PHYSICO-CHEMICAL STUDIES OF SOME SCHIFF BASE COMPLEXES OF TRANSITION METALS IN PURE AND MIXED SOLVENT MEDIA

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By

DHIRAJ BRAHMAN

M.Sc. in Chemistry

Supervisor

DR. BISWAJIT SINHA

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NORTH BENGAL

DECEMBER, 2013

Dedicated
To
My Beloved Parents

DECLARATION

I declare that the thesis entitled **"PHYSICO-CHEMICAL STUDIES OF SOME SCHIFF BASE COMPLEXES OF TRANSITION METALS IN PURE AND MIXED SOLVENT MEDIA"** has been prepared by me under the guidance of Dr. Biswajit Sinha, Assistant Professor, Department of Chemistry, University of North Bengal. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

DHIRAJ BRAHMAN,
Department of Chemistry,
University of North Bengal,
Darjeeling-734013,
West Bengal, India

DATE:

CERTIFICATE

I declare that Mr. DHIRAJ BRAHMAN has prepared the thesis entitled **"PHYSICO-CHEMICAL STUDIES OF SOME SCHIFF BASE COMPLEXES OF TRANSITION METALS IN PURE AND MIXED SOLVENT MEDIA"** for the award of Ph. D degree of University of North Bengal, under my guidance. He has carried out the work at the Department of Chemistry, University of North Bengal.

Dr. Biswajit Sinha,
Department of Chemistry,
University of North Bengal,
Darjeeling-734013,
West Bengal, India

DATE:

ABSTRACT

Chapter I contains a brief overview of some important Schiff bases, their transition metal complexes and their varied applications. It also contains a brief introduction to solvation, solute (ion)-solvent and solute (ion)-solute (ion) interactions. Object and application of the present investigation as well as importance and scope of different physico-chemical properties like apparent molar volumes, partial molar volumes at infinite dilution, the viscosity *B*-coefficient, etc., have been mentioned. Importance of different solutes and solvents, used in the present investigation, has also been outlined.

In chapter II theoretical background for the research works embodied in this thesis has been given in detail with special reference to different physico-chemical parameters studied in Solution Chemistry. A brief overview of solvent effects on reactions rates and theoretical approach for the study of partial molar volumes and solvation was given in this chapter.

Chapter III describes the experimental methods employed for the measurement of different thermodynamic and transport properties. This chapter also contains provenance and purity of the different chemicals used and describes the syntheses and physicochemical characterization of the Schiff bases and their transition metal complexes used as solutes in the present investigation.

Chapter IV describes the ion-ion and ion-solvent interactions for N, N$^{/}$-ethylene-bis(salicylideneiminato)-diaquochromium(III) chloride dissolved in solutions of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate and methanol at 298.15, 308.15 and 318.15 K under ambient pressure. The derived parameters like apparent molar volume (ϕ_V), the slope (S_V^*), standard partial molar volume (ϕ_V^0), standard transfer volume ($\Delta_t\phi_V^0$), the viscosity *B*-coefficient, etc., were discussed on the basis of ion-ion and ion-solvent interactions. Thermodynamics of viscous flow were discussed on the basis of the transition state theory.

In chapter V the densities, viscosities and refractive indices of N, N$^{/}$-ethylene-bis(salicylideneiminato)-diaquochromium(III) chloride in aqueous solutions of dimethylsulfoxide were reported at 298.15, 308.15 and 318.15 K under atmospheric pressure. The derived parameters like apparent molar volume (ϕ_V), standard partial molar volume (ϕ_V^0), the slope (S_V^*), standard isobaric partial molar expansibility (ϕ_E^0) and its temperature dependence $(\partial\phi_E^0/\partial T)_P$, the viscosity *B*-coefficient, its temperature dependence ($\partial B/\partial T$), solvation number (S_n) and apparent molar refractivity (R_D), etc., were discussed on the basis

of ion-ion and ion-solvent interactions. Further ionic viscosity *B*-coefficients ($B_{\pm}$) and ionic solvation numbers ($S_{n,\pm}$) were determined and discussed accordingly.

Chapter VI describes standard partial molar volumes (ϕ_V^0) and viscosity *B*-coefficients of N, N$^{/}$-ethylenebis-(salicylideneiminato)cobalt(II) in different binary solutions of 1,4-dioxane and methanol at 298.15, 303.15, 308.15 and 313.15 K under ambient pressure. The derived parameters like standard partial molar volume (ϕ_V^0), viscosity *B*-coefficient, standard partial molar expansibility (ϕ_E^0), etc., were discussed in terms of solute-solvent and solvent-solvent interactions. Various results indicated that the studied ternary system is characterized by structural changes and strong solute-solvent interactions.

In this chapter VII standard partial molar volumes (ϕ_V^0) and viscosity *B*-coefficients of iron(III)-N, N$^{/}$-ethylene-bis(salicylideneiminato)-chloride in different aqueous methanol solutions were determined from solution density and viscosity measurements at temperatures 298.15, 303.15, and 313.15 K under ambient pressure. Standard partial molar volume (ϕ_V^0), viscosity *B*-coefficient, the standard partial molar expansibility (ϕ_E^0) and its temperature dependence at constant pressure, $(\partial \phi_E^0 / \partial T)_P$ for the experimental solutions were used to reveal the nature of different interactions in the ternary solutions. UV-VIS absorption spectra of the ternary solutions also supported the results obtained.

Chapter VIII describes the standard partial molar volumes (ϕ_V^0) and viscosity *B*-coefficients of iron(III)-N, N$^{/}$-ethylene-bis(salicylideneiminato)-chloride in binary mixtures of N, N-dimethylformamide and acetonitrile at 298.15, 303.15, 308.15 and 313.15 K under ambient pressure. In the investigated temperature range, the relation: $\phi_V^0 = a_0 + a_1T + a_2T^2$, was used to determine the temperature dependence of the standard partial molar volume $(\partial \phi_V^0 / \partial T)_P$, i.e., standard partial molar expansibility (ϕ_E^0); its temperature dependence, $(\partial \phi_E^0 / \partial T)_P$ and viscosity *B*-coefficients were used to reveal the nature and degree of solute-solvent and solvent-solvent interactions in the ternary solutions.

In this chapter IX the standard partial molar volumes (ϕ_V^0) and viscosity *B*-coefficients of salicylaldehyde anil zinc (II) in different molar solutions of tetrabutylammonium bromide in methanol were determined from solution density and viscosity measurements at 298.15, 308.15 and 318.15 K under ambient pressure. Apparent molar volume (ϕ_V) and solution density (ρ)

were further used to determine isobaric apparent molar expansibility (ϕ_E), standard isobaric partial molar expansibility (ϕ_E^0) and its temperature dependence at constant pressure, $(\partial\phi_E^0/\partial T)_P$ for the solutions to study the nature of different interactions in the ternary solutions. The transition state theory was applied to analyze the viscosity *B*-coefficients of the ternary solutions on the basis of the activation parameters of viscous flow. The overall results indicated strong solute-solvent interactions between the complex and the solvent mixtures. UV-Visible absorption spectra of the ternary solutions also supported the results obtained.

In chapter X non-covalent interactions between of {N, N$^{/}$-bis[(2-pyridinyl)methylene]-1, 2-benzenediamine]-bis(nitrato)}Cu(II) with pyridoxine hydrochloride in methanol were investigated at 298.15, 308.15 and 318.15 K under ambient pressure. The derived parameters like apparent molar volume (ϕ_V), the slope (S_V^*), standard partial molar volume (ϕ_V^0), standard transfer volume ($\Delta_t\phi_V^0$), isobaric apparent molar expansibility (ϕ_E), standard isobaric partial molar expansibility (ϕ_E^0), the viscosity *B*-coefficient, its temperature derivative ($\partial B/\partial T$), solvation number (S_n), etc., were discussed on the basis of specific or nonspecific solute-cosolute and solute-solvent interactions. Spectrophotometric results indicated 1:1 solute-cosolute interaction between the complex and pyridoxine hydrochloride.

Finally chapter XI contains the concluding remarks on the research works embodied in this thesis.

PREFACE

I started the research work presented in this thesis entitled "**PHYSICO-CHEMICAL STUDIES OF SOME SCHIFF BASE COMPLEXES OF TRANSITION METALS IN PURE AND MIXED SOLVENT MEDIA**" in 2009 under the supervision of Dr. Biswajit Sinha at the Department of Chemistry, University of North Bengal, India with the aim to investigate on the solution thermodynamics of some Schiff base complexes of transition metals in different pure and mixed solvent media.

The process of solvation of a solute by solvent molecules is of primary importance in many branches of chemistry such as chemical syntheses or complex formation processes, etc. The solvation of ions or solutes and its source in terms of solute-solvent or ion-solvent and solvent-solvent interactions constitute an important area in solution chemistry. Solvent affects both molecular structure and electronic structure of solutes. Knowledge of their interactions helps in better understanding of the profile of solutes or solvents, i.e., whether the added solute modifies or distorts the structure of the solvent and vice-versa. For a particular chemical reaction, the reactivity is influenced by the preferential solvation of the reactant and its transition state through non-specific and specific solute-solvent or ion-solvent interactions. In order to analyze solute-solvent or ion-solvent interactions, over the years great interest was paid to the behavior of solutions of electrolytes and non-electrolytes in pure solvents and binary solvent mixtures.

But such studies on the solution behavior of some Schiff bases and their metal complexes in non-aqueous and mixed solvents with a view to investigate solute-solute and solute-solvent interactions under varied conditions are very limited in the literature. Studies on thermodynamic properties of the metal complexes in solution phase may provide valuable information regarding their solution behavior and appropriate understanding of their physico-chemical properties would enable chemists to choose the solvent that will (i) enhance the rate of chemical reactions, (ii) solubility during the chemical processes and (iii) reverse the direction of equilibrium reactions, etc. Hence the present dissertation is an attempt to explore the thermodynamic properties of some Schiff base metal complexes in solution phase with special reference to solute-solvent (ion-solvent) and solute-solute (ion-ion) interactions.

Acknowledgement

At the first opportunity I erratically feel short of words to articulate my heartfelt gratitude and deep indebtedness to Dr. Biswajit Sinha, my supervisor for his proficient supervision through the splendid path of my research with great endurance. His constant support, fruitful discussions and valuable suggestions at different stages are really a great motivation. He is truly a "Guru" for me in the serenity of mind, hard work and patience towards others. The support and encouragement of all the other faculty members of the Department of Chemistry, N. B. U in the whole stage of my research was of colossal help. I sincerely appreciate the help rendered by all the non-teaching staffs of this department during the crucial stage of my research and I am grateful to all of them for their kind-heartedness.

I evoke with gratitude the selfless help and involvement of my lab mates Mr. Abhijit Sarkar, Mr. Rashmidipta Biswas, Mr. Sanjoy Saha, Mr. Rajendra Pradhan, Mr. Bijan Pandit at different stages of my work. Amongst all of my friends at the Department of Chemistry, N. B. U Mr. Anand Pariyar, Mr. Raju Subba, Dr. Rajani Dewan are the chief contributors to what all I have been able do as part of my research. I also express my heartfelt gratitude to my parents and brothers for their love, affection and encouragement during this period.

I am happy to acknowledge the services of SAIF-NEHU (SHILONG), CDRI, (Lucknow), IIT (Chennai) for their help in sample analyses. I would also like to record my thankfulness to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi, India (No. F 540 / 27 / DRS / 2007, SAP-1) for financial and instrumental assistance as well as to the University Grants Commission, New Delhi, India for granting me UGC-BSR Research Fellowship in Science (Ref. No: 4-1/2008 (BSR)) during my research period. Above all my praises are due to God, without the poise of whom the whole episode would have had condensed to nothing.

Mr. Dhiraj Brahman
Research Scholar
Department of Chemistry
University of North Bengal
Darjeeling -734013, WB, INDIA

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CHAPTER I

Introduction

Schiff bases, derived from an amine and aldehydes or ketones, are an important class of ligands in chemistry that coordinate to metal ions via azomethine nitrogen and they have been studied extensively.[1-4] Schiff bases are called "privileged" ligands, because of their easy preparative procedures and applications in many fields.[5] Schiff bases have been playing an important role in the development of coordination chemistry. Schiff bases and their transition metal complexes are being studied by many chemists because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas. [6-8] Many of the studies on Schiff base metal complexes are centered on their catalytic activities in a large number of homogenous and heterogeneous reactions.[9] Most of the biological and chemical reactions occur in solution phase and solvation plays a crucial role in various processes taking place in solution phase[10] and thus studying the solvation processes is important for understanding solvent effects on chemical reactions. Therefore the introductory part of the thesis deals with a brief discussion on the Schiff base ligands and their transition metal complexes, general application of Schiff base complexes and the solvation phenomenon including various interactions occurring in solution phase viz. solute-solute or ion-ion interactions and solute-solvent or ion-solvent interactions.

1.1. Chemistry of Schiff Bases

Schiff bases are the compounds containing azomethine group (-HC=N-) usually formed by the condensation of primary amines with a carbonyl compound.[11-13] Schiff bases were first reported by Hugo Schiff in 1864.[14] The common structural feature of this class of compounds is the presence of azomethine linkage with a general formula $RHC=N-R^{/}$, where R and $R^{/}$ are alkyl, aryl, cycloalkyl or heterocyclic groups which may be variously substituted. Details regarding the preparation of Schiff base are spread out in the literature. The general synthetic route of formation of Schiff base is given in figure 1.1.

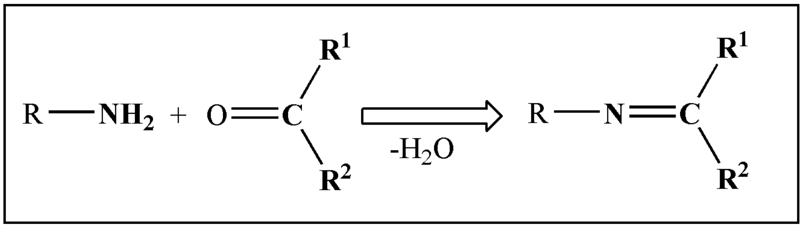

Fig. 1.1. Condensation reaction for of Schiff base formation. R^1 and R^2 groups may be variably substituted.

Like aldehydes, ketones are also able to form Schiff base ligands. However, ketones form Schiff bases less readily than the aldehydes. Again Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerize[15] but those of aromatic aldehydes having effective conjugated systems are more stable. The presence of lone pair of electrons in an sp^2 hybridized orbital of nitrogen atom of azomethine group is of considerable chemical and biological importance[16] and impart excellent chelating ability, especially when used in combination with one or more donor atoms close to the azomethine group.

In general, the donor nature of the ligand depends both on the type of carbonyl compound used and the nature of amine employed in the condensation reaction. Schiff base may act as bi-, tri-, tetra- or polydentate ligands depending on the number of donor sites present in their structure. Some examples are illustrated in figure 1.2 below:

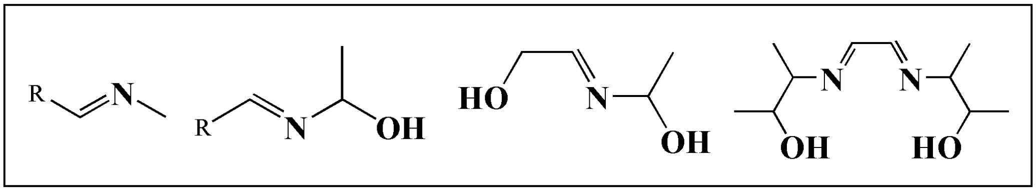

Fig. 1.2. Schiff bases with mono-, bi-, tri- and tetra donor sites.

A majority of Schiff bases, derived from salicyldehyde and 1,2-diamines such as ethylenediamine, have ONNO tetradentate donor sites and possess a wide variety of applications.[17,18] When the aldehyde is salicyaldehyde and the diamine is 1,2-diaminoethane or ethylenediamine, the resulting Schiff base is called "Salen" and when the diamine is 1,2-phenylenediamine the resulting condensation product is called “Salophen”. Some examples of Schiff bases with varying dentacity are depicted in figure 1.3.

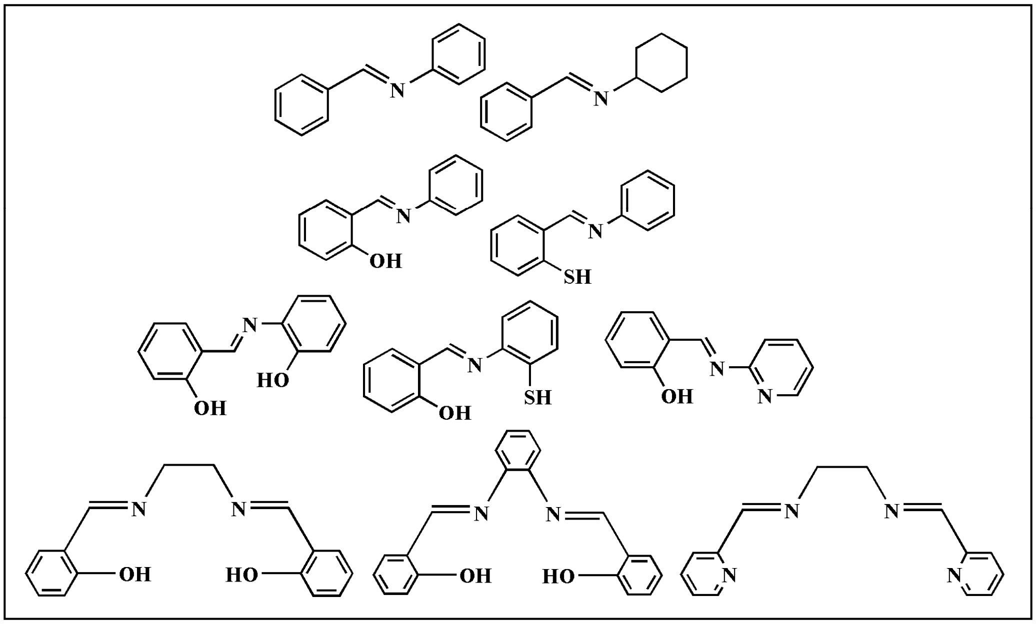

Fig. 1.3. Schiff bases with different dentacity.

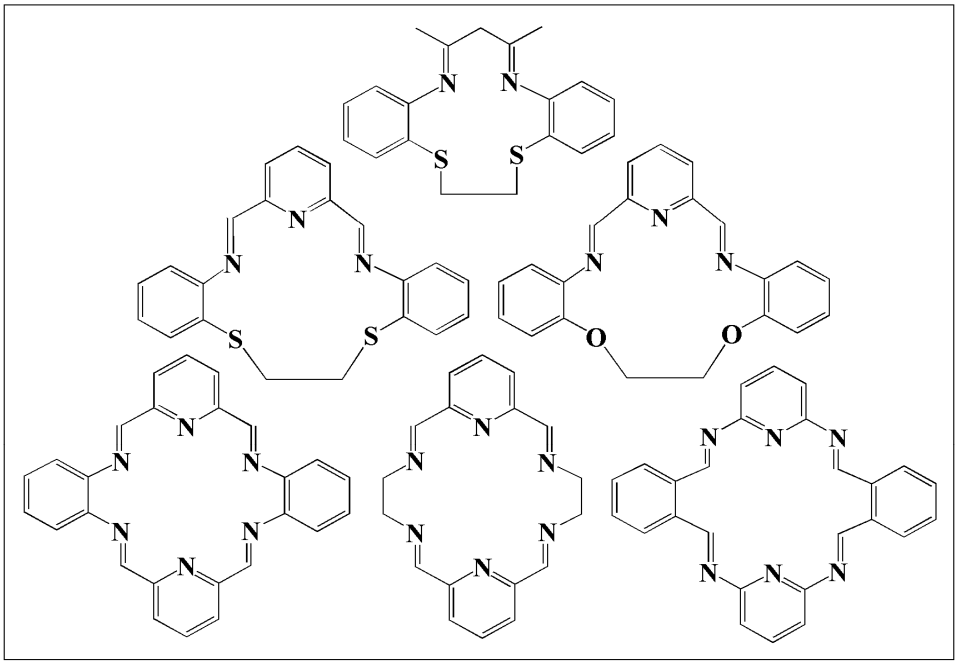

Fig. 1.4. Schiff base macrocycles with different dentacity.

In addition to these, a large number of Schiff base macrocycles were prepared by self condensation reaction of appropriate formyl- or keto- and primary amine precursors and they find wide range of applications in the development of supramolecular chemistry.[19, 20]A few examples of Schiff base macrocycles are depicted in figure 1.4.

Schiff bases have a number of applications, viz. preparative use, identification, detection and determination of aldehydes or ketones, purification of carbonyl or amino compounds or protection of these groups during complex or sensitive reactions. They also form basic units in certain dyes.[21] In azomethine derivatives, the (-HC=N-) linkage is essential for biological activity, several azomethine were reported to possess remarkable antibacterial, antimalerial activities.[22, 23] Schiff bases appear to be an important intermediate in a number of enzymatic reactions involving interaction of an enzyme with an amino or carbonyl group of the substrate. Condensation of primary amine in an enzyme usually that of a lysine residue with a carbonyl group of the substrate to form an imine or Schiff base is one of the most important types of catalytic mechanism in biochemical process. Also in organic syntheses, Schiff base formation reactions are useful in making carbon-nitrogen bonds.[21]

For several reasons, Schiff bases have been found to be most convenient and attractive ligands for forming complexes with different metal ions. Firstly, steric and electronic effects around the metal core can be finely tuned by a suitable selection of bulky or electron withdrawing or donating substituent incorporated into the Schiff bases.[24] Secondly, the donor atoms (N and O) of the chelated Schiff bases exert two opposite electronic effects: the phenolate oxygen is hard donor and stabilizes the higher oxidation states of the metal atom; whereas the imine nitrogen is borderline donor and stabilizes the lower oxidation state of the metal ion.[25] The basicity of the Schiff bases also plays a key role in the formation and stabilization of the complexes. The –OH and –SH groups present in the Schiff bases can induce tautomerism in the compound leading to complexes with different structures. A large number of salen complexes show keto-enol tautomerism as shown in figure 1.5.

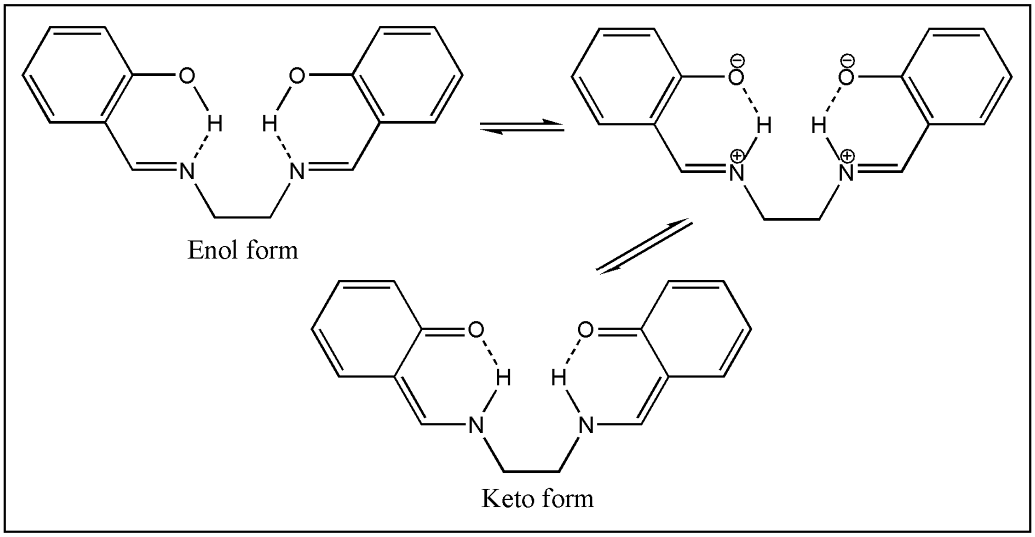

Fig. 1.5. Keto-enol tautomerism in salen Schiff base ligand.

Also the deprotonation of thiolic, alcoholic and phenolic groups are favoured due to the stabilization of various oxidation states of the central metal ion.[26]

1.2. Transition Metal Complexes of Schiff Bases

Schiff bases act as a good chelating ligands for almost all the metal ions. Thus Schiff base complexes of transition metals remain as an important and popular topic in chemistry.[27] Organometallic compounds of Schiff bases have played a vital role in coordination chemistry, mainly due to their ease of preparation, structural variability and widespread applications such as catalyst, functional materials, antibacterial reagents etc.[28-30] Transition metal complexes of Schiff bases are known to chemist since 1840, when a dark green crystalline solid, bis(salicyldimino)Cu(II) has been isolated from the reaction of cupric acetate, salicyladehyde and aqueous ammonia.[31]

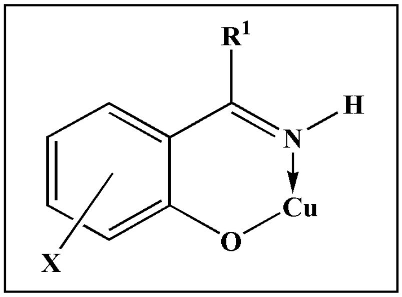

Fig. 1.6. Structure of bis(salicyladimino)Cu(II).

General Introduction

In recent years, there has been considerable interest in the chemistry of transition metal complexes of Schiff bases. This is due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning the metal centered electronic factor and enhancing the solubility and stability of either homogenous or heterogeneous catalysts.[32] A large number of publications[33-38] ranging from purely synthetic to modern physico-chemical and biochemically relevant studies of metal complexes of Schiff bases revealed that such complexes are very much concerned with the development of modern coordination chemistry. In fact, Schiff bases are able to stabilize many different metals in various oxidation states and thus control the performance of metals in large variety of useful catalytic transformations.[39] In this regard metal complexes of Schiff bases derived from salicylaldehyde and various amines have been widely investigated.[40, 41] In the area of bioinorganic chemistry interest in Schiff base complexes has centered on the role of such complexes in providing synthetic models for the metal containing sites in metalloprotiens and metalloenzymes.[42, 43]

The interest in the design, synthesis and characterization of the transition metal complexes of unsymmetrical Schiff base ligands has come from the rationalization that coordinated ligands around central metal ions in natural systems are unsymmetrical.[44] Unsymmetrical Schiff base ligands have offered many advantages over their symmetrical counterparts in the elucidation of the composition and the geometry of the metal binding sites in the metalloprotein and the metallo enzymes and the selectivity of the natural systems with synthetic materials.[45] In recent years, transition metal complexes of multidentate Schiff base ligands containing both amino and hydroxyl groups for coordination with metals ions have attracted much attention.[46] Among many potential Schiff base ligands, salen ligands attracted many chemists to explore the field of coordination chemistry with a new dimension. The tenability of carbon skeleton around coordinating atom (O or N) may be attributed to salen's ability to form chelate frameworks with novel architecture and properties for multitude applications.[47] Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions.[48]

Although Schiff base metal complexes were known since the mid nineteenth century, after the work of Jorgensen and Werner these metal complexes have gained interest of many chemists in the field of coordination chemistry.[49] Pfeiffer and his co-workers[50] reported a series of complexes derived from Schiff bases of salicylaldehyde and its substituted analogues. Of all the Schiff base complexes, those derived from salicyladiimines have been thoroughly studied so far. The advantage of the salicyladiimines ligand system is the considerable flexibility of the synthetic procedures that resulted in the preparations of a wide variety of complexes with a given metal whose properties are often dependent on the ligand structure. Complexes of transition metal ions with Schiff bases provide a large and growing class of compounds with both stereochemical and magnetochemical interest. Characteristically, several distinct compounds may be isolated from a reaction mixture and the products may differ in the coordination number of the metal ion, the stereochemistry of the ligand isomers or the degree of molecular complexity.[51] Metal complexes of Schiff bases are generally prepared by treating metal salts with Schiff base ligands under suitable experimental conditions. An elaborate discussion on synthesis and characterization of Schiff base metal complex are available in numerous literature.[52,53]

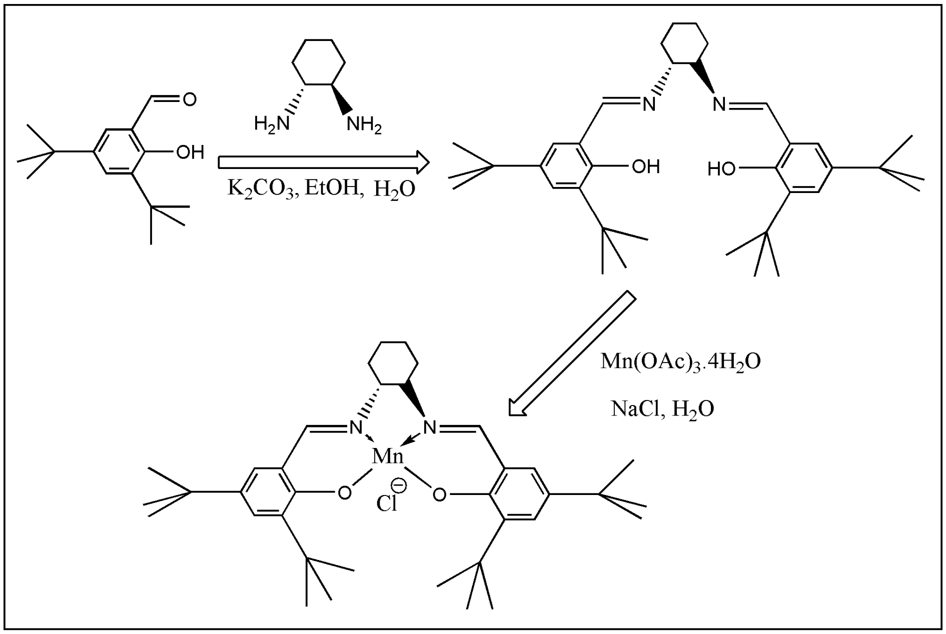

Fig. 1.7. Synthesis of Jacobsen's catalyst.

The synthesis of well-known Mn(III) Schiff base complex, “Jacobsen’s catalyst” is presented in figure 1.7. The Schiff base can be obtained by condensation between trans-1,2-diaminocyclohexane and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and finally Jacobsen’s catalyst can be prepared from the ligand by treatment with Mn(III) acetate followed by oxidation with air. Similar type of Mn(III) complex can be obtained from salophen Schiff base and is presented in figure 1.8.

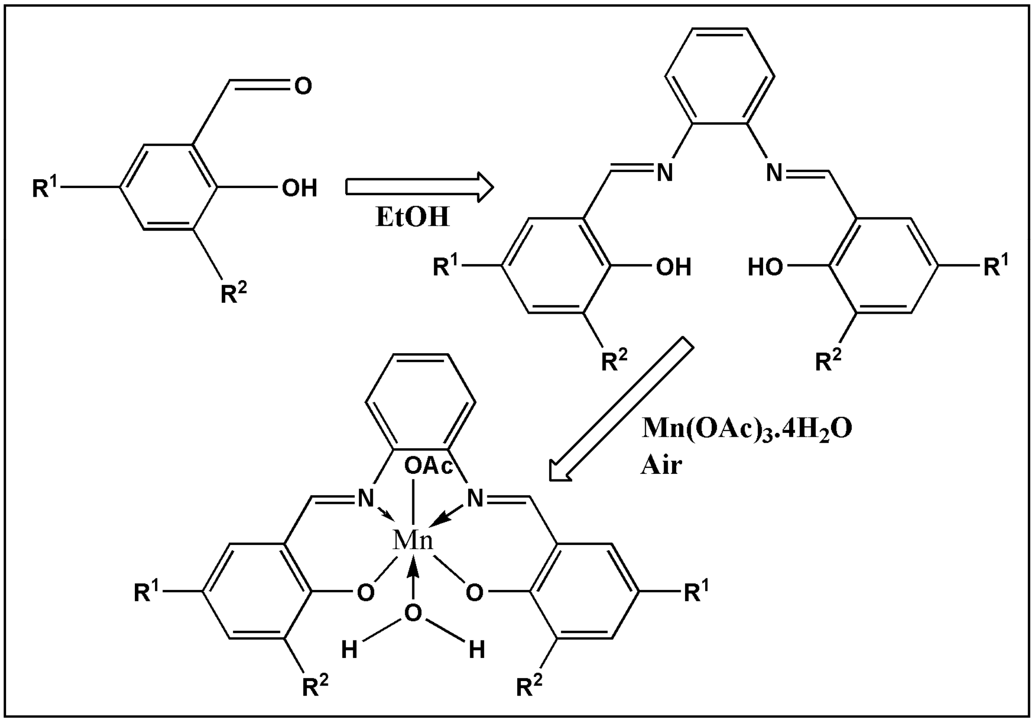

Fig. 1.8. Procedure for synthesis of Mn(III) salophen complex.

Cozzi[5] has outlined five different synthetic routes commonly employed for the preparation of Schiff base metal complexes and these are depicted in figure 1.9. Apart from these, many complexes of Co(II), Ni(II), Fe(III), Cr(III), Zn(II) and many other metal ions with different Schiff base ligands were synthesized and characterized by different techniques.[54] Thus Schiff base complexes are known to offer: (i) ease and flexibility of the synthetic procedure, (ii) diverse properties and (iii) use as biological models or biologically active compounds.

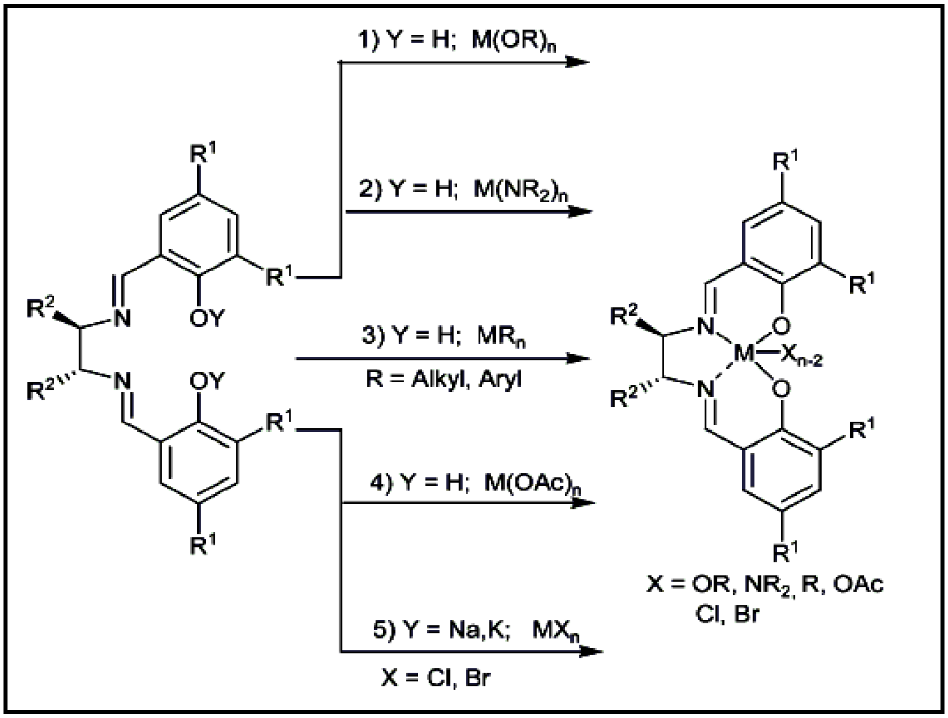

Fig. 1.9. Different synthetic routes of preparation of transition metal Schiff base complexes.

1.3. Application of Transition Metal Complexes of Schiff bases

A large number of Schiff bases and their metal complexes have been studied for their interesting and important properties such as their ability to reversibly bind oxygen[55], photochromic properties[56], complexing ability towards toxic metals etc. Schiff base complexes are considered to be among the most important stereochemical models in transition metal coordination chemistry due to their preparative accessibility and structural variety[57]. A considerable number of Schiff base complexes have potential interest, being used as more or less successful models of biological compounds[58]. Not only they have played an important role in the development of modern coordination chemistry, but they can also be found at key points in the development of inorganic biochemistry, catalysis, optical materials, etc.[59] Thus some important applications of Schiff base complexes of transition metals are outlined here.

1.3.1. As Catalysts

Schiff base complexes catalyze a large number of homogenous and heterogeneous reactions. They play a major role in such reactions and their activities may be varied by altering metal ions, coordination sites and the ligand types. Catalytic activities of Schiff base metal complexes are abundantly found in the literature.[60] Many Schiff base complexes of metal ions show high catalytic activities. Chiral Schiff base complexes are more selective in various reactions such as oxidation, hydroxylation, aldol condensation and epoxidation, etc.[27] A number of asymmetric chemical transformations employed ONO type chiral Schiff base complexes possessing ions of transition metals like Zn(II), Cu(II), V(IV) etc. Uchida and Katsuki reported that Co(III) salen complexes are excellent catalyst for Bayer-Villiger oxidation.[61] Also the Co(salen) and its analogues are found to be good catalyst for oxidation of phenols and alcohols in presence of dioxygen as oxidant. However Co(salen) needs an axial ligand (such as pyridine or donor solvent molecules) for being catalytically active and binding dioxygen.[62] A few catalytically active Co(II) Schiff base complexes are depicted in figure 1.10.

The oxidation of hydrocarbons using Schiff base complexes has been a field of academic and industrial interest to analyze the catalytic activities of various metal complexes.[63] Schiff base complexes of Cr(III), Mn(III), Fe(II), Co(II), Ni(II) and Zn(II) have been tested for oxidation of cyclohexane.[64] Mn(III) complexes of N, N/-ethylenebis-(salicylideneaminato)salen; N, N/-ethylenebis-(5-chlorosalicylidenaminato)Cl salen; N, N/-ethylene bis-(5-bromosalicylideneaminato)Br salen and N,N/- ethylene bis-(5-nitrosalicyli-2,2-diene aminato)NO salen were encapsulated in zeolites-Y for aerobic oxidation of styrene to benzaldehyde, styrene oxide and phenyl acetaldehyde.[65]

Mn(III) complexes of salen, Br_2salen and (*tert*-butyl)$_4$salen Schiff base ligands encapsulated in zeolites were active catalysts in the oxidation of styrene using molecular oxygen as oxidant.[66] The Co(II) complex of N,N/-bis(salicylidene)-1,2-phenylenediamine was used as a catalyst in oxidation of benzyl alcohol. The Mn(II) salen complexes showed catalytic activities in asymmetric oxidation of silyl ketone acetals with high enantioselectivity. A few Mn^{III}(salen) complexes are depicted in figure 1.11.

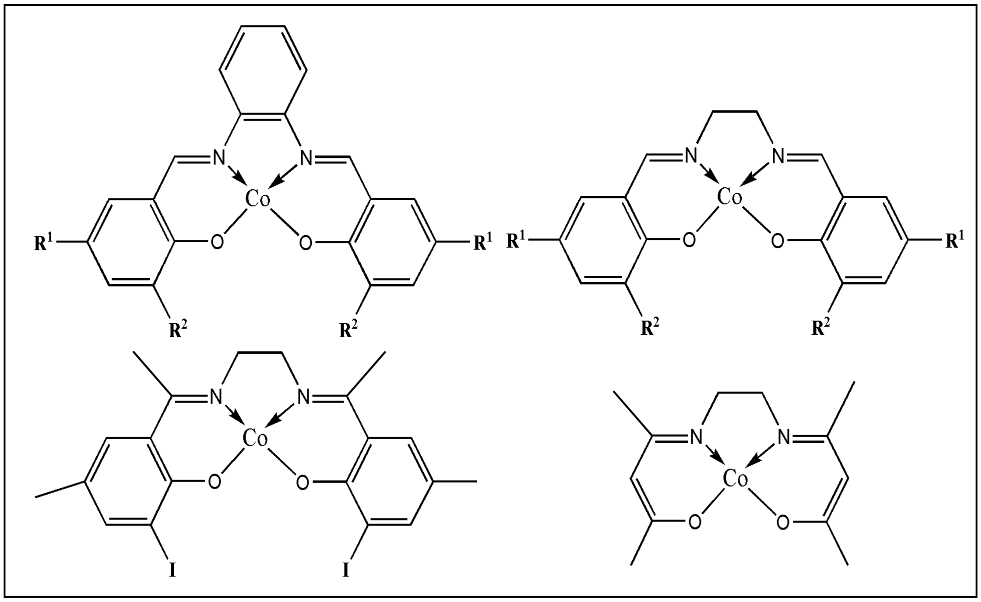

Fig. 1.10. Catalytically active Co(II) Schiff base complexes.

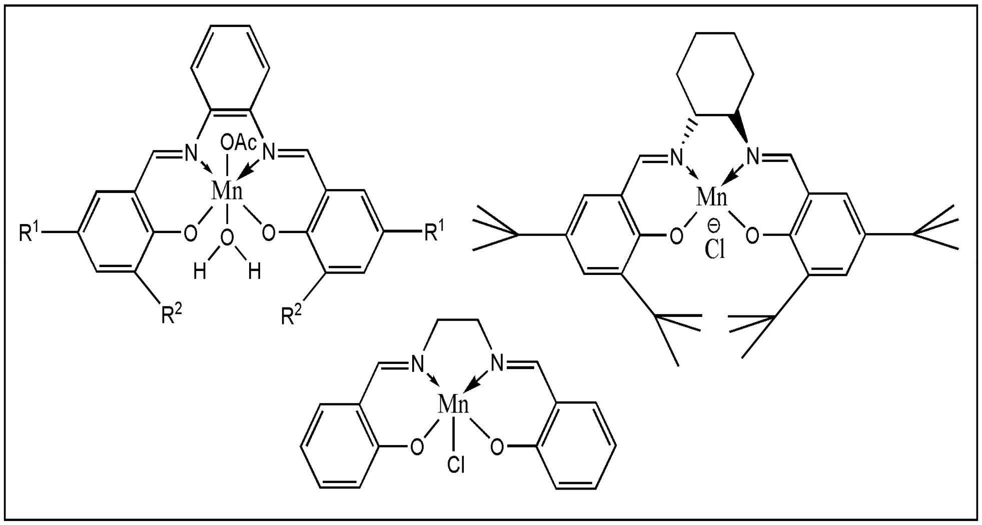

Fig. 1.11. Some Mn^{III}(salen) complexes.

Dinuclear Schiff base complexes of transition metal ions are more efficient catalysts than mononuclear complexes probably due to the synergic effect of two metal ions.[67] The dinuclear Schiff base complexes of Cu(II) were used as catalysts in oxygen activation.[68] Dinuclear complexes of Cu(II) and Pd(II) is shown in figure 1.12.

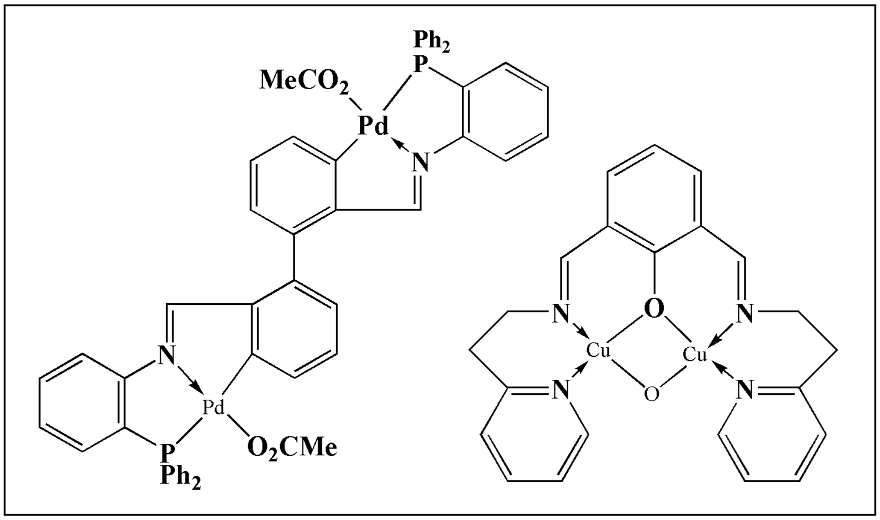

Fig. 1.12. Binuclear complex of Pd(II) and Cu(II).

Also the interest in polymerization of olefins has recently increased due to the observed catalytic activities of Schiff base complexes in synthesis of commercially important branched and linear polyethylene. Literature is full of examples in which complexes of Schiff base ligands were employed as catalyst in polymerization reactions.[69] The zicronium, titanium, and vanadium complexes of phenoxyimine were also used successfully in the polymerization of ethylene. The ring opening polymerization of cycloalkenes is now-a-days efficiently catalyzed by Schiff base metal complexes at low temperatures.[70] The ring opening of large cycloalkanes is usually a difficult process but Schiff base complexes of Co(II) and Cr(III) were effective in these reactions with significant enantioselectivity.[71] Phosphine substituted in N-heterocyclic carbene Schiff base ligands has enhanced ring closing metathesis reaction to synthesize functionalized olefins. The chiral Schiff base complexes of salen and binapthyl were used as an efficient catalyst in Michael addition reaction. The Heck reaction, an industrially useful process to synthesize fine chemicals and pharmaceuticals, was successfully catalyzed by using Schiff base complexes.[72] The Mn(II) complexes of bis(2-pyridinaldehyde) ethylenediamine, bis(2-pyridinaldehyde) propylenediamine ligands were used in epoxidation of olefins but reasonable epoxide selectivity was possible only in the presence of PhIO oxidant.[73] Cr(III) salen complexes catalyzed the epoxidation of unfunctionalized *trans*-olefins.[74] The Cr(III) and Mn(II) complexes based on [N, N$'$-bis(3,5-di-*tert*-butylsalicylidene)]- (1,2-

diamino hexane) Schiff base ligand showed exceptionally high enantioselectivity in epoxidation reactions.[75] Co(II) salen complexes were used in the asymmetric nucleophilic ring opening of *meso*-epoxides in the presence of benzoic acid.[76] Costa *et. al.*[77] studied the catalytic activity of Pd(II) complexes of Schiff bases possessing nitrogen donors during hydrogenation of alkenes and alkynes under mild conditions. A very efficient catalytic activity is exhibited by mono and dinuclear Pd(II) complexes of Schiff bases possessing *tert*-butyl groups on the salicyl ring with steric constraints towards reduction of cyclohexene and nitrobenzene. Various Schiff base metal complexes are found to be an excellent catalyst in many other academically and industrially important reactions such as reduction of ketones, allylic alkylation reaction, hydrosilation, decomposition of hydrogen peroxide, carbonylation reaction, benzylation reaction, isomerization, cyclopropanation, cyanide addition, dimerization and Diels-Alder reaction, etc. Thus Schiff base complexes of transition metal ions have played a significant role in various reactions to enhance the yield and product selectivity. The convenient route of synthesis and thermal stability of Schiff base ligands have contributed significantly for their possible application in catalysis as metal complexes. The transition metals in combination with different Schiff base ligands showed high catalytic activities in reactions of industrial importance and academic interests.

1.3.2. As Electroluminescent Materials

Organic electroluminescence (EL) devices have attracted large interest in recent years due to flat-panel display applications.[78] Organic dyes, chelate metal complexes and polymers are three major categories of materials used in the fabrication of organic electroluminescent (EL) devices. Out of the three, chelate metal complexes having high-luminance blue emitting nature find use as materials for RGB (red, green, and blue) emission. Many salicylaldehyde-derived Schiff base metal complexes with the formation of inner complex have been investigated as EL materials.[79] Schiff base complexes, especially those of Zn(II), are now-a-days used as electroluminescent materials.[80] Wei *et al.*[81] prepared blue luminescent zinc and beryllium complexes of the Schiff bases derived from calixarene. Xie *et al.*[82] reported the crystal structure, thermal stability and optoelectron properties of bis[salicylidene-

(4-dimethylamino)aniline]Zn(II). This complex exhibits very good light emission and charge transporting performance in organic light emitting diodes (OLEDs). Yang *et al.*[83] have synthesized N, N$^{/}$-bis-(salicylidene)-ethylenediamine-Zn(II) iodide and used as a Dye-sensitized solar cells. Synthetic route of N, N$^{/}$-bis(salicylidene)-ethylenediamine-Zn(II) iodide is shown in figure 1.13.

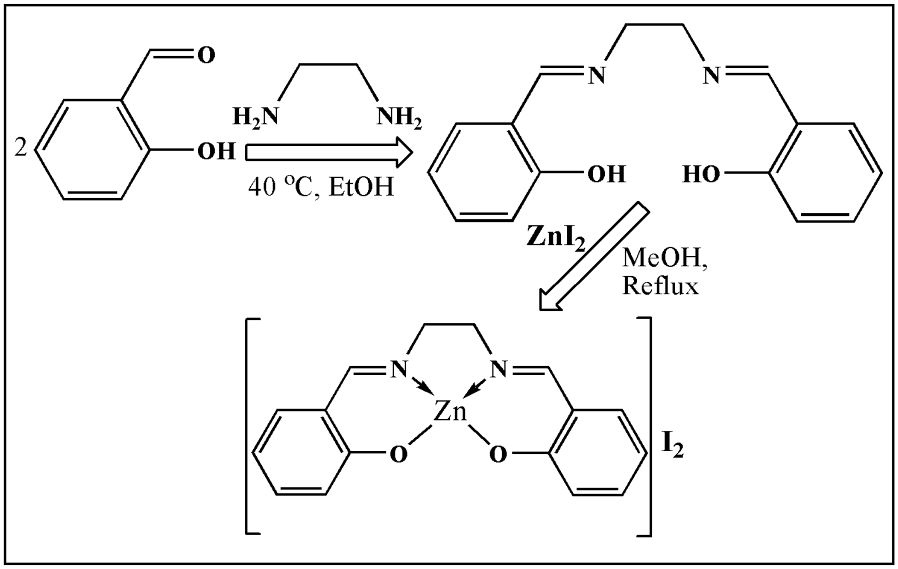

Fig. 1.13. Synthetic route of N, N$^{/}$-bis-(salicylidene)-ethylenediamine-Zn(II) iodide.

These experimental reports point to the possible application of Schiff base complexes as emitting materials in full colour flat-panel displays. Cozzi *et al.*[84] reviewed the photophysical properties of the Schiff base complexes with several metal ions. They evaluated the photophysical properties of salen complexes for possible use in the luminescent probes. Mixed valence Schiff base complexes are considered as functional materials for optoelectronics and molecular magnets. Some of the Schiff base complexes may find applications in the development of new molecular switches.

1.3.3. As Electrochemical Sensors

Schiff bases have been used as carriers in the preparation of potentiometric sensors for determining cations and anions.[85] A ruthenium(III) Schiff base complex was used in the fabrication of chloride PVC-based membrane sensor.[86] It shows high selectivity toward Cl^- ion over several organic and inorganic anions and was successfully applied for the determination of Cl^- ion in serum samples. It could also be used as an indicator electrode in the potentiometric titration of Cl^- ion with $AgNO_3$ solution. Gupta *et al.*[87] reported a potentiometric Al^{3+}-sensor based on the use N, N$^/$-bis-(salicylidene)-1,2-cyclohexanediamine as a neutral carrier in PVC matrix. It was successfully applied for direct determination of Al^{3+} in biological, industrial and environmental samples. It has been used as an indicator electrode in potentiometric titration of Al^{3+} ion with EDTA.

1.3.4. In Biological and Medicinal Applications

Many ligands have been designed to mimic the function of natural carriers in recognizing and transporting specific metal ions, anions or neutral molecules and in understanding and reproducing the catalytic activity of metallo-enzymes and proteins.[1] Schiff bases are known to be an important intermediate in many enzymatic reactions involving interaction of an enzyme with an amine or carbonyl group of the substrate.[88] In past few decades, a number of transition metal complexes have been exploited for the design of new drugs due to their diverse biological activities. Synthetic chemists are interested in studying the efficiency of the biosynthetic machinery by designing biomimetic reactions that approximate natural reaction pathways. Schiff bases can accommodate different metal centers with various coordination modes allowing successful synthesis of homo and heterometallic complexes with varied stereochemistry. This feature is employed for modeling active sites in biological systems.[89] Transition metals are essential catalyst involved in many electron transport systems. For instance iron is the principal electron carrier in biological oxidation and reduction reactions.[90] Haem (Fe^{2+}) and hematin (Fe^{3+}) groups are the coenzymes often associated with protoporphyrin IX for a number of redox enzymes. These include catalases, which catalyze the dismutation of H_2O_2, and peroxidases, which catalyze the reduction of alkyl hydroperoxides. Wang *et al.*[91] have reported that Fe(salen) could effectively catalyze the reduction of O_2 and H_2O_2. Salen metal complexes have been designed as nucleic acids reagents to induce specific damages in DNA or RNA. In the 1980s the chemical nuclease activity of transition metal complexes was discovered and is recently used extensively in bio-engeering. Literature survey reveals that a large number of Schiff base complexes are excellent

DNA cleavagers.[92] Mn(III) salen complexes can produce enantiospecific recognition and cleavage of right handed double helical DNA.[93] In addition to these, Co(salen) and Ru(salen) complexes were also designed as DNA cleavers. Almost all the transition metal complexes of Schiff base ligand shows excellent antiviral, antimalerial, antibacterial and antitubercular activity.[94] The potent biological activity can be related to the presence of nitrogen atom with a lone pair of electron in it and that the nitrogen can participate in hydrogen bonding with NH or OH groups present in biomolecules.

1.3.5. Other Applications

Many Schiff base compounds are found to be good corrosion inhibitors. Emregul and Atakol [95] studied the corrosion behavior of iron with three different Schiff base compounds and they found that these compounds have excellent inhibition efficiency. Literature survey reveals an increased attention to Schiff base compounds as corrosion inhibitors especially in acidic environments for various metals.[96]

1.4. Solvent Effects

Most of the chemical and biological processes occur in solution phase. The role of solvation in chemistry and biology is obvious. The influence of the solvent on chemical phenomena has been observed for a long time and it has received the attention of researchers from both experimental and theoretical fields related to chemistry. The presence of a solvent influences the outcome of a chemical reaction through the interaction of the local environment with the individual species undergoing the reactions. The solvent, on one level, provides an energy path for the stabilization of energetic products formed during reactions and provides physical barriers to the motion of the reactive species. On a more subtle level, the solvent perturbs the potential energy curves that govern these reactions.[97] Since the solvent species around a solute form a structure that determines the outcome of chemical and/or biological events, the solvent species are not just "spectator" species but are part of the chemical or biochemical process. Solvation has been proved to be of fundamental importance in diverse areas like biological activities and atmospheric processes.[98] Solvated ions appear in high concentrations in living organisms where their presence or absence can fundamentally alter the functions of life. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common[99] and the exchange of solvent molecules around ions in solutions is fundamental in understanding of the reactivity of ions in solution.[100] Solvated ions also play a key role in electrochemical applications simply because the conductivity of electrolytes depends on the ion-solvent interactions.[101] Majority of the chemical reactions are usually performed in solutions and solvents can influence reactions in a number of ways. Solvents may be used as a reaction medium to bring reactants together, as a reactant to react with a solute to make it dissolved and as a carrier to deliver chemical compounds in solutions to their point of use in the required amounts.

Solvents also control the temperature in exothermic and endothermic reactions. In endothermic reactions, heat could be supplied through a heated inert solvent having a high heat capacity while in exothermic reactions, the surplus heat can be removed by allowing the solvent to boil or absorb heat. If reactions involve solid reactants, solvents could be used to create a homogenous reaction phase (i.e., solution) through which the solid reactants can be brought into contact. It is important to select the most appropriate solvent so as to get most effective results or optimum yield of the products. A good solvent should be able to meet all the necessary standards such as it should be an inert to all the reaction conditions, the boiling point of the solvent should be appropriate, at the end of the reaction there should not be any difficulty in its removal and it should dissolve the reagents and reactants. In essence, the reaction rates are influenced by differential solvation of the starting material and the transition state by the solvent. When the reactant molecules proceed to the transition state, the solvent molecules orient themselves to stabilize the transition state. If the transition state is stabilized to a greater extent than the starting material then the reaction proceeds faster. If the starting material is stabilized to a greater extent than the transition state then the reaction proceeds slower. However, such differential solvation requires rapid relaxation (re-orientation) of the solvent (from the transition state orientation back to the ground-state orientation). Thus, equilibrium-solvent effects are observed in reactions that tend to have sharp barriers and weakly dipolar, rapidly relaxing solvents.

1.4.1. Solvation

The term solvation refers to the surrounding of each dissolved molecule or ion by a shell of more or less tightly bound solvent molecules. This solvent shell is the result of intermolecular forces between solute and solvent. During the solvation process, a relatively small amount of solute dissolves in relatively large amount of solvent to form a homogeneous phase through a variety of intermolecular forces such as solvent-solvent, solute-solvent and solute-solute interactions. The solute-solute interactions gradually disappear and replaced by solute-solvent interactions during the dissolving process. The solute molecules will perturb the structure of the solvent when they enter into the solution and they create some more or less ordered solvation shell around themselves. For the dissolving process to be spontaneous, the lowering of the free energy resulting from the solvation must exceed the free energy increase due to the annihilation of the interactions that existed between the solute molecules and between the solvent molecules. If the liberated solvation energy is lower than the lattice energy, then the overall process of dissolution is endothermic and if the solvation energy is higher than the lattice energy, then the overall process is called exothermic.

1.4.2. Preferential Solvation

The solvation phenomena in mixture of solvents e.g., binary, ternary, etc., is more complicated than in pure solvents. In addition to the different types of interactions between solute and solvent, the interactions between solvent mixtures play a significant role in the solvation process. This leads to the large deviation from the ideal behavior expected from the Raoult's law of vapor pressure depression for binary mixture. Solute may induce a significant change in the composition of the solvent mixture in the solvation sphere than the bulk composition. This is generally known as selective solvation or preferential solvation.[102] This phenomenon is graphically represented in figure 1.14.

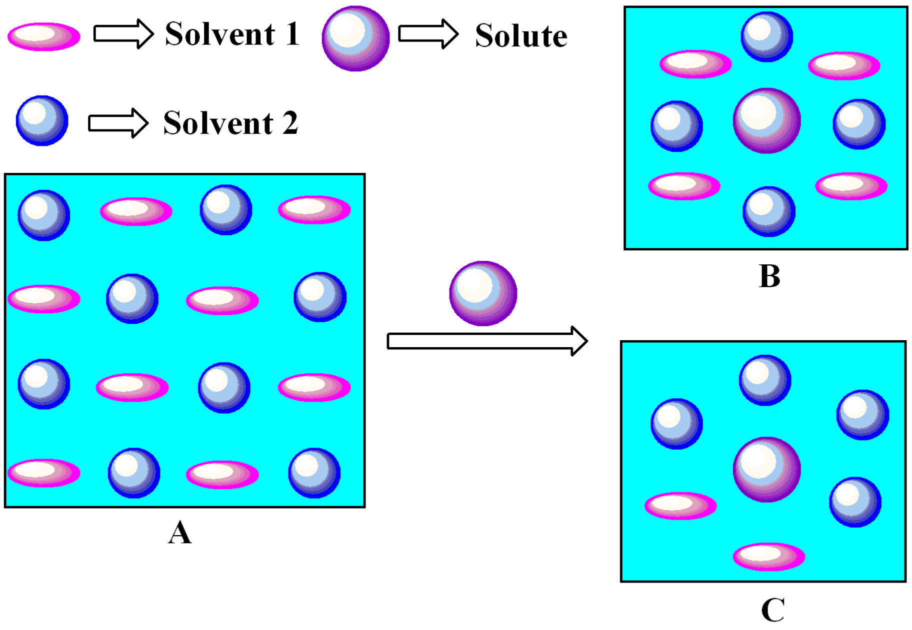

Fig. 1.14. Schematic representation of preferential solvation, A: binary mixture of solvent 1 and solvent 2; B: ideal solvation of the solute; C: preferential solvation of the solute by solvent 1.

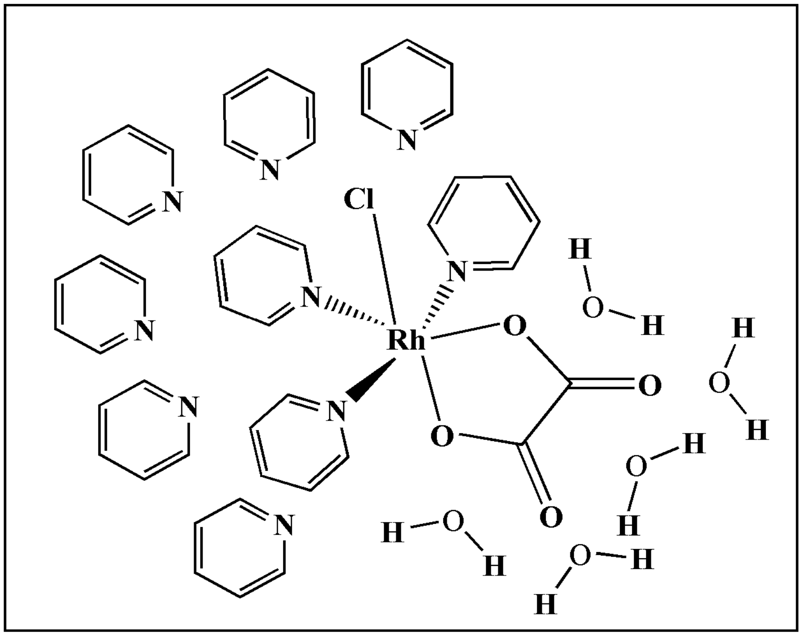

Fig. 1.15. Selective solvation of different parts of chloro-oxalato-tripyridine rhodium(III) complex by pyridine and water.

Solute with a dipole may preferentially be solvated at two different loci with different composition of the binary mixture. This type of selective solvation has been suggested for the solubilization of chloro-oxalato-tripyridine rhodium(III) complex, it is neither soluble in water nor in pyridine but is soluble in 1:1 mixture of the two solvents due to selective solvation of different units, i.e. the pyridine unit of the complex by pyridine and the oxalate unit by water.[102] The selective solvation of the complex is depicted in figure 1.15.

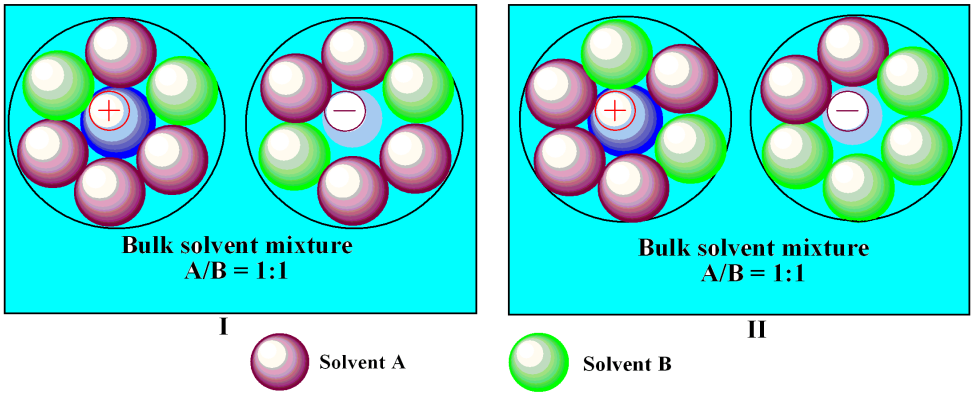

Fig. 1.16. Schematic model for the selective solvation of ions by one component of a binary 1:1 mixture of the solvents A and B: (I) Homoselective solvation: both ions are preferentially solvated by the same solvent A; (II) heteroselective solvation: the cation is preferentially solvated by A and the anion by B.

When in a mixture of two solvents both ions of a binary salt are solvated preferably by the same solvent, the solvation is referred to as homoselective solvation. Similarly, if the cation and the anion are preferably solvated by different solvents, the solvation is referred to as heteroselective solvation and is shown in figure 1.16.[102] Preferential solvation commonly results from specific (e.g., hydrogen-bonding) and nonspecific (dielectric enrichment)[103] solute-solvent interactions. It can also be a result of solvent-solvent interactions.[104]

1.5. Ion-Solvent or Solute-Solvent Interaction

The process of solvation of a solute by solvent molecules is of primary importance in many branches of chemistry such as chemical syntheses or complex formation processes. Thus solvation of ions or solutes and its source in terms of solute-solvent or ion-solvent and solvent-solvent interactions constitute an important area in chemistry, since solute-solvent or ion-solvent interactions play a major role in controlling the chemical reaction rate, chemical equilibrium position, etc. Solvent affects both molecular structure and electronic structure of solutes. Knowledge of their interactions helps in better understanding of the profile of solutes or solvents, i.e., whether the added solute modifies or distorts the structure of the solvent.[105] For a particular chemical reaction it was shown that the reactivity is influenced by the preferential solvation of the reactant and/or transition state through non-specific and specific solute-solvent or ion solvent interactions. In the solvation process, changes in energy of transition states are of critical importance. In order to analyze solute-solvent or ion-solvent interactions, great interest has been paid to the behavior of solutions of electrolytes and non-electrolytes in pure solvents and binary solvent mixtures.[106, 107]

Ion-solvent or solute-solvent interactions can be defined by starting with a solid ionic crystal or a neutral solid and then reducing the forces holding the ions together in the crystal or solvation of neutral molecules by some kind interactions between the solute molecules and the solvent. A stage is reached when the inter-ionic forces in case of ionic crystal are so weakened that the ions acquire a new degree of freedom that produces the mobile ions due to freedom of transnational motion. All these alterations are possible with the addition of a solvent that can influence the inter-ionic forces within the crystal and there is a considerable energy of interaction between the ions and the solvent molecules. These interactions are collectively termed as ion-solvent interactions. A schematic representation of dissolution of an ionic crystal by the action of a solvent is shown in figure 1.17.

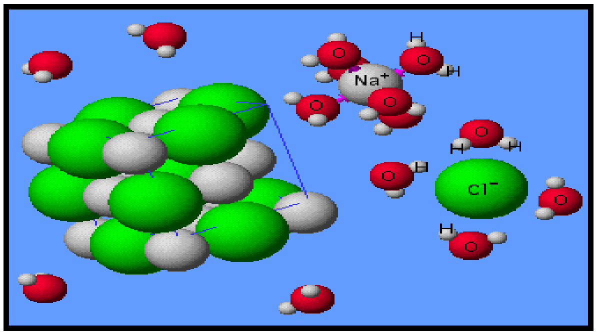

Fig. 1.17. Dissolution of an ionic crystal in a solvent.

Ions orient dipoles. The spherically symmetrical electric field of the ion may tear solvent dipoles out of the solvent lattice and orient them with appropriate charged end towards the central ion. Thus, viewing the ion as a point charge and the solvent molecules as electric dipoles, ion-dipole forces become the principal source of ion-solvent interactions. The majority of reactions occurring in solutions are chemical or biological in nature. It was presumed earlier that the solvent only provides an inert medium for chemical reactions. The significance of ion-solvent interactions was realized after extensive studies in aqueous, non-aqueous and mixed solvents were undertaken.[108, 109]

The organic solvents have been classified based on the dielectric constants, organic group types, acid base properties or association through hydrogen bonding,[109] donor-acceptor properties,[110] hard and soft acid-base principles,[111] etc. As a result, the different solvents show a wide divergence of properties ultimately influencing their thermodynamic, transport and acoustic properties in presence of electrolytes and non-electrolytes in these solvents. The determination of thermodynamic, transport and acoustic properties of different electrolytes or non-electrolytes in various solvents would thus provide important information in this direction. Henceforth, in the development of theories of electrolytic solutions, much attention has been devoted to the controlling forces- 'ion-solvent interactions' in infinitely dilute solutions wherein ion-ion interactions are almost absent. By separating these functions into ionic contributions, it is also possible to determine the contributions due to cations and anions in the solute (ion)-solvent interactions. Thus ion-solvent interactions play a key role in understanding the physico-chemical properties of solutions.

1.6. Ion-Ion or Solute-Solute Interaction

Ion-solvent interactions are only a part of the story of an ion related to its environment. The surrounding of an ion sees not only solvent molecules but also other ions. The mutual interactions between these ions constitute the essential part- 'ion-ion interactions'. The degree of ion-ion interactions affects the properties of solution and depends on the nature of electrolyte under investigation. Ion-ion interactions, in general, are stronger than ion-solvent interactions. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but ion-solvent interactions or ion-solvation still remains a complex process. As proton transfer reactions are particularly sensitive to the nature of the solvent and it has become clear that the solvents significantly influence a majority of the solutes. Conversely, the nature of the strongly structured solvents, such as water, is substantially modified by the presence of solutes.

1.7. Object and Application of the Research work

In recent years there has been an increasing interest in the study of physico-chemical properties of solute-solvent systems. The physico-chemical properties play a pivotal role in interpreting the intermolecular interactions among mixed components and efforts in recent years have been directed at an understanding of such properties at microscopic and macroscopic levels. In order to gain insight into the mechanism of such interactions thermodynamic, transport and acoustic studies on mixed solvent systems are highly useful. Most chemical and biological reactions prevail in solution phase and the understanding of chemical reactions is largely based on the behavior of reactants in the studied solutions. Solvent parameters such as dielectric constant, density, viscosity and refractive index are useful parameters in elucidating various solvent properties for explaining solvent effects in many chemical processes. Due to complexity of intermolecular interactions, the development of a generally valid model for solution is not an easy task. Thus, models with non-specific solute-solvent interactions like van der Waals interactions are mainly dealt with.[112] Many biological processes including transporting, signaling, metabolism, etc., are also controlled by solvation.[113,114] Several theoretical treatments have been developed to link quantitatively the solvent effects to the bulk properties of solvent. The simplest model amongst these treatments is given by Onsager[115] and Kirkwood.[116] Various approaches were suggested over the years for ascertaining the number of solvent molecules closely associated with ions and the number of those solvent molecules released from the solvation shell of ions to the bulk on ion pair formation. Certain ions, such as transition metal cations, have geometrically well-defined first solvation shells[117] but they are further solvated in a second concentric solvation shell with much less well-defined geometries and solvation numbers. However most ions are solvated in a not clearly defined manner, not only in the closest vicinity of the ions but also beyond that, due to non-directional electrostatic ion-dipole or ion-induced dipole interactions.[118] In solution chemistry the way for proper understanding of the different phenomena regarding the molecular interactions forms the basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents. Estimates of ion-solvent interactions can be had thermodynamically and also from the determination of partial molar volumes, viscosity *B*-coefficient and limiting ionic conductivities, etc.

The solute-solute and solute-solvent interactions have been subject of wide interest in many area of chemistry. The influence of these solute-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in diverse areas such as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction.[119] Knowledge of ion-solvent or solute-solvent interactions in non-aqueous solutions is very important in many practical problems concerning energy transport, heat transport, mass transport, reaction kinetics and fluid flow. Besides finding applications in engineering branch, the study is important from practical and theoretical point of view in understanding liquid theories. The non-aqueous systems have been of immense importance to the technologist and theoretician as many chemical processes occur in these systems.

In recent years, there has been increasing interest in the behavior of some Schiff bases and their metal complexes in non-aqueous and mixed solvents with a view to investigate solute-solute and solute-solvent interactions under varied conditions. Although in recent years considerable attention has been paid to the synthesis, characterization and application of Schiff base metal complexes,[120] much less works are reported regarding their thermodynamic properties in solution phase. A proper understanding of solution properties may help in elucidating their behavior in solution phase. Literature survey reveals that only a few works on the thermodynamic properties of Schiff bases in pure and mixed solvent media have been reported. Shekaari *et al.*[121] have reported the thermodynamic properties of salophen Schiff base in ionic liquid medium. They have also studied the thermophysical properties of some

Schiff base ligands in various solvent mixtures.[122, 123] Apart from these, Baluja *et al.*[124] has reported the acoustical studies of some Schiff bases in 1,4-dioxane and dimethylformamide solutions. Mishra *et al.*[125] have reported the ultrasonic studies of some 3*d* metal complexes of Schiff bases. Ergin[126] studied the equivalent conductivities and ion association constants of some tris-(ethylenediamine)Co(III) complexes in dimethyl sulfoxide at different temperatures. Ikeuchi *et al.*[127] have reported the densities and viscosities of Tris(acetylacetonato)Co(III) complex in various solvents.

Studies on thermodynamic properties of these metal complexes in solution phase may provide valuable information regarding their solution behavior and appropriate understanding of their physico-chemical properties would enable chemists to choose solvent that will (i) enhance the rate of chemical reactions, (ii) solubility during the chemical process and (iii) reverse the direction of equilibrium reactions. Thus studies on transport properties of Schiff base metal complexes along with the thermodynamic properties would give valuable information about different molecular interactions in their solutions. The influence of these solute-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving complex ions. The changes in ionic solvation have important applications in diverse areas such as organic and inorganic synthesis, studies of reaction mechanisms and extractions. Also it is apparent that the real understanding of the molecular interactions in solution phase is a difficult task. The aspect embraces a wide range of topics but we have embarked on a series of investigations based on the volumetric, viscometric, refractometric, and spectrophotometric methods to study the chemical nature of the structure of solutes and solvents and their mutual and specific interactions in solution.

1.8. Importance and Scope of the Physico-Chemical Parameters

The solvation of solute is of primary importance in many fields ranging from synthetic chemistry to biological phenomenon. It is well known that the solvation process is complex since the solvation process is affected by the behavior of both solute and solvent resulting from their molecular structure as well as hydrophilic-hydrophobic properties.[128] Fundamental thermodynamic and thermophysical properties are essential sources of information necessary for a better understanding of the non-ideal behavior of complex systems, because of the fact that physical and chemical effects are caused by molecular interactions, intermolecular forces, etc. of unlike molecules.[129] The study of physico-chemical properties involve the interpretation of the nature of intermolecular interactions among the mixed components. The interactions between molecules can be established from a study of some physical parameters such as density, viscosity, conductance, refractive index as well as electronic spectroscopy and infrared spectroscopy, etc.[130, 131] From a practical point of view, these properties are necessary for the development of thermodynamic models required in adequate and optimized processes of the chemical, petrochemical, pharmaceutical and other industries. Measurement of thermodynamic and transport properties such as density and viscosity of solutes in pure solvent and binary solvent mixtures at various temperatures are useful to understand the nature of interactions occurring in solution and helpful to practical chemical engineering purposes.[132]

Density of solution and related volumetric properties are essential for theoretical as well as practical aspects. The density is useful in conversion of concentration unit and in the investigation of interactions in solutions. The density of fluid is an important parameter for research and industrial fields. Density is used to solve a variety of problems such as quality control in the production of industrial liquids or concentration determination in the food and beverage industries as in measuring sugar and alcohol concentration. The density data are used to calculate the apparent molar volumes and partial molar volumes at infinite dilution. Apparent molar volumes and partial molar volumes give a direct measure for displacement of solvent by solute and thus reflect the compatibility of the solute with the solvent. Studies of the apparent molar volumes and partial molar volumes of electrolytes and non-electrolytes are used to examine the ion-ion/solute-solute, ion-solvent/solute-solvent and solvent-solvent interactions. In addition, density is required for the estimation of other chemical properties such as molar refraction and viscosity, etc.

Knowledge of viscosity of fluids is essential in most engineering calculations where fluid flow, mass transport and heat transport are important factors. Viscosity is the property of a fluid liquid or gas that mainly characterizes its flow behavior.

Viscosity varies with temperature and in general, the viscosity of a simple liquid decreases with increasing temperature and vice-versa. Viscosity data provides valuable information about the nature and strength of forces operating within and between the unlike molecules. Recently the employment of computer simulation of molecular dynamics has lead to significant improvement towards a successful molecular theory of transport properties in fluids and a proper understanding of molecular motions and interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents.[133, 134] Viscosity measurement has also proved to be a valuable tool for the physical chemist, since the viscosity coefficient is profoundly influenced by the size, shape and arrangement of the molecules. Also a potentially rewarding approach in the study of ion-solvent interaction involves the estimation of the free energy and related thermodynamic quantities for the transfer of individual ion or solute from one solvent to another.[135]

The study of physico-chemical behavior of solute in solution from refractive index measurement has gained much importance. In electrolytic solution ion-ion, ion-solvent and solvent-solvent interactions can be fully understood from the refractive index studies.[136] Refractive index is one of the important properties of a liquid or solution and refractive index can be measured easily with a high degree of accuracy. The molar refractivity reflects arrangements of the electron shell of ions in molecules and yields information about the electronic polarization of ions. The molar refractivity measures the change in the properties due to polarization or deformation of the electron shells of ions under the influence of neighboring surroundings.[137]

Again in a solute-solvent system the electronic interactions of various electronically excited states of the solute and solvent molecules may be also substantial. When absorption spectra are measured in solvents of different polarity, it is found that these solvents modify positions, intensities and shapes of the absorption bands. These changes are results of intermolecular solute-solvent interaction forces such as ion-dipole, dipole-dipole, dipole induced dipole, hydrogen bonding, etc. The interaction force tends to alter the energy difference between ground and excited state of the absorbing species containing the chromospheres. Thus, solvent effects on absorption spectra can be used to provide information about solute-solvent as well as solvent-solvent interactions. These facts, therefore, prompted us to undertake the study of physico-chemical properties of Schiff base metal complexes in pure and mixed solvent media. Furthermore, the thermodynamic properties derived from experimental density, viscosity and refractive index data and subsequent interpretation of the nature and the strength of intermolecular interactions helps in testing and development of various theories of solution.

1.9. Importance of Solutes and Solvents Used

The importance of solutes and solvents used in the works embodied in this thesis is outlined below.

1.9.1 Solutes

Basically transition metal Schiff base complexes such as Co^{II}(salen), Fe^{III}(salen)Cl, [Cr^{III}(salen)$(H_2O)_2$]Cl, Zn^{II}(salianil), [Cu^{II}-(1,2-diaminophenyl)-N, $N^{/}$-bis-(2-pyridinecarboxaldimine)] have been used as solutes. Salen complex of Co(II), i.e., N, $N^{/}$-bis(salicylaldehyde)-ethylenediimino cobalt(II), abbreviated as Co(salen) is a tetradentate Schiff base complex. Tsumaki[138] reported that solid samples of Co(salen) can bind oxygen reversibly. Since then there has been a continuous and increasing interest in this complex and its derivatives as well as in other dioxygen binding Schiff-base Co(II) complexes such as Co(acacen) and Cobaloxime. In the 1940's Cobalt(II) complexes with salen type ligands were extensively studied for oxygen storage for military purposes.[139-140] They are also considered to be models for many active centers of enzymes, Co(salen) complexes catalyze the oxidation of certain p-substituted phenolics to p-benzoquinones with dixoygen as oxidant.[141] Co(salen) has a low spin configuration with square planar donor atom symmetry. Ochai *et al.*[142] have suggested from their kinetic and thermodynamic studies that oxygenation of Co(salen) is possible when solvent with high donor ability such as DMSO, pyridine, etc. are incorporated as coaxial ligand. They also indicated that the oxygenation of Co(II)L complex forms either $O_2 \cdot CoL$ (1:1 adduct) or $LCo \cdot O_2 \cdot CoL$ (2:1 adduct), of which the 2:1 adduct is thermodynamically favored.[142] Co(salen) can be potentially applied for dioxygen-storage and dioxygen-separation processes.[143] They can also be used as a DNA cleavers.

The coordination compounds of iron containing the salen ligand have been known since 1933 and have been extensively studied due to their specific physical and biological properties.[144, 145] The great potential of the $[Fe(salen)]^+$ cations lies in its ability to catalyze redox reactions in organic syntheses,[146] e.g., oxidation, aldol condensation and epoxidation, etc. In addition to these, other practical applications have recently been reported such as its use in sensing electrodes for glucose or uric acid or electrochemical sensors for the determination of NO in solution.[147] Fe(III) salen and Fe(III) porphyrins bear some structural and chemical similarities. As in Fe(III) porphyrins, the Fe atom of Fe(salen)Cl is penta- coordinated in a pyramidal geometry with the tetradentate ligand in square planar coordination, the fifth chloride ligand is an apical position and open sixth coordination site. Fe(III) salen, analogously to Fe(III) porphyrins, shows catalytic activity towards the bland oxidation of hydrocarbons and undergoes electron transfer reactions mimicking the catalytic functions of peroxidases.[148] Fe(salen) is also used in the application of electro-catalytic reduction of hydrogen peroxide and oxygen and also DNA cleavage.[149]

Among the many transition metal ions Cr(III) is an essential nutrient that has been implicated as glucose tolerance factor (GTF) in the maintenance of normal carbohydrate and lipid metabolism.[150] The Schiff base complex of Cr(III), $[Cr(salen)(H_2O)_2]Cl$ is used as a new kind of GTF models in diabetic rats.[151] The cation, $[Cr(salen)(H_2O)_2]^+$ can also be used as a DNA cleaver. This Cr(III) Schiff base complexes have been shown to bring about apoptosis in lymphocyte cell cultures.[152] Organic electroluminescent (EL) devices have attracted a large interest in recent years due to flat-panel display applications. Among many classes of Zn(II) complexes as electroluminescent materials, complexes with organic ligands containing the azomethine C=N bond and a donor oxygen or nitrogen atoms are of special interest as because these systems exhibit intense luminescence in the blue region of visible spectrum.[153] Many salicylaldehyde-derived Schiff base metal complexes have been investigated as EL materials. (Salicylaldehyde-anil) Zn(II) complex were used as light emitting material in EL device.[154]

A number of aldehydes and ketones have been found to react with o-phenylenediamine leading to the formation of an azomethine linkage exhibiting a broad spectrum of biological activities. During the last decade the coordination chemistry of Schiff bases derived from 2-pyridinecarboxaldehyde has received much attention.[155] Recently, there has been tremendous interest in studies related to the interaction of transition metal ions with nucleic acid because of their relevance in the development of new reagents for biotechnology and medicine.[156] There has also been substantial interest in the rational design of novel transition metal complexes that can bind and cleave duplex DNA with high sequence and structure selectivity. The Cu(II) complex of 1, 2-diaminophenyl-N, $N^{/}$-bis-(2-pyridinecarboxaldimine) has been reported to be a potential DNA cleaver.[157]

1.9.2. Solvents

Methanol, acetonitrile, N, N-dimethylformamide, dimethyl sulfoxide, water and 1,4- dioxane were chosen as main solvents in the research works embodied in this thesis. The study of these solvents, in general, is of great interest because of their wide applications as solvents and solubilizing agents in many industries ranging from pharmaceuticals to cosmetics.

1,4-dioxane is very hygroscopic and miscible in all proportions with water. Its dielectric constant and dipole moment are 2.209 and 0.45 D, respectively at 25 ^{o}C. However, its dipole moment rises with increase in temperature suggesting formation of boat form.[158] N, N- dimethylformamide is a non-associative aprotic protophilic solvent with a liquid range of –60 to 153 ^{o}C, low vapour pressure and good solubility for a wide range of substances. It is slightly basic and a popular solvent in visible and near UV spectrometry (>270 nm) and for polarographic work. It is also used in the separation of saturated and unsaturated hydrocarbons and serves as solvents for vinyl resins, acid gases, polyacrylic fibres and catalysts in carbonylation reaction as well as in organic syntheses. It has also been used as a model for peptide linkage in studies of protein denaturation.[159, 160]

General Introduction

Alcohols have varied applications in chemical and cosmetic industries. These are useful in enology and as alternative energy sources.[161] A knowledge of their physico-chemical characteristics helps to understand their behavior in a better way. Methanol is used as solvent for paints and varnishes, antifreeze for automobile radiators, motor fuel, denaturant for ethanol, etc. It is obtainable commercially in adequate purity for most purposes, the principle impurity being up to 0.05% water that is removed by distillation or by use of molecular sieves and anhydrous calcium hydride. However, it is worth mentioning that 1,4-dioxane differs from alcohols in its behaviour towards water. Alcohols are usually structure makers whereas 1,4-dioxane acts as a net structure breaker.[162]

Dimethyl sulfoxide, an aprotic solvent having both polar and non-polar groups, is an important solvent in chemistry, biotechnology and medicine for the dissolution of various substances and as an anti-depressing agent for living cells. It has useful properties for application in organic syntheses[163] and in electrochemical systems.[164] It's dipolar character of makes it a good nucleophilic agent and it tends to enhance the reaction rates and yields of many organic syntheses by stabilizing charged intermediates in the reaction. It's polarity and physical properties, coupled with the stability of some potentially useful electrode materials, makes this solvent theoretically promising for high-energy density battery applications.

Acetonitrile molecules are aprotic and highly polar (μ = 3.7 D at 25 °C) with their dipoles oriented anti-parallel to each other and the strongly ordered in structure due to dipole-dipole interactions.[165] Water is the most widely used solvent in the chemical industries, since it is the most physiological and best tolerated excipient. However, in some cases, water cannot be used as a solvent because the active substance or the solute is insoluble or slightly soluble in it. The non-aqueous solvents with common characteristics of being soluble or miscible in water are thus used. Such solvents can be used to prepare binary mixtures and they can serve different purposes such as increasing water solubility, modifying the viscosity, absorption of the dissolved substance, etc.

1.9.3. Mixed Solvents

Mixed solvents rather than single pure liquids are of utmost practical importance in most of chemical and industrial processes as they provide a wide range of mixtures of two or more components in varying proportions so as to permit continuous adjustment of desired properties of medium.[166] Design of mixed solvents of required solvating power with suitable liquid state range to predict the solubility and chemical stability of solutes is a highly interdisciplinary field of research in condensed matter physics, chemistry, biology, pharmaceutical and soft material sciences.[167] Water is the best-known polar solvent with a structure determined to a great extent by the hydrogen bonding between its molecules. Other well known protic solvents are the alcohols that possess one acidic hydrogen atom on the -OH group.[168] Water as well as methanol is a continuum random network of hydrogen bonds and this determines the special physical structure of both the liquids. Their unusual properties are a result of this network structure.[169] Alcohols may be considered as derivatives of water with one hydrogen atom replaced by an alkyl group. The presence of an unshared electron in the oxygen outer shell imparts an important feature in the structure of alcohols. Alcohols become water-like in their physical properties as their ratio of hydroxyl groups to the C–H bonds increases. Water-methanol mixtures show many interesting non-ideal properties which can be linked to rather strong interspecies interactions leading to significant changes in the structure and dynamics of these mixtures at molecular level.[170] In alcohol-water system, mixing process is dominated by the entropy contributions to the mixing process. Due to the strong hydrophilic part these smaller alcohols are completely soluble in water. However it is well known from experimental results that the hydrophobic part contributes substantially to the thermodynamic properties of water-alcohol mixtures. The hydrophobic parts of these molecules are also responsible for the minimum in partial volume for methanol in water-methanol mixtures.[171] Dimethyl sulphoxide plays an important role in biology as a cryoprotective agent and has also widespread pharmacological application as a solvent.[172] Dimethyl sulfoxide and its mixtures with other solvents (particularly water) have aroused much interest among scientists in the last few decades.[173] The effects of dimethyl sulfoxide on water structure have been proposed and considered important to understand the functions of dimethyl sulphoxide in biological systems. Many observations suggest that (dimethyl sulphoxide + water) complexes form by hydrogen bonding of water protons to the SO group. The strong non-ideality of the variation of the dielectric constant with composition[174] is paralleled by similar positive deviations of viscosity, density and reflective index[175] and negative deviations of heat mixing. The maximum deviations occur at mole fraction of 0.30 to 0.40, suggesting the probable existence of stable DMSO hydrate or at least strong hydrogen bonded association between the two molecules.[176] On the other hand, it is found that DMSO enhances the hydrogen-bonding network of water, possibly through the ''hydrophobic'' hydration of the methyl groups.[177]

Acetonitrile and N, N- dimethylformamide are versatile compounds because of their wide range of applicability as solvents in chemical and technological processes.[178] They have nearly the same dielectric constants ($\varepsilon_{r,\mathrm{ACN}} = 36.0$, $\varepsilon_{r,\mathrm{DMF}} = 37.6$).[179(a)] These solvents have different Gutmann donor numbers (ACN: 14.1, DMF: 26.6),[179(b)] making them considerably different in their solvating capacities. While N, N- dimethylformamide solvates only the cations, acetonitrile strongly solvates both the cations and the anions. Mixtures of acetonitrile and N, N-dimethylformamide is, therefore, expected to be a good solvent for the study of solvation process of solutes.

Binary systems of 1, 4-dioxane with alcohols are interesting from a consideration of the low polarity of 1, 4-dioxane and for the type of interactions between the components of the mixture. 1, 4-dioxane can form hydrogen bonds with methanol and due to this the self-association of alcohols is reduced or perturbed in favor of hydrogen-bonded structures when mixed together leading to intermolecular association between methanol and 1,4-dioxane molecules. Papanastasiou *et al.*[180] suggested that the binary mixtures of 1,4-dioxane and methanol forms two intermolecular complexes (1,4-dioxane : methanol) of the types 1:1 and 1:2 and that 1, 4-dioxane can associate through hydrogen bonds by either of its two oxygen atoms.

Tetraalkylammonium ions ($\mathrm{R_4N^+}$) find much use in various areas of chemistry, e.g., in phase-transfer catalysis, as hydrophobic cations used for precipitating large anions or as a series of ions with properties that gradually change with their size. The tetraalkylammonium cations are generally classified as 'hydrophobic', but the manifestation of hydrophobicity is not the same for all of the relevant properties.[181] Solutions of tetraalkylammonium salts have been of widespread interest to solution chemists during recent years, mostly because of the unusual structural effects that these salts impart on solvent structure. In methanol solution, tetrabutylammonium bromide shows net methanol structure breaking ability.[182] Thus the thermodynamic studies of solvent mixtures consisting of salts like tetrabutylammonium bromide can give better insight into the effect of electrostatic and hydrophobic interactions in the studied systems.

In the past few decades, there has been growing concern about the environmental effects of the toxic releases from chemical industries. This has led to the search for "greener" alternatives for volatile organic compounds. Ionic liquids are one of the more popular alternatives, mainly due to their insignificant vapor pressure, thermal and chemical stabilities, and excellent recyclability.[183] Ionic liquids are salts composed of voluminous organic ions with asymmetric, flexible and charge-delocalized molecular structures. Because of their unique properties and varieties, ionic liquids are considered as high-performance fluids for a wide range of engineering and material science applications both in processes like syntheses, catalyses, separations and in devices such as optical components, lubricants, batteries, etc. They are also considered as promising alternative media for a more sustainable chemical industry and are often referred to as green solvents.[184] The binary mixtures of such trialkyl-substituted imidazolium-based ionic liquids with organic solvents are interesting for fundamental research for understanding the relation between structure and mixture properties, especially by comparing them with corresponding dialkyl-substituted mixtures.[185] Successful and effective application of ionic liquids as solvent media in organic transformations, extractions, electrochemical and microbiological processes require a precise knowledge of intermolecular interactions of these compounds with other conventional chemical systems. The chemical constitution of ionic liquids determines the nature of intramolecular and intermolecular interactions and thus the macroscopically observable properties such as thermodynamic and transport properties, etc.[186, 187]

1.10. Method of Investigation

The phenomena of solute-solute, solute-solvent and solvent-solvent interactions are intriguing. It is desirable to explore these interactions using different experimental techniques. For physico-chemical investigation important methods of densitometry, viscometry, refractometry and UV-visible spectroscopy were used in the research works embodied in this thesis. Thermodynamic properties of solutions are not only useful for estimation of feasibility of chemical reactions in solution but they also offer one of the better methods of investigating the theoretical aspects of solution structure. Thermodynamic properties like apparent molar volume, partial molar volume, partial molar expansibility, etc. obtained from density measurements are generally convenient parameters for interpreting solute-solute and solute-solvent interactions in solution. The apparent and partial molar volumes of electrolyte solutions have proved to be very useful tools in elucidating structural interactions (i.e., ion-ion or solute-solute ion-solvent or solute-solvent, and solvent-solvent interactions) occurring in solution. The viscosity of electrolyte and non-electrolyte solutions is another important parameter to study their solution behavior. The temperature and concentration dependence of viscosities of electrolyte and non-electrolyte solutions help to understand ion-solvent or solute-solvent (solvation) and long-range ion-ion electrostatic interactions. The change in solvent viscosity by the addition of electrolytes is attributed to inter-ionic and ion-solvent effects. The viscosity *B*-coefficients gives a satisfactory interpretation of ion-solvent or solute-solvent interactions such as the effects of solvation, preferential solvation and long range structure-breaking or structure-making capacity of the solutes. Refractometric studies also render an insight into the different molecular interactions prevailing in solutions containing mixed solvent systems and helps in understanding of the behavior of the solutes with different solvents. In addition to these, UV-visible spectroscopy is used to support the results obtained from density, viscosity and refractive index measurements.

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CHAPTER II

Physico-Chemical Parameters Studied in Solution Chemistry

The development of our knowledge about solutions goes hands in hands with the developments in chemistry since times unknown. The alchemist's search for a universal solvent "Alkahest" provided ancient chemists experiences that arose the earliest chemical rule: "like dissolves like".[1] Raoult systematically studied the effects of dissolved nonionic substances on the freezing and boiling point of liquids and his observation that the vapour pressure of a solvent above a solution is proportional to the mole fraction of the solvent in solution is known as Raoult's law.[2] The difficulty in explaining the effects of inorganic solutes on the physical properties of solutions lead in 1884 to Arrhenius's theory of incomplete and complete dissociation of ionic solutes into cations ans anions in solution. Arrhenius derived his dissociation theory from a comparison of the results obtained from measurements of conductivity and osmotic pressure of dilute electrolyte solutions.[3] The further development of solution chemistry reminds us the pioneering work of Ostwald (1853-1932), Nernst (1864-1941), Lewis (1875-1946), Debye (1884-1966), Bjerrum (1879-1958) and E. Huckel (1896-1980) and the likes.[1]

Anyway solution chemistry stands as an important branch of chemistry wherein studies on the change in properties that arise when one substance dissolves in another substance is made. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. The mixing of different solute or solvent with another solvent/solvent mixtures gives rise to solutions that generally do not behave ideally, i.e., deviate from Raoult's law. This deviation from ideality is expressed in terms of many thermodynamic parameters, by excess properties in case of liquid-liquid mixtures and apparent molar properties in case of solid-liquid mixtures. These thermodynamic properties of solvent mixtures corresponds to the difference between the actual property and the property if the system behves ideally and thus are useful in the study of molecular interactions and arraangements. In particular, they reflect the interaction that take place between solute-solute, solute-solvent and solvent-solvent species. However, the exact structure of the solvent molecules in solution is unknown with certainity many times. The addition of an ion or solute modifies the solvent structure to an extent that can also modify or perturb the solute molecules. The extent of solute (ion)-solvation is dependent upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. The ion-solvent interactions can also be studied from the thermodynamic point of view where the changes in free energy, enthalpy and entropy, etc. associated with a particular reaction can be qualitatively and quantitatively evaluated by using various physico-chemical techniques and analysis of the data on physico-chemical properties can help to reach conclusions regarding the factors associated with the ion-solvent interactions can be worked out.

Such phenomena thus pave the path for research in solution chemistry to elucidate the nature of interaction through experimental studies involving densitometry, viscometry, conductometry, refractometry and other suitable methods like UV-Visible, infrared and NMR spectroscopy. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated and thus the present research work is intimately related to the studies of solute-solute and solvent-solvent interactions of some Schiff base transition metal complexes in some industrially and biologically important solvent systems.

2.1. Density

The physico-chemical properties of solvent mixtures have attracted much attention from both theoretical and engineering applications points of view. Many engineering applications require quantitative data on the density of solvent mixtures. Such properties also provide information about the nature and molecular interactions between liquid mixture components. The volumetric information includes 'Density' as a function of mass, volume and mole fraction and excess volumes of mixing. One of the well-recognized approaches to the study of molecular interactions in fluids is the use of thermodynamic methods. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. Fundamental properties such as enthalpy, entropy and Gibbs energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these macroscopic properties in terms of molecular phenomena is difficult. Sometimes higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. Various concepts regarding molecular processes in solutions like electrostriction,[4] hydrophobic hydration,[5] micellization[6] and co-sphere overlap during solute-solvent interactions[7] to a large extent have been derived and interpreted from the partial molar volume data of many compounds.

2.1.1. Partial Molar Volumes

According to phase rule: $F = C - P + 2$, for a single phase and a one component system, $F = 2$. This means minimum two properties of a 'one component one phase' system must be known to specify its state. These properties are usually pressure and temperature since these variables can be controlled easily. Similarly for a two component system, $F = 3$. Hence for a two-component system, any extensive thermodynamic property Y (such as V, G, H, S, etc.) can be expressed as:

$$Y = f(P,T,n_1,n_2) \tag{1}$$

where n_1 and n_2 are mole numbers of the solvent and the solute, respectively and the total differential becomes,

$$\begin{aligned} dY = {} & (\partial Y/\partial P)_{T,\,n_1,n_2}\,dP + (\partial Y/\partial T)_{P,n_1,n_2}\,dT \\ & + (\partial Y/\partial n_2)_{P,T,n_1}\,dn_1 + (\partial Y/\partial n_1)_{P,T,n_2}\,dn_2 \end{aligned} \tag{2}$$

The partial molar property $\overline{Y}_i$ is defined as:

$$\overline{Y}_i = (\partial Y/\partial n_i)_{P,T,n_j} \tag{3}$$

At constant temperature and pressure equation (1) becomes,

$$Y = f(n_1,n_2) \tag{4}$$

and consequently the total differential becomes,

$$dY = (\partial Y / \partial n_2)_{P,T,n_1} dn_1 + (\partial Y / \partial n_1)_{P,T,n_2} dn_2 \qquad (5)$$

Equation (5) can be written more compactly as:

$$dY = \overline{Y}_1 dn_1 + \overline{Y}_2 dn_2 \qquad (6)$$

Of all the extensive thermodynamic properties, the volume is the easiest to visualize and the molar volume of a pure substance can be determined simply from density measurements. This visualization also holds true for partial molar volume defined as:

$$\overline{V_i} = (\partial V / \partial n_i)_{P,T,n_j} \qquad (7)$$

thus equation (6) becomes,

$$dV = \overline{V_1} dn_1 + \overline{V_2} dn_2 \qquad (8)$$

and its integral form is:

$$V = n_1 \overline{V_1} + n_2 \overline{V_2} \qquad (9)$$

For an ideal solution, its volume is just the sum of the molar volumes of the solute and the solvent, e.g., benzene and toluene solution.

$$V = n_1 V_1^* \; n_2 V_2^* \qquad (10)$$

where V_1^* and V_2^* are molar volumes of the solvent and the solute, respectively. But for a non-ideal solution, e.g., water and ethanol solution, according to equation (9) it is the partial molar volumes that are additive or extensive. Thus partial molar volume of a component is not equal to its molar volume and partial molar volumes of components vary with composition of the mixture.

2.1.2. Apparent Molar Volume

The experimental determination of partial molar volume is quite simple and involves the careful measurement of the densities of solutions of known concentrations. The calculation is simplified by the use of a related quantity called apparent molar volume (ϕ_V); it is the volume due to added solute per mole in the solution.

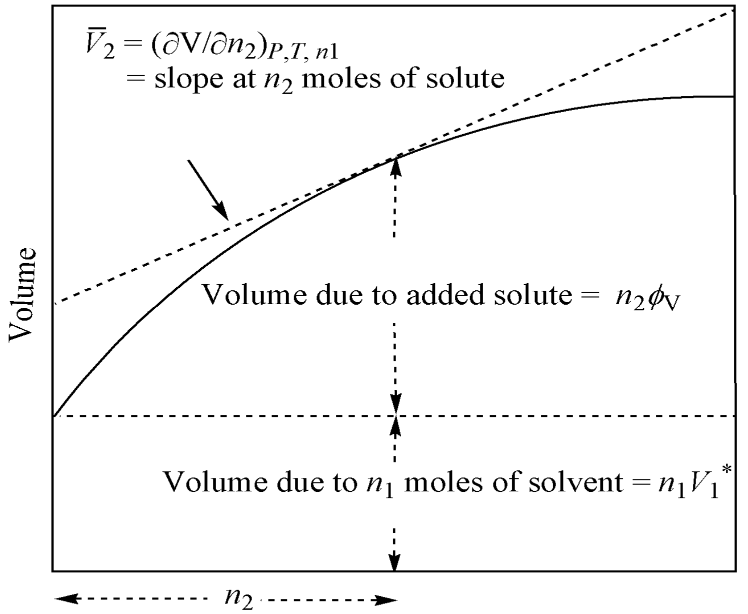


Fig. 2.1. Dependence of the total volume of a solution on the volume of the pure solvent and the apparent molar volume (ϕ_V) of the solute.

Figure 2.1 depicts the volume changes of a solution as n_2 moles of a solute are added to a fixed n_1 moles of a solvent and shows that apparent molar volume (ϕ_V) is,

$$\phi_V = \frac{V_{\text{solution}} - V_{\text{solvent}}}{\text{moles of solute}} = \frac{V - n_1V_1^*}{n_2} \tag{11}$$

and the volume of the solution at any particular added n_2 moles of the solute is given by:

$$V = n_1V_1^* + n_2\phi_V \tag{12}$$

However, it does not make any sense to define apparent molar volume for the solvent because number of moles of both the solute and solvent can't be held constant simultaneously. The apparent molar volume can be measured easily and it gives estimates of the partial molar volumes of both the solute and solvent. Partial differentiation of equation (12) with respect to n_2 at constant n_1 gives the partial molar volume of the solute,

$$\overline{V}_2 = (\partial V / \partial n_2)_{n_1} = \phi_V + n_2 (\partial \phi_V / \partial n_2)_{n_1} \qquad (13)$$

For the determination of apparent molar volume (ϕ_V) from experimental data it is more convenient[4] to use the molarity scale (c) for solute concentration and densities (ρ). The apparent molar volumes (ϕ_V) of solutes can be calculated by using the following relation:[4]

$$\phi_V = M/\rho_1 - 1000(\rho - \rho_1)/(c\rho_1) \qquad (14)$$

where M is the molecular weight of the solute, ρ_1 and ρ are the densities of solvent and solution, respectively. However, if concentrations are expressed in terms of molality (m) of the solute, equation (14) can also be expressed as:[4]

$$\phi_V = M/\rho - 1000(\rho - \rho_1)/(m\rho\rho_1) \qquad (15)$$

The extrapolation of the apparent molar volume of an electrolyte/a solute to infinite dilution and the expression of the concentration dependence of the apparent molar volume have been made by four major equations over a period of years – the Masson equation,[8] the Redlich-Meyer equation,[9] the Owen-Brinkley equation[10] and the Pitzer equation.[11] Masson found that the apparent molar volume (ϕ_V) of electrolytes follows a linear relation with the square root of the solute molarities (c):

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \qquad (16)$$

where ϕ_V^0 is the limiting apparent molar volume or standard partial molar volume (equal to the partial molar volume at infinite dilution, $\overline{V}_2^0$) and S_V^* is the corresponding slope. The majority of ϕ_V data in water[12] and nearly all ϕ_V data in non-aqueous[13-17] solvents have been extrapolated to infinite dilution through the use of equation (16).

However, Redlich and Meyer[9] have shown that equation (16) cannot be more than a limiting law and for a given solvent and temperature, the slope S_V^* should depend only upon the valence type. They suggested an equation for representing ϕ_V as follows:

$$\phi_V = \phi_V^0 + A_V\sqrt{c} + b_V c \tag{17}$$

$$\text{where } A_V = kw^{3/2} \tag{18}$$

A_V is the theoretical slope, based on molar concentration, including the valence factor:

$$w = 0.5\sum_i^j \nu_i z_i^2 \tag{19}$$

$$\text{and, } k = N_A^2 e^2 (8\pi/1000\varepsilon_r^3 RT)^{1/2}[(\partial \ln \varepsilon_r/\partial P)_T - \beta/3] \tag{20}$$

where β is the compressibility of the solvent. But the variation of dielectric constant (ε_r) with pressure was not known accurately enough, even in water, to calculate accurate values of the theoretical limiting slope.

The Redlich-Meyer[9] extrapolation equation adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions. However, studies[18-20] on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Actually, the volume contributed to a solvent by the addition of 1 mole of an ion is difficult to determine. This is so because, upon entry into the solvent, the ions change the volume of the solution due to a breakup of the solvent structure near the ions and the compression of the solvent under the influence of the ion's electric field, i.e., Electrostriction [21] which is a general phenomenon and whenever there are electric fields of the order of 10^9-10^{10} V m^{-1}, the compression of ions and molecules is likely to be significant. However, for polyvalent electrolytes, the more complete Owen-Brinkley[10] equation can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of ϕ_V. The Owen-Brinkley equation derived by including the ion-size parameter (a) is given by:

$$\phi_V = \phi_V^0 + A_V \tau(\kappa a)\sqrt{c} + 0.5 w_V \theta(\kappa a) + 0.5 K_V c \qquad (21)$$

where the symbols have their usual significance.[10] However, equation (21) has not been widely employed for the treatment of results for non-aqueous solutions. Pogue and Atkinson[22] used the Pitzer formalism to fit the apparent molar volume data. The Pitzer equation for the apparent molal volume of a single salt $\mathrm{M}_{\nu_\mathrm{M}}\mathrm{X}_{\nu_\mathrm{X}}$ is:

$$\begin{aligned}\phi_V = \phi_V^0 + V|z_\mathrm{M} z_\mathrm{X}|A_V|2b\,\mathrm{In}(I + \mathrm{b}I^{1/2}) + \\ 2\nu_\mathrm{M}\nu_\mathrm{X} RT[mB_\mathrm{MX}^\nu + m^2(\gamma_\mathrm{M}\gamma_\mathrm{X})^{1/2} C_\mathrm{MX}^\nu]\end{aligned} \qquad (22)$$

where

$$B_\mathrm{MX}^\nu = (\partial\beta^0/\partial P)_T + (\partial\beta^1/\partial P)_T(2/\alpha^2 I)[1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})] \qquad (23)$$

$$C_\mathrm{MX}^\nu = (\partial C^\phi/\partial P)_T/2 \qquad (24)$$

$$\nu = \nu_\mathrm{M} + \nu_\mathrm{X} \qquad (25)$$

$$\alpha = 2.0\,(\mathrm{kg/mol})^{1/2} \qquad (26)$$

$$\mathrm{b} = 1.2\,(\mathrm{kg/mol})^{1/2} \qquad (27)$$

and other symbols have their usual significance.[22]

2.1.3. Ionic Partial Molar Volume

The individual ionic partial molar volumes provide information relevant to the general question of the structure near the ion, i.e., its solvation. The calculation of the ionic limiting partial molar volumes in organic solvents is, however, a difficult. At present most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods originally developed for aqueous solutions[23] to non-aqueous electrolyte solutions. In the last few years, the method suggested by Conway *et al.*[23] has been used most frequently. These authors used the method to determine the limiting partial molar volumes of the anion for a series of homologous tetraalkylammonium chlorides, bromides and iodides in aqueous solution. They plotted the limiting partial molar volume, $\phi^0_{V,\mathrm{R_4NX}}$ for a series of these salts with a common halide ion as a function of the formula weight of the cation, $M_{\mathrm{R_4N^+}}$ and obtained straight lines for each series and suggested the following equation:

$$\phi^0_{V,\mathrm{R_4NX}} = \phi^0_{V,\mathrm{X^-}} + bM_{\mathrm{R_4N^+}} \tag{28}$$

The extrapolation to zero cationic formula weight thus provided the limiting partial molar volumes of the halide ions, $\phi^0_{V,\mathrm{X^-}}$. When an ion is introduced into a solvent, ϕ^0_V can be expressed as: [24]

$$\phi^0_{V,\mathrm{ion}} = \phi^0_{V,\mathrm{int}} + \Delta V \tag{29}$$

where $\phi^0_{V,\mathrm{int}}$ is the intrinsic volume of the ion and ΔV is the change in volume of the system due to ion-solvent interactions. Some authors [25] have suggested that the anion solvation can be considered as negligible in electrolyte solutions. These authors argued that the solvation number at infinite dilution is a measure of the extent to which the cation is solvated. Therefore equation (29) can also be expressed as:

$$\phi^0_{V,\mathrm{ion}} = \phi^0_{V,\mathrm{int}}(\mathrm{R_4N^+}) + \Delta V \tag{30}$$

and the term $\phi^0_{V,\mathrm{int}}(\mathrm{R_4N^+})$ can be calculated with the help of the following relation: [26]

$$\phi^0_{V,\mathrm{int}}(\mathrm{R_4N^+}) = 2.52\, r^3_{\mathrm{R_4N^+}} \tag{31}$$

where $r_{\mathrm{R_4N^+}}$ is the crystallographic radii of the $\mathrm{R_4N^+}$ ion. Uosaki *et al.*[27] used this method for the separation of some literature values and of their own $\phi^0_{V,\mathrm{R_4NX}}$ values into ionic contributions in organic electrolyte solutions. Krumgalz [26] applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

However, Millero [28] on the basis of Frank and Wen model [29] has expressed the standard partial molar volume of an ion ($\phi^0_{V,\mathrm{ion}}$) by the relation:

$$\phi^0_{V,\mathrm{ion}} = \phi^0_{V,\mathrm{int}} + \phi^0_{V,\mathrm{elect}} + \phi^0_{V,\mathrm{disord}} + \phi^0_{V,\mathrm{caged}} \tag{32}$$

where $\phi^0_{V,\mathrm{elect}}$ is the electrostriction partial molar volume due to ion-solvent interactions, $\phi^0_{V,\mathrm{disord}}$ is the disordered partial molar volume due void space and $\phi^0_{V,\mathrm{caged}}$ is the caged partial molar volume due to a caged water structure around ions containing hydrophobic groups such as the tetraalkylammonium ions. It is difficult to determine the importance of the various contributions to $\phi^0_{V,\mathrm{ion}}$. Millero[28] has examined $\phi^0_{V,\mathrm{ion}}$ values in water and methanol with the help of following relations: [30]

$$\phi^0_{V,\mathrm{ion}} = 2.52r^3 + A^{/} r^2 - B^{/} z^2 / r \tag{33}$$

$$\phi^0_{V,\mathrm{ion}} = 2.52(r+a)^3 - B^{//} z^2 / r \tag{34}$$

where r is the crystallographic radii of the ion, z is ionic charge, a, $A^{/}$, $B^{/}$ and $B^{//}$ are constants. These constants like ionic entropies show no simple correlation to any of the common physical properties. The electrostriction of an ion can be estimated, when dielectric saturation is negligible, by the Drude-Nernst equation: [31]

$$\phi^0_{V,\mathrm{elect}} = -\frac{N_A z^2 e^2}{2\varepsilon_r r}(\partial \ln \varepsilon_r / \partial P) = -\frac{B^{///} z^2}{r} \tag{35}$$

where ε_r is the dielectric constant of the solvent , $B^{///}$ is a solvent dependent constant and other symbols have their usual significance.[31] For highly ordered solvents there is strong competition between ion and other solvent molecules to increase the order. While ions attempts to orient solvent molecules around themselves, the solvent molecules attempt to stay in the highly structured bulk liquid. This leads to a relatively large disturbed region surrounding the solvated ions thus leading to large values for $\phi^0_{V,\mathrm{disord}}$ and S^0_{ion} (partial molar entropy of the ion). For solvents with less ordered structure, ion-solvent interactions are in favor of the ion and the solvent molecules will be influenced by the ions. This leads to a smaller voids space surrounding the ion and consequently a smaller $\phi^0_{V,\mathrm{disord}}$, negative $\phi^0_{V,\mathrm{elect}}$ and S^0_{ion} values. Thus the actual number of solvent molecules ordered by an ion depends on both the degree of the solvent structure and the dielectric constant of the solvent.

2.1.4. Standard Partial Molar Volume of Transfer

Studies on partial molar volume of solutes at infinite dilution have proved to be useful practice for exploring solute (or ion)-solvent and solvent–solvent interactions in aqueous,[12] non-aqueous,[26, 32] and mixed solvents.[33] Since the solute-solute or ion-ion interactions are absent at infinite dilution, the difference or changes in the partial molar volume of the solute in a particular solvent system from that in a reference solvent, i.e., transfer volume reflects the extent and nature of solute-solvent or ion-solvent and solute-cosolute interactions. These changes are expressed by means of a transfer function, $\Delta_{\mathrm{t}}\phi^0_V$, defined as:

$$\Delta_{\mathrm{t}}\phi^0_V = \phi^0_V\,(\mathrm{solute} + \mathrm{cosolute} + \mathrm{solvent}) - \phi^0_V\,(\mathrm{solute} + \mathrm{solvent}) \tag{36}$$

This transfer function gives a measure of the differences in solute-solvent interactions between the reference solvent and solvent system or mixed solvent. Franks *et al.*[34] showed that the partial molar volume of a non-electrolyte is a combination of it's intrinsic volume $\phi^0_{V,\mathrm{int}}$ and volume $\phi^0_{V,\mathrm{solv}}$ due to its interactions with the solvent. The intrinsic volume is considered to have two types of contributions, i.e., $\phi^0_{V,\mathrm{int}} = \phi_{V,\mathrm{vw}} + \phi_{V,\mathrm{void}}$; where $\phi_{V,\mathrm{vw}}$ is the van der Waals volume and $\phi_{V,\mathrm{void}}$ is voids or empty spaces therein the solution. Shahidi *et al.*[35] modified this equation to include the contribution of interactions of a non-electrolyte solute with the solvent as follows:

$$\phi^0_{V,\mathrm{int}} = \phi_{V,\mathrm{vw}} + \phi_{V,\mathrm{void}} - n\sigma_s \tag{37}$$

where σ_s is the shrinkage in volume produced by the interactions of hydrogen bonding groups present in the solute with solvent molecules (water) and n is the potential number of hydrogen bonding sites in the solute. For electrolytes and zwitterioninc solutes, the shrinkage is caused by the electrostriction and hence the equation (37) can be expressed as:

$$\phi^0_{V,\mathrm{int}} = \phi_{V,\,\mathrm{vw}} + \phi_{V,\,\mathrm{void}} - \phi_{V,\,shrinkage} \qquad (38)$$

and generally $\phi_{V,\,\mathrm{vw}}$ and $\phi_{V,\,\mathrm{void}}$ are taken[36] to have same magnitude in water and in mixed solvent for the same type of solutes. Thus, $\phi^0_{V,\mathrm{int}}$ depends on $\phi^0_{V,\mathrm{shrinkage}}$, which is controlled by the extent of electrostriction in the solution. The cosphere overlap model developed by Gurney[37]and Frank and Evans[38] can also be utilized to analyze $\Delta_{\mathrm{t}}\phi^0_V$ values in terms of solute-cosolute interactions. According to this model properties of water molecules in the hydration cosphere depend on the nature of the solute molecules. When two solute particles come close enough so that their cospheres overlap, some of the cosphere material is displaced leading to changes in the thermodynamic properties. The following types of interactions are possible: (i) polar-ionic and polar-polar group interactions (e.g., ion-dipole, ion-quadrupole, ion-induced dipole interactions), (ii) polar-non-polar and non-polar-non-polar group interactions (e.g., hydrophobic-hydrophilic interactions, hydrophobic-hydrophobic interactions), etc., depending on the nature of the solvent and solute molecules. The first type of interaction contributes positive volumes of transfer, while the second and third type of interactions contribute negative volumes of transfer. The overlap of hydration cospheres of charged species reduces electrostriction and leads to a decrease in $\phi^0_{V,\mathrm{shrinkage}}$ resulting into positive $\Delta_{\mathrm{t}}\phi^0_V$ values.[37] Kozak *et al.*[39] proposed a theory based on the McMillan-Mayer theory of solutions that permit the formal separation of effects due to interactions between pairs of solute molecules and those due to interactions involving three or more solvent molecules. Friedman and Krishnan[40] as well as Franks and Evans[38] further developed this approach to include the solute-cosolute interactions in the solvation sphere. According to this treatment, the thermodynamic function $\Delta_{\mathrm{t}}\phi^0_V$ can be expressed as:

$$\Delta_{\mathrm{t}}\phi^0_{V,} = 2Z_{12}m_2 + 3Z_{122}m_2^2 + 4Z_{1222}m_2^3 \qquad (39)$$

where Z_{12}, Z_{122} and Z_{1222} are the pair, triplet and quartet interaction coefficients, respectively and m_2 is the molality of the cosolute in the solution.

However, it is difficult to interpret the changes in $\Delta_{\mathrm{t}}\phi_V^0$ with solvent composition in terms of ionic effects because of treating the electrolytes as a whole. Obtaining individual ionic thermodynamic quantities involves adoption of some extra-thermodynamic assumptions (as discussed for partial molar volume in section 2.1.3 above) in order to split the transfer function $\Delta_{\mathrm{t}}\phi_V^0$ into ionic components. Maestre *et al.*[41] used the hypothesis of reference electrolyte ($\mathrm{Ph_4AsBPh_4}$) method to split $\Delta_{\mathrm{t}}\phi_V^0$ into ionic contributions by means of the following relations:

$$\Delta_{\mathrm{t}}\phi_V^0(\mathrm{Ph_4AsBPh_4}) = 2\Delta_{\mathrm{t}}\phi_V^0(\mathrm{Ph_4As^+}) = 2\Delta_{\mathrm{t}}\phi_V^0(\mathrm{BPh_4{}^-}) \tag{40}$$

$$\Delta_{\mathrm{t}}\phi_V^0(\mathrm{Ph_4AsBPh_4}) = \Delta_{\mathrm{t}}\phi_V^0(\mathrm{Ph_4AsCl}) + \Delta_{\mathrm{t}}\phi_V^0(\mathrm{NaBPh_4}) - \Delta_{\mathrm{t}}\phi_V^0(\mathrm{NaCl}) \tag{41}$$

Thus once $\Delta_{\mathrm{t}}\phi_V^0(\mathrm{Ph_4As^+})$ or $\Delta_{\mathrm{t}}\phi_V^0(\mathrm{BPh_4{}^-})$ has been obtained, other single ion volumes of transfer can be had from the whole electrolyte data. According to Conway,[42] the partial molar volume of an ion at infinite dilution can be split into three terms:

$$\phi_{V,\mathrm{ion}}^0 = \phi_{V,\mathrm{int}}^0 + \phi_{V,\mathrm{elect}}^0 + \phi_{V,\mathrm{struc}}^0 \tag{42}$$

where $\phi_{V,\mathrm{int}}^0$ is a positive term consisting of the molar volume of the ion itself, $\phi_{V,\mathrm{elect}}^0$ is a negative term owing to the electrostriction of the solvent and $\phi_{V,\mathrm{struc}}^0$ is the structural contribution to the volume. The last term can be further split into two parts: one negative corresponding to the accommodation of the ion in a cavity in the solvent and the other positive resulting from a local reinforcement of the solvent structure. So equation (42) in terms of transfer volume becomes:

$$\Delta_{\mathrm{t}}\phi_{V,\mathrm{ion}}^0 = \Delta_{\mathrm{t}}\phi_{V,\mathrm{elect}}^0 + \Delta_{\mathrm{t}}\phi_{V,\mathrm{struc}}^0 \tag{43}$$

The term $\Delta_t \phi^0_{V,\text{int}}$ vanishes because $\phi^0_{V,\text{int}}$ is the crystallographic volume of the ion and $\Delta_t \phi^0_{V,\text{ion}}$ will thus depend on the balance between electrostriction and structural contributions.

2.1.5. Apparent Molar Expansibility

The apparent molar expansibility (ϕ_E) of a solution is defined by $\phi_E = (\partial \phi_V / \partial T)_P$ and combining this equation with the equation (11), we have:

$$\phi_E = \frac{\alpha V - \alpha_1 n_1 V_1^*}{n_2} \tag{44}$$

where α and α_1 are the coefficients of thermal expansion of the solution and the solvent, respectively and are defined as: $\alpha = -\rho^{-1}(\partial \rho / \partial T)_P$ and $\alpha_1 = -\rho_1^{-1}(\partial \rho_1 / \partial T)_P$. The apparent molar expansibility (ϕ_E) can be calculated from densities and their temperature coefficients by the equations:

$$\phi_E = \alpha_1 \phi_V + \frac{1000(\alpha - \alpha_1)}{c} \tag{45}$$

and

$$\phi_E = \alpha \phi_V + \frac{1000(\alpha - \alpha_1)}{m \rho_1} \tag{46}$$

2.1.6. Standard Partial Molar Expansibility

The standard partial molar expansibilities (ϕ_E^0) can be determined from the relation:[4]

$$\phi_E = \phi_E^0 + S_E \sqrt{c} \tag{47}$$

When solute concentrations are in molalities (m), equation (47) can be written as:

$$\phi_E = \phi_E^0 + S_E \sqrt{m} \tag{48}$$

and $(\partial \phi_E^0 / \partial T)_P$ values can then be obtained from the slope of a least squares linear regression of ϕ_E^0 values against experimental temperatures (T).

Alternatively, the temperature dependence of ϕ_V^0 for various investigated electrolytes in various solvents can be expressed as:

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \tag{49}$$

where a_0, a_1 and a_2 are the coefficients for a solute and T is the absolute temperature. The partial molar expansibilities (ϕ_E^0) can be obtained by differentiating equation (49) with respect to T at constant pressure P,

$$\phi_E^0 = (\partial \phi_V^0 / \partial T)_P = a_1 + 2a_2 T \tag{50}$$

Thus the standard molar expansibilities (ϕ_E^0) change in magnitude with the change of temperature. Since partial molar heat capacities of electrolytes are commonly negative and on the basis of the structural model,[43] the explanation in terms of structure breaking leads to the prediction that $(\partial C_P^0 / \partial P)_T$ should be positive; hence on the basis of the thermodynamic equation,

$$(\partial C_P^0 / \partial P)_T = -T(\partial^2 \phi_V^0 / \partial T^2)_P \tag{51}$$

it is evident structure breaking solutes should have negative $(\partial^2 \phi_V^0 / \partial T^2)_P$ values. Similar reasoning indicates that positive $(\partial^2 \phi_V^0 / \partial T^2)_P$ should be associated with the structure-making solutes. Hence, according to Hepler[43] the sign of $(\partial \phi_E^0 / \partial T)_P$ can be used to reveal the long–range structure-making and breaking capacity of the electrolytes/solutes in the solvent systems. The general thermodynamic expression used is as follows:

$$(\partial \phi_E^0 / \partial T)_P = (\partial^2 \phi_V^0 / \partial T^2)_P = 2a_2 \tag{52}$$

If the sign of $(\partial\phi_E^0/\partial T)_P$ is positive the electrolyte/solute is a structure maker and when the sign of $(\partial\phi_E^0/\partial T)_P$ is negative, it is a structure breaker.

2.1.7. Ionic Partial Molar Expansibility

If $\phi_{V,\text{ion}}^0$ values are available at several temperatures (T), $\phi_{E,\text{ion}}^0$ values can be obtained from the slopes of a plot of $\phi_{V,\text{ion}}^0$ values against T. Partial molar expansibilities (ϕ_E^0) of the electrolytes can be split into ionic contributions by following the relation:

$$\phi_E^0 = \phi_{E,+}^0 + \phi_{E,-}^0 \tag{53}$$

where $\phi_{E,+}^0$ and $\phi_{E,-}^0$ are the partial molar expansibility of the cation and anion, respectively. Millero and coworkers[44] examined $\phi_{E,\text{ion}}^0$ values of a large number of ions in water at 298.15 K. For simple monovalent cations and anions they found that $\phi_{E,\text{ion}}^0$ varies in size or radius in the inverse order as observed by Fajans and Johnson[45] and that ion-water interactions are different for cations and anions of similar size. Similar to $\phi_{V,\text{ion}}^0$, $\phi_{E,\text{ion}}^0$ can also be resolved into different contributions according to Frank and Wen model[29] for the hydration of ions as expressed by the relation:

$$\phi_{E,\text{ion}}^0 = \phi_{E,\text{int}}^0 + \phi_{E,\text{elect}}^0 + \phi_{E,\text{disord}}^0 + \phi_{E,\text{caged}}^0 \tag{54}$$

According to this model the intrinsic expansibility, $\phi_{E,\text{int}}^0$, is the volume change due to expansion of the ion and can be neglected for monovalent ions. However, this term in equation (54) is dictated mostly by the expansibility of covalent bonds in the ions with hydrocarbon portion. The electrostriction expansibility, $\phi_{E,\text{elect}}^0$, is the volume change due to changes in electrostriction region and is negative as well as proportional to z^2/r; where z is the charge on the ion and r is its crystal radius. The disordered expansibility, $\phi_{E,\text{disord}}^0$, is due to changes in a disordered region and it is different for cations and anions of same size owing to different orientation of water molecules in the first electrostricted region. This term depends on the temperature and magnitude of z^2/r. Thus for ions with a large electrostricted region (i.e., large z^2/r), the disordered region is very small or even nonexistent. However, for ions with a small electrostricted region (i.e., small z^2/r), the disordered region is also an important contribution. The caged expansion, $\phi^0_{E,\text{caged}}$, is due to the changes in highly structured water around the hydrocarbon portion of an ion and is important for ions with hydrocarbon portion, it is positive and increases in magnitude with the size of the hydrocarbon portion of the ion.

2.2. Viscosity

Viscosity, the force required to produce unit rate of shear between two layers separated by unit distance, is an important transport property of liquids and is used for the determination of ion-solvent interactions and studied extensively. Viscosity is not a thermodynamic quantity but viscosity of an electrolytic solution along with the thermodynamic property, ϕ^0_V, i.e., the standard partial molar volume gives a lot of information and insight regarding ion-solvent interactions and the nature of structures in the electrolytic solutions.

2.2.1. Viscosity of Electrolyte Solution

The viscosity relationships of electrolytic solutions are highly complicated. Because ion-ion and ion-solvent interactions are occurring in the solution and separation of the related forces is a difficult task. But from careful analysis, vivid and valid conclusions can be drawn regarding the structure and the nature of the solvation of the particular system. As viscosity is a measure of the friction between adjacent, relatively moving parallel planes of the liquid, anything that increases or decreases the interaction between the planes will raise or lower the friction and thus, increase or decrease the viscosity. If large spheres are placed in the liquid, the planes will be keyed together in increasing the viscosity. Similarly, increase in the average degree of hydrogen bonding between the planes will increase the friction between the planes, thereby increasing viscosity.

An ion with a large rigid co-sphere for a structure-promoting ion will behave as a rigid sphere placed in the liquid and increase the inter-planar friction. Similarly, an ion increasing the degree of hydrogen bonding or the degree of correlation among the adjacent solvent molecules will increase the viscosity. Conversely, ions destroying correlation would decrease the viscosity. In 1905 Grüneisen[46] performed the first systematic measurement of viscosities of a number of electrolytic solutions over a wide range of concentrations. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In 1929, Jones and Dole[47] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations (c):

$$\eta/\eta_1 = \eta_r = 1 + A\sqrt{c} + Bc \qquad (55)$$

The above equation can be rearranged as:

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (56)$$

where A and B are constants specific to ion-ion and ion-solvent interactions. The equation is applicable equally to aqueous and non-aqueous solvent systems with negligible ionic association and has been used extensively. The term $A\sqrt{c}$, originally ascribed to Grüneisen effect (due to the long-range coulombic forces between the ions) can, in principle, be discussed in the light of Debye-Hückel theory[48] of inter-ionic attractions. The A-coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory[49, 50] and is given by the Falkenhagen Vernon[50] equation:

$$A_{\text{Theo}} = \frac{0.2577\Lambda_0}{\eta_1(\varepsilon_r T)^{0.5}\lambda_+^0\lambda_-^0}[1 - 0.6863(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda_0})^2] \qquad (57)$$

where Λ_0, λ_+^0 and λ_-^0 are the limiting molar conductances of the electrolyte as a whole and its cation and anion, respectively; other symbols have their usual significance. When A-coefficients obtained by fitting η_r values to equation (56) for aqueous solutions[51] were compared with the values calculated from equation (55), good agreement was observed. But the accuracy was poor with partially aqueous solutions.[52] Crudden *et al.*[53] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analyzed by the equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha_{\mathrm{IP}}\, c}}{\alpha_{\mathrm{IP}}\, c} = B_i + B_P\left(\frac{1-\alpha_{\mathrm{IP}}}{\alpha_{\mathrm{IP}}}\right) \tag{58}$$

where A, B_i and B_P are characteristic constants and α_{IP} is the degree of dissociation of ion pair. Thus extrapolation of a plot of $(\eta_r - 1 - A\sqrt{\alpha_{\mathrm{IP}}\, c})/\alpha_{\mathrm{IP}}\, c$ versus to $(1-\alpha_{\mathrm{IP}})/\alpha_{\mathrm{IP}} = 0$ gave the intercept B_i. However for the most of the electrolytic solutions both in aqueous and non-aqueous media, the equation (56) is valid up to 0.1 (M)[4, 54, 55] within experimental errors. At higher concentrations the extended Jones-Dole equation (59), involving an additional coefficient *D*, originally used by Kaminsky,[56] is given below:

$$\eta/\eta_1 = 1 + A\sqrt{c} + Bc + Dc^2 \tag{59}$$

The significance of the coefficient *D* is also not always meaningful and therefore, equation (56) is the most popular. The plots of $(\eta/\eta_1 - 1)/\sqrt{c}$ against $\sqrt{c}$ for the electrolytes should give the value of A-coefficient. But sometimes, the values are negative or considerably scattered and also deviate from linearity.[4, 57, 58] Thus, instead of determining A- coefficient from the plots or by the least square method, the A-coefficients should be calculated by using Falkenhagen-Vernon equation (57). According to the inter-ionic attraction theory of electrolytes the ions tend to build and maintain a space lattice structure in solution and opposes any influence or force that tend to disturb this space lattice structure; thus the inter-ionic forces tend to stiffen or increase the viscosity of the solution. Thus it is expected that A-coefficient will have a negative value for all strong electrolytes and a value of zero for non-electrolytes.[47] The B-coefficient may be either positive or negative and it is actually the ion-solvent interaction parameter. The effect of solute size on the B-coefficient is apparent from hydrodynamic theories applicable to particles in a fluid continuum. When penetration between the solute and solvent occurs, the steric effect may contribute to the B-

coefficient and thus B-coefficient is greatly sensitive to the “rigidity” or “flexibility” of the solute. Thus the B-coefficient is determined by the solute/ion size and the nature of the solvent. The B-coefficients are obtained as slopes of the straight lines using the least square method and intercepts equal to the A values. The factors influencing B- coefficients are: [59, 60] (i) ionic solvation and the action of the field of the ion produces long-range order in solvent molecules and thereby increase η or B-values, (ii) destruction of the three dimensional bulk structure of solvent molecules that decreases η values, (iii) high molar volume and low dielectric constant yield high B-values for similar solvents and (iv) steric hindrance of the primary solvation of ions due to high molar volume solvents or poor solvation of either ion of the binary electrolyte yield reduced B-values.

In structured solvents like water, a solute with or without a primary solvation sheath can apparently affect the degree of ‘structure’ of the solvent molecules at relatively long distances. A ‘structure-making’ solute lowers the average effective temperature of the solvent molecules and thus increases the viscosity of the solution and leads to a high B-coefficient values. Because of the exponential relationship between viscosity and temperature, [54] a rise in temperature of the solution causes B-coefficients to fall, this fall being greater at low than at high temperatures. Such behaviour can be used to identify ‘structure-making’ solutes.[61] Conversely, ‘structure-breaking’ solutes should have rather low B-coefficient that increases with temperature.[54] If solvation decreases with increasing temperature, B-coefficient of a solvated species should also fall and consequently both primary solvation and structure making should have high B-coefficient at low temperature and negative values of $\partial B / \partial T$.

2.2.2. Ionic Viscosity B-Coefficients

Viscosity B-coefficients, as determined experimentally by using the Jones-Dole equation, do not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contributions from cations and anions to the total ion-solvent interaction. The division of viscosity B-values into ionic components is quite arbitrary and based on some extra-thermodynamic assumptions. The following methods have been used for the division of B-values in the ionic components:

(1) Cox and Wolfenden[62] carried out the division on the assumption that B_{ion} values of Li^+ and IO_3^- in LiIO_3 are proportional to the respective ionic volumes that are proportional to the third power of the respective ionic mobilities. The method of Gurney[37] and also of Kaminsky[56] is based on:

$$B_{\text{K}^+} = B_{\text{Cl}^-} \text{ (in water)} \tag{60}$$

The argument in favour of this assignment is based on the fact that the B-coefficients for KCl is very small and that the mobilities of K^+ and Cl^- are very similar over the temperature range 15-45 ºC. The assignment is supported by other thermodynamic properties. Nightingle,[63] however, preferred RbCl or CsCl to KCl on mobility considerations.

(2) The method suggested by Desnoyers and Perron[64] is based on the assumption that the Et_4N^+ ion in water is probably closest to be neither structure breaker nor a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation, [65]

$$B = 0.0025\ \phi^0_{V,\,\text{ion}} \tag{61}$$

and with an accurate value of the partial molar volume of the ion, $\phi^0_{V,\,\text{ion}}$, it is possible to calculate a value of 0.359 for $B_{\text{Et}_4\text{N}^+}$ in water at 25 ºC. Sacco *et al.*[66] proposed the "reference electrolytic" method for the division of B-values. Thus, for tetraphenyl phosphonium tetraphenyl borate (Ph_4PBPh_4) in water, we have:

$$B_{\text{Ph}_4\text{B}^-} = B_{\text{Ph}_4\text{P}^+} = B_{\text{Ph}_4\text{PBPh}_4}/2 \tag{62}$$

As Ph_4PBPh_4 is sparingly soluble in water, $B_{\text{Ph}_4\text{PBPh}_4}$ can be obtained from:

$$B_{\text{Ph}_4\text{PBPh}_4} = B_{\text{NaBPh}_4} + B_{\text{Ph}_4\text{PBr}} - B_{\text{NaBr}} \tag{63}$$

The values obtained are in good agreement with those obtained by other methods. The criteria adopted for the separation of B-coefficients in non-aqueous solvents differ from those generally used in water. However, the methods[58, 59, 67, 68] are based on the equality of equivalent conductance of the counter ions at infinite dilution.

According to Krumgalz[69, 70] the method for the resolution of B-coefficients into ionic parts is based on the fact that the large tetraalkylammonium cations ($\mathrm{R_4N^+}$) are not solvated[71, 72] in organic solvents. Thus, the ionic B-values for large tetraalkylammonium ions, $\mathrm{R_4N^+}$ (where R > Bu) in organic solvents, are proportional to their ionic dimensions. So, we have:

$$B_{\mathrm{R_4NX}} = a + b r^3_{\mathrm{R_4N^+}} \tag{64}$$

where $a = B_{\mathrm{X^-}}$ and b is a constant dependent on temperature and solvent nature. The extrapolation of the plot of $B_{\mathrm{R_4NX}}$ (R > Pr or Bu) against $r^3_{\mathrm{R_4N^+}}$ to zero cation dimension gives directly $B_{\mathrm{X^-}}$ in the proper solvent and thus B-ion values can be had. The B-ion values can also be calculated from the equations:

$$B_{\mathrm{R_4N^+}} - B_{\mathrm{R'_4N^+}} = B_{\mathrm{R_4NX}} - B_{\mathrm{R'_4NX}} \tag{65}$$

$$B_{\mathrm{R_4N^+}} \Big/ B_{\mathrm{R'_4N^+}} = r^3_{\mathrm{R_4N^+}} \Big/ r^3_{\mathrm{R'_4N^+}} \tag{66}$$

by using the radii of the tetraalkylammonium ions ($r^3_{\mathrm{R_4N^+}}$ and $r^3_{\mathrm{R'_4N^+}}$) calculated from the conductometric data.[73]

Gill and Sharma[74] used $\mathrm{Bu_4NBPh_4}$ as a reference electrolyte. The method of resolution is based on the assumption, like Krumgalz, that $\mathrm{Bu_4N^+}$ and $\mathrm{Ph_4B^-}$ ions with large R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of $\mathrm{Bu_4N^+}$ (5.00Å) and $\mathrm{Ph_4B}$ (5.35 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents used by Gill and co-workers. They proposed the equations:

$$B_{\mathrm{Ph_4B^-}} \Big/ B_{\mathrm{Bu_4N^+}} = r^3_{\mathrm{Ph_4B^-}} \Big/ r^3_{\mathrm{Bu_4N^+}} = (5.35/5.00)^3 \tag{67}$$

and, $$B_{\mathrm{Bu_4NBPh_4}} = B_{\mathrm{Bu_4N^+}} + B_{\mathrm{Ph_4B^-}} \tag{68}$$

The method requires only the B-values of Bu_4NBPh_4 and is equally applicable to mixed non-aqueous solvents. The B-ion values obtained by this method agree well with those reported by Lawrence *et al.*[66] in different organic solvents using the assumption as given below:

$$B_{[\mathrm{(i-Am)_3BuN^+}]} = B_{\mathrm{Ph_4B^-}} = 1/2 B_{[\mathrm{(i-Am)_3BuNPh_4B}]} \tag{69}$$

Lawrence *et al.*[66] used tetrabutylammonium tetrabutylborate (Bu_4NBBu_4) as 'reference electrolyte' because the cation and anion are symmetrical in shape and have almost equal van der Waals volumes. Thus, we have:

$$B_{\mathrm{Bu_4N^+}} \Big/ B_{\mathrm{Bu_4B^-}} = V_{W(\mathrm{Bu_4N^+})} \Big/ V_{W(\mathrm{Bu_4B^-})} \tag{70}$$

$$\text{or, } B_{\mathrm{Bu_4N^+}} = B_{\mathrm{Bu_4NBBu_4}} \Big/ [1 + V_{W(\mathrm{Bu_4B^-})} \Big/ V_{W(\mathrm{Bu_4N^+})}] \tag{71}$$

A similar division can be made for Ph_4PBPh_4 system. Lawrence *et al.*[66] made the viscosity measurements of tetraalkylammonium bromides (from Pr to Hept.) in DMSO and HMPT. The B-coefficients, $B_{\mathrm{R_4NBr}} = B_{\mathrm{Br^-}} + a[f(r_{\mathrm{R_4N^+}})]$, were plotted as functions of the van der Waals volumes. The $B_{\mathrm{Br^-}}$ values thus obtained were compared with the accurately determined $B_{\mathrm{Br^-}}$ value using Bu_4NBBu_4 and Ph_4PBPh_4 as 'reference electrolyte'. They concluded that the 'reference electrolyte' method is the best available method for division into ionic contributions.

Jenkins and Pritcheit[75] observed that $B_{\mathrm{Cs^+}} = B_{\mathrm{I^-}}$, as suggested by Krumgalz,[71] to be more reliable than $B_{\mathrm{K^+}} = B_{\mathrm{Cl^-}}$ in aqueous solutions. Anyway, it is apparent that almost all these methods are based on certain approximations and anomalous results may arise unless proper mathematical theory is developed to calculate B-values.

2.2.3. Temperature Dependence of Ionic Viscosity *B* - Coefficients

A regularity in the behavior of $B_{\pm}$ and $\partial B_{\pm}/\partial T$ has been observed both in aqueous and non-aqueous solvents and useful generalizations have been made by Kaminsky.[76] He observed that (i) within a group of the periodic table the B-ion values decrease as the crystal ionic radii increase, (ii) within a group of periodic table, the temperature co-efficient of B_{ion} values increase as the ionic radius increases. The results can be summarized as follows:

For structure breaking ions-

$$\text{(i) } A \text{ and } \partial A/\partial T > 0 \tag{72}$$

$$\text{(ii) } B_{\text{ion}} < 0 \text{ and } \partial B_{\text{ion}}/\partial T > 0 \tag{73}$$

For structure making ions-

$$\text{(iii) } B_{\text{ion}} > 0 \text{ and } \partial B_{\text{ion}}/\partial T < 0 \tag{74}$$

An ion when surrounded by a solvent sheath, the properties of the solvent in the solvational layer may be different from those present in the bulk structure. This is well reflected in the 'Co-sphere' model of Gurney,[37] A, B, C zones of Frank and Wen[29] and hydrated radius of Nightingle.[63] The viscosity of a dilute electrolyte solution has been equated to the viscosity of the solvent (η_0) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighborhood. Thus, the Jones-Dole equation becomes,

$$\eta = \eta_1 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_1 + \eta(A\sqrt{c} + Bc) \tag{75}$$

where η^*, the positive increment in viscosity, is caused by coulombic interaction. B-coefficient can thus be interpreted in terms of the competitive viscosity effects. Following Stokes, Mills and Krumgalz[69] we can write for B_{ion} as:

$$B_{\text{ion}} = B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} + B_{\text{ion}}^{\text{Str}} + B_{\text{ion}}^{\text{Reinf}} \tag{76}$$

whereas according to Lawrence and Sacco:[66]

$$B_{\text{ion}} = B_{\text{w}} + B_{\text{solv}} + B_{\text{shape}} + B_{\text{ord}} + B_{\text{disord}} \tag{77}$$

$B_{\text{ion}}^{\text{Einst}}$ is the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions (the term corresponds to η^{E} or B_{shape}). $B_{\text{ion}}^{\text{Orient}}$ is the positive increment arising from the alignment or structure making action of the electric field of the ion on the dipoles of the solvent molecules (the term corresponds to η^{A} or B_{ord}). $B_{\text{ion}}^{\text{Str}}$ is the negative increment related to the destruction of the solvent structure in the region of the ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centrosymetrically and solvent to keep its own structure (this corresponds to η^{D} or B_{disord}). B_{disord} is the positive increment conditioned by the effect of 'reinforcement of the water structure' by large tetraalkylammonium ions (R_4N^+) due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent in organic solvents. B_{w} and B_{solv} account for viscosity increases and attributed to the van der Waals volume and the volume of the solvation of ions. Thus, small and highly charged cations like Li^+ and Mg^{2+} form a firmly attached primary solvation sheath around these ions ($B_{\text{ion}}^{\text{Einst}}$ or η^{E} positive). At ordinary temperature, alignment of the solvent molecules around the inner layer also cause increase in $B_{\text{ion}}^{\text{Orient}}(\eta^{A})$, $B_{\text{ion}}^{\text{Str}}(\eta^{D})$ is small for these ions. Thus, B_{ion} will be large and positive as $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} > B_{\text{ion}}^{\text{Str}}$. However, $B_{\text{ion}}^{\text{Einst}}$ and $B_{\text{ion}}^{\text{Orient}}$ would be small for ions of greatest crystal radii (within a group) like Cs^+ or I^- due to small surface charge densities resulting in weak orienting and structure forming effect. $B_{\text{ion}}^{\text{Str}}$ would be large due to structural disorder in the immediate neighborhood of the ion due to competition between the ionic field and the bulk structure. Thus $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} < B_{\text{ion}}^{\text{Str}}$ and B_{ion} is negative. Ions of intermediate size (e.g., K^+ and Cl^-) have a close balance of viscous forces in their vicinity, i.e., $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} = B_{\text{ion}}^{\text{Str}}$, so that B_{ion} is close to zero. Large molecular ions like tetraalkylammonium ions (R_4N^+) have large $B_{\text{ion}}^{\text{Einst}}$ because of large size but

$B_{\text{ion}}^{\text{Orient}}$ and $B_{\text{ion}}^{\text{Str}}$ would be small, i.e., $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{Orient}} >> B_{\text{ion}}^{\text{Str}}$ and B_{ion} would be positive and large. The value would be further reinforced in water arising from $B_{\text{ion}}^{\text{Reinf}}$ due to hydrophobic hydrations. The increase in temperature will have no effect on $B_{\text{ion}}^{\text{Einst}}$. But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion leading to decrease in $B_{\text{ion}}^{\text{Str}}$. $B_{\text{ion}}^{\text{Orient}}$ will decrease slowly with temperature as there will be less competition between the ionic field and reduced solvent structure. The positive or negative temperature co-efficient will thus depend on the change of the relative magnitudes of $B_{\text{ion}}^{\text{Orient}}$ and $B_{\text{ion}}^{\text{Str}}$. Moreover, the temperature-induced change in viscosity of ions (or entropy of solvation or mobility of ions) would be more pronounced in case of smaller ions than in case of the larger ions. So there is a correlation between viscosity, entropy of solvation and temperature dependent mobility of ions. Thus, the ionic B-coefficient and the entropy of solvation of ions have been used as probes of ion-solvent interactions and can provide information about the structure making and structure breaking character of ions.

2.2.4. Viscosity of Non-Electrolyte Solutions

Thermodynamics of non-electrolytes cover an area of knowledge at least equal in magnitude to that of electrolyte solutions. Hildebrand and Scott have thoroughly discussed this subject, mostly in non-polar solvents.[77] According to Falkenhagen,[49, 50] *A*- coefficient values for uncharged solutes are zero. Solution viscosities (η) of non-electrolytes can be analyzed with the modified Jones-Dole equation: [37, 54]

$$\eta_r = 1 + Bc \tag{78}$$

where $\eta_r = \eta/\eta_1$; η_1, η and c are viscosities of the solvents, viscosities of the solutions and molar concentration of the solute in the studied solutions, respectively. *A*- coefficients may be found to be zero or very close to zero within the experimental error limit with Jones-Dole equation (56) fitted to the experimental viscosity data. If such cases the experimental viscosities can be fitted to the following linear regression relation giving equal weights to all the viscosities:[78]

$$\eta = C' + B'c \tag{79}$$

where B' and C' are constants; C' values are found to agree with the observed η_1 values within the experimental error limit and B' is related to *B*- coefficients by the following relation:[78]

$$B = B'/C' \tag{80}$$

2.2.5. Viscosity *B*-Coefficient of Transfer

Similar to $\Delta_t \phi_V^0$, viscosity *B*-coefficient of transfer ($\Delta_t B$) is free from solute-solute or ion-ion interactions and provides information about solute-cosolute interactions. $\Delta_t B$ values can be calculated from the following relation:

$$\Delta_t B = B\,(\text{solute} + \text{c}\mathit{osolute} + \text{solvent}) - B\,(\text{solute} + \text{solvent}) \tag{81}$$

and can be discussed with the aid of Gurney's 'Co-sphere' model.[37] Generally negative $\Delta_t B$ values indicate that the solute is in less structured environment in the solution compared to that in the solvent and positive $\Delta_t B$ values indicate that the solute is in more structured environment in the solution compared to that in that solvent. These results reflect the influence of 'solvent structure modification' by the solute and cosolute molecules.

2.2.6. Effects of Shape and Size on Viscous Flow

Stokes and Mills[54] have dealt in the aspect of shape and size extensively. The ions in solution can be regarded to be rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein[65] leads to the equation:

$$\eta/\eta_1 = 1 + 2.5\phi \tag{82}$$

where ϕ is the volume fraction occupied by the particles. Modifications of the equation have been proposed by: (i) Simha[79] on the basis of departures from spherical shape and (ii) Vand[80] on the basis of dependence of the flow patterns around the neighboring particles at higher concentrations. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monoatomic cations). Thus we have from equation (82):

$$2.5\phi = A\sqrt{c} + Bc \tag{83}$$

Since $A\sqrt{c}$ term can be neglected in comparison with Bc and $\phi = c\phi^0_{v,\,\text{ion}}$, where $\phi^0_{v,\,\text{ion}}$ is the partial molar volume of the ion, we get:

$$2.5\,\phi^0_{v,\,\text{ion}} = B \tag{84}$$

In the ideal case, the ionic $B_\pm$-coefficient is a linear function of partial molar volume of the ion, $\phi^0_{v,\,\text{ion}}$ with slope to 2.5. Thus, $B_\pm$ can be equated to:

$$B_\pm = 2.5\phi^0_{v,\,\text{ion}} = 2.5\times 4/3(\pi R^3_\pm N_A/1000) \tag{85}$$

assuming that the ions behave like rigid spheres with an effective radii, $R_\pm$ moving in a continuum and 2.5 is the shape factor for a sphere. $R_\pm$, calculated by using the equation (85), should be close to crystallographic radii or corrected Stoke's radii [81] if the ions are scarcely solvated and behave as spherical entities. But, in general, $R_\pm$ values of the ions are higher than the crystallographic radii indicating appreciable solvation. The number n_s of solvent molecules bound to the ion in the primary solvation shell can be easily calculated by comparing the Jones-Dole equation with the Einstein's equation:[65]

$$B_\pm = 2.5/1000(V_i + n_s V_S) \tag{86}$$

where V_i is the molar volume of the bare ion and V_S, the molar volume of the solvent. The equation (86) has been used by a number of workers to study the nature of solvation and solvation number.

2.2.7. Thermodynamics of Viscous Flow

Like diffusion, viscosity can be treated by means of the theory of absolute reaction rates.[82] As a gas is considered to consist of molecules moving about in empty space, a liquid may be regarded as made up of “holes” moving about in matter. Thus “holes” are to be taken as playing the same part in a liquid as moles do in gas phase. The energy required to create a hole of molecular dimension in a liquid is equal to the energy of vaporization per molecule of the liquid.[82] If two layers of molecules in a liquid are apart by a distance λ_1 and one layer slides over the other under the influence of a force f per square centimeter and Δu is the difference in the velocity of the two layers, then the coefficient of viscosity is given by the relation: $\eta = f\lambda_1 / \Delta u$. The passage of a molecule from one equilibrium position to another such position in the same layer requires that a suitable hole is available and energy must be utilized to create such a hole in the liquid. The process is shown in figure 2.2 below.

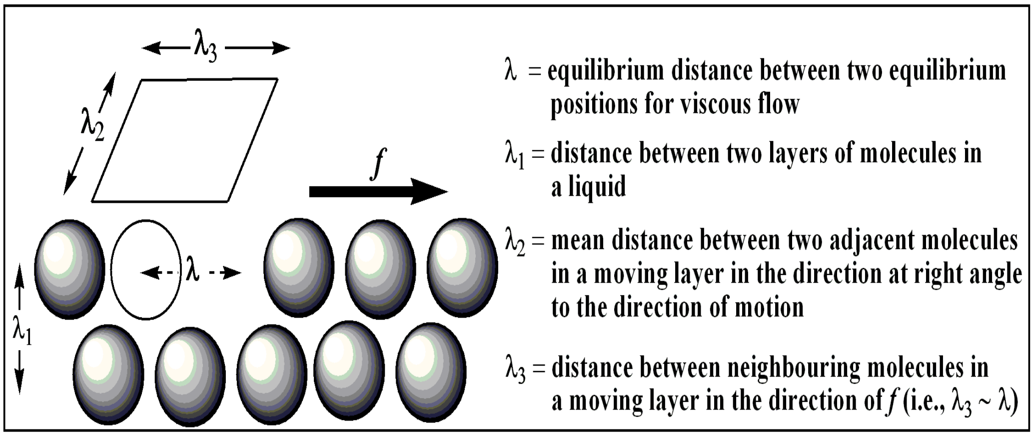


Fig. 2.2. Passage of a molecule from one equilibrium position to another position in the same layer of a liquid with the creation of a suitable hole.

This process can be discussed with the aid of a symmetrical potential energy barrier depicted in figure 2.3.

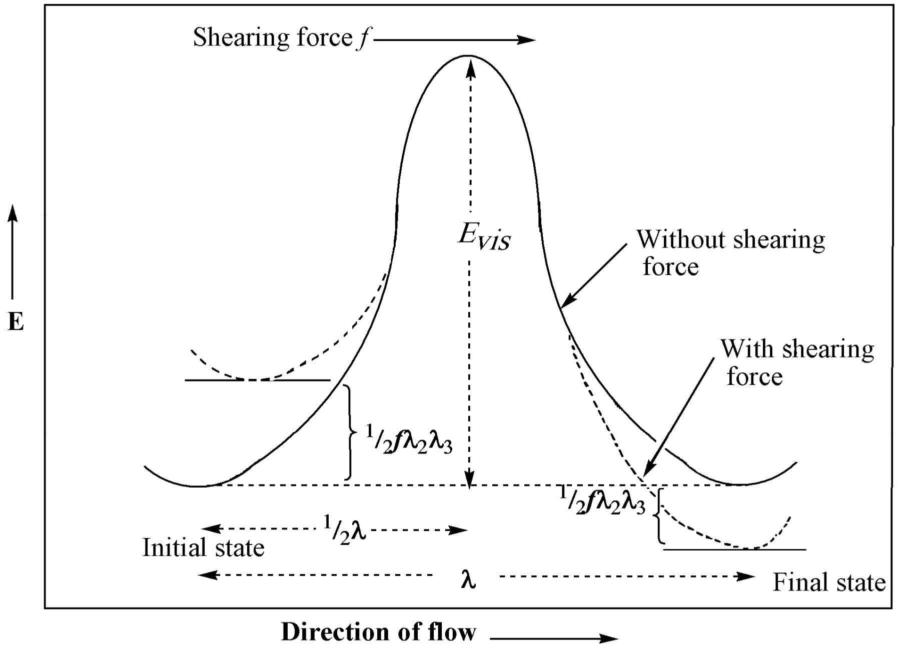


Fig. 2.3. Potential energy barrier for viscous flow with and without shearing force.

As the potential energy barrier has been taken as symmetrical, the distance between the initial equilibrium position and the activated state is $\lambda/2$. The applied force acting on a molecule in the direction of motion is thus $f\lambda_2\lambda_3$, since $\lambda_2\lambda_3$ is the effective area per molecule. So the energy acquired by the moving molecule that reached the top of the potential energy barrier is $f\lambda_2\lambda_3\lambda/2$. This energy reduces the height of the energy barrier in the forward direction by the amount of $f\lambda_2\lambda_3\lambda/2$ and increases the height of the energy barrier in the backward direction by the same amount. With some assumptions and statistical thermodynamic treatments, described in the literature,[82] the viscosity (η) of a solution can be represented by the Eyring's relation:[82]

$$\eta = Ae^{E_{vis}/RT} = (hN/V)e^{\Delta G^{*}/RT} = (hN/V)e^{(\Delta H^{*}/RT - \Delta S^{*}/R)} \qquad (87)$$

where E_{vis} = the experimental energy of activation determined from a plot of $\ln\eta$ against $1/T$; $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the free energy, enthalpy and entropy for the activation of viscous flow, respectively. The total activation energy for viscous flow may be regarded as consisting of two parts: (i) the energy required forming the hole, (ii) that required for the molecule to move into the hole and most of the energy is required for the preparation of the holes rather that required to move the molecules into the holes. According to equation (87), the free energy of activation for viscous flow per mole of the solvent/solvent mixture ($\Delta\mu_1^{0\neq}$) as:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_1\phi_{V,1}^0 / hN_A) \tag{88}$$

where N_A , $\phi_{V,1}^0$ are the Avogadro's number and the molar volume of the solvent, respectively. The other symbols have their usual significances. For a binary mixture used as solvents, $\phi_{V,1}^0$ is taken as the mole fraction average of molecular weights of components normalized by densities at the experimental temperatures. The above relation can also be expressed as: [52, 83]

$$\ln(\eta_1\phi_{V,1}^0 / hN_A) = -\frac{\Delta S_1^{0\neq}}{R} + \left(\frac{\Delta H_1^{0\neq}}{R}\right)\frac{1}{T} \tag{89}$$

So a linear regression of the ($\ln(\eta_1\phi_{V,1}^0 / hN_A)$ data against $1/T$ provides the $\Delta H_1^{0\neq}$ and $\Delta S_1^{0\neq}$ values. A correlation between viscosity *B*- coefficients and the deviation between the contribution per mole of a solute to the free energy of activation for viscous flow of the solution ($\Delta\mu_2^{0\neq}$) and the free energy of activation of viscous flow per mole of the pure solvent or solvent mixture ($\Delta\mu_1^{0\neq}$) was suggested by Feakins *et al.*[83] in the form of the following relation:

$$B = (\nu\phi_{V,1}^0 - \phi_{V,2}^0) + \phi_{V,1}^0\left(\frac{\Delta\mu_2^{0\neq} - \nu\Delta\mu_1^{0\neq}}{RT}\right) \tag{90}$$

where the coefficient ν is 1 for non-electrolytes, 2 for 1:1 electrolytes and so on. Thus $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values can be obtained from equation (90) by using the *B*-coefficient values. $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values can also be expressed as:

$$\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT} = -\frac{\Delta S_2^{0\neq} - \Delta S_1^{0\neq}}{R} + \left\{\frac{\Delta H_2^{0\neq} - \Delta H_1^{0\neq}}{R}\right\}\frac{1}{T} \tag{91}$$

where $\Delta S_i^{0\neq}$ and $\Delta H_i^{0\neq}$ are the standard partial molar entropy and enthalpy of activation for viscous flow per mole of i^{th} component in the solution. So a linear regression treatment of equation (91) provides the values of $(\Delta S_2^{0\neq} - \Delta S_1^{0\neq})$ and $(\Delta H_2^{0\neq} - \Delta H_1^{0\neq})$ from the corresponding slopes and intercepts. According to equation (90), $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity *B*-coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms. In many cases $\Delta\mu_1^{0\neq}$ are almost invariant of the solvent compositions and temperatures, implying that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity *B*-coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms. The $\Delta\mu_2^{0\neq}$ values contain the change in the free energy of activation of solute molecules as well as the contribution from the movement of solute molecules. If $\Delta\mu_2^{0\neq}$ values are positive and greater than $\Delta\mu_1^{0\neq}$ values at the experimental temperatures, the solute (ion)-solvent interactions is stronger in the ground state than in the transition state and in the transition state the solvation of the solute (ions) becomes less favored energetically. However, a popular method uses the following relations,

$$d(\Delta\mu_2^{0\neq})/dT = -\Delta S_2^{0\neq} \tag{92}$$

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \tag{93}$$

for the calculation of the entropy and enthalpy of activation of viscous flow for the solute, respectively.

2.2.8. Solvation Number

Bockris[84] suggested that the term ‘primary solvation’ should refer to the comparatively firm attachment of solvent molecules to the ions in such a way that an ion and its solvent molecules move as an entity in an electrolyte transport process, the solvent molecules having lost their own translation degree of freedom and ‘secondary solvation’ would designate all other solvent molecules. There are few cases where the inner sheath of water molecules is permanent in a log-term sense and the water molecules are firmly attached by coordinate links. Chromium and cobalt are transition elements with such a marked tendency to form coordinate links.[85] For a given ion, the solvation number depends on the manner of this association of solvent molecules and the method by which it is determined. The first solvation shell constitutes the set of immediate neighbouring solvent molecules around ion. If the solvent molecules interact strongly or coordinate with the ion and thus they constitute the primary solvation of the ion. The second solvation shell is the set of solvent molecules that are next nearest neighbours of the ion. Solvent molecules belonging to the primary and secondary solvation of the ion are oriented by its field in a manner that is incompatible with the normal mutual orientation of the solvent molecules in the bulk solvent. There will exist a region around the ion with solvent molecules having neither the central orientation nor the bulk orientation. This disordered region is called the thawed zone.[86]

Anyway, if the limiting conductance of the ion is known, the effective radius of the solvated ion can easily be determined from the Stokes' law.[81] The volume of the solvation shell V_S, can be written as:

$$V_S = (4\pi/3)(r_S^3 - r_C^3) \qquad (94)$$

where r_C is the crystal radius of the ion; the solvation number, S_n would then be obtained from:

$$S_n = V_S / V_0 \qquad (95)$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects[81] from:

$$V_S^0 = 4.35 r_S^3 \qquad (96)$$

where V_S^0 is expressed in mol.L^{-1} and r_S in angstroms. However, the method of determination of solvation number is not applicable to ions of medium size though a number of empirical equation[87] and theoretical corrections[88-91] have been suggested. Alternatively, solvation numbers S_n can easily be had from the relation:[92]

$$S_n = B / \phi_V^0 \tag{97}$$

S_n is indicative of the formation of a primary solvation sphere around a solute and the range 0-2.5 for S_n indicates unsolvated solutes in the solution.[92] If values of ionic viscosity *B*-coefficients ($B_\pm$) are available, ionic solvation numbers ($S_{n,\pm}$) can also be calculated from the equation (97) by using ionic partial molar volumes ($\phi_{V,\pm}^0$) of the ions.

2.3. Conductance

The modern theory of electrolytes dates back from the work of Debye and Hückel in 1923. Debye and Hückel took as their model an electrolyte completely dissociated into rigid spherical ions and ionic interaction was computed by Coulomb's law by assuming the medium to be a continuum. The familiar Debye and Hückel limiting law predicted that the thermodynamic behaviour of a dilute electrolyte solution depends on valency, temperature and properties of the solvent and throws light on the long-term electrostatic interactions in dilute solutions. Conducting power of an ion is also influenced by interionic forces and ion-solvent interactions. The conductometric method in conjunction with viscosity measurements gives us much information regarding the ion-ion and ion-solvent interactions. The successful application of the Debye-Hückel theory of interionic attraction was made by Onsager[93] to derive the Kohlrausch's equation representing the molar conductance of an electrolyte. For solutions of a single symmetrical electrolyte the equation is given by:

$$\Lambda = \Lambda_0 - S\sqrt{c} \tag{98}$$

where, $S = \alpha\Lambda_0 + \beta$ (99)

$$\alpha = (ze)^2\,\kappa \big/ 3(2+\sqrt{2})\varepsilon_r k_B T\sqrt{c} = 82.406\times10^4\, z^3 \big/ (\varepsilon_r T)^{3/2} \tag{100a}$$

$$\beta = z^2 e\, F\kappa \big/ 3\pi\eta\sqrt{c} = 82.487\, z^3 \big/ \eta\sqrt{\varepsilon_r T} \tag{100b}$$

The equation took no account for the short-range interactions and also of shape or size of the ions in solution (κ^{-1} is the radius of the ionic atmosphere). The ions were regarded as rigid charged spheres in an electrostatic and hydrodynamic continuum, i.e., the solvent.[94] In the subsequent years, Pitts (1953)[95] and Fuoss and Onsager (1957)[96, 97] independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions.

However, the Λ_0 values obtained for the conductance at infinite dilution using Fuoss-Onsager theory differed considerably[94] from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned.[98-100] The original Fuoss-Onsager equation was further modified by Fuoss and Hsia[101] who recalculated the relaxation field, retaining the terms which had previously been neglected. The results of conductance theories can be expressed in a general form by:

$$\Lambda = \Lambda_0 - \alpha \Lambda_0 \sqrt{c} \big/ (1+\kappa a)(1+\kappa a/\sqrt{2}) - \beta\sqrt{c} \big/ (1+\kappa a) + G(\kappa a) \qquad (101)$$

where $G(\kappa a)$ is a complicated function of the variables. The simplified form:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2 \sqrt[3]{c} \qquad (102)$$

is generally employed in the analysis of experimental results. However, it has been found that these equations have certain limitations, in some cases it fails to fit experimental data. Some of these results have been discussed elaborately by Fernandez-Prini.[98, 102, 103] Further correction of the equation (102) was made by Fuoss and Accascina.[96] They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2 \sqrt[3]{c} - \mathrm{F}\Lambda c \qquad (103)$$

where, $\mathrm{F}c = 4\pi R^3 N_A/3$. In most cases, however, J_2 is made zero but this leads to a systematic deviation of the experimental data from the theoretical equations. It has been observed that Pitt's equation gives better fit to the experimental data in aqueous solutions.[104]

2.3.1. Ionic Association

Conductance measurements help us to determine the values of the ion-pair association constant, K_A for the process:

$$\mathrm{M}^{Z+} + \mathrm{A}^{Z-} = \mathrm{MA} \tag{104}$$

$$K_A = (1-\alpha_{\mathrm{IP}}) / \alpha_{\mathrm{IP}}^2 c \gamma_\pm^2 \tag{105}$$

$$\alpha = 1 - \alpha_{\mathrm{IP}}^2 K_A c \gamma_\pm^2 \tag{106}$$

where $\gamma_\pm$ is the mean activity coefficient of the free ions at concentration $\alpha_{\mathrm{IP}} c$. For strongly associated electrolytes, the constant, K_A and Λ_0 has been determined using Fuoss-Kraus equation[105] or Shedlovsky's equation:[106]

$$T(z)/\Lambda = 1/\Lambda_0 + K_A/\Lambda_0^2 . c\gamma_\pm^2 \Lambda / T(z) \tag{107}$$

where $T(z) = F(z)$ (Fuoss-Kraus method) and $1/T(z) = S(z)$ (Shedlovsky's method):

$$F(z) = 1 - z(1 - z(1 - ....)^{-1/2})^{-1/2} \tag{108a}$$

$$\text{and } 1/T(z) \equiv S(z) = 1 + z + z^2/2 + z^3/8 + \ .... \tag{108b}$$

A plot of $T(z)/\Lambda$ against $c\gamma_\pm^2 \Lambda/T(z)$ should be a straight line having $1/\Lambda_0$ for its intercept and K_A/Λ_0^2 for its slope. Where K_A is large, there will be considerable uncertainty in the determined values of Λ_0 and K_A from equation (107). The Fuoss-Hsia[101] conductance equation for associated electrolytes is given by:

$$\begin{aligned}\Lambda = \Lambda_0 - S\sqrt{\alpha_{\mathrm{IP}} c} + E(\alpha_{\mathrm{IP}}\, c)\ln(\alpha_{\mathrm{IP}}\, c) + J_1(\alpha_{\mathrm{IP}}\, c) - \\ J_2(\alpha_{\mathrm{IP}}\, c)^{3/2} - K_A \Lambda \gamma_\pm^2 (\alpha_{\mathrm{IP}}\, c)\end{aligned} \tag{109}$$

The equation was modified by Justice.[107] The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha_{\mathrm{IP}}\,(\Lambda_0 - S\sqrt{\alpha_{\mathrm{IP}}\,c}) + E(\alpha_{\mathrm{IP}}\,c)\ln(\alpha_{\mathrm{IP}}\,c) + J_1(R)\alpha_{\mathrm{IP}}\,c - J_2(R)(\alpha_{\mathrm{IP}}\,c)^{3/2} \tag{110}$$

$$(1-\alpha_{\mathrm{IP}})/\alpha_{\mathrm{IP}}^2 c\gamma_\pm^2 = K_A \tag{111}$$

$$\ln\gamma_\pm = -k_{\mathrm{B}}\sqrt{q}/(1+k_{\mathrm{B}}R\sqrt{\alpha_{\mathrm{IP}}\,c}) \tag{112}$$

The conductance parameters are obtained from a least square treatment after setting, $R = q = e^2/2\varepsilon_r\,k_{\mathrm{B}}T$ (Bjerrum's critical distance). According to Justice the method of fixing the J-coefficient by setting, $R = q$ clearly permits a better value of K_A to be obtained. From the experimental values of the association constant K_A, one can use two methods in order to determine the distance of closest approach, a, of two free ions to form an ion-pair. The following equation has been proposed by Fuoss:[97]

$$K_A = (4\pi N_A\,a^3/3000)\exp(e^2/a\,\varepsilon_r\,k_{\mathrm{B}}\,T) \tag{113}$$

In some cases, the magnitude of K_A was too small to permit a calculation of a. The distance parameter was finally determined from the more general equation due to Bjerrum:[108]

$$K_A = 4\pi N_A\,a/1000\int_{r=a}^{r=q} r^2\exp(z^2e^2/r\varepsilon_r\,k_{\mathrm{B}}T)\,dr \tag{114}$$

The equations neglect specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. The method was successfully utilized by Douheret.[109]

2.3.2. Limiting Equivalent Conductance

The limiting equivalent conductance of an electrolyte can be easily determined from the theoretical equations and experimental observations. At infinite dilutions, the motion of an ion is limited solely by the interactions with the surroundings solvent molecules, as the ions are infinitely apart. Under these conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \qquad (115)$$

At present, limiting equivalent conductance is the only function that can be divided into ionic components using experimentally determined transport number of ions, i.e.,

$$\lambda_+^0 = t_+ \Lambda_0 \qquad \text{and} \qquad \lambda_-^0 = t_- \Lambda_0 \qquad (116)$$

Thus, from accurate value of λ^0 of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions.[110] However, accurate transference number determinations are limited to few solvents only. Spiro[111] and Krumgalz[112] have made extensive reviews on the subject.

In absence of experimentally measured transference numbers, it would be useful to develop indirect methods to obtain the limiting equivalent conductance in organic solvents for which experimental transference numbers are not yet available. The method has been summarized by Krumgalz[112] and some important points are mentioned below:

(i) Walden equation,[113] $$(\lambda_\pm^0)_{\text{water}}^{25} \cdot \eta_{0,\text{water}} = (\lambda_\pm^0)_{\text{acetone}}^{25} \cdot \eta_{0,\text{ acetone}} \qquad (117)$$

(ii) $$\left.\begin{aligned} \lambda_{\text{pic}}^0 . \eta_0 &= 0.267 \\ \lambda_{\text{Et}_4\text{N}^+}^0 . \eta_0 &= 0.296 \end{aligned}\right|^{113,114} \text{based on } \Lambda_{\text{Et}_4\text{N}_{\text{pic}}}^0 = 0.563 \qquad (118)$$

Walden considered the products to be independent of temperature and solvent. However the $\Lambda_{\text{Et}_4\text{N}_{\text{pic}}}^0$ values used by Walden was found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

$$\text{(iii) } \lambda_{25}^0(\text{Bu}_4\text{N}^+) = \lambda_{25}^0(\text{Ph}_4\text{B}^-)^{114} \qquad (119)$$

The equality holds good in nitrobenzene and in mixture with CCl_4 but not realized in methanol, acetonitrile and nitromethane.

$$\text{(iv)}\ \lambda^{0}_{25}(\text{Bu}_4\text{N}^+) = \lambda^{0}_{25}(\text{Bu}_4\text{B}^-)^{115} \qquad (120)$$

The method appears to be sound as the negative charge on boron in the Bu_4B^- ion is completely shielded by four inert butyl groups as in the Bu_4N^+ ion but this phenomenon was not observed in case of Ph_4B^-.

(v) The equation suggested by Gill[116] is:

$$\lambda^{0}_{25}(\text{R}_4\text{N}^+) = zF^2 \big/ 6\pi N_A \eta_1 [r_i - (0.0103\varepsilon_r + r_y)] \qquad (121)$$

where z and r_i are charge and crystallographic radius of proper ion, respectively; η_1 and ε_r are solvent viscosity and dielectric constant of the medium, respectively; r_y = adjustable parameter taken equal to 0.85 Å and 1.13 Å for dipolar non-associated solvents and for hydrogen bonded and other associated solvents, respectively. In a paper,[112 (b)] Krumgalz examined the Gill's approach more critically using conductance data in many solvents and found the method reliable in three solvents, e.g., butan-1-ol, acetonitrile and nitromethane.

$$\text{(vi)}\ \lambda^{0}_{25}[(\text{i}-\text{Am})_3\text{BuN}^+] = \lambda^{0}_{25}(\text{Ph}_4\text{B}^-)^{117} \qquad (122)$$

It has been found from transference number measurements that the $\lambda^{0}_{25}[(\text{i}-\text{Am})_3\text{BuN}^+]$ and $\lambda^{0}_{25}(\text{Ph}_4\text{B}^-)$ values differ from one another by 1%.

$$\text{(vii)}\ \lambda^{0}_{25}(\text{Ph}_4\text{B}^-) = 1.01\lambda^{0}_{25}(\text{i}-\text{Am}_4\text{B}^-)^{118} \qquad (123)$$

The value is found to be true for various organic solvents. Krumgalz[112] suggested a method for determining the limiting ion conductance in organic solvents. The method is based on the fact that large tetraalkyl (aryl) onium ions are not solvated in organic solvents due to the extremely weak electrostatic interactions between solvent molecules and the large ions with low surface charge density and this phenomenon can be utilized as a suitable model for apportioning Λ_0 values into ionic components for non-aqueous electrolytic solutions.

2.4. Refractive Index

The dimensionless optical property refractive index (n_D) is very sensitive to changes in molecular organization of pure liquids, solutions and mixtures. The ratio of the speed of light in vacuum to that in another substance is defined as the refractive index (n_D) of the substance, i.e.,

$$n_D = \frac{\text{Speed of light in vacuum}}{\text{Sped of light in the substance}} \tag{124}$$

The most significant works on refractive index were results of independent studies by Lorentz and Lorenz.[119] They deduced a theoretical relationship between refractive index (n_D) and density (ρ) of a substance as given by the relation:

$$R_\mathrm{S} = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{1}{\rho} \tag{125}$$

where R_S stands for specific refraction. Accordingly, the molar refraction (R_M) can be defined by multiplying both sides of equation (125) by molar mass (M) of the substance and thus molar refractivity (R_M) is given by:

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{\rho} \tag{126}$$

However, for mixture molar refractivity (R_M) can be obtained from the relation:

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \sum_{i=1}^{n} \frac{x_i M_i}{\rho} \tag{127}$$

where x_i and M_i are the mole fraction and molecular weight of the i th component in the mixture, respectively. Molar refraction is a fundamental property of a compound and it is apparently independent on the phase. Physically, it can be regarded as the actual or hard-core volume of a mole of substance, since the surrounding environment created by the solvent or the presences for other solutes does not significantly affect this quantity.[120] For most organic compounds, molar refraction can be estimated based on atomic refractions and refraction of bonds.[120] However, such information is very rare or even non-existent for many class of inorganic or organometallic solid substances or materials e.g., metal complexes. Hence equation (127) is undoubtedly very useful to determine molar refraction of a substance from a mixture or solution experiment. The applications of refractive index individually or combined with other properties, such as density and dielectric permittivity are abundant. The most frequent uses of refractive index and molar refraction data are to assess purity of a compound, to calculate the molecular electronic polarizability, to estimate liquid viscosity, to determine molecular structure and size,[120] and to calculate the dipole moment of a molecule when combined with a relative permittivity measurement.

According to Marcus *el al.*[121] the apparent molar refractivity (R_D) of a solute can be expressed as:

$$R_D = \frac{1000}{c}\left[\frac{n_D^2 - 1}{n_D^2 + 2} - \frac{1}{\rho_1}\left(\rho - \frac{cM}{1000}\right)\frac{n_{D,1}^2 - 1}{n_{D,1}^2 + 2}\right] \tag{128}$$

where n_D and $n_{D,1}$ are the refractive indices of the solution and solvent or solvent mixture, respectively and other symbols have their usual meanings. Again the molecular polarizability (α_{M}),[122] measures the ability of the molecular orbitals to be deformed under an electrical field and when the structure of a molecule becomes more complex, its electron cloud becomes more decentralized and thus the polarizability of the molecule increases. As R_D is directly proportional to the molecular polarizability,[123] the increasing trend in R_D values indicates an overall increase in the molecular polarizabilities as expressed by the relation:[121]

$$\alpha_{\mathrm{M}} = \frac{3R_{\mathrm{M}}}{4\pi N_A} \tag{129}$$

2.5. Solvent Effects on Reaction Rates

When reactants are dissolved, the standard molar Gibbs energy of solvation, ΔG^0_{solv} is liberated due to the intermolecular interactions between solvent and solute. For the simple isomerization reaction A ↔ B in the solvents I and II with different solvation capacities to solvate A and B, the difference in the molar transfer Gibbs energies of reactant A and product B, $\Delta\Delta G^0(\text{I} \rightarrow \text{II})$ is given by,[124]

$$\begin{aligned}\Delta G^0(\text{II}) - \Delta G^0(\text{II}) &= \Delta\Delta G^0(\text{I} \rightarrow \text{II}) \\ &= \Delta G^0_{\text{t}}(\text{B}, \text{I} \rightarrow \text{II}) - \Delta G^0_{\text{t}}(\text{A}, \text{I} \rightarrow \text{II}) \qquad (130)\end{aligned}$$

This corresponds to the Gibbs energy diagram shown in figure 2.4. The difference in the molar transfer Gibbs energies of reactant A and product B, $\Delta\Delta G^0(\text{I} \rightarrow \text{II})$ determines the solvent effect on the position of this equilibrium. As shown in figure 2.4 when $\Delta G^0_{\text{t}}(\text{B}, \text{I} \rightarrow \text{II}) > \Delta G^0_{\text{t}}(\text{A}, \text{I} \rightarrow \text{II})$, the equilibrium is displaced towards B on changing the solvent from I to II.

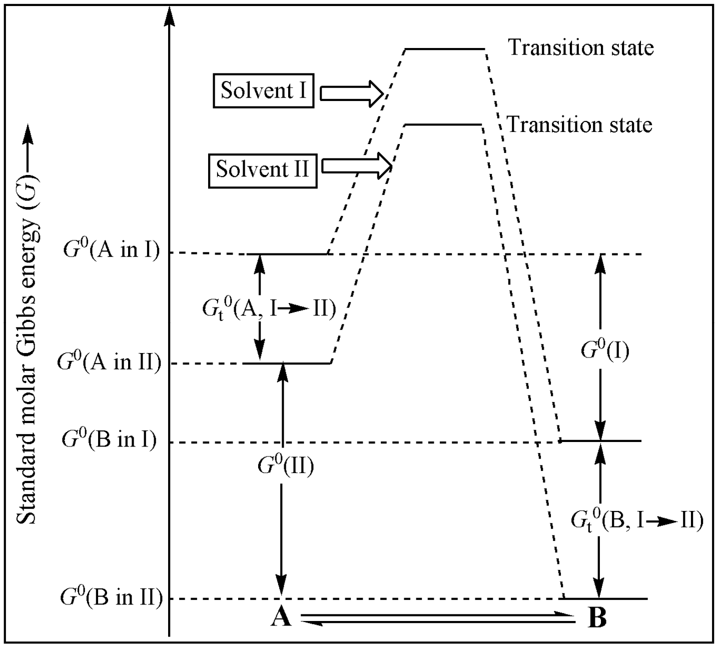


Fig. 2.4. One-dimensional Gibbs energy diagram for an equilibrium reaction, A ↔ B in the solvents I and II. $\Delta G^0(\text{I})$ and $\Delta G^0(\text{II})$: standard molar Gibbs energies of reaction in solvents I and II, respectively; $\Delta G^0_{\text{t}}(\text{A}, \text{I} \rightarrow \text{II})$ and $\Delta G^0_{\text{t}}(\text{B}, \text{I} \rightarrow \text{II})$: standard molar Gibbs energies of transfer of the solutes A and B from solvent I to solvent II, respectively.[124]

The required standard molar Gibbs energies of transfer can be obtained from activity coefficients by using the equation (131):

$$\Delta G_t^0(\mathrm{X}, \mathrm{I} \rightarrow \mathrm{II}) = -RT\ln(\gamma_\mathrm{I}/\gamma_\mathrm{II}) \qquad (131)$$

where γ_I and γ_II refers to activity coefficients of solute X in solvents I and II. A quantitative description of the influence of the solvent on the position of chemical equilibria by means of physical or empirical parameters of solvent polarity is only possible in favorable and simple cases due to the complexity of intermolecular solute/solvent interactions. However, much progress has recently been made in theoretical calculations of solvation enthalpies of solutes that can participate as reaction partners in chemical equilibria. If the solvation enthalpies of all participants in a chemical equilibrium reaction carried out in solvents of different polarity are known, then the solvent influence on this equilibrium can be quantified.[125]

In addition, the solvation capability or polarity of a solvent is not described by its relative permittivity alone. Besides the purely electrostatic Coulomb interactions, there exist other specific and unspecific interaction forces such as ion-dipole, dipole-dipole, hydrogen bonding, ion-pair formation, etc. For example, 1,3-dicarbonyl compounds can exist in three tautomeric forms as shown in figure 2.5 below:

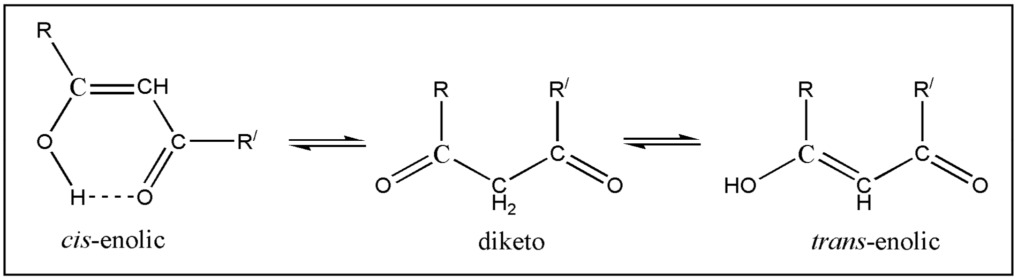


Fig. 2.5. Three tautomeric forms of 1,3-dicarbonyl compounds.

Since open chain 1,3-dicarbonyl compounds rarely remain in the *trans*-enolic form and if this form is neglected, the above equilibrium is simply the keto-enol equilibrium. It has been found that increasing solvent polarity diminishes the enol content. The enol form is the least polar of the two tautomers because intramolecular hydrogen bonding reduces the dipole-dipole repulsion of the carbonyl groups and this is unreduced in the diketo form. Furthermore, the enol stabilization due to the intramolecular hydrogen bonding will be more pronounced when intermolecular hydrogen bonding with the solvent does not compete. Thus, a change to a more polar solvent with a tendency towards intermolecular hydrogen bonding (EPD solvents) is generally associated with a decline in enol content. In a nonpolar solvent, stronger solvation leads to a higher degree of order of the solvent molecules and hence to a decrease in the entropy. In contrast, polar solvent molecules show a high degree of order even in the absence of a dipolar solute. Such solvent effects can also be found for other tautomerisms, e.g. lactim/lactam, azo/hydrazone, ring/chain equilibria, etc.[124]

The dependence of the reaction rate on the medium can be studied through two approaches: (i) comparison of the reaction rates in gas phase and in solution and (ii) comparison of the reaction rates in different solvents. Until recently only few reactions that occur in solution have been studied in gas phase[126] and hence approach (ii) is normally adopted. There are two ways in which solvents can affect the reaction rates of homogeneous chemical reactions: (i) through static or equilibrium solvent effects and (ii) through dynamic or frictional solvent effects[127-133] The static effects of solvents on rate constants can be understood in terms of transition state theory. According to this theory, solvents can modify the Gibbs energy of activation by differential solvation of the reactants and the activated complex and consequently activation enthalpies, activation entropies and activation volumes are influenced. Reaction rates are very sensitive to barrier heights, e.g., a change of only 8.4 kJ/mol in an activation barrier can alter the reaction rate at room temperature by a factor of 31.

The Hughes-Ingold rules of solvent effects on reaction rates are based of equilibrium solvation of the activated complex. Solvents can also influence reaction rates through dynamic or frictional effects. For broad barrier reactions in strongly dipolar solvents, non-equilibrium solvation of the activated complex can occur and solvent reorientation may influence the reaction rate. In the extreme case, solvent reorientation becomes rate limiting and the transition state theory breaks down. In this situation, rate constants depend on the solvent dynamics and will vary with friction coupled with solvent’s properties like density, internal pressure or viscosity. For a chemical reaction as shown in figure 2.6:

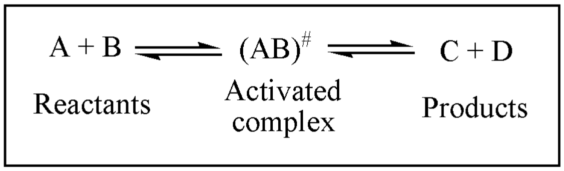
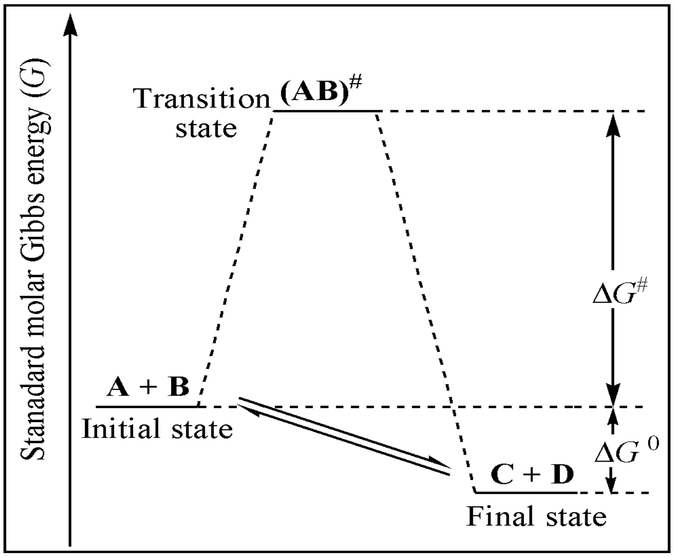


Fig. 2.6. Reactants A and B react through the activated complex $(AB)^{\#}$ to products C and D.

Fig. 2.7. One-dimensional Gibbs energy diagram for the above reaction in solution. ΔG^0: standard molar Gibbs energies of reaction, $\Delta G^{\neq}$: standard molar Gibbs energies of activation for the reaction from the left to the right.[134]



The influence of solvent on reaction rates is best treated with the transition state theory and its Gibbs energy diagram is shown in figure 2.7. The change in the Gibbs energy of activation in going from one solvent to another is evaluated as the relative modification in Gibbs energy by differential solvation of the reactants and the activated complex (shown in figure 2.8) and it is assumed that the reactants and the activated complex are in thermal equilibrium with the solvent.

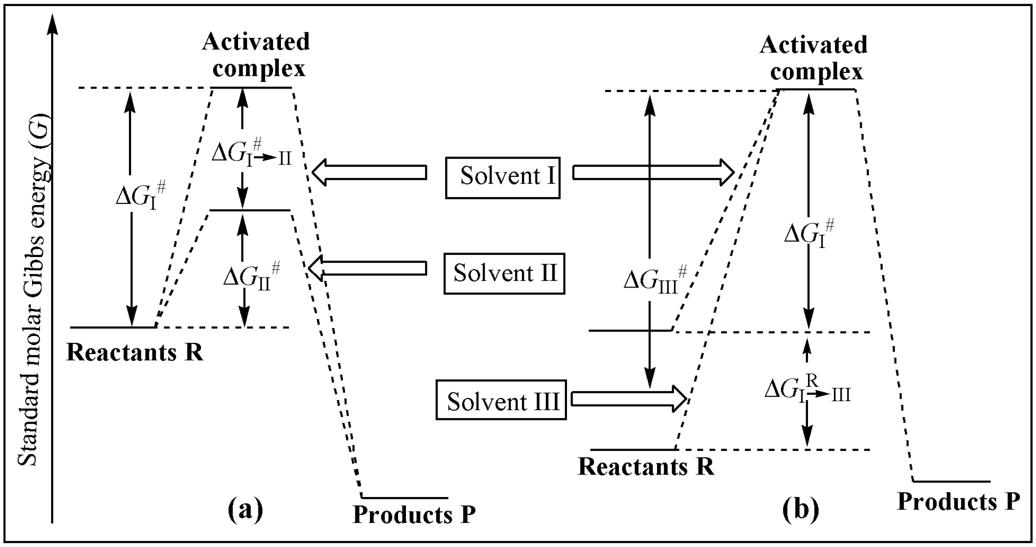


Fig. 2.8. One-dimensional Gibbs energy diagram for a chemical reaction in three different solvents I, II and III. (a) Reaction with non-solvated (solvent I) and solvated (solvent II) activated complex (preferential solvation of the activated complex); (b) Reaction with non-solvated (solvent I) and solvated (solvent II) reactants (preferential solvation of the reactants). $\Delta G_{\mathrm{I}}^{\#}$, $\Delta G_{\mathrm{II}}^{\#}$ and $\Delta G_{\mathrm{III}}^{\#}$: standard molar Gibbs energies of activation in solvents I, II and III, respectively. $\Delta G_{\mathrm{I}\to\mathrm{II}}^{\#}$ and $\Delta G_{\mathrm{I}\to\mathrm{III}}^{\mathrm{R}}$: standard molar Gibbs energies of transfer of the activated complex and the reactants from solvent I to solvents II and III, respectively.[134]

The smaller the $\Delta G^{\neq}$ value, the greater is the reaction rate. The fastest reaction (with $\Delta G^{\neq} = 0$) is given by $RT/N_A h$ corresponding to the frequency for the passage of the activated complex through the transition state. At 25 °C, this value is $6\times10^{12}\ \mathrm{s}^{-1}$, a typical value for the molecular vibrations. In principle, it is not sufficient to study only the change in $\Delta G^{\neq}$, because this term is related to an enthalpy and entropy terms ($\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$); thus there are four types of reaction rate control: (i) cooperative effects when both $\Delta H^{\neq}$ and $T\Delta S^{\neq}$ have same sign, (ii) enthalpy controlled reactions when $\Delta H^{\neq}$ and $T\Delta S^{\neq}$ have opposite effects and $\Delta H^{\neq} > T\Delta S^{\neq}$, (iii) entropy controlled reactions when $\Delta H^{\neq}$ and $T\Delta S^{\neq}$ have opposite effects and $\Delta H^{\neq} < T\Delta S^{\neq}$, and (iv) compensating effects when $\Delta H^{\neq}$ and $T\Delta S^{\neq}$ have opposite effects but nearly equal. The solvation of the products, however, does not have any influence on the reaction rate. This is because the initial reactants and the activated complex are solvated usually to different extents and the difference between both Gibbs transfer energies determines the reaction rate in solution.

2.6. Solvent Effects of UV-Visible Spectra of Solutions

When absorption spectra are measured in solvents of different polarity, the positions, intensities and shapes of the absorption bands usually gets modified by these solvents.[135-138] These changes are a result of intermolecular solute-solvent interactions forces such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc; all these forces alter the energy difference between the ground and excited state of the absorbing species. Theories of solvent effects on absorption spectra assume principally that the chemical states of the isolated and solvated chromophore-containing molecules are the same and treat these effects only as a physical perturbation of the relevant molecular states of the chromophores.[139-141] Thus, solvent effects on absorption spectra can provide information about solute solvent interactions[135-138] and can also provide information on primary solvation of solvated ion.[142] The solvent effect on spectra resulting from electronic transitions is primarily dependent on the chromophore and the nature of the transitions. The electronic transitions of particular interest are $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ as well as charge-transfer absorptions. It has been established experimentally that only those molecules with π-electrons for which the charge distribution and consequently the dipole moment in the electronic ground state is different from that in the excited state exhibit pronounced solvatochromism. This term is used to describe the pronounced change in position of a UV-Visible absorption band that accompanies a change in the polarity of the solvent. A hypsochromic (or blue) shift with increasing solvent polarity is called negative solvatochromism and the corresponding bathochromic (or red) shift is termed as positive solvatochromism. Interestingly, solutions of pyridinium N-phenolate betaine dye are red coloured in methanol, violet in ethanol, blue in isoamyl alcohol, green in acetone and yellow in anisol; thus covering the whole visible range. This extraordinary large solvent induced shift of the visible $\pi \rightarrow \pi^*$ absorption band of intra-molecular charge transfer character (from the phenolate to the pyridinium moiety) has been used to introduce an empirical solvent scale called $E_{\mathrm{T}}(30)$.[143-145] Differential solvation of the highly dipolar, zwitterionic electronic ground state and the less dipolar first excited state leads to the large negative solvatochromism.[146] Usually long-wave length absorption band undergoes a bathochromic shift as the solvent polarity increases, if the excited state is more polar than the ground state and if the ground state is more polar than the excited state, hypsochromic shift occurs with increasing solvent polarity. For metal complexes of ligands with π-electron system two kinds of solvent-dependent charge transfer absorptions depending on the relative electron-donor/electron acceptor properties of the metal and ligand: (i) metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT). Strong solvatochromism for both types of charge transfer transitions were observed.

2.7. Theoretical Approach

2.7.1. Molecular Theory for Partial Molar Volume

There are mainly two theoretical approaches based on statistical mechanics of liquids to the calculation of the partial molar volume. One of them is the scaled particle theory (SPT).[147-149] The SPT yields an approximate expression for free energy of cavity formation into a fluid. Hirata and Arakawa[150] obtained an analytical expression for the partial molar volume of cavity formation by taking the pressure derivative of the cavity formation free energy and succeeded in extracting the intrinsic volume of ions in aqueous solution. However, the SPT has two essential difficulties in its application to the systems of chemical and biochemical interest. First, the application of the original SPT is limited to spherical solute only. The other difficulty is with the SPT is its inefficiency in calculating the electrostatic effects on the partial molar volume. Irisa, Nagayama, and Hirata[151] resolved the former problem by extending the theory to arbitrary shaped solutes. They succeeded in calculating the partial molar volume of molecular solutes by using the extended SPT.[152] However, the latter problem remains unresolved even though the combination with dielectric continuum models was proposed.[153, 154] The other approach is based on the Kirkwood-Buff (KB) solution theory.[155] In the KB theory, the partial molar volume of a solute is given by:

$$\phi_V^0 = k_B T \kappa_T - \int_0^\infty [g(r)-1] 4\pi r^2 \partial r \qquad (132)$$

where κ_T is the isothermal compressibility of solution, k_B is the Boltzman constant and $g(r)$ is the radial distribution function between the solute and solvent. If the radial distribution function is obtained, the partial molar volume can be readily calculated through this equation. Molecular simulation may possibly give the radial distribution function. But attempts to combine the KB theory with molecular simulation are still limited to small molecules.[156-158] Another approach is to employ molecular liquid theories such as the reference hypernetted chain (RHNC)[159] and the reference interaction site model (RISM).[160] The RHNC theory coupled with the KB theory was applied to the partial molar volume of ions in aqueous solution.[161,162] With the KB theory, the RISM theory has succeeded in calculating and analyzing the partial molar volume for various molecular systems: ions,[163, 164] hydrocarbons[165, 166] and biomolecules[167, 168] in aqueous solution as well as other non-aqueous solutions.[169, 170] Recently, the RISM theory was further developed to describe the three-dimensional spatial correlation functions of solvent around a solute molecule.[171, 172] The theory, called 3D-RISM theory, was also combined with the KB theory and was applied for the analysis of the partial molar volumes of biomolecules.[173-179] Thus, the RISM theory is the most successful method for investigating the partial molar volume and other thermodynamic properties in solution chemistry.

2.7.2. Solvation Models

There are essentially two methods:[180] the *ab initio* calculation and the semi-empirical CNDO-type approach. In the *ab initio* calculation, the difference in energy between a solvate and the separate constituents is determined as a function of the geometry, i.e., bond angles and bond length. Solvation energy is then maximized with respect to these parameters. The solvent molecules may be regarded as rigid spheres having the same geometry as in the free state. The calculation employs the self-consistent field version of molecular orbital theory to solve the Schrödinger equation for the solvate and for the constituents separately neglecting electron correlation. The main problem is the proper choice of the basis set of orbitals (Gaussian or Slater type). After all the difference in energy between a solvate and the separate constituents is obtained with minimum error and with a given basis set the full molecular Hamiltonian is used for the calculation. The semi-empirical calculations employ an approach suggested by Pople *at al.*[181] The approach involves complete neglect of differential overlap (CNDO) of the basis set of orbitals. With a given basis set of orbitals this decreases the number of integrals to be calculated. This version is called CNDO/2 and involves empirical parameters based on ionization potential and electron affinities in the Hamiltonian and the energy of the system is expressed as a sum of one-atom and two-atom terms.

In molecular dynamic (MD) approach, a limited number of ions and molecules and Newtonian mechanics of movement of all particles in solution is studied. This requires the knowledge of the intermolecular energy of interactions between a pair of particles. Computer simulation approaches may be useful in this regard and the last few decades witnessed some interesting trends in the development of solvation models and computer softwares. A. Galindo *et al.* [182, 183] have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibrium of electrolytic aqueous solutions. The water molecules are modeled as hard spheres with four short-range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of different diameter to describe the anion and cation. The Debye-Hückel and mean spherical approximations are used to describe the interactions. Good agreement with experimental data was found for a number of aqueous electrolyte solutions.

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CHAPTER III

3.1. Source and Purification of the Chemicals Used

3.1.1. Solvents

Methanol (CH_4O, M.W. 32.04), dimethylsulfoxide (C_2H_6SO, M.W. 78.13), 1,4-dioxane ($C_4H_8O_2$, M.W. 88.11), N, N-dimethylformamide (C_3H_7NO, M.W. 73.10) and acetonitrile (C_2H_3N, M. W. 41.05) were used for preparing different binary solvent mixtures used as solvents in the research works embodied in this thesis. All these solvents were of spectroscopic grade and were used as received from the vendors. Their purities were ascertained by comparing their measured densities and viscosities to literature values[1-21] as listed in the respective chapters. Provenance and purity of these solvents are given in table 3.1.

Table 3.1. Provenance and purity of the solvents used.

Chemical	Source	Mass fraction purity	CAS No
Methanol	Merck, India	>0.998 [a]	67-56-1
Dimethylsulfoxide	S. D. Fine Chemicals, India	>0.995 [a]	67-68-5
1,4-dioxane	Merck, India	>0.998 [a]	123-91-1
N, N-dimethylformamide	Merck, India	>0.998 [a]	68-12-2
Acetonitrile	Merck, India	>0.988 [a]	75-05-8

[a] Moisture content as prescribed by the respective vendors were 0.05%.

3.1.2. Mixed Solvents

Methanolic solutions of the ionic liquid 1-butyl-2, 3-dimethyl imidazolium tetrafluoroborate ([bdmim]BF_4), aqueous dimethylsulphoxide solutions, binary mixtures of 1,4-dioxane with methanol, aqueous methanol solutions, binary mixtures of N, N- dimethylformamide with acetonitrile, methanolic solutions of tetrabutylammonium bromide (Bu_4NBr) as well as methanolic solutions of pyridoxine hydrochloride were used as mixed solvents for different investigations reported in this dissertation. De-ionized water was collected from a de-ionization plant of the university, N. B. U and then distilled twice in an all glass distilling set along with alkaline $KMnO_4$ solution to remove any organic matter[22] therein. For preparing aqueous solutions doubly distilled de-ionized water with a specific conductance of 1×10^{-6} $S\,cm^{-1}$ at 298.15 K was used. During the preparation of various liquid-liquid binary solvents, respective pure components were taken separately in air-tight glass stoppered bottles and thermostated at 298.15 K for sufficient time. When the thermal equilibrium was ensured, the required masses of each component were transferred to thoroughly cleaned and dried bottles, shaken well and stoppered. However, for preparing solid-liquid solvent systems required mass of the sold component was mixed with required mass of the liquid component with necessary adjustments to achieve exact mass fraction of the solid component in the mixed solvent system. During all the mixing processes adequate precautions were adopted to prevent contamination from CO_2, moisture and other impurities. The relative error in solvent composition was estimated to be about 1%.

Stock solutions of the solutes, i.e., different Schiff base complexes in different mixed solvents were prepared by mass and the working solutions were prepared by mass dilution. Solute molalities (m) were converted into molarities (c) by using experimental density values.[23] All solutions were prepared afresh and degassed with dry nitrogen before use. The uncertainty in molarity (c) of the solutes in solutions was evaluated to be ±0.0001 mol.dm^{-3}.

3.1.3. Solutes

The Schiff base complexes, viz., N, N$^{/}$-ethylene-bis(salicylideneiminato)-diaquochromium(III) chloride, N, N$^{/}$-ethylenebis-(salicylideneiminato)Co(II), iron(III)-N, N$^{/}$-ethylene-bis(salicylideneiminato)-chloride, salicylaldehyde anil zinc(II), {N, N$^{/}$-bis[(2-pyridinyl)methylene]-1, 2-benzenediamine]-bis(nitrato)}Cu(II) were used as solutes and were prepared by following standard literature procedures.[24-29] Schiff bases are generally synthesized by the condensation of aldehydes and amines. In the present investigation the aldehydes employed were salicylaldehyde and pyridine-2-carboxaldehyde. The amines chosen were 1,2-ethylenediamine, 1,2-phenylenediamine and aniline. Provenance and purity of these chemicals are given in table 3.2.

Table 3.2. Provenance and purity of the amines and aldehydes used.

Chemical	Source	Mass fraction purity	CAS No
1,2-ethylenediamine	S. D. Fine Chemicals, India	>0.995	107-15-3
1,2-phenylenediamine	S. D. Fine Chemicals, India	>0.995	95-54-5
Aniline	S. D. Fine Chemicals, India	>0.995	62-53-3
Salicylaldehyde	S. D. Fine Chemicals, India	>0.995	90-02-08
Pyridine-2-carboxaldehyde	S. D. Fine Chemicals, India	>0.995	1121-60-4

3.1.3.1. Synthesis of SalenH$_2$

N, N$^{/}$-bis-(salicylaldehyde)-ethylenediimine, abbreviated as SalenH$_2$, was prepared by refluxing an ethanolic solution of 1,2-ethylenediamine (0.01 mole, 0.67 ml) and salicylaldehyde (0.02 mol, 2.15 ml) for 1 hour. The bright yellow crystalline solid was filtered and washed with ethanol several times and dried in a vacuum desiccator over anhydrous CaCl$_2$ for several hours. The purity of the compound was checked by elemental analysis (Calc: C, 71.62; H, 6.01; N, 10.44; O, 11.93; found: C, 71.42; H, 5.98; N, 10.32; O, 11.88) and IR spectroscopy with major IR peaks at (KBr, cm^{-1}): 3435, 2910, 2840, 1630, 1595, 750. The molecular structure of SalenH$_2$ and its IR spectrum are shown in figures 3.1 and 3.2, respectively.

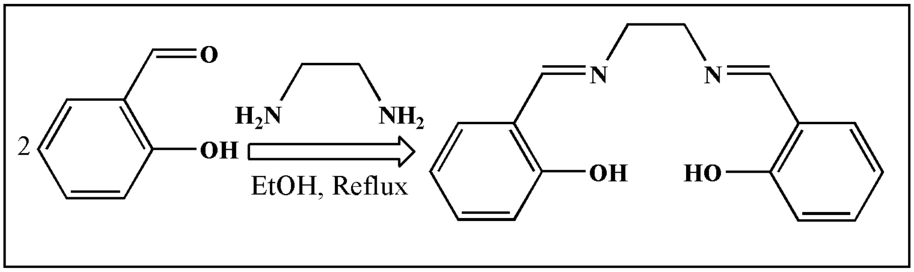

Fig 3.1. Synthesis of SalenH$_2$.

Its melting point was determined by open capillary method to be at 128 °C and its UV-Visible spectrum in methanol two major absorption bands at 254 and 316 nm along with a weak peak at 404 nm (shown in figure 3.3).

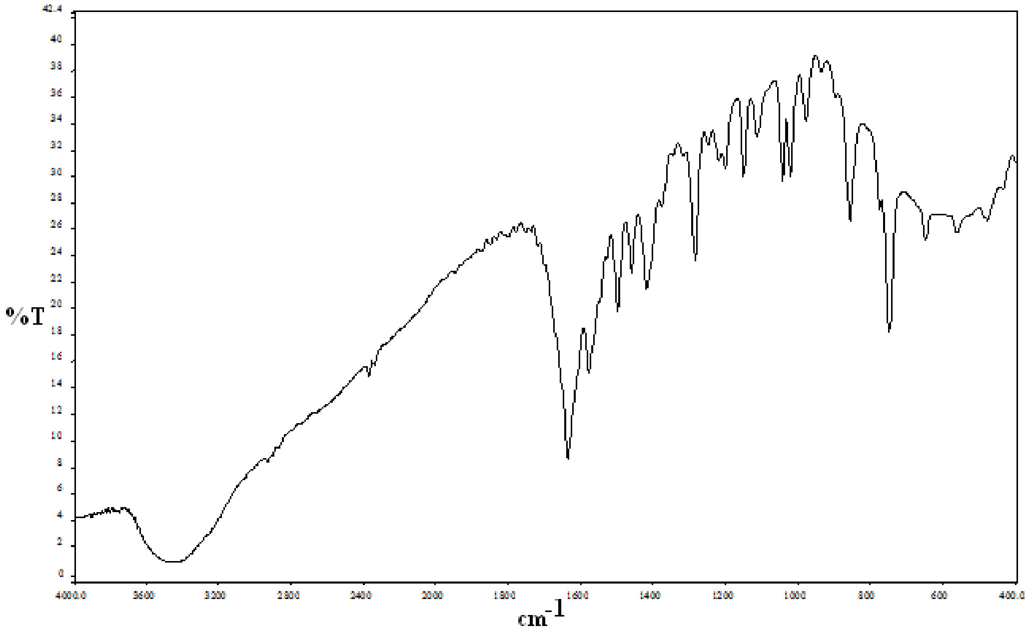

Fig. 3.2. IR spectrum (KBr, cm^{-1}) of $SalenH_2$.

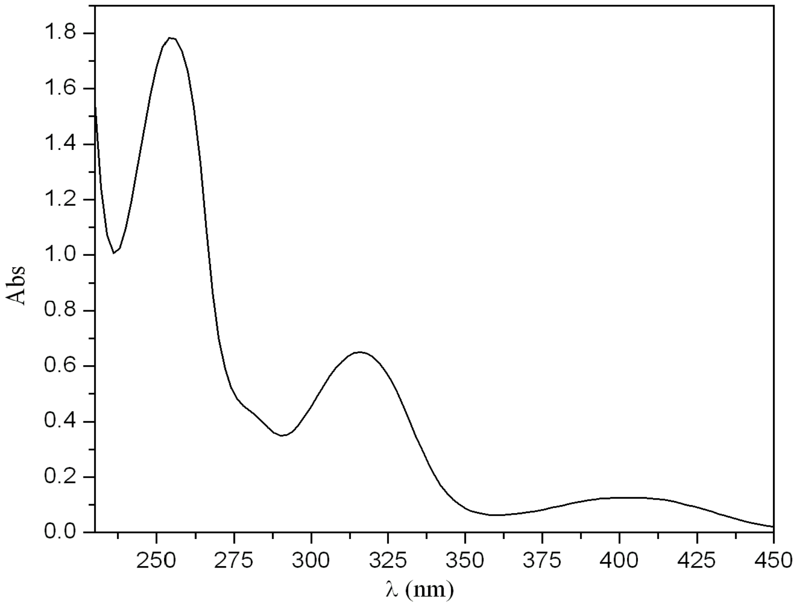

Fig. 3.3. UV-Visible spectrum of $SalenH_2$ in methanol at 298.15 K.

3.1.3.2. Synthesis of $[Cr^{III}(Salen)(H_2O)_2]Cl$

N, N′-ethylenebis-(salicylideneiminato)-diaquochromium(III) chloride, $[Cr(salen)(H_2O)_2]Cl$ was prepared by a slight modification of a literature method[24] from equimolar quantities of $CrCl_3.6H_2O$ and the Schiff base, $SalenH_2$ in ethylene glycol-water-methanol (1:1:3) mixture. Salicylaldehyde (0.1 mol) and ethylenediamine (0.05 mol) were added to a solution of $CrCl_3.6H_2O$ (0.05 mol) dissolved in a mixture of ethylene glycol-water-methanol (1:1:3). The mixture was refluxed for about 30 min and then Na_2CO_3 (0.03 mol) was added gradually to the solution, followed by refluxing the solution for about 3-4 hours and by concentrating the solution. The reddish-brown precipitate of the complex thus obtained was dried and recrystallized several times from 80% MeOH to obtain reddish orange crystals of the complex. The complex was kept in a vacuum desiccator over anhydrous $CaCl_2$ for several hours. The purity of the complex was checked by elemental analysis (Calc: C, 49.30; H, 4.65; N, 7.19; Cr, 13.34; Found: C, 49.05; H, 4.84; N, 7.13; Cr, 13.38) and IR spectroscopy. The molecular structure of the complex $[Cr(salen)(H_2O)_2]Cl$ is shown in figure 3.4.

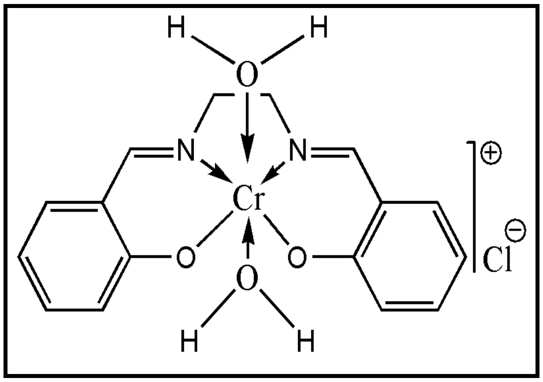

Fig. 3.4. The molecular structure of the complex $[Cr(salen)(H_2O)_2]Cl$.

The IR spectrum of the complex $[Cr(salen)(H_2O)_2]Cl$ (shown in figure 3.5) showed the major absorptions at 1629.7 (1627 [30]), 1600.6 (1575, 1597 [30]), and 1539.1 (1530[30]) cm^{-1} attributable to $\nu_{C=N}$, $\nu_{C=C}$ stretching frequencies and the absorptions at 2943.2 and 3450.3 cm^{-1} are attributable to coordinated water molecules and $\nu_{C\text{-}H}$ stretching frequencies.[24]

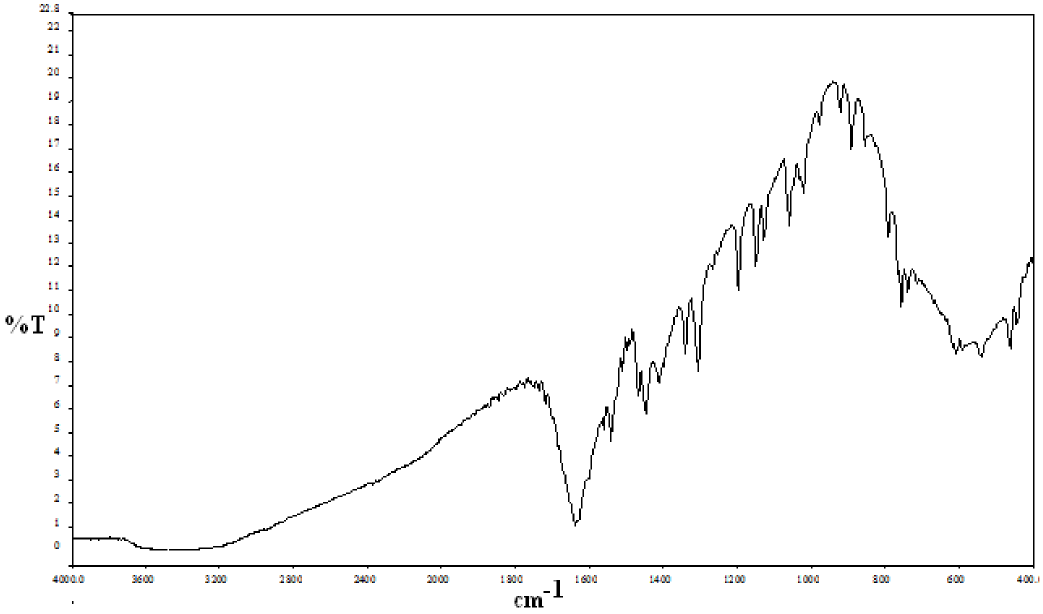

Fig. 3.5. IR spectrum (KBr, cm^{-1}) of the complex $[Cr(salen)(H_2O)_2]Cl$.

Magnetic moment of the complex, measured with a Sherwood scientific magnetic balance, was found to be 3.83 B.M (3.85 B.M[30]) at room temperature.

3.1.3.3. Synthesis of Co^{II}(Salen)

N, N′-Ethylene-bis(salicylideneiminato)cobalt(II) or Co^{II}(salen) was prepared by a slight modification of a known method [25, 26] by adding cobalt acetate, $Co(OAc)_2.4H_2O$ (1.245 g, 5 mmol) dissolved in 40 mL methanol to a 30 mL methanolic solution of $SalenH_2$ (1.337 g, 5 mmol). The mixture was refluxed for 3 hours at 70 °C. The red crystalline precipitate of the cobalt complex was filtered off, washed, and dried in *vacuo* at room temperature for about 6-8 hrs (84% yield). The product was recrystallised from methanol and kept a vacuum desiccator over anhydrous $CaCl_2$. The molecular structure of the complex Co(salen) is shown in figure 3.6.

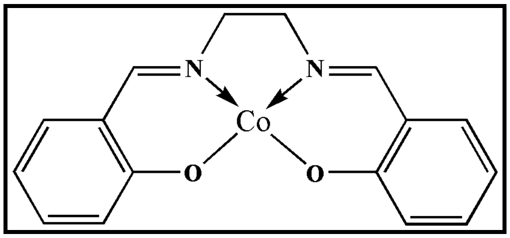

Fig. 3.6. The molecular structure of Co(salen).

The purity of the complex was checked by elemental analysis (Found: C, 59.10; H, 4.33; N, 8.63; O, 10.01.; Co, 18.11; Calc: C, 59.09; H, 4.34; N, 8.61; O, 9.84; Co, 18.12) and IR spectroscopy. Characteristic IR bands (shown in figure 3.7) for the prepared complex (KBr, cm^{-1}) are: 1626.80 (1623.86[31]) for $\nu_{C=N}$, 1332.44 (1332.44[31]) for $\nu_{C=O}$, 430.70 (430.70[31]) for ν_{Co-O} and 468.32 (468.32[31]) for ν_{Co-N}. Magnetic moment, measured with a Sherwood scientific magnetic balance, was found to be 2.71 B.M (2.75 B.M[31]) at room temperature. UV-Visible spectrum of the complex in methanol showed a major absorption band at 388 nm as shown in figure 3.8).

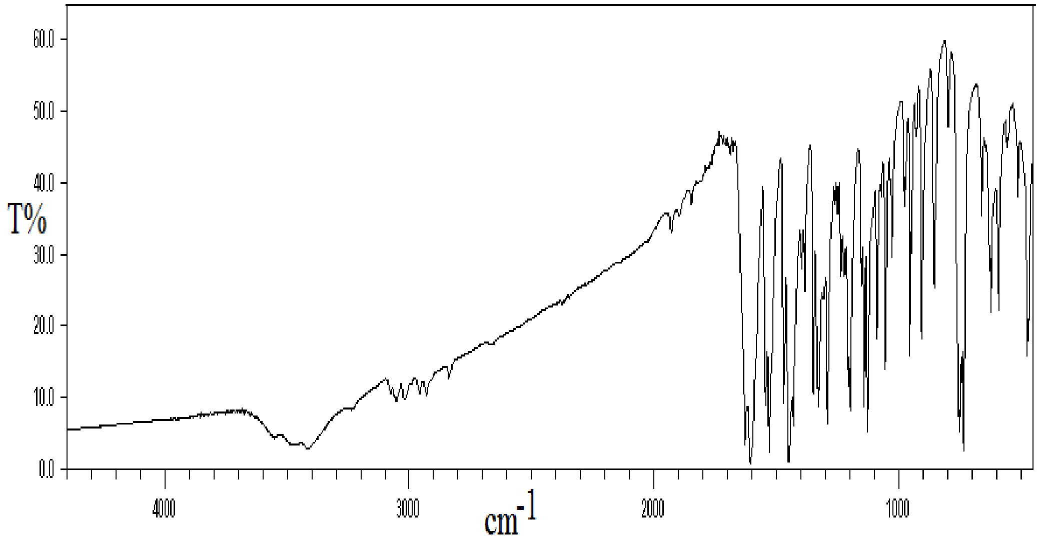

Fig. 3.7. IR spectrum (KBr, cm^{-1}) of Co(salen).

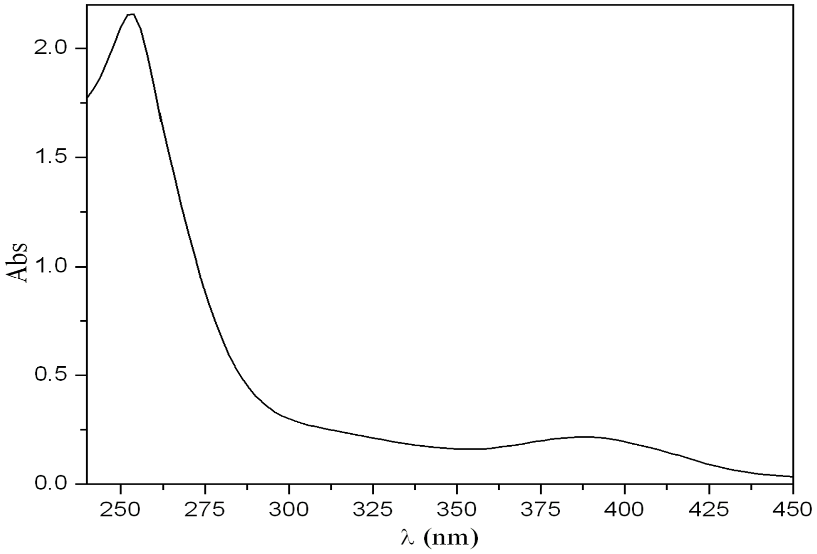

Fig. 3.8. UV-Visible spectrum of Co(salen).

3.1.3.4. Synthesis of [Fe^{III}(Salen)Cl]

Iron(III)-N, N$^{/}$-ethylene-bis(salicylideneiminato)-chloride, Fe^{III}(salen)Cl was prepared by a slight modification of a known method [27] from equimolar quantities of $FeCl_3.6H_2O$ and the Schiff base, $SalenH_2$ in ethanol. Metallation was achieved by adding triethylamine (NEt_3, 1.3 mL) and $FeCl_3.6H_2O$ (1.08 g, 4mmol), dissolved in 30 mL ethanol, to a 30 mL ethanolic solution of $SalenH_2$ (1.07 g, 4mmol). The mixture was refluxed for 30 min at 60 °C, concentrated in vacuum to approximately 15 mL at room temperature. The deep brown microcrystalline solid was filtered, dried in vacuum at 50-60 °C and was recrystallized finally from ethanol and was kept in a vacuum desiccator over anhydrous $CaCl_2$. The molecular structure of the complex, Fe^{III}(salen)Cl is shown in figure 3.9.

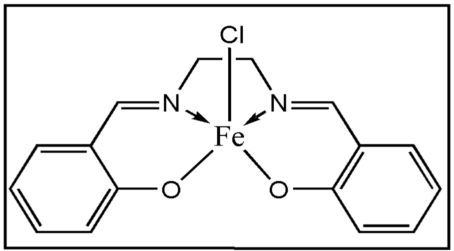

Fig. 3.9. The molecular structure of Fe^{III}(salen)Cl.

The purity of the complex was checked by elemental analysis (Found: C, 53.64; H, 4.01; N, 7.94; Cl, 9.85; Fe, 15.60; Calc: C, 53.74; H, 3.95; N, 7.84; Cl, 9.91; Fe, 15.63) and IR spectroscopy (shown in figure 3.10). Characteristic IR bands for the prepared complex (KBr, cm^{-1}) are 585.76, 617.44, 757.92, 795.02, 904.87, 1445.82, 1544.35, 1629.76, 3448.17.

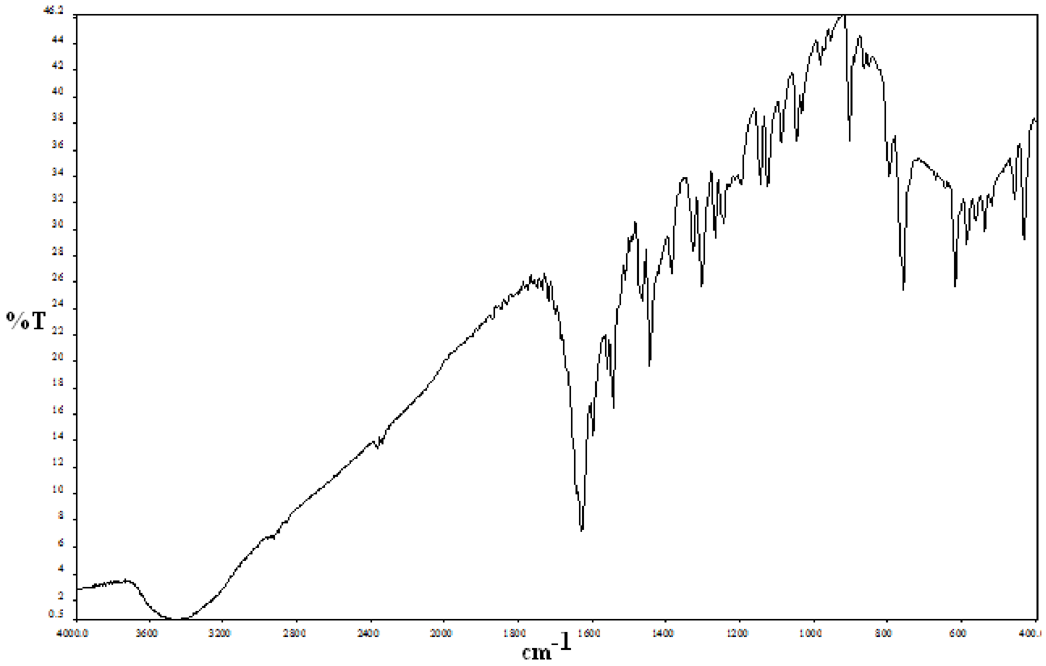

Fig. 3.10. IR spectrum (KBr, cm^{-1}) of Fe^{III}(salen)Cl.

Magnetic moment, measured with a Sherwood scientific magnetic balance, was found to be 5.31 B.M (5.29 B.M [32]) at room temperature. UV-Visible spectrum of the complex in methanol showed major absorption bands at 254, 316 nm and 404 nm as shown in figure 3.11).

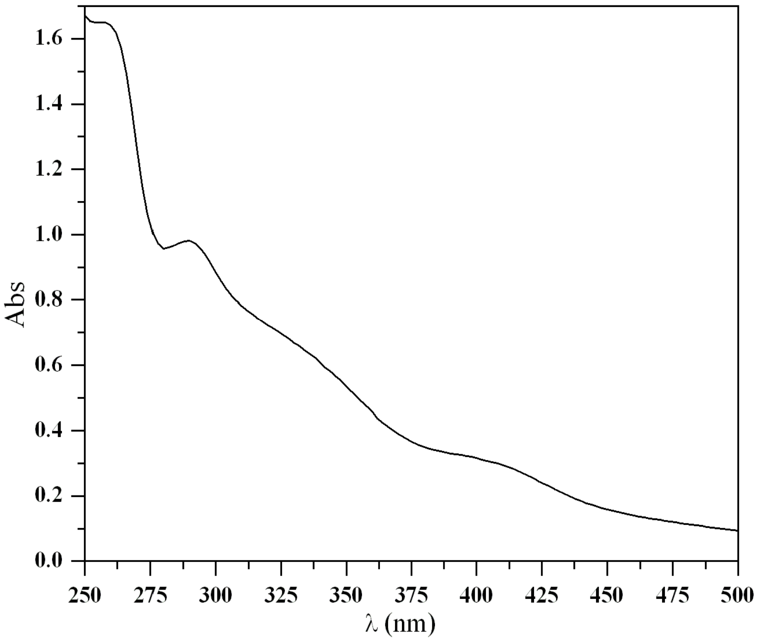

Fig. 3.11. UV-Visible spectrum of Fe^{III}(salen)Cl.

3.1.3.5. Synthesis of salicylaldehyde anil zinc (II)

Salicylaldehyde anil, abbreviated as SA, $C_{13}H_{11}NO$ and its zinc(II) complex, abbreviated as SAZ, $C_{26}H_{24}N_2O_4Zn$ were prepared by following literature method [28] with slight modifications. SA was prepared by condensation reaction between salicylaldehyde and aniline, taken in 1:1 molar ratio and stirred for 3-4 hours at 140-150 ^{o}C. The yellow precipitate of SA was filtered, washed with little MeOH, followed by diethylether and then recrystalized from MeOH. A methanol solution of zinc acetate, $Zn(O_2CCH_3)_2.2H_2O$ and SA (in 1:2 molar ratio) was stirred for 1-2 hours at ambient temperature and SAZ was obtained as yellowish green product. It was filtered, dried in vacuum at 50-60 ^{o}C and was finally recrystallized from methanol and was kept in a vacuum desiccator over anhydrous $CaCl_2$. The molecular structures of the ligand SA and the complex SAZ are depicted in figure 3.12.

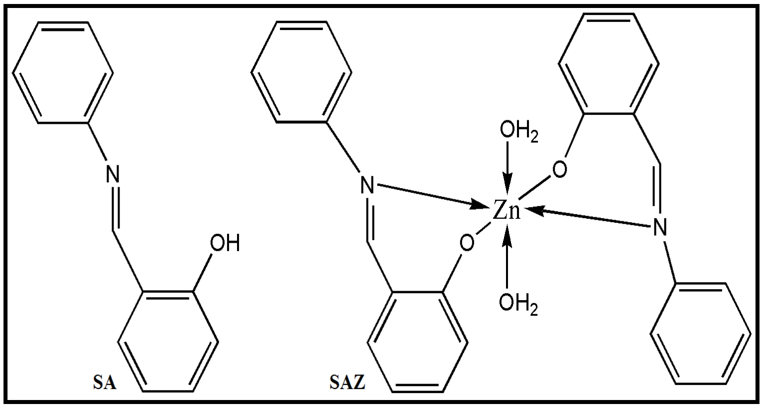

Fig. 3.12. The molecular structures of the ligand SA and the complex SAZ.

The purity of the complex was checked by elemental analysis (Found: C, 63.21; H, 4.05; N, 5.64; O, 12.92; Zn, 13.22; Calc: C, 63.23; H, 4.09; N, 5.67; O, 12.96; Zn, 13.24) and IR spectroscopy. Characteristic IR bands (shown in figure 3.13) for the prepared complex (KBr, cm^{-1}) are 1616.1 (1606.8 [33]), 1589.2, 1253.1 (1253 [33]), 1174.1, 596 (608 [33]), 547.7, 3435 (3435 [33]). UV-Visible spectrum of the complex in methanol showed major absorption bands at 226, 296 and 382 nm (shown in figure 3.14).

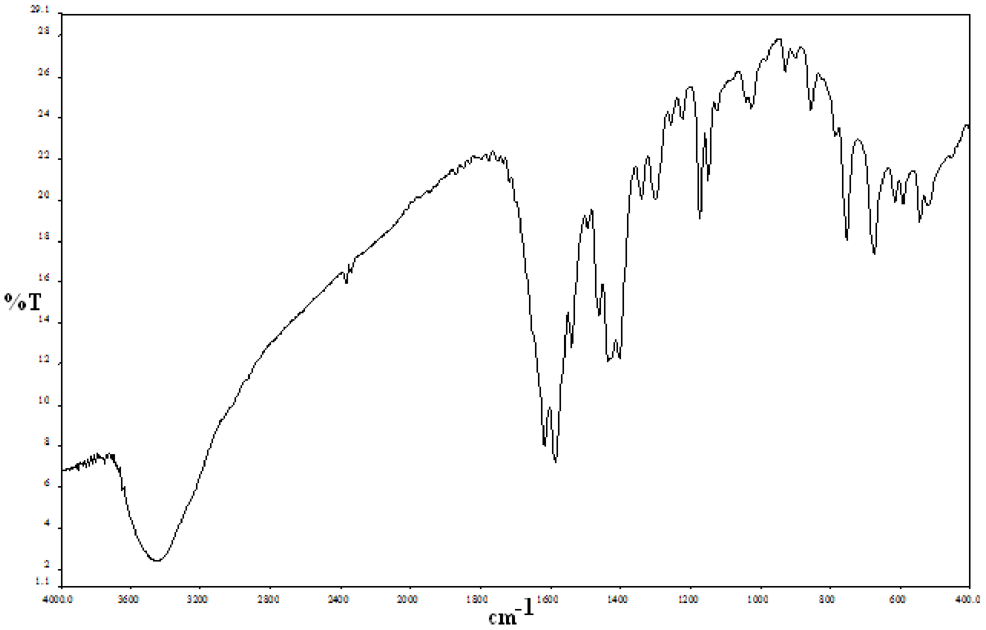

Fig. 3.13. IR spectrum of the complex SAZ.

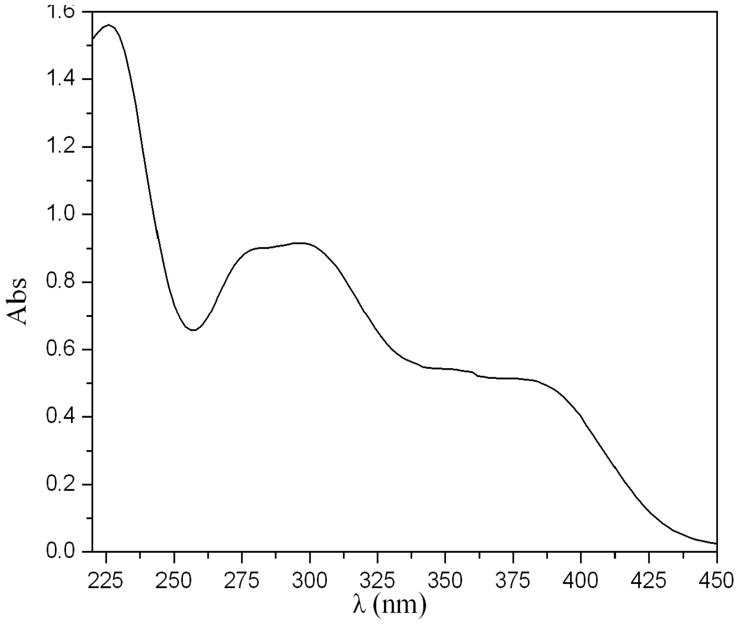

Fig. 3.14. UV-Visible spectrum of the complex SAZ.

3.1.3.6. Synthesis of {N, N$^{/}$-bis[(2-pyridinyl)methylene]-1, 2-benzenediamine]-bis(nitrato)}Cu(II)

The Cu(II) complex was prepared by following a literature method.[29] The ligand, 1,2-diaminophenyl-N, N$^{/}$-bis-(2-pyridinecarboxaldimine) was prepared from a mixture of pyridine-2-carboxaldehyde (10 mmol, 1.92 ml) and 1,2-phenylenediamine (5 mmol, 0.54 g) in methanol. The reaction mixture was refluxed for 4-5 hours and a pale yellow colored solution of the ligand (L) was obtained. Next a methanolic solution of $Cu(NO_3)_2.3H_2O$ (10 mmol) was added dropwise to the ligand solution till a green colored solution appeared. This solution was then refluxed for 4 hours to get the desired complex, $CuL(NO_3)_2$ in the final solution. The solution was left in a fuming hood at room temperature for slow evaporation of the solvent. The product was filtered, dried and kept in a vacuum desiccator. The molecular structure of $CuL(NO_3)_2$ is depicted in figure 3.15.

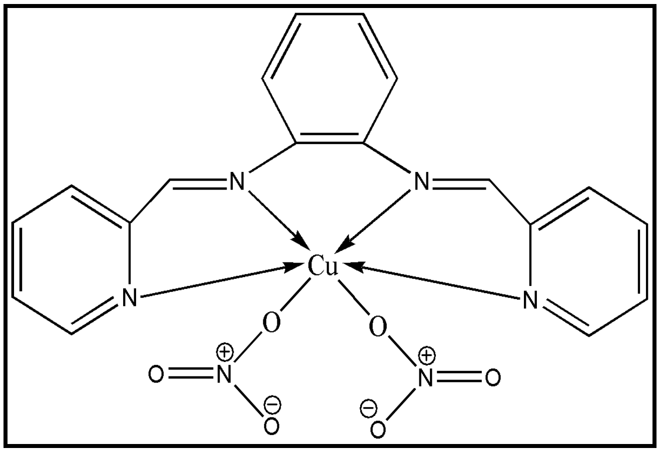

Fig. 3.15. The molecular structure of $CuL(NO_3)_2$.

The purity of the complex was checked by elemental analysis (Found: C, 45.57; H, 2.94; N, 17.70; Cu, 13.40; Calc: C, 45.63; H, 2.98; N, 17.73; Cu, 13.41) and IR spectroscopy (shown in figure 3.16). Characteristic IR bands for the prepared complex (KBr, cm^{-1}) are 2345.3, 1624.5, 1299.0, 1050.2, 750.3, 665.0, 452.2. Magnetic moment was measured to be 1.82 B.M at room temperature. UV-Visible spectrum of the complex in methanol showed a major absorption bands at 330 nm as shown in figure 3.17.

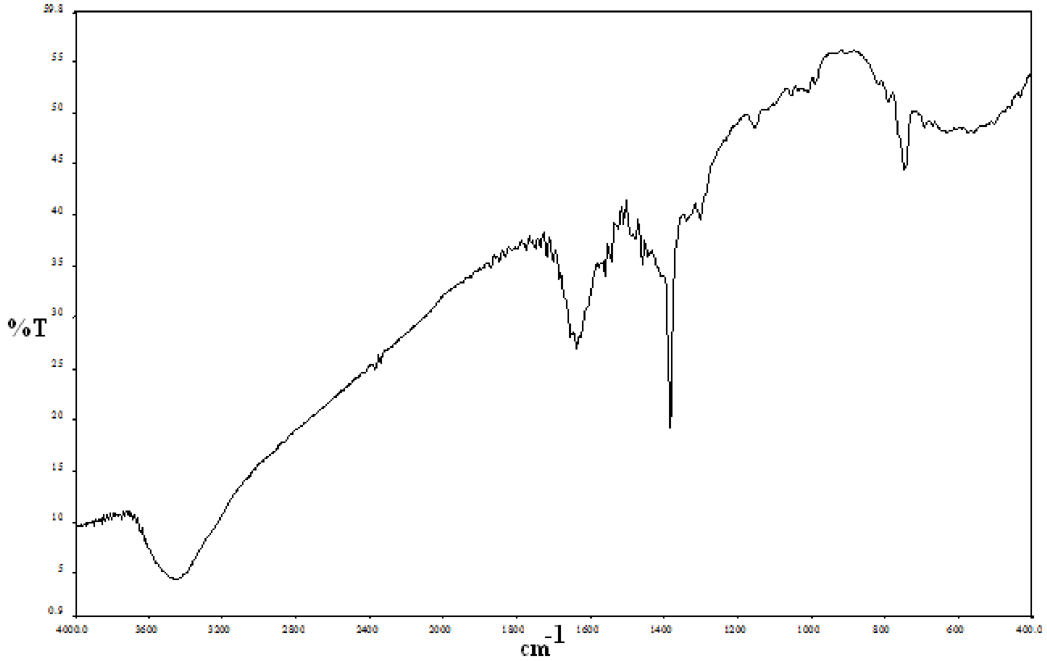

Fig. 3.16. IR spectrum of CuL(NO_3)$_2$.

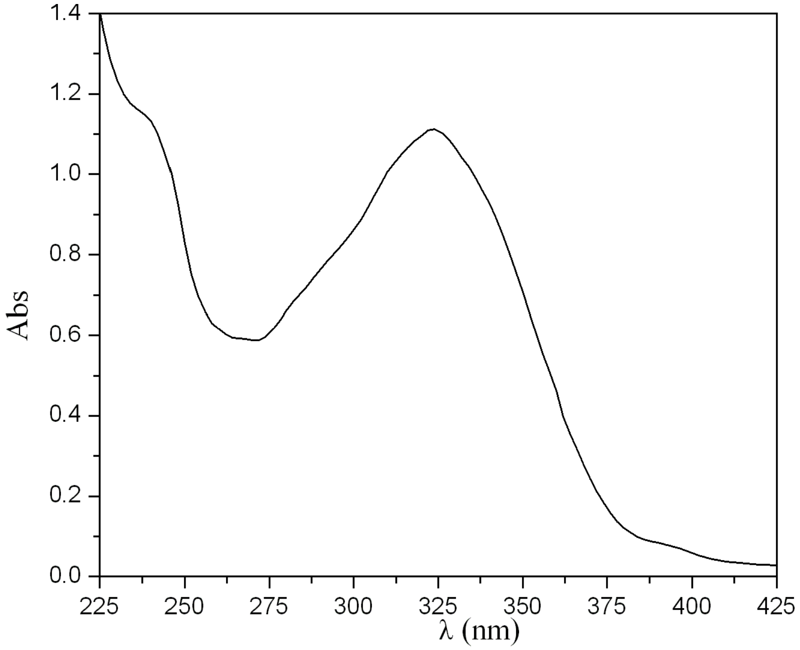

Fig. 3.17. UV-Visible spectrum of CuL(NO_3)$_2$.

Provenance and purity of all these synthesized chemicals are given in table 3.3.

Table 3.3. Provenance and purity of the synthesized Schiff base complexes.

Complex	Mol. Formula	M. Wt	Mass Frac. purity	CAS No
N, N$^{/}$-ethylenebis-(salicylideneiminato)-diaquochromium(III) chloride	$C_{16}H_{18}CrN_2O_4Cl$	389.77	>0.985	31274-22-3
N, N$^{/}$-Ethylene-bis(salicylideneiminato)cobalt(II)	$C_{16}H_{14}CoN_2O_2$	325.23	>0.985	14167-18-1
Iron(III)-N, N$^{/}$-ethylene-bis(salicylideneiminato)-chloride	$C_{16}H_{14}N_2O_2ClFe$	357.59	>0.985	38586-93-5
Salicylaldehyde anil zinc (II)	$C_{26}H_{24}N_2O_4Zn$	493.87	>0.985	14741-04-9
{N, N$^{/}$-bis[(2-pyridinyl)methylene]-1, 2-benzenediamine]-bis(nitrato)}Cu(II)	$C_{18}H_{14}CuN_6O_6$	473.89	>0.985	1000062-59-8

3.1.4. Other Solutes Used

Other solutes used in different research works embodied in this thesis are 1-butyl-2-3-dimethylimidazolium tetrafluoroborate ($C_9H_{17}BF_4N_2$, M. Wt. 240.05), tetrabutylammonium bromide (Bu_4NBr, M. Wt. 322.37), $CrCl_3.6H_2O$, $Co(O_2CCH_3)_2.4H_2O$, $FeCl_3.6H_2O$, $ZnO_2CCH_3)_2.2H_2O$, $Cu(NO_3)_2.3H_2O$ and pyridoxine hydrochloride ($C_8H_{11}ClNO_3$, M. Wt. 205.64). All these chemicals were of analytical grade (A. R) and were procured from different commercial sources. The ionic liquid 1-butyl-2-3-dimethylimidazolium tetrafluoroborate was dried under vacuum (0.004 mbar) at 65 ^{o}C overnight and kept under argon at all times. Tetrabutylammonium bromide was purified by dissolving it in a mixed alcohol medium and then recrystallised from solvent ether medium[34] and was dried in a vacuum desiccator for few hours before use.

Table 3.4. Provenance and purity of other chemicals used.

Chemical	Source	Mass fraction purity	CAS No
1-Butyl-2,3-dimethylimidazolium tetrafluoroborate ($C_9H_{17}BF_4N_2$)	Sigma-Aldrich, Germany	>0.985	402846-78-0
$CrCl_3.6H_2O$	S. D. Fine Chemicals, India	>0.995	10060-12-5
$Co(O_2CCH_3)_2.4H_2O$	S. D. Fine Chemicals, India	>0.995	6147-53-1
$FeCl_3.6H_2O$	Merck, India	>0.995	10025-77-1
$Cu(NO_3)_2.3H_2O$	S. D. Fine Chemicals, India	>0.995	10031-43-3
$Zn(O_2CCH_3)_2.2H_2O$	S. D. Fine Chemicals, India	>0.995	5970-45-6
Tetrabutylammonium bromide (Bu_4NBr)	Merck, India	>0.985	1643-19-2
Pyridoxine hydrochloride ($C_8H_{11}ClNO_3$)	S. D. Fine Chemicals, India	>0.985	58-56-0

Pyridoxine hydrochloride was taken in darkened glass bottle and kept in a vacuum desiccator over fused $CaCl_2$ for several hours before use. Except these solutes all the remaining salts were used as obtained from the vendors. Provenance and purity of these chemicals are given in table 3.4.

3.2. Experimental Methods

3.2.1. Physico-chemical methods used to characterize synthesized compounds

A variety of physico-chemical methods have been employed to characterize the structure of Schiff base ligands and their metal chelates. A brief account of these methods is given below.

a) Elemental analysis

CHN analyses of all the synthesized compounds were done on a Perkin–Elmer (Model 240C) analyzer. The metal content in the complexes were determined by using Atomic Absorption Spectrophotometer (Varian SpectrAA 50B). It was calibrated with Sigma-Aldrich standards for a particular metal and concentration determinations were done with weighted amount of the complexes digested in concentrated nitric acid and diluted to definite volumes. Figure 3.18 shows the AAS instrument used for the analysis of metal contents in the complexes.

Fig. 3.18. Atomic Absorption Spectrophotometer (Varian SpectrAA 50B).

b) Magnetic susceptibility measurement

The magnetic susceptibility measurements were done at room temperature on a Sherwood Scientific Ltd magnetic susceptibility balance (Magway MSB Mk1). The MSB works on the basis of a stationary sample and moving magnets. The pairs of magnets are placed at opposite ends of a beam so placing the system in balance. Introduction of the sample between the poles of one pair of magnets produces a deflection of the beam that is registered by means of phototransistors. A current is made to pass through a coil mounted between the poles of the other pair of magnets, producing a force restoring the system to balance. At the position of equilibrium, the current through the coil is proportional to the force exerted by the sample and can be measured as a voltage drop. Figure 3.19 shows the magnetic susceptibility balance used.

Fig. 3.19. The magnetic susceptibility balance.

The solid sample is tightly packed into weighed sample tube with a suitable length (*l*) and noted the sample weight (*m*). Then the packed sample tube was placed into tube guide of the balance and the reading (*R*) was noted. The mass susceptibility, χ_g, is calculated using:

$$\chi_g = C_{\mathrm{Bal}} \times l \times \frac{(R - R_0)}{m \times 10^9} \qquad (1)$$

where l = the sample length (in cm), m = the sample mass (in g), R = the reading for the tube plus sample, R_0 = the empty tube reading and C_{Bal} = the balance calibration constant. Thus molar susceptibility is $\chi_M = \chi_g \times \mathrm{M.\,Wt\ of\ the\ sample}$. The molar susceptibility is the corrected with diamagnetic contribution. The effective magnetic moment, μ_{eff}, is then calculated by using the following expression:

$$\mu_{eff} = 2.83\sqrt{T \times \chi_A} \quad \mathrm{B.M} \qquad (2)$$

where χ_A is the corrected molar susceptibility. The MSB was calibrated with $Hg[Co(SCN)_4]$ before the measurements.

c) Infrared spectra

FT–IR spectra of Schiff bases and their complexes were recorded as either KBr pellets with a Perkin-Elmer FT-IR spectrophotometer (Spectrum RX-1) in the range 400-4000 cm^{-1}. KBr for IR spectroscopy from Sigma-Aldrich, Germany was used for preparing the pellets after drying the salt in a drying pistol over anhydrous $CaCl_2$ for 24 hours and then kept in vacuum desiccator over anhydrous $CaCl_2$ before use. Figure 3.20 shows the Perkin–Elmer FT-IR spectrophotometer (Spectrum RX-1) used.

Fig. 3.20. Perkin–Elmer FT-IR spectrophotometer (Spectrum RX-1).

d) Electronic spectra

Electronic spectra of the ligands and its complexes in various solvents were recorded on a Jasco V-530 double beam UV-VIS Spectrophotometer at 298.15 K. Figure 3.21 shows the UV-VIS Spectrophotometer used. It was coupled with a thermostatic arrangement and maintained at 298.15 K. A quartz cell of 1 cm path length was used for the spectral measurements.

Fig. 3.21. Jasco V-530 double beam UV-VIS Spectrophotometer.

e) Conductivity

Systronic Conductivity meter- 308 is used for measuring specific conductivity of electrolytic solutions. It is a microprocessor based instrument and can provide both automatic and manual temperature compensation. The instrument shows the conductivity of the solution under test at the existing temperature or with temperature compensation. Provision for storing the cell constant and the calibrating solution type is provided with the help of battery backup. This data can be further used for measuring the conductivity of an unknown solution without recalibrating the instrument even after switching it off. The conductance measurements were carried out on this conductivity bridge by using a dip-type immersion conductivity cell, CD-10 with a cell constant of 1.0 ± 10% cm^{-1}. The instrument was standardized by using 0.1 (M) KCl solution. The cell was calibrated by the method of Lind and co-workers.[35] Measurements were made in a thermostatic water bath maintained at the experimental temperature with an accuracy of ± 0.01 K.

Fig. 3.22. Systronic Conductivity meter-308.

The conductivities were measured at a frequency of 1 kHz and were uncertain to 0.3%. Figure 3.22 shows the Conductivity meter used.

3.2.2. Mass measurement

Mass measurements were made on digital electronic analytical balance (Mettler Toledo, AG 285, Switzerland) as shown in figure 3.23.

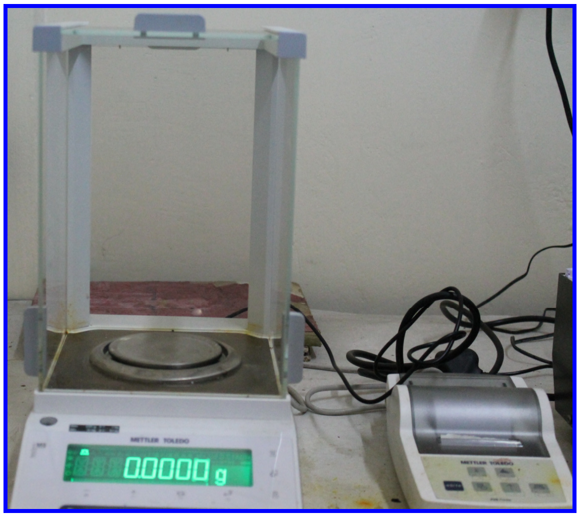

Fig. 3.23. Digital electronic analytical balance (Mettler Toledo, AG 285).

It can measure mass to a very high precision and accuracy. The weighing pan is inside a transparent enclosure with doors so that dust does not collect and any air currents in the room do not affect the balance's operation. The mass measurements were accurate to ± 0.01 mg.

3.2.3. Density measurement

The density was measured with the help of Anton Paar densitometer (DMA 4500M) as shown in figure 3.24.

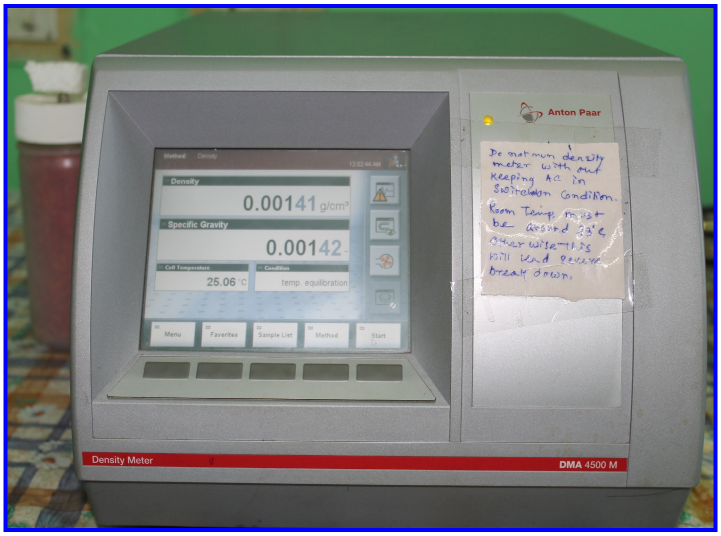

Fig. 3.24. Anton Paar densitometer (DMA 4500M).

In the digital densitometer, the mechanic oscillation of the U-tube is electromagnetically transformed into an alternating voltage of the same frequency. The period of oscillation (τ) can be measured with high resolution and stands in simple relation to the density (ρ) of the sample in the oscillator: [36]

$$\rho = \mathrm{A}\tau^2 - \mathrm{B} \tag{3}$$

where A and B are the respective instrument constants of each oscillator. Their values are determined by calibrating with two liquids of precisely known densities ρ_1 and ρ_2. The densities of the two liquids that are used for special adjustment have to differ by at least $\Delta\rho = 0.01\ \mathrm{g.cm^{-3}}$ and τ values of the adjustment media have to differ by at least 0.0001. Modern instruments calculate and store the constants A and B after the two calibration measurements mostly performed with air and water. They employ suitable measures to compensate various parasitic influences on the measuring result, e.g., the influence of the sample's viscosity and the non-linearity caused by the measuring instrument's finite mass.

The densitometer was calibrated at the experimental temperatures with doubly distilled, degassed water and dry air at atmospheric pressure. The temperature was kept constant with an accuracy of $\pm 1\times10^{-2}\ \mathrm{K}$ by using an automatic built–in Peltier technique. The stated repeatability and accuracy of the densities were $\pm 1\times10^{-5}\ \mathrm{g\cdot cm^{-3}}$ and $\pm 5\times10^{-5}\ \mathrm{g\cdot cm^{-3}}$, respectively. However, when the accuracy of the measured densities was tested with the density of an aqueous NaCl solution of known molality using the data given by Pitzer,[36] the estimated uncertainty of the density measurements for most of the solutions was found to be better than $\pm 2\times10^{-5}\ \mathrm{g\cdot cm^{-3}}$.

3.2.4. Measurement of Viscosity

The kinematic viscosities were measured by means of capillary viscometers: a suspended-level Ubbelohde viscometer and Cannon type Ubbelohde viscometer. The time of efflux of a constant volume of the experimental liquid through the capillary was measured with the aid of a digital stopwatch capable of measuring times accurate to ± 0.01s. The viscometer was always kept in a vertical position in the thermostatic bath with an accuracy of ± 0.01 K of the desired temperature. After attainment of thermal equilibrium, the flow times of pure liquids and liquid mixtures were measured thrice and the average of the readings was taken into account. During the measurements adequate precautions were taken to minimize evaporation loses. The efflux time for water at 298.15 K was measured to be 428.9 s. Viscosity of a solution (η) is obtained from the following equation,

$$\eta = (Kt - L/t)\rho \tag{4}$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The values of the constants K and L, determined by using water and methanol as the calibrating liquids, were found to be 1.9602×10^{-3} and 4.2019 respectively. The kinetic energy corrections were done from these values and they were found to be negligible. The uncertainty in viscosity measurements, based on our work on several pure liquids, was within $\pm 4\times10^{-4}\,\mathrm{mPa\cdot s}$. Figure 3.25 depicts the capillary viscometers used for measuring viscosities of the solutions studied.

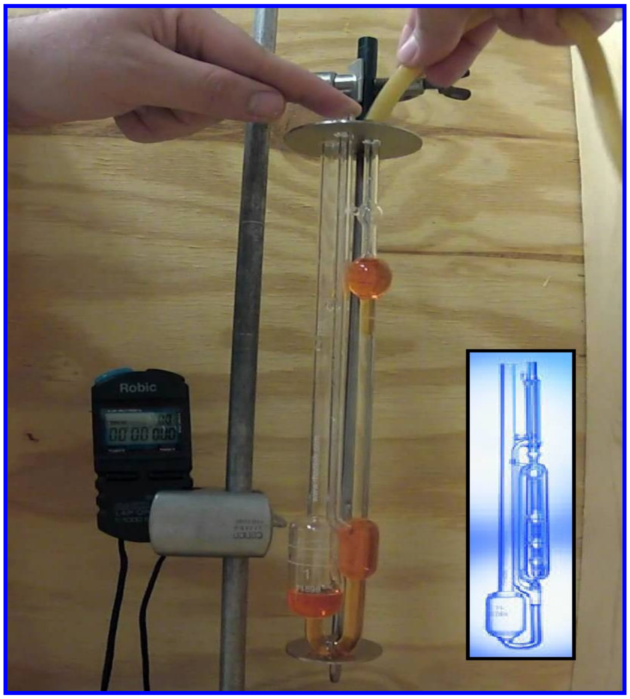

Fig. 3.25. Capillary viscometers: A suspended-level Ubbelohde viscometer. Inset: Cannon type Ubbelohde viscometer.

3.2.5. Refractive index measurement

Refractive indices were measured with an Abbe-refractometer (Cyberlab, MA01527, USA) against Sodium D light at 298.15 K. Water was circulated through the refractometer from a thermostatic bath maintained to ± 0.01 K of 298.15 K. It was calibrated by measuring the refractive indices of doubly distilled, degassed water at 298.15 K. The uncertainty in refractive indices was within ± 0.0002. Figure 3.26 shows the refractometer used.

Fig. 3.26. Abbe Refractometer (Cyberlab, MA01527, USA).

3.2.6. Spectrophotometric measurements

Absorption spectra of Schiff base complexes in different mixed solvent systems were recorded on a Jasco V-530 double beam UV-VIS spectrophotometer as mentioned above. During spectrophotometric measurements stock solution of a Schiff bases complex ($5.0\times10^{-5}\,\mathrm{mol\cdot L^{-1}}$) was prepared in the mixed solvent systems and 2.0 mL of it was taken in the quartz cell and absorption was measured against a selected spectroscopic grade reference solvent. Then 10 μL of a co-solvent or a solution of co-solute (of fixed concentration) in a mixed solvent or in the reference solvent was added in a stepwise fashion through a 10 μL pre-calibrated Hamilton syringe. The absorbance of the solution was measured at each step within 30 seconds after mixing.

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CHAPTER IV

Partial molar volumes and viscosity *B*-coefficients for N, N$^{/}$-ethylene-bis(salicylideneiminato)-diaquochromium(III) chloride in methanolic solutions of 1- butyl- 2, 3-dimethylimidazolium tetrafluoroborate at *T* = (298.15, 308.15 and 318.15) K*

4.1. Introduction

Chemical reactions and equilibria in solutions, very often, involve ionic species. In all such systems ions interact with one another and with the solvent molecules surrounding them. Chemical reactions and thermodynamic parameters in such systems largely depend on the extent of ion-ion and ion-solvent interactions. Depending on the extent of the inter-ionic interactions and ion-solvent interactions, solutions of ionic species may contain ion pairs like contact, solvent separated and solvent shared ion pairs.[1] Among the many potential materials, Schiff bases are considered as "privileged ligands" and they are easily obtained from the condensation of aldehydes and amines.[2, 3] Transition metal complexes of Schiff bases can catalyze various reactions such as oxidation, hydroxylation, and epoxidation,[4, 5] etc. The chemistry of transition metal complexes containing salen-type Schiff base ligands is of enduring significance, since such complexes have common features with metalloporphyrins regarding their electronic structure and catalytic activities,[6] etc. Schiff base complexes of Cr(III) such as N, N$^{/}$-ethylene-bis(salicylideneiminato)-diaquochromium(III) chloride, [Cr(salen)$(H_2O)_2$]Cl is a new kind of GTF model[7] and can reduce the symptoms of diabetes like hyperglycemia and cholesterol.[8, 9] On the other hand, Ionic liquids are organic electrolytes generally with asymmetric organic cations and non-coordinating counter inorganic anions.[10, 11] Because of their unique properties and variety, ionic liquids are regarded as high-performance fluids and find a wide range of engineering and material science applications.[12-15] Sometimes the catalytic activities of transition metal salen complexes improve by the addition of ionic liquids to the reaction mixture[16] and exploration the potentiality of ionic liquids as reaction media is very demanding in relation to green chemistry. Also the addition of co-solvents like water, methanol, etc., has been found to strongly affect various physico-chemical properties of ionic liquids.[17] Hence various thermophysical

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properties of systems comprising of transition metal complex, ionic liquid and molecular solvents can provide valuable information about ion-ion and ion-solvent interactions that probably characterize their solution thermodynamics and structure in solution phase and such information would permit developing a convenient experimental procedure for a suitable biphasic reusable catalytic system. Anyway, to the best of our knowledge there is no report of the physico-chemical properties of the system: $[Cr(salen)(H_2O)_2]Cl$ + $[bdmim]BF_4$ + MeOH in the literature. Hence in this chapter we reported some physico-chemical properties of the ternary mixtures of $[Cr(salen)(H_2O)_2]Cl$ + $[bdmimBF_4]$ + MeOH at 298.15, 308.15 and 318.15 K under ambient pressure and discussed the results in terms of ion-ion and ion-solvent interactions.

4.2. Experimental section

4.2.1. *Materials*

A. R. grade $CrCl_3.6H_2O$; 1,2-ethylenediamine and salicylaldehyde, each of purity > 99%, were procured from SD Fine chemicals, India. The ionic liquid 1-butyl-2,3-dimethyl imidazolium tetrafluoroborate of purity > 98% was procured from Sigma-Aldrich, Germany. Spectroscopic grade methanol (minimum assay, GC > 99.8% with 0.05% of water) was procured Merck, India. All the chemicals were used as received from the vendor. The various binary solvent mixtures were prepared by mass and necessary adjustments were done to achieve exact molar solutions (0.005, 0.01, 0.015 and 0.02 mol dm^{-3}) of $[bdmim]BF_4$ in methanol at 298.15 K. The relative error in solvent composition was about 1%. The physical properties of these solvent mixtures are given in table 4.1 and compared to the literature values[18-21] whenever available. $[Cr(salen)(H_2O)_2]Cl$ was prepared by a slight modification of a literature method[22] from equimolar quantities of $CrCl_3.6H_2O$ and the Schiff base, $SalenH_2$ in ethylene glycol-water-methanol (1:1:3) mixture. The preparation and physicochemical characterization of the complex has been described in chapter III. The molecular structures of the complex and the ionic liquid are shown in figure 4.1.

Stock solutions of the complex in different solvent mixtures were prepared by mass and the working solutions were prepared afresh before use by mass dilution. The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The conversion of molality into molarity was accomplished by using experimental density values whenever needed.

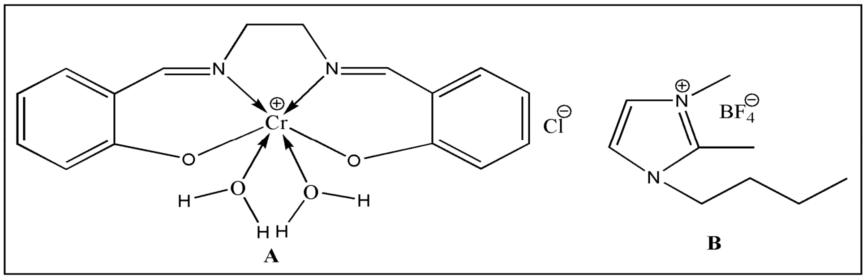

Fig. 4.1. Molecular structure of A) $[Cr(salen)(H_2O)_2]Cl$, and B) $[bdmim]BF_4$.

The uncertainty in molarity of $[Cr(salen)(H_2O)_2]Cl$ solutions was evaluated to ± $0.0001\ mol{\cdot}dm^{-3}$. Solutions of the comnplex $[Cr(salen)(H_2O)_2]Cl$ respond to $AgNO_3$ test for Cl^- ions and it actually behaves as a 1:1 electrolyte.[7]

4.2.2. *Apparatus and procedure*

The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M). The densitometer was calibrated at the experimental temperatures with doubly distilled and degassed water and dry air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $\pm 1\times10^{-2}\ K$ using the built–in Peltier technique. The estimated uncertainty of the density measurements for most of the solutions was found to be better than $\pm 2\times10^{-5}\ g\cdot cm^{-3}$. The viscosity was measured by means of a suspended Canon-type Ubbelohde viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled, degassed water and purified methanol.[18, 23, 24] It was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a digital stopwatch correct to ± 0.01s. In all determinations, an average of triplicate measurements was taken into account and adequate precautions were taken to minimize evaporation loses during the actual measurements. The uncertainty in viscosity measurements, based on our work on several pure liquids, was within $\pm 4\times10^{-4}\ mPa\cdot s$. Details about the density and viscosity measurements have been given in Chapter III.

Table 4.1. Densities (ρ) and viscosities (η) of different mixtures of methanol (1) + [bdmim]BF$_4$ (2) at T = (298.15 to 318.15) K

$c_{[\text{bdmim}]\text{BF}_4}$ [a]	T/K	$\frac{\rho \cdot 10^{-3}}{\text{kg} \cdot \text{m}^{-3}}$		$\frac{\eta}{\text{mPa} \cdot \text{s}}$	
		Expt.	Lit.	Expt.	Lit.
0.000	298.15	0.78661	0.7866[18] 0.78645[19] 0.78659[20] 0.78656[21]	0.5450	0.547[18] 0.542[19] 0.5446[20] 0.5422[21]
	308.15	0.77715	0.7769[18] 0.77710[19] 0.77728[20] 0.77720[21]	0.4760	0.471[18] 0.469[19] 0.4747[20] 0.4742[21]
	318.15	0.76774	0.76774[20] 0.76770[21]	0.4183	0.4185[20] 0.4174[21]
0.005	298.15	0.78759		0.5520	
	308.15	0.77801		0.4870	
	318.15	0.76849		0.4271	
0.010	298.15	0.78804		0.5649	
	308.15	0.77852		0.4978	
	318.15	0.76943		0.4360	
0.015	298.15	0.78845		0.5747	
	308.15	0.77898		0.5043	
	318.15	0.76992		0.4446	
0.020	298.15	0.78896		0.5845	
	308.15	0.77946		0.5130	
	318.15	0.77036		0.4532	

[a] Molarity of [bdmim]BF$_4$ in methanol.

4.3. Results and discussion

The experimental values of molalities (m), densities (ρ), viscosities (η) and derived parameters for the experimental solutions of [Cr(salen)(H$_2$O)$_2$]Cl in different mixed solvents at various temperatures are reported in table 4.2.

Table 4.2. Molalities (m), densities (ρ), viscosities (η), and apparent molar volumes (ϕ_V) of [Cr (salen)(H_2O)$_2$]Cl in different mixtures of methanol (1) + [bdmim]BF_4 (2) at T = (298.15 to 318.15) K

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{\rho\cdot 10^{-3}}{\text{kg}\cdot\text{m}^{-3}}$	$\frac{\eta}{\text{mPa}\cdot\text{s}}$	$\frac{\phi_V\cdot 10^{6}}{\text{m}^{3}\cdot\text{mol}^{-1}}$
0.000 [a]			
T/K = 298.15			
0.0076	0.78720	0.5486	369.83
0.0102	0.78739	0.5508	371.61
0.0128	0.78758	0.5541	372.64
0.0153	0.78776	0.5574	373.55
0.0192	0.78803	0.5618	375.36
0.0230	0.78829	0.5660	376.72
T/K = 308.15			
0.0076	0.77775	0.4806	370.60
0.0102	0.77795	0.4828	371.36
0.0128	0.77814	0.4850	373.07
0.0153	0.77833	0.4893	373.34
0.0192	0.77861	0.4947	374.99
0.0230	0.77888	0.4989	376.22
T/K = 318.15			
0.0076	0.76835	0.4228	371.28
0.0102	0.76855	0.4261	372.63
0.0128	0.76875	0.4293	373.39
0.0153	0.76894	0.4326	374.10
0.0192	0.76923	0.4369	375.36
0.0230	0.76951	0.4421	376.32
0.005 [a]			
T/K = 298.15			
0.0076	0.78818	0.5556	369.52
0.0102	0.78837	0.5578	371.30
0.0128	0.78855	0.5601	372.64
0.0153	0.78874	0.5633	373.23
0.0192	0.78901	0.5667	375.05
0.0230	0.78926	0.5709	377.10
T/K = 308.15			
0.0076	0.77861	0.4916	370.34
0.0102	0.77881	0.4948	371.09
0.0128	0.77899	0.4970	373.09
0.0153	0.77918	0.5003	374.15
0.0192	0.77946	0.5047	375.58
0.0230	0.77973	0.5088	376.67
T/K = 318.15			
0.0076	0.76910	0.4316	371.05
0.0102	0.76930	0.4338	372.40
0.0128	0.76949	0.4360	373.44
0.0153	0.76968	0.4392	374.98
0.0192	0.76997	0.4436	376.01

[a] Molarity of [bdmim]BF_4 in methanol.

Contd…

0.0230	0.77024	0.4477	377.56
0.010[a]			
T/K = 298.15			
0.0076	0.78863	0.5685	369.38
0.0102	0.78882	0.5708	371.16
0.0128	0.78900	0.5730	372.49
0.0153	0.78918	0.5752	374.15
0.0192	0.78944	0.5796	375.97
0.0230	0.78970	0.5838	377.65
T/K = 308.15			
0.0076	0.77912	0.5023	370.18
0.0102	0.77932	0.5046	370.93
0.0128	0.77950	0.5078	372.93
0.0153	0.77969	0.5100	373.99
0.0192	0.77996	0.5144	375.63
0.0230	0.78024	0.5196	376.50
T/K = 318.15			
0.0076	0.77004	0.4405	370.77
0.0102	0.77024	0.4427	372.11
0.0128	0.77043	0.4449	373.15
0.0153	0.77062	0.4481	374.68
0.0192	0.77090	0.4524	375.92
0.0230	0.77118	0.4566	377.26
0.015[a]			
T/K = 298.15			
0.0076	0.78904	0.5793	369.26
0.0102	0.78923	0.5815	371.03
0.0128	0.78941	0.5838	372.36
0.0153	0.78959	0.5860	374.01
0.0192	0.78985	0.5893	375.84
0.0230	0.79010	0.5935	378.22
T/K = 308.15			
0.0076	0.77958	0.5089	370.04
0.0102	0.77977	0.5111	372.41
0.0128	0.77995	0.5144	374.09
0.0153	0.78014	0.5166	374.92
0.0192	0.78041	0.5209	376.35
0.0230	0.78067	0.5251	378.51
T/K = 318.15			
0.0076	0.77053	0.4491	370.62
0.0102	0.77073	0.4513	371.96
0.0128	0.77092	0.4535	373.00
0.0153	0.77111	0.4567	374.52
0.0192	0.77139	0.4611	375.76
0.0230	0.77166	0.4652	377.84
0.020[a]			
T/K = 298.15			
0.0076	0.78955	0.5891	369.10
0.0102	0.78974	0.5914	370.87
0.0128	0.78992	0.5936	372.20

[a] Molarity of [bdmim]BF_4 in methanol. **Contd…**

0.0153	0.79010	0.5958	373.85
0.0192	0.79035	0.5992	376.51
0.0230	0.79061	0.6023	378.05
T/K = 298.15			
0.0076	0.78006	0.5176	369.89
0.0102	0.78025	0.5198	372.26
0.0128	0.78043	0.5220	373.94
0.0153	0.78062	0.5242	374.77
0.0192	0.78088	0.5286	377.06
0.0230	0.78115	0.5327	378.35
T/K = 298.15			
0.0076	0.77097	0.4577	370.48
0.0102	0.77117	0.4599	371.82
0.0128	0.77136	0.4621	372.86
0.0153	0.77155	0.4653	374.39
0.0192	0.77182	0.4696	376.50
0.0230	0.77210	0.4728	377.69

[a] Molarity of [bdmim]BF_4 in methanol.

4.3.1. *Standard partial molar volumes*

The apparent molar volumes (ϕ_V) were obtained from the solution densities using the following relation:

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_1)}{m\rho\rho_1} \qquad (1)$$

where M is the molar mass of [Cr(salen)$(H_2O)_2$]Cl, m is the molality of the solution, ρ_1 and ρ are the densities of the solvent and solution, respectively. As the plots of ϕ_V against square root of molar concentration ($\sqrt{m}$) were linear, ϕ_V values were fitted to Masson equation:[25]

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \qquad (2)$$

where intercept ϕ_V^0 is the partial molar volume at infinite dilution and is, by definition, free from ion-ion or solute-solute interactions; and thus provides a measure of ion-solvent or solute-solvent interactions. On the other hand, the slope S_V^* provides information regarding ion-ion or solute-solute interactions. The ϕ_V^0 values were determined by fitting the dilute data ($m < 0.1$) to equation (2) by using least squares linear regression and the correlation coefficients (R^2) were within the range

Table 4.3. Standard partial molar volumes (ϕ_V^0), the slopes (S_V^*) and standard deviations (σ) for $[Cr(salen)(H_2O)_2]Cl$ in different mixtures of methanol (1) + $[bdmim]BF_4$ (2) at T = (298.15 To 318.15) K

T/K	$\frac{\phi_V^0 \cdot 10^6}{m^3 \cdot mol^{-1}}$	$\frac{S_V^* \cdot 10^6}{m^3 \cdot kg^{1/2} \cdot mol^{-3/2}}$	$\frac{\sigma \cdot 10^6}{m^3 \cdot mol^{-1}}$
		0.000 [a]	
298.15	360.79 (±0.31)	104.80 (±2.57)	0.15
308.15	362.73 (±0.54)	88.35 (±4.48)	0.26
318.15	364.71 (±0.21)	76.62 (±1.76)	0.10
		0.005 [a]	
298.15	359.83 (±0.61)	111.77 (±5.03)	0.29
308.15	361.19 (±0.62)	103.20 (±5.10)	0.30
318.15	362.27 (±0.34)	100.46 (±2.84)	0.16
		0.010 [a]	
298.15	358.11 (±0.17)	128.99 (±1.39)	0.08
308.15	360.89 (±0.68)	104.76 (±5.61)	0.32
318.15	361.85 (±0.28)	101.87 (±2.30)	0.13
		0.015 [a]	
298.15	357.15 (±0.45)	136.93 (±3.71)	0.21
308.15	359.64 (±0.75)	123.82 (±6.16)	0.36
318.15	360.82 (±0.49)	110.21 (±4.03)	0.23
		0.020 [a]	
298.15	356.47 (±0.54)	142.46 (±4.43)	0.25
308.15	358.96 (±0.64)	129.51 (±5.26)	0.31
318.15	360.14 (±0.51)	116.06 (±4.22)	0.25

[a] Molarity of $[bdmim]BF_4$ in methanol. Standard errors are given the parenthesis.

0.98311-0.99930. ϕ_V^0 and S_V^* values along with standard deviations (σ) for the studied solutions at the experimental temperatures are reported in table 4.3. It shows that ϕ_V^0 values are positive for all the studied solutions and such values progressively decrease as the content of $[bdmim]BF_4$ in the ternary solutions increases. So it is evident that the ternary solutions are characterized by the presence of strong ion-solvent interactions. For the present ternary systems positive ϕ_V^0 values may be attributed to the solvation of different ionic species (due to dissociation of the complex and $[bdmim]BF_4$) in MeOH through ion-dipole interactions. But when the concentration of $[bdmim]BF_4$ increases these interactions decrease due to columbic interactions among different ionic species. Presence of ion-ion interactions is well reflected by the positive S_V^* values for all the studied solutions. Again S_V^* values increase progressively as the concentration of $[bdmim]BF_4$ increases in the studied solutions indicating that solute ([bdmim]BF_4)-cosolute ([Cr(salen)$(H_2O)_2$]Cl) interactions are further strengthened at high concentrations of [bdmim]BF_4. It is because of the fact that the more ions are dispersed in experimental solutions due to dissociation of both the complex [Cr(salen)$(H_2O)_2$]Cl and [bdmim]BF_4 into their constituent ions. Thus both the complex and [bdmim]BF_4 behave as strong electrolytes in the studied solutions. But decrease in S_V^* values at higher temperatures indicates that thermal agitation hampers columbic interactions between the ions and creates room for more solvent molecules around them in the solutions, i.e., ionic solvation increases. A perusal of table 4.3 also shows that ϕ_V^0 values decrease with an increase in concentration of [bdmim]BF_4 indicating enhancement of different possible ion-ion interactions and such interactions probably cause some loosely bound solvent molecules (MeOH) around the solutes (or their constituent ions) to be released into the hydrogen-bonded bulk structure of the solvent (MeOH). Thus resulting in lower values of ϕ_V^0 at higher concentration of [bdmim]BF_4. Again the ϕ_V^0 values increase as the experimental temperature increases from 298.15-318.15 K and thus suggest that ion-solvent interactions improve at higher temperatures probably due to favorable (stronger) solvation of solute or caging effect at higher temperatures. Anyway, S_V^* values are always smaller than ϕ_V^0 values for all the studied solutions and thus indicate that ion-solvent interactions are more prominent than the ion-ion interactions. The dependence of ϕ_V^0 values for the complex [Cr(salen)$(H_2O)_2$]Cl on the solvent composition and temperature is shown in figure 4.2.

4.3.2. *Standard partial molar volume of transfer*

To understand the nature of solute-cosolute interactions, we have calculated the partial molar volume of transfer ($\Delta_t\phi_V^0$) from the following relation:

$$\Delta_t\phi_V^0 = \phi_V^0\,([\mathrm{Cr(salen)(H_2O)_2]Cl} + [\mathrm{bdmin]BF_4} + \mathrm{MeOH}) - \phi_V^0\,([\mathrm{Cr(salen)(H_2O)_2]Cl} + \mathrm{MeOH}) \qquad (3)$$

$\Delta_t\phi_V^0$ is, by definition, free from solute-solute interactions and provides information about solute-cosolute interactions as at infinite dilution interactions between individual solute molecules are negligible ($\Delta_t\phi_V^0$ are depicted in figure 4.3).

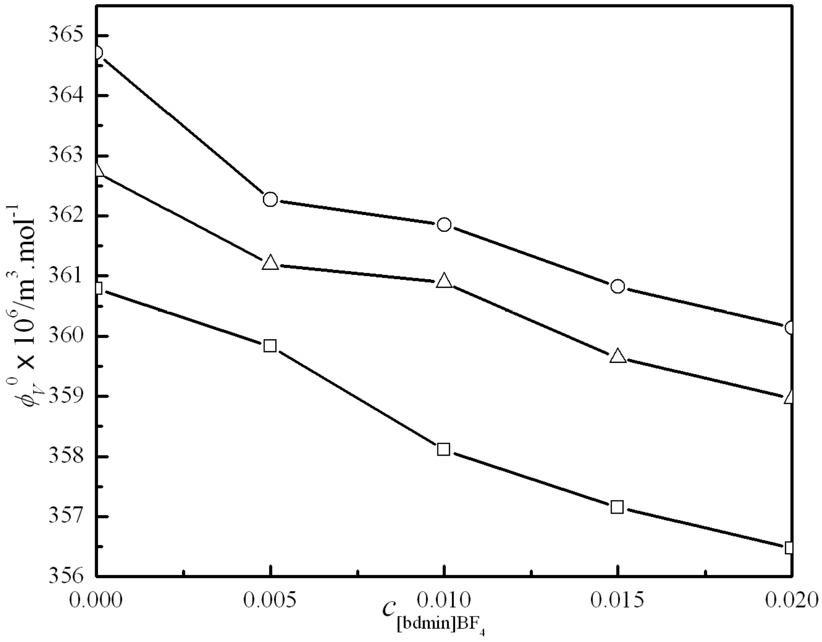

Fig. 4.2. Dependence of standard partial molar volumes (ϕ_V^0) for [Cr(salen)(H_2O)$_2$]Cl on the molarity ($c_{[\text{bdmim}]\text{BF}_4}$) of [bdmim]$BF_4$ in the solvent mixtures at T = (298.15-318.15) K. Symbols: □, 298.15 K; Δ, 308.15 K; ○, 318.15 K.

According to the cosphere overlap model,[26] the interactions between [Cr(salen)(H_2O)$_2$]Cl and [bdmim]BF_4 can be categorized as follows: (i) The polar–ionic group interactions between the polar N-groups of [Cr(salen)(H_2O)$_2$]Cl and the ions of [bdmim]BF_4, (ii) Polar-polar group interactions between the polar groups of [Cr(salen) (H_2O)$_2$]Cl and the imidazolium ring of [bdmim]BF_4, (iii) Polar-non-polar group interactions between N-group of [Cr(salen) (H_2O)$_2$]Cl and the non-polar alkyl chains of [bdmim]BF_4, (iv) Nonpolar-nonpolar group interactions between non-polar groups of [Cr(salen)(H_2O)$_2$]Cl and alkyl chain of [bdmim]BF_4. Amongst the above interactions while the interactions of types (i) and (ii) lead to positive $\Delta_t\phi_V^0$ values (since there is reduction in the electrostriction effect), interactions of (iii) and (iv) types lead to negative $\Delta_t\phi_V^0$ values. Thus the negative $\Delta_t\phi_V^0$ values for the ternary solutions studied indicate the dominance of polar–non-polar group and non-polar-non-polar group interactions over polar-ionic group and polar-polar group interactions between [Cr(salen) (H_2O)$_2$]Cl and [bdmim]BF_4.

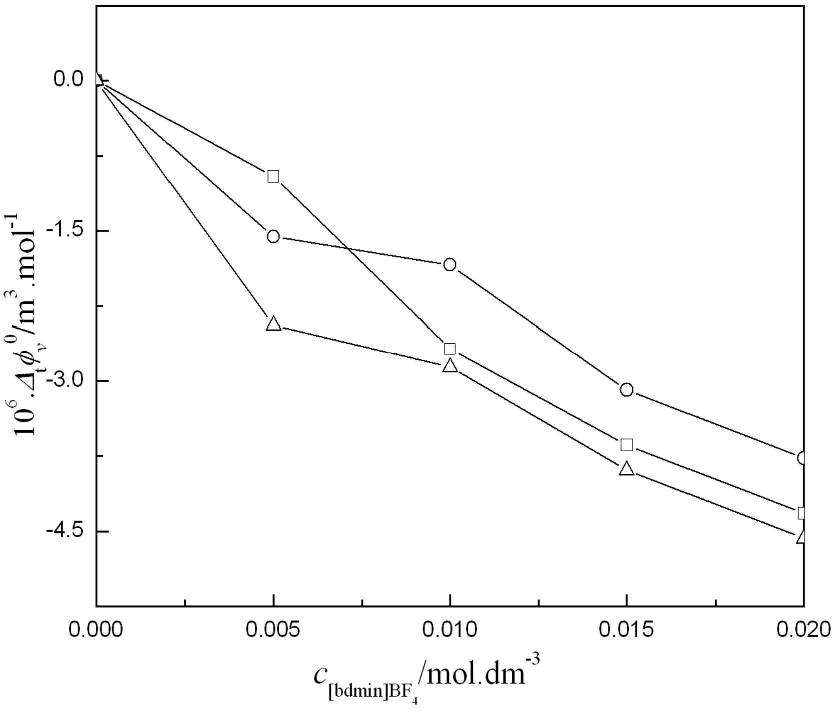

Fig. 4.3. Plots of standard partial molar volumes of transfer ($\Delta_t\phi_V^0$) for [Cr(salen)(H$_2$O)$_2$]Cl at different temperatures: □, 298.15 K; Δ, 308.15 K; ○, 318.15 K.

4.3.3. *Partial molar expansibilities*

The temperature dependence of apparent molar volumes ϕ_V is slightly positive as evident from table 4.2 and the temperature dependence of standard partial molar volumes (ϕ_V^0) can be expressed as follows: [27]

$$\phi_V^0 = a_0 + a_1 T \tag{4}$$

where a_0, a_1 and T are regression coefficients and absolute temperature, respectively. The regression coefficients a_0, a_1 were obtained from a least square linear regression with correlation coefficient (R^2) values falling within the range (0.94936-0.99899). The temperature dependence of standard partial molar volumes (ϕ_V^0) is depicted in figure 4.4.

The partial molar expansibilities (ϕ_E^0) measure the variation of volume with temperature and can be obtained from the relation:

$$\phi_E^0 = (\partial\phi_V^0 / \partial T)_P = a_1 \tag{5}$$

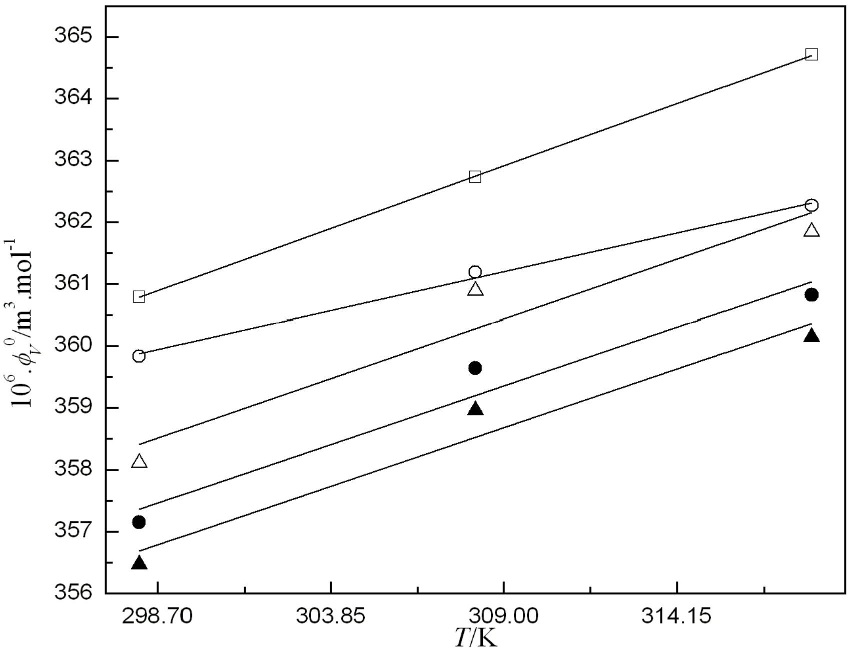

Fig. 4.4. Temperature dependence of standard partial molar volumes (ϕ_V^0) for [Cr(salen)(H_2O)$_2$]Cl as a function of the molarity ($c_{[\text{bdmim}]\text{BF}_4}$) of [bdmim]$BF_4$ in the solvent mixtures: $c_{[\text{bdmim}]\text{BF}_4} = 0.000$, □; $c_{[\text{bdmim}]\text{BF}_4} = 0.005$, ○; $c_{[\text{bdmim}]\text{BF}_4} = 0.010$, Δ; $c_{[\text{bdmim}]\text{BF}_4} = 0.015$, ●; $c_{[\text{bdmim}]\text{BF}_4} = 0.020$, ▲.

The ϕ_E^0 values for the complex were found to be 0.183×10^{-6}, 0.184×10^{-6}, 0.187×10^{-6}, 0.122×10^{-6} and $0.196\times10^{-6}\ \text{m}^3\cdot\text{mol}^{-1}$ in the solvent mixtures with 0.020, 0.015, 0.010, 0.005 and 0.000 $\text{mol}\cdot\text{dm}^{-3}$ of [bdmim]BF_4 in the solvent mixtures, respectively. The positive ϕ_E^0 values increase as the content of [bdmim]BF_4 in the ternary mixtures increase up to 0.010 $\text{mol}\cdot\text{dm}^{-3}$ of [bdmim]BF_4 and then slightly decreased. These facts are probably due to structural perturbation influenced by the gradual disappearance of caging/packing effect[28, 29] as the content of [bdmim]BF_4 in the ternary solutions increases. The positive ϕ_E^0 values suggest release of some loosely bound MeOH molecules from the secondary solvation sphere of [Cr(salen)(H_2O)$_2$]Cl to the bulk structure and thus there are concomitant increase in apparent molar volumes (ϕ_V) and standard partial molar volumes (ϕ_V^0). However, increase in ϕ_E^0 values with increasing content of [bdmim]BF_4 in the ternary mixtures is rather slight probably due to the solvophobic and solvophilic solvations of the solutes or their ions in the solutions.[30]

4.3.4. *Viscometric results*

The viscosity results were analysed by using the Jones-Dole equation:[31, 32]

$$(\eta/\eta_1 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (6)$$

where $\eta_r = \eta/\eta_1$, η_1 and η are the viscosities of solvent and solution, respectively, *A* is the Falkenhagen coefficient and *B* is Jones-Dole coefficient. *A*-coefficient accounts for the ion-ion or solute-solute interactions and *B*-coefficient gives a measure of structural modifications induced by the ion-solvent or solute-solvent interactions.[33] The viscosity *A*- and *B*- coefficients were estimated from the intercepts and slopes by a least squares linear regression of equation (6) and are listed in table 4.4 along with their standard errors. Table 4.4 reveals that viscosity *B*- coefficients are positive and increase with increase in experimental temperature but decrease as the content of [bdmim]BF_4 in the ternary solution increases.

The viscosity *B*-coefficient[33, 34] is another avenue into the effects of ion-solvent or solute-solvent interactions on the solution viscosity and thereby provides valuable information regarding solvation of solutes and their effect on the solvent in the vicinity of the solute molecules. The positive viscosity *B*-coefficients for the studied solutions reinforce the presence of strong ion-solvent or solute-solvent interactions but these interactions are weakened with an increase of [bdmim]BF_4 concentration, i.e., increase in [bdmim]BF_4 concentration causes net structural loss but at higher temperatures there is structural gain in the solutions. Although, theoretically the viscosity *A*-coefficients should be positive for electrolytes but we obtained negative values for the viscosity *A*-coefficients for all the solvent compositions. The negative values for the viscosity *A*-coefficients is probably partly due to low surface charge density on the cations and partly due to strong electrolytic nature of both the complex and the ionic liquid[31] in MeOH.

Table 4.4. Viscosity *A*- and *B*-coefficients for $[\mathrm{Cr(salen)(H_2O)_2}]\mathrm{Cl}$ with standard deviations (σ) for linear regression of equation (6) and solvation number (S_n) in different mixtures of methanol (1) + $[\mathrm{bdmim}]\mathrm{BF_4}$ (2) with standard deviations (σ) at T = (298.15 to 318.15) K

Parameters	298.15 K	308.15 K	318.15 K
		0.000[a]	
$\frac{A}{\mathrm{dm}^{3/2}\cdot\mathrm{mol}^{-1/2}}$	-0.202 (±0.011)	-0.227 (±0.027)	-0.237 (±0.012)
$\frac{B}{\mathrm{dm}^{3}\cdot\mathrm{mol}^{-1}}$	3.685 (±0.105)	4.416 (±0.261)	5.043 (±0.114)
σ	0.005	0.013	0.006
S_n	10.21 (±0.30)	12.17 (±0.74)	13.83 (±0.32)
		0.005[a]	
$\frac{A}{\mathrm{dm}^{3/2}\cdot\mathrm{mol}^{-1/2}}$	-0.153 (±0.008)	-0.157 (±0.009)	-0.181 (±0.012)
$\frac{B}{\mathrm{dm}^{3}\cdot\mathrm{mol}^{-1}}$	3.042 (±0.075)	3.715 (±0.089)	4.090 (±0.121)
σ	0.004	0.005	0.006
S_n	8.45 (±0.22)	10.29 (±0.26)	11.29 (±0.34)
		0.010[a]	
$\frac{A}{\mathrm{dm}^{3/2}\cdot\mathrm{mol}^{-1/2}}$	-0.147 (±0.008)	-0.169 (±0.012)	-0.178 (±0.013)
$\frac{B}{\mathrm{dm}^{3}\cdot\mathrm{mol}^{-1}}$	2.928 (±0.079)	3.681 (±0.117)	4.013 (±0.121)
σ	0.004	0.006	0.006
S_n	8.18 (±0.22)	10.20 (±0.34)	11.09 (±0.34)
		0.015[a]	
$\frac{A}{\mathrm{dm}^{3/2}\cdot\mathrm{mol}^{-1/2}}$	-0.085 (±0.006)	-0.145 (±0.010)	-0.175 (±0.013)
$\frac{B}{\mathrm{dm}^{3}\cdot\mathrm{mol}^{-1}}$	2.422 (±0.052)	3.405 (±0.089)	3.949 (±0.124)
σ	0.003	0.005	0.006
S_n	6.78 (±0.15)	9.47 (±0.27)	10.95 (±0.36)
		0.020[a]	
$\frac{A}{\mathrm{dm}^{3/2}\cdot\mathrm{mol}^{-1/2}}$	-0.067 (±0.004)	-0.121 (±0.012)	-0.151 (±0.015)
$\frac{B}{\mathrm{dm}^{3}\cdot\mathrm{mol}^{-1}}$	2.212 (±0.041)	3.030 (±0.109)	3.642 (±0.140)
σ	0.002	0.006	0.007
S_n	6.20 (±0.12)	8.44 (±0.32)	10.11 (±0.40)

[a] Molarity of $[\mathrm{bdmim}]\mathrm{BF_4}$ in methanol. Standard errors are given the parenthesis.

Anyway, such values of the viscosity *A*-coefficients indicate weak ion-ion or solute - solute interactions suggesting that the complex acts a strong electrolyte in the studied concentration range in MeOH. Thus viscometric results concur with those obtained from volumetry.

Similar to $\Delta_t\phi_V^0$, viscosity *B*-coefficient of transfer ($\Delta_t B$) is free from solute-solute interactions and provides information regarding solute-co solute interactions. $\Delta_t B$ values were obtained from the following relation:

$$\Delta_t B = B([\mathrm{Cr(salen)(H_2O)_2]Cl} + [\mathrm{bdmin]BF_4} + \mathrm{MeOH}) - B([\mathrm{Cr(salen)(H_2O)_2]Cl} + \mathrm{MeOH}) \quad (7)$$

$\Delta_t B$ values for the ternary solutions studied were depicted in figure 4.5 as a function molarity of [bdmim]BF_4 and simply concur with the trends of solute-cosolute interactions reflected by $\Delta_t\phi_V^0$ values. The sign of $(\partial B/\partial T)$ values provides important information regarding long-range structure making or structure breaking ability of solute in solvent media. In general the sign of $(\partial B/\partial T)$ is negative for a solvent structure maker and *vice-versa*. The positive $(\partial B/\partial T)$ values[35] for studied system indicate that [Cr(salen)(H_2O)$_2$]Cl acts as solvent structure breaker in studied solutions.

4.3.5. *Solvation numbers*

Solvation numbers S_n for the complex [Cr(salen)(H_2O)$_2$]Cl in the experimental solvent media were calculated from the relation:[35]

$$S_n = B/\phi_V^0 \quad (8)$$

S_n is indicative of the formation of a primary solvation sphere around a solute and the range 0-2.5 for S_n indicates unsolvated solutes in the solution.[35] So an inspection of S_n values given in table 4.4 indicated that the complex remains solvated and its solvation decreases at higher concentration of [bdmim]BF_4 in the studied solutions but increases at higher temperatures. Such trends in S_n values are due to the fact that [bdmim]BF_4 itself interacts with MeOH and thus decreases solvation of the complex or its ions. However, higher temperatures favor solvation of the complex as already discussed on the basis of ϕ_V^0 values.

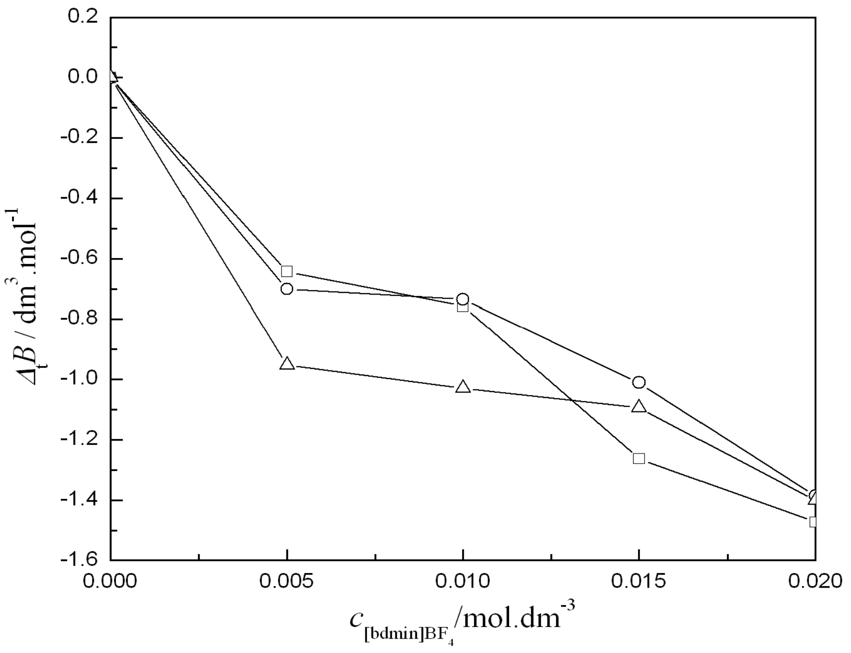

Fig. 4.5. Plots of viscosity *B*-coefficients of transfer ($\Delta_t B$) for [Cr(salen)(H_2O)$_2$]Cl at different temperatures: □, 298.15 K; Δ, 308.15 K; ○, 318.15 K.

4.3.6. *Thermodynamics of viscous flow*

While viscosity *B*-coefficient is very useful, greater insight into viscous flow can be had from the thermodynamic activation parameters. According to Eyring *et al.*[34] the application of statistical thermodynamics to the hole model of viscous flow (based on the absolute reaction rate theory) impart the free energy of activation for viscous flow per mole of the solvent/solvent mixture, $\Delta\mu_1^{0\neq}$ as:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_1\phi_{V,1}^0 / hN_A) \tag{9}$$

where N_A , $\phi_{V,1}^0$ are the Avogadro's number and the molar volumes of the solvent, respectively. The other symbols have their usual significances. For the binary mixtures of MeOH + [bdmim]BF$_4$ used as solvents, $\phi_{V,1}^0$ is taken as the mole fraction average of molecular weights of MeOH and [bdmim]BF$_4$ normalized by densities at the experimental temperatures. The above relation can also be expressed as: [33, 36]

$$\ln(\eta_1\phi_{V,1}^0 / hN_A) = -\frac{\Delta S_1^{0\neq}}{R} + \left(\frac{\Delta H_1^{0\neq}}{R}\right)\frac{1}{T} \tag{10}$$

A linear regression of the data ($\ln(\eta_1\phi_{V,1}^0/hN_A)$ and $10^3/T$) with $R^2 \approx 0.99879-0.99999$ provided the $\Delta H_1^{0\neq}$ and $\Delta S_1^{0\neq}$ values. Such regression lines are shown in figure 4.6.

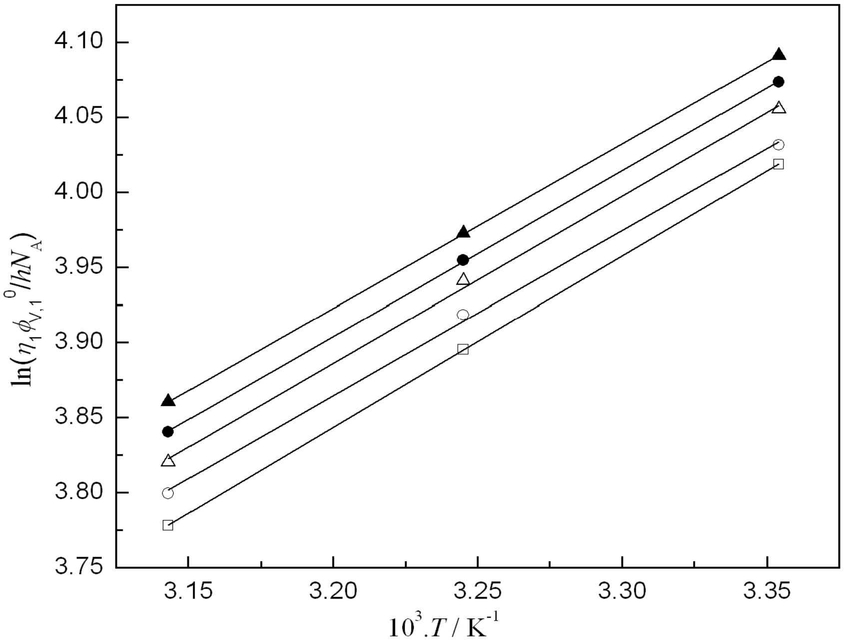

Fig. 4.6. Plots of $\ln(\eta_1\phi_{V,1}^0/hN_A)$ against $10^3 \times T^{-1}$ for different solvent mixtures as a function of the molarity ($c_{[\mathrm{bdmim}]\mathrm{BF}_4}$) of [bdmim]BF$_4$ in the solvent mixtures: $c_{[\mathrm{bdmim}]\mathrm{BF}_4}$ = 0.000, □; $c_{[\mathrm{bdmim}]\mathrm{BF}_4}$ = 0.005, ○; $c_{[\mathrm{bdmim}]\mathrm{BF}_4}$ = 0.010, Δ; $c_{[\mathrm{bdmim}]\mathrm{BF}_4}$ = 0.015, ●; $c_{[\mathrm{bdmim}]\mathrm{BF}_4}$ = 0.020, ▲.

A correlation between viscosity *B*- coefficients and the deviation between the contribution per mole of a solute to the free energy of activation for viscous flow of the solution ($\Delta\mu_2^{0\neq}$) and the free energy of activation of viscous flow per mole of the pure solvent or solvent mixture ($\Delta\mu_1^{0\neq}$) was suggested by Feakins *et al.*[36] in the form of the following relation:

$$B = (\nu\phi_{V,1}^0 - \phi_{V,2}^0) + \phi_{V,1}^0\left(\frac{\Delta\mu_2^{0\neq} - \nu\Delta\mu_1^{0\neq}}{RT}\right) \tag{11}$$

where the coefficient ν is 2 for 1:1 electrolytes. Thus $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values were obtained from equation (11) by using the *B*- coefficient values obtained from equation (6). $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values can also be expressed as:

$$\frac{\Delta\mu_2^{0\neq}-\Delta\mu_1^{0\neq}}{RT}=-\frac{\Delta S_2^{0\neq}-\Delta S_1^{0\neq}}{R}+\left\{\frac{\Delta H_2^{0\neq}-\Delta H_1^{0\neq}}{R}\right\}\frac{1}{T} \tag{12}$$

where $\Delta S_i^{0\neq}$ and $\Delta H_i^{0\neq}$ are the standard partial molar entropy and enthalpy of activation for viscous flow per mole of i^{th} component in the solution. So a linear regression treatment of equation (12) with $R^2 \approx 0.94828-0.99862$ provided the values of $(\Delta S_2^{0\neq}-\Delta S_1^{0\neq})$ and $(\Delta H_2^{0\neq}-\Delta H_1^{0\neq})$ from the corresponding slopes and intercepts. The regression lines are shown in figure 4.7.

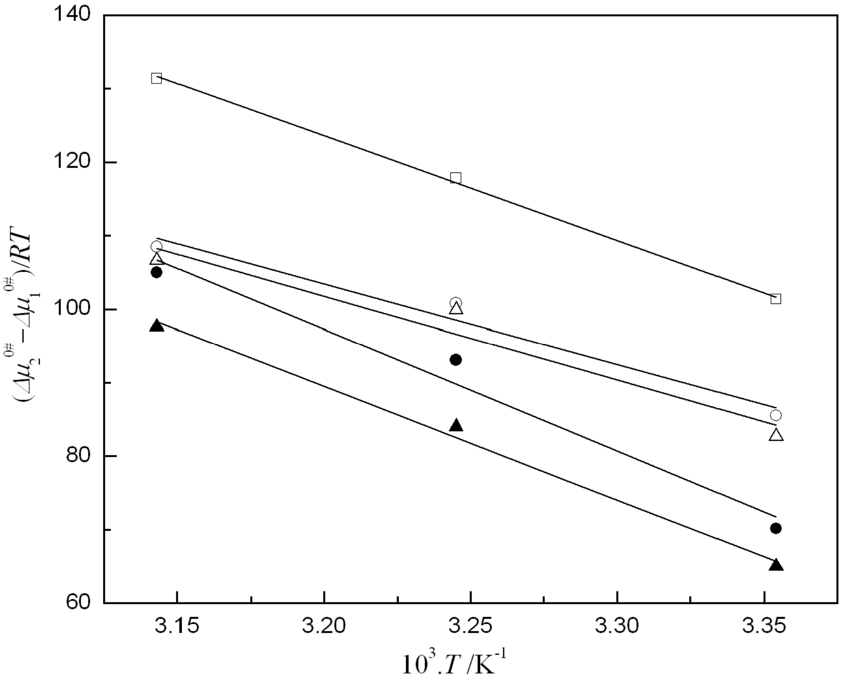

Fig. 4.7. Plots of $(\Delta\mu_2^{0\neq}-\Delta\mu_1^{0\neq})/RT$ against $10^3\times T^{-1}$ for [Cr(salen)(H$_2$O)$_2$]Cl as a function of the molarity ($c_{[\text{bdmim}]\text{BF}_4}$) of [bdmim]BF$_4$ in the solvent mixtures: $c_{[\text{bdmim}]\text{BF}_4}$ = 0.000, □; $c_{[\text{bdmim}]\text{BF}_4}$ = 0.005, ○; $c_{[\text{bdmim}]\text{BF}_4}$ = 0.010, Δ; $c_{[\text{bdmim}]\text{BF}_4}$ = 0.015, •; $c_{[\text{bdmim}]\text{BF}_4}$ = 0.020, ▲.

The parameters $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$ and $(\Delta\mu_2^{0\neq}-\Delta\mu_1^{0\neq})$ are reported in table 4.5. $\Delta H_1^{0\neq}$, $\Delta H_2^{0\neq}$, $\Delta S_1^{0\neq}$ and $\Delta S_2^{0\neq}$ are reported in table 4.6. According to equation (11), $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity *B*-coefficients and $(\phi_{V,2}^0-\phi_{V,1}^0)$ terms.

Table 4.5. Values of $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$ and ($\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}$) for $[Cr(salen)(H_2O)_2]Cl$ in different mixtures of methanol (1) + $[bdmim]BF_4$ (2) at T = (298.15 to 318.15) K

T/K	$\frac{\Delta\mu_1^{0\neq}}{kJ \cdot mol^{-1}}$	$\frac{\Delta\mu_2^{0\neq}}{kJ \cdot mol^{-1}}$	$\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\#}}{kJ \cdot mol^{-1}}$
		0.000 [a]	
298.15	9.961 (±0.001)	261.181 (±0.105)	251.219 (±0.105)
308.15	9.980 (±0.001)	311.789 (±0.261)	301.809 (±0.262)
318.15	9.994 (±0.001)	357.441 (±0.114)	347.447 (±0.115)
		0.005 [a]	
298.15	9.993 (±0.001)	222.021 (±0.075)	212.028 (±0.076)
308.15	10.039 (±0.001)	268.214 (±0.089)	258.175 (±0.089)
318.15	10.050 (±0.001)	296.937 (±0.121)	286.887 (±0.121)
		0.010 [a]	
298.15	10.052 (±0.001)	214.979 (±0.079)	204.927 (±0.079)
308.15	10.097 (±0.001)	265.996 (±0.117)	255.899 (±0.118)
318.15	10.105 (±0.001)	292.065 (±0.121)	281.960 (±0.121)
		0.015 [a]	
298.15	10.097 (±0.001)	184.077 (±0.052)	173.980 (±0.053)
308.15	10.132 (±0.001)	248.684 (±0.090)	238.552 (±0.091)
318.15	10.158 (±0.001)	287.912 (±0.124)	277.753 (±0.124)
		0.020 [a]	
298.15	10.141 (±0.001)	171.266 (±0.041)	161.126 (±0.042)
308.15	10.177 (±0.001)	225.328 (±0.110)	215.150 (±0.111)
318.15	10.211 (±0.001)	268.319 (±0.141)	258.108 (±0.141)

[a] Molarity of $[bdmim]BF_4$ in methanol.

Table 4.5 shows that $\Delta\mu_1^{0\neq}$ are almost invariant of the solvent compositions and temperatures, implying that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity B-coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms. The $\Delta\mu_2^{0\neq}$ values contain the change in the free energy of activation of solute molecules in presence of solvent as well as the contribution from the movement of solute molecules. $\Delta\mu_2^{0\neq}$ values are positive and greater than $\Delta\mu_1^{0\neq}$ values at all the experimental temperatures for all the experimental solvent media suggesting that solute (ion)-solvent interactions is stronger in the ground state than in the transition state and in the transition state the solvation of the solute (ions) is less favoured energetically. Also $\Delta\mu_2^{0\neq}$ values increase as the temperature increases but decreases as the content of [bdmim]BF_4 in ternary solutions increase. Such a trend of $\Delta\mu_2^{0\neq}$ values indicate that solute (ion)-solvent interactions increase with a rise in temperature making the viscous flow more difficult but the flow is somewhat favourable at higher content of [bdmim]BF_4 in the studied solutions.

Table 4.6. Values of $\Delta H_1^{0\neq}$, $\Delta H_2^{0\neq}$, $\Delta S_1^{0\neq}$ and $\Delta S_2^{0\neq}$ for [Cr(salen)(H_2O)$_2$]Cl in different mixtures of methanol (1) + [bdmim]BF_4 (2).

Solvent	$\frac{\Delta H_1^{0\neq}}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta H_2^{0\neq}}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta S_1^{0\neq}}{\mathrm{J\cdot mol^{-1}\cdot K^{-1}}}$	$\frac{\Delta S_2^{0\neq}}{\mathrm{J\cdot mol^{-1}\cdot K^{-1}}}$
0.000 ^{a}	9.475	-1174.648	-1.634	-4816.753
	(±0.002)	(±3.057)	(±0.008)	(±9.923)
0.005 ^{a}	9.142	-897.697	-2.874	-3764.690
	(±0.021)	(±10.777)	(±0.069)	(±35.010)
0.010 ^{a}	9.265	-947.594	-2.661	-3881.267
	(±0.022)	(±15.367)	(±0.073)	(±49.995)
0.015 ^{a}	9.182	-1368.061	-3.073	-5219.174
	(±0.005)	(±15.655)	(±0.017)	(±50.858)
0.020 ^{a}	9.091	-1277.390	-3.522	-4864.610
	(±0.002)	(±6.829)	(±0.007)	(±22.183)

^{a} Molarity of [bdmim]BF_4 in methanol. Standard errors are given the parenthesis.

Furthermore according to Feakins *et al.* [33, 36] the first contribution to the effect of the solute on the activation free energy of the solvent molecule originates from the difference between the solvation energies of the solute in the ground state solvent and the transition state solvent or free energy of transfer, $\Delta G_2^{0\neq}(1 \rightarrow 1')$ between them. The second contribution to $\Delta\mu_2^{0\neq}$ comes from the movement of the solute through its own viscous transition state, $\Delta G_2^{0\neq}(2 \rightarrow 2')$. So the term $\Delta\mu_2^{0\neq}$ can also expressed as:

$$\Delta\mu_2^{0\neq} = \Delta G_2^{0\neq}(1 \rightarrow 1') + \Delta G_2^{0\neq}(2 \rightarrow 2') \qquad (13)$$

The values $\Delta G_2^{0\neq}(2 \rightarrow 2')$ can be approximated to the $\Delta\mu_1^{0\neq}$ values and the values $\Delta G_2^{0\neq}(1 \rightarrow 1')$ simply become equal to $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values. Thus, the quantity

$(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ is the change in the activation energy per mole of solute on replacing one mole of solvent by one mole of solute in an infinite dilution. The values of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ obtained are positive for all the solvent mixtures and increase almost linearly as the temperature increases for all the solvent mixtures and decrease with further addition of [bdmim]BF_4 in the ternary solutions. The positive $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values and their positive temperature dependence as well as similar trends in viscosity *B*-coefficients indicate the structure breaking ability of the complex and the transfer of the complex molecules from the ground state solvent to the transition state solvent is energetically hindered, although $\Delta H_2^{0\neq}$ values are negative for all the solvent media. This indicates that that the flow is exothermic but hindered by the negative $\Delta S_1^{0\neq}$ and $\Delta S_2^{0\neq}$ values. Such negative activation entropies probably originate from a combined effect of favourable solvation of the different ionic species, coloumbic interactions amongst them and hydrogen bonded bulk structure of MeOH. Thus for the present solutions under investigation viscous flow is an enthalpy driven process.

4.4. Conclusion

In summary, partial molar volumes ϕ_V^0 and viscosity *B*-coefficients for [Cr(salen)(H_2O)$_2$]Cl in the ternary solutions indicate the presence of strong solute-solvent interactions; these interactions strengthen at higher temperatures but decrease at higher content of [bdmim]BF_4 in the studied solutions. Also [Cr(salen)(H_2O)$_2$]Cl acts as a net structure breaker for the studied solutions.

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CHAPTER V

Ion-solvent and ion-ion interactions in solutions of N, N/-ethylenebis-(salicylideneiminato)-diaquochromium(III) chloride in aqueous dimethylsulphoxide at T = (298.15, 308.15 and 318.15) K

5.1. Introduction

Ion solvation is an important phenomenon in many contexts of chemistry as solvated ions are ubiquitous on earth. The exchange of solvent molecules around ions or solvated ions in solutions is fundamental to the understanding of the reactivity of ions in solutions.[1] Solvents can influence or control the outcome of a chemical reaction through the interaction of the local environment with the individual species undergoing the reactions.[2] Thus the knowledge of ion-solvent interactions is fundamentally important in many areas of chemistry. In this regard physico-chemical properties like apparent molar volume and viscosity *B*-coefficient and apparent molar refraction, etc., of solutions provide an avenue into the process of solvation of solutes in different solvents, especially in mixed solvents.

Dimethylsulfoxide (DMSO) is a polar aprotic solvent. It finds important applications in organic synthesis[3] and electrochemistry,[4] etc. The dipolar nature of DMSO imparts itself a good nucleophilic character and thus it can influence ion-solvation as well as stabilize charged intermediates in many organic reactions.[5] Although water and DMSO are miscible over the entire concentration range, the physical properties of the mixtures deviate from linearity to those of each constituent. Within the entire composition range, the mixtures can be divided into three regions: one belonging to a highly water rich region with quasi-clathrate structure, another region with $2H_2O.DMSO$ type associates up to $x_{\text{DMSO}} \approx 0.03$ and another region dominated by dipolar structures due to dipole-dipole interactions.[6-7] Thus when a solute is dissolved in such aqueous solutions ion-solvent, ion-ion and solvent-solvent interactions will show dramatic changes in different thermophysical properties like densities, viscosities and refractive indices, etc., of the solutions.

Again among the many potential organic materials, Schiff bases with azomethine linkage and their transition metal complexes are important compounds as because of their wide variety of applications like industrial, biological, analytical, medicinal, pharmaceutical and catalytic applications.[8-10] Cr^{3+} is biologically significant at all the levels of living organisms.[11] For example it has positive roles in controlling carbohydrate and lipid metabolism.[12] Hence various thermophysical properties of solutions comprising of transition metal complex such as $[Cr(salen)(H_2O)_2]Cl$ in aqueous binary mixtures of DMSO can provide valuable information about ion-ion and ion-solvent interactions that probably characterize their solution thermodynamics and structure in solution phase. Such information would permit tuning the composition of selected solvent mixture for maximum product yield in many organic reactions that are catalyzed by transition metal complexes. Anyway, to the best of our knowledge there is no report on the physico-chemical properties of the system: $[Cr(salen)(H_2O)_2]Cl + H_2O +$ DMSO in the literature. Hence in this chapter some physico-chemical properties of the ternary mixtures of $[Cr(salen)(H_2O)_2]Cl + H_2O +$ DMSO at 298.15, 308.15 and 318.15 K under ambient pressure were reported and the results were discussed in terms of ion-ion and ion-solvent interactions.

5.2. Experimental section

5.2.1. *Materials*

A. R. grade $CrCl_3.6H_2O$; 1,2-ethylenediamine and salicylaldehyde, each of purity > 99%, were procured from SD Fine chemicals, India. All these chemicals were used as received from the vendor. Spectroscopic grade DMSO (minimum assay, GC > 99.5% with 0.05% of water) was procured from SD Fine chemicals, India and used as received. Doubly distilled de-ionized water with a specific conductance $< 1\times10^{-6}\ \mathrm{S\,cm^{-1}}$ at 298.15 K was used for preparing binary solvent mixtures. Various binary solvent mixtures were prepared by mass and necessary adjustments were done to achieve exact mass factions (w_2 = 0.80, 0.60, 0.40 and 0.20) of DMSO in the binary solvent mixtures at 298.15 K. The relative error in solvent composition was about 1%. The physical properties of these solvent/solvent mixtures are given in table 5.1 and are compared to the literature values [2, 13-15] whenever available.

Table 5.1. Densities (ρ), viscosities (η) and refractive indices (n_D) of different aqueous DMSO solutions at T = (298.15-318.15) K.

$w_2{}^a$	T/K	$\frac{\rho\cdot 10^{-3}}{\mathrm{kg\cdot m^{-3}}}$		$\frac{\eta}{\mathrm{mPa\cdot s}}$		n_D	
		Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
1.00	298.15	1.09581	1.09541[2] 1.09602[13] 1.096107[14]	1.9661	1.9660[2] 2.0006[13]	1.4769	1.4768 [15]
	308.15	1.08540	1.08538[2] 1.08524[13] 1.090731[14]	1.6533	1.6523[2] 1.6623[13]		
	318.15	1.07541	1.07450[2] 1.07683[13]	1.4886	1.4875[2] 1.3849[13]		
0.80	298.15	1.09847	1.09842[13]	3.4457	3.4496[13]	1.4524	1.4523[15]
	308.15	1.09491	1.09482[13]	2.7334	2.7340[13]		
	318.15	1.08841	1.08838[13]	2.0656	2.0653[13]		
0.60	298.15	1.08292	1.08231[2] 1.08284[13] 1.078822[14]	3.4207	3.4210[2] 3.4594[13]	1.4233	1.4232[15]
	308.15	1.07284	1.07280[2] 1.07796 [13] 1.068819[14]	3.1050	3.1050[2] 2.6810[13]		
	318.15	1.06505	1.05710[2] 1.07492[13]	2.7772	2.7753[2] 2.1496[13]		
0.40	298.15	1.05353	1.05347[2] 1.04502[13] 1.053939[14]	2.2202	2.2210[2] 2.2379[13]	1.3915	1.3913[15]
	308.15	1.04538	1.04530[2] 1.05125[13]	1.9217	1.9210[2] 1.7346[13]		
	318.15	1.03813	1.03801[2] 1.04781[13]	1.4977	1.4975[2] 1.3196[13]		
0.20	298.15	1.02428	1.02420[2] 1.02384[13] 1.023623[14]	1.3419	1.3400 [2] 1.3496 [13]	1.3605	1.3600[15]
	308.15	1.01524	1.01520[2] 1.02101[13] 1.019312[14]	1.0544	1.0537 [2] 1.0928 [13]		
	318.15	0.97926	0.97920[2] 1.01753[13]	0.8473	0.8482 [2] 0.8496 [13]		

[a] Mass fraction of DMSO in the solvent mixtures.

[Cr(salen)(H_2O)$_2$]Cl was prepared by a slight modification of a literature method[16] and the details of the synthesis and physico-chemical characterization of [Cr(salen)(H_2O)$_2$]Cl has already been described in chapter III. The molecular structures of the ligand, SalenH$_2$ and the complex are shown in figure 5.1.

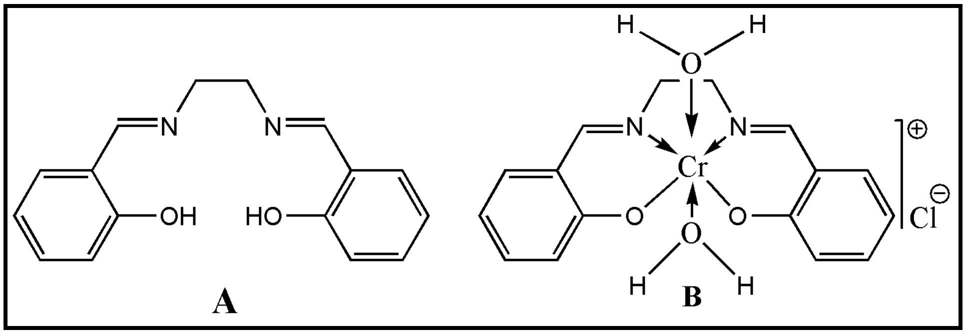

Fig. 5.1. Molecular structure of A) SalenH_2 and B) [Cr(salen)(H_2O)$_2$]Cl.

Stock solutions of the complex in different solvent mixtures were prepared by mass and the working solutions were prepared afresh before use by mass dilution. The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The conversion of molality into molarity was accomplished by using experimental density values whenever needed. The uncertainty in molarity of [Cr(salen)(H_2O)$_2$]Cl solutions was evaluated to $\pm 0.0001\ \text{mol}\cdot\text{dm}^{-3}$. Solutions of the complex [Cr(salen)(H_2O)$_2$]Cl responded to $AgNO_3$ test for Cl^- ions and it is reported to behave as a 1:1 electrolyte.[17]

5.2.2. *Apparatus and procedure*

The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M). The densitometer was calibrated at the experimental temperatures with doubly distilled, degassed water and dry air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $\pm 1\times10^{-2}\,\text{K}$ by using the built–in Peltier technique. The estimated uncertainty of the density measurements for most of the solutions was found to be better than $\pm 2\times10^{-5}\,\text{g}\cdot\text{cm}^{-3}$. The viscosity was measured by means of a suspended Canon-type Ubbelohde viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled, degassed water and purified methanol.[18-20] It was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a digital stopwatch correct to ± 0.01s. In all determinations, an average of triplicate measurements was taken into account and adequate precautions were taken to minimize evaporation loses during the actual measurements. The uncertainty in viscosity measurements, based on our work on several pure liquids, was within $\pm 4\times10^{-4}\,\mathrm{mPa\cdot s}$. Refractive indices were measured with an Abbe refractometer at 298.15 K. Water was circulated through the refractometer from a water bath maintained to ± 0.01 K of 298.15 K. The refractometer was calibrated with doubly distilled, degassed water before each series of measurements. The uncertainty in refractive indices was within ±0.0002. Details of density, viscosity and refractive index measurements have been described in chapter III.

5.3. Results and discussion

The experimental values of molalities (m), densities (ρ), viscosities (η) and apparent molar volumes (ϕ_V) for the experimental solutions of [Cr(salen)(H_2O)$_2$]Cl in different aqueous DMSO mixtures at various temperatures are reported in table 5.2.

5.3.1. *Standard partial molar volumes*

The apparent molar volume (ϕ_V) of a solute is defined as the difference between the volume of the solution and the volume of the pure solvent per mole of solute.[21] The apparent molar volumes (ϕ_V) were obtained from the following relation:

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_1)}{m\rho\rho_1} \qquad (1)$$

where M is the molar mass of [Cr(salen)(H_2O)$_2$]Cl , m is the molality of the solution, ρ_1 and ρ are the densities of the solvent and solution, respectively. Table 5.2 shows that apparent molar volumes (ϕ_V) decrease with increasing temperature and the water-content in the ternary mixtures.

Table 5.2. Molalities (m), densities (ρ), viscosities (η) and apparent molar volumes (ϕ_V) of $[Cr(salen)(H_2O)_2]Cl$ in aqueous DMSO solutions at T = (298.15 to 318.15) K

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{\rho\cdot10^{-3}}{\text{kg}\cdot\text{m}^{-3}}$	$\frac{\eta}{\text{mPa}\cdot\text{s}}$	$\frac{\phi_V\cdot10^{6}}{\text{m}^{3}\cdot\text{mol}^{-1}}$
1.00 [a]			
T/K = 298.15			
0.0110	1.09704	1.9754	262.32
0.0147	1.09744	1.9804	263.00
0.0183	1.09782	1.9868	263.78
0.0220	1.09821	1.9932	264.31
0.0276	1.09879	2.0014	265.10
0.0332	1.09936	2.0099	265.83
T/K = 308.15			
0.0110	1.08666	1.6637	261.62
0.0147	1.08707	1.6685	262.31
0.0183	1.08747	1.6734	262.63
0.0220	1.08785	1.6782	264.02
0.0276	1.08844	1.6848	264.91
0.0332	1.08902	1.6918	265.71
T/K = 318.15			
0.0110	1.07670	1.4988	260.77
0.0147	1.07712	1.5022	261.48
0.0183	1.07752	1.5069	262.27
0.0220	1.07792	1.5103	263.22
0.0276	1.07852	1.5167	264.29
0.0332	1.07911	1.5237	265.21
0.80 [a]			
T/K = 298.15			
0.0110	1.09971	3.4553	261.16
0.0146	1.10010	3.4608	261.96
0.0183	1.10049	3.4677	262.91
0.0220	1.10088	3.4746	263.51
0.0275	1.10145	3.4849	264.35
0.0331	1.10202	3.4948	265.13
T/K = 308.15			
0.0110	1.09617	2.7450	260.18
0.0146	1.09656	2.7503	261.37
0.0183	1.09696	2.7555	262.10
0.0220	1.09735	2.7608	262.93
0.0275	1.09792	2.7679	264.00
0.0331	1.09850	2.7764	264.69
T/K = 318.15			
0.0110	1.08969	2.0737	259.62
0.0146	1.09009	2.0772	260.62
0.0183	1.09050	2.0809	261.25
0.0220	1.09089	2.0844	262.40
0.0275	1.09148	2.0898	263.18

[a] Mass fraction of DMSO in the solvent mixtures.

Contd…

0.0331	1.09205	2.0954	264.44
0.60^{a}			
T/K = 298.15			
0.0111	1.08422	3.4304	259.79
0.0148	1.08464	3.4359	260.46
0.0186	1.08505	3.4428	261.81
0.0223	1.08545	3.4483	262.61
0.0279	1.08605	3.4572	263.55
0.0336	1.08664	3.4670	264.65
T/K = 308.15			
0.0111	1.07417	3.1144	258.93
0.0148	1.07459	3.1184	260.20
0.0186	1.07502	3.1238	260.99
0.0223	1.07542	3.1291	262.20
0.0279	1.07602	3.1378	263.55
0.0336	1.07662	3.1448	264.68
T/K = 318.15			
0.0111	1.06640	2.7890	258.46
0.0148	1.06683	2.7928	259.55
0.0186	1.06726	2.7981	260.72
0.0223	1.06767	2.8033	261.79
0.0279	1.06828	2.8104	263.15
0.0336	1.06889	2.8173	264.31
0.40^{a}			
T/K = 298.15			
0.0114	1.05493	2.2300	259.02
0.0153	1.05539	2.2337	260.03
0.0191	1.05582	2.2373	261.42
0.0229	1.05625	2.2410	262.32
0.0287	1.05690	2.2478	263.38
0.0345	1.05752	2.2533	264.81
T/K = 308.15			
0.0114	1.04680	1.9311	258.56
0.0153	1.04727	1.9346	259.39
0.0191	1.04771	1.9382	260.69
0.0229	1.04815	1.9417	261.52
0.0287	1.04879	1.9470	263.32
0.0345	1.04943	1.9510	264.45
T/K = 318.15			
0.0114	1.03957	1.5052	257.94
0.0153	1.04004	1.5072	259.19
0.0191	1.04049	1.5106	260.26
0.0229	1.04093	1.5126	261.34
0.0287	1.04158	1.5162	263.09
0.0345	1.04223	1.5203	264.19
0.20^{a}			
T/K = 298.15			
0.0118	1.02579	1.3492	258.23
0.0157	1.02627	1.3512	259.26
0.0196	1.02674	1.3544	260.32

[a] Mass fraction of DMSO in the solvent mixtures.

Contd…

0.0236	1.02721	1.3564	261.50
0.0295	1.02790	1.3600	262.69
0.0355	1.02858	1.3640	264.02
	T/K = 308.15		
0.0118	1.01677	1.0600	257.78
0.0157	1.01726	1.0619	258.63
0.0196	1.01774	1.0637	259.58
0.0236	1.01821	1.0655	261.11
0.0295	1.01891	1.0676	262.32
0.0355	1.01961	1.0716	263.40
	T/K = 318.15		
0.0118	0.98085	0.8538	257.14
0.0157	0.98136	0.8556	258.04
0.0196	0.98185	0.8573	259.59
0.0236	0.98236	0.8590	260.27
0.0295	0.98308	0.8609	262.02
0.0355	0.98381	0.8635	263.20

[a] Mass fraction of DMSO in the solvent mixtures.

Such trends indicate that the interactions between solute and solvent as well as those between solute-solute or solute-cosolute change with temperature and solvent compositions. However, more clear information regarding solute-solvent or solute- interactions can be had from limiting apparent molar volumes at infinite dilution or standard partial molar volumes (ϕ_V^0) of the solute.

As the plots of ϕ_V against square root of molar concentration ($\sqrt{m}$) were linear in the studied concentration range of the solute at all experimental temperatures, ϕ_V values were fitted to Masson equation:[22]

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \tag{2}$$

where intercept ϕ_V^0 stands for the standard partial molar volume and provides a measure of ion-solvent interactions and the slope S_V^* provides information regarding ion-ion interactions. The ϕ_V^0 values were determined by fitting the dilute data ($m < 0.1$) to equation (2) using a least squares linear regression and the correlation coefficient (R^2) values were within the range 0.97594-0.99918. The values of ϕ_V^0 and S_V^* along with standard deviations (σ) for [Cr(salen)(H_2O)$_2$]Cl in different aqueous DMSO mixtures at the experimental

Table 5.3. Standard partial molar volumes (ϕ_V^0), slopes (S_V^*) and corresponding standard deviations (σ) for [Cr(salen)(H_2O)$_2$]Cl in aqueous DMSO solutions at T = (298.15 To 318.15) K

T/K	$\phi_V^0 \cdot 10^6$ / $\mathrm{m^3 \cdot mol^{-1}}$	$S_V^* \cdot 10^6$ / $\mathrm{m^3 \cdot kg^{1/.2} \cdot mol^{-3/2}}$	$\sigma \cdot 10^6$ / $\mathrm{m^3 \cdot mol^{-1}}$
		1.00 ^{a}	
298.15	257.55 (±0.10)	45.53 (±0.65)	0.04
308.15	255.61 (±0.52)	55.41 (±3.55)	0.25
318.15	254.43 (±0.22)	59.01 (±1.53)	0.11
		0.80 ^{a}	
298.15	255.77 (±0.17)	51.79 (±1.14)	0.08
308.15	254.17 (±0.24)	58.62 (±1.67)	0.12
318.15	253.11 (±0.30)	61.68 (±2.09)	0.15
		0.60 ^{a}	
298.15	252.98 (±0.33)	63.70 (±2.22)	0.16
308.15	251.08 (±0.22)	74.22 (±1.53)	0.11
318.15	250.37 (±0.13)	76.20 (±0.89)	0.06
		0.40 ^{a}	
298.15	251.17 (±0.30)	73.09 (±2.01)	0.14
308.15	250.06 (±0.42)	77.19 (±2.81)	0.20
318.15	249.22 (±0.24)	80.80 (±1.64	0.12
		0.20 ^{a}	
298.15	250.18 (±0.18)	73.16 (±1.22)	0.09
308.15	249.58 (±0.44)	73.63 (±2.95)	0.21
318.15	248.54 (±0.39)	77.77 (±2.56)	0.18

^{a}Mass fraction of DMSO in the solvent mixtures.
Standard errors are given the parenthesis.

temperatures are reported in table 5.3. The intercept ϕ_V^0 is a measure of ion-solvent or solute-solvent interactions and the S_V^* value is a volumetric coefficient that characterizes pair-wise interaction between the solvated species or ion-ion interaction in solution phase. For a particular solute the ϕ_V^0 values depend on its intrinsic volume, the dielectric constant and the structure of the solvent system. Due to its dipolar nature, DMSO is a good nucleophile and can influence ion-solvation [5]. Also the structure and dielectric constant of aqueous DMSO solutions varies with the water-content due to dipole-dipole interactions [6, 7]. The ϕ_V^0 values for the complex systems gradually decrease with the advent of more water in solvent mixtures when compared to those values in pure DMSO. Thus it is evident that the studied solutions are characterized by strong ion-solvent interactions and such interactions gradually decrease leading to release of the loosely bound DMSO molecules around the complex, [Cr(salen)(H_2O)$_2$]Cl back to the bulk solution in order to promote hydrogen bonded structures with water molecules, because of the fact that DMSO enhances the hydrogen bonding network of water, possibly through the "hydrophobic" hydration of the methyl group [23, 24], thus resulting in lower values of ϕ_V and ϕ_V^0 at higher mass fractions (w_2) of water in the ternary solutions. Again both the ϕ_V and ϕ_V^0 values decrease as the experimental temperatures increase. The decrease in ϕ_V^0 values with an increase in experimental temperatures can be ascribed to the thermal effects that probably disrupts the weak interactions between the ions and solvent molecules, i.e., causes desolvation effect and this desolvation effect favors associated structure of the bulk solvent system as expected for the chosen solvents used in this study. So ϕ_V values do not increase rather they decrease.

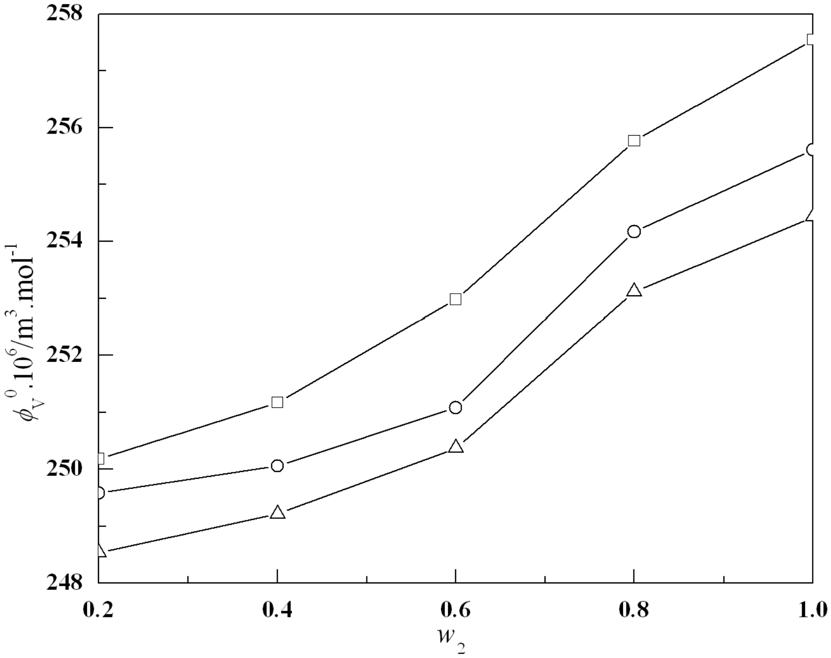

Fig. 5.2. Dependence of standard partial molar volume (ϕ_V^0) of [Cr(salen)(H_2O)$_2$]Cl on the mass fractions (w_2) of DMSO in the solvent mixtures at T = (298.15-318.15) K. Symbols: □, 298.15 K; ○, 308.15 K; Δ, 318.15 K.

The lower ϕ_V^0 values at higher water content also indicate that the complex probably remains preferentially more solvated by DMSO rather than by water. Dependence of ϕ_V^0 values on the solvent composition (w_2) is depicted in figure 5.2.

A perusal of table 5.3 reveals that for all the studied solutions, S_V^* values increase as both the water-content (in solvent mixtures) and experimental temperatures increase. For the studied solutions S_V^* values indicate the presence of ion-ion interactions and these interactions further strengthen in water rich solvent mixtures, because dielectric constants of the solvent mixtures increase with more water [25] and the more ions are dispersed in solutions due to dissociation of the complex $[Cr(salen)(H_2O)_2]Cl$ into its constituent ions, *i.e.*, $[Cr(salen)(H_2O)_2]^+$ and Cl^-. Hence more ion-ion interactions prevail in studied solutions. The increase in S_V^* values with increase in experimental temperatures can also be ascribed to thermal agitations of the systems at enhanced temperatures. An increase in the experimental temperatures increases kinetic energy of the system; thus more collisions between the constituent ions are possible and more collisions lead to increase in ion-ion interactions. Anyway, the S_V^* values are always smaller as compared to the ϕ_V^0 values for all the studied solutions and this fact indicates that the ion-solvent interaction plays a dominant role than the ion-ion interactions in characterizing the volumetric properties of studied systems.

5.3.2. *Partial molar expansibilities*

Apparent molar volumes (ϕ_V) and densities (ρ) at the experimental temperatures were used to calculate the apparent molar expansibilities (ϕ_E) of $[Cr(salen)(H_2O)_2]Cl$ solutions using the relation:[26]

$$\phi_E = \alpha\phi_V + \frac{1000(\alpha - \alpha_1)}{m\rho_1} \tag{3}$$

where α and α_1 are the coefficients of isobaric thermal expansion of the solvent and solution, respectively and other symbols have their usual significance. α and α_1 are defined as: $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$ and $\alpha_1 = -\rho_1^{-1}(\partial\rho_1/\partial T)_P$.The partial molar expansibilities (ϕ_E^0) were then determined from the relation:[26]

$$\phi_E = \phi_E^0 + S_E\sqrt{m} \qquad (4)$$

$(\partial\phi_E^0/\partial T)_P$ values were obtained from the slope of a linear fit of ϕ_E^0 values (a least squares linear regression used) against experimental temperature (T) with the correlation coefficient (R^2) values within the range 0.89052-0.99960. The ϕ_E^0 values are an important indicator of solute-solvent interactions and helps in interpretation of the long-range structure making or breaking properties of solutes.[27] The ϕ_E^0 values along with corresponding errors for different experimental solutions at different temperatures are given in table 5.4. It reveals that ϕ_E^0 values are negative. Negative expansibility, i.e., decreasing volume with increasing temperatures, is a characteristic property of aqueous solution of hydrophobic solutes.[28] DMSO is slightly polar due to the S=O group and it can participate in hydrophobic and hydrophilic interactions with water and such interactions cause redistribution of hydrogen bonded network of water structure. This redistribution results in changes in the packing of the solutions. The complex, [Cr(salen)(H_2O)$_2$]Cl, also has hydrophobic and hydrophilic fragments in its structure. So the negative ϕ_E^0 values most probably reflect an overall outcome of the hydrophobic and hydrophilic interactions prevailing in the solutions. According to Hepler[29] if the term $(\partial\phi_E^0/\partial T)_P$ is small negative or positive, the solute is a structure maker otherwise it is a structure breaker. The $(\partial\phi_E^0/\partial T)_P$ values for different ternary solutions are given in table 5.4. It shows that the $(\partial\phi_E^0/\partial T)_P$ values are small negative for all the studied solutions. Thus [Cr(salen)(H_2O)$_2$]Cl seems to act a net structure maker in aqueous DMSO solutions.

Table 5.4. Partial molar expansibilities (ϕ_E^0), slopes (S_E) and temperature dependence of partial molar expansibilities $(\partial\phi_E^0/\partial T)_P$ for [Cr(salen)(H_2O)$_2$]Cl in aqueous DMSO solutions at T = (298.15 to 318.15) K

Solvent	$\frac{\phi_E^0 \cdot 10^{-6}}{\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}}$			$\frac{S_E \cdot 10^{-6}}{\mathrm{m^3 \cdot kg^{1/2} \cdot mol^{-1} \cdot K^{-1}}}$			$\frac{\left(\frac{\partial \phi_E^0}{\partial T}\right)_p \cdot 10^{-6}}{\mathrm{m^3 \cdot mol^{-1} \cdot K^{-2}}}$
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	
1.00 [a]	-0.386 (±0.012)	-0.398 (±0.013)	-0.408 (±0.013)	0.628 (±0.085)	0.649 (±0.091)	0.665 (±0.090)	-1.120 (±0.013)
0.80 [a]	-0.247 (±0.020)	-0.250 (±0.020)	-0.254 (±0.021)	0.473 (±0.140)	0.480 (±0.141)	0.487 (±0.143)	-0.346 (±0.024)
0.60 [a]	-0.332 (±0.013)	-0.342 (±0.0142)	-0.349 (±0.0142)	0.570 (±0.092)	0.590 (±0.097)	0.600 (±0.097)	-0.851 (±0.045)
0.40 [a]	-0.277 (±0.024)	-0.283 (±0.025)	-0.289 (±0.025)	0.338 (±0.161)	0.346 (±0.165)	0.353 (±0.168)	-0.626 (±0.011)
0.20 [a]	-0.603 (±0.020)	-0.620 (±0.020)	-0.690 (±0.023)	0.101 (±0.131)	0.104 (±0.133)	0.119 (±0.150)	-4.365 (±0.884)

[a] Mass fraction of DMSO in the solvent mixtures. Standard errors are given the parenthesis

5.3.3. *Viscometric results*

The solute-solvent/ion-solvent interactions can also be discussed in terms of the changes in dynamic property such as viscosity and conductivity, etc. For the solutions under investigation, solution viscosities were analyzed by using the Jones-Dole equation: [30, 31]

$$(\eta/\eta_1 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (5)$$

where $\eta_r = \eta/\eta_1$; η_1, η and *c* are the viscosities of solvent, the viscosities of solution and molarity of the solute in the solutions, respectively. *A* is the Falkenhagen coefficient[32, 33] that depends on the long range coulombic forces related to ion-ion interactions and *B* is an adjustable parameter related to the size of the ions and ion-solvent interactions. *B*-coefficient also gives a measure of structural modifications induced by the ion-solvent or solute-solvent interactions.[34]

Viscosity *A*- and *B*- coefficients, listed in table 5.5, were estimated from the intercepts and slopes by a least squares linear regression of equation (5) with the correlation coefficient (R^2) values within the range 0.99273-0.99970. Table 5.5 shows that *A*- coefficients are negative (except in solvent mixture with w_2 = 0.20 at 308.15 and 318.15 K) and increase when both the water-content in the solvent mixtures and experimental temperatures increase. Although, theoretically the viscosity *A*-coefficients should be positive for electrolytes but we obtained negative values for the viscosity *A*-coefficients for most of the solvent compositions. The negative values for the viscosity *A*-coefficients is probably partly due to low surface charge density on the cation, $[Cr(salen)(H_2O)_2]^+$ and partly due to strong electrolytic nature of the complex[30] in aqueous DMSO solutions. Anyway, it is obvious that ion-ion or solute-solute interactions increase at higher temperature and higher water-content (higher dielectric constant[25]) in the ternary mixtures. These facts are probably due to increase in dissociation of the complex and more collisions between the ions at higher temperatures. Thus these trends in *A*-coefficients concur with the trends in S_V^* values discussed earlier.

Table 5.5. Viscosity *A*- and *B*-coefficients for [Cr(salen)(H_2O)$_2$]Cl with standard deviations (σ) for linear regression of equation (5) and solvation number (S_n) in aqueous DMSO solutions at T = (298.15 to 318.15) K

Parameters	298.15 K	308.15 K	318.15 K
		1.00^{a}	
$\frac{A}{\text{dm}^{3/2}\cdot\text{mol}^{-1/2}}$	-0.060 (±0.004)	-0.030 (±0.003)	-0.023 (±0.003)
$\frac{B}{\text{dm}^{3}\cdot\text{mol}^{-1}}$	0.942 (±0.025)	0.819 (±0.019)	0.781 (±0.023)
σ	0.002	0.001	0.002
S_n	3.66 (±0.10)	3.20 (±0.08)	3.07 (±0.09)
		0.80^{a}	
$\frac{A}{\text{dm}^{3/2}\cdot\text{mol}^{-1/2}}$	-0.044 (±0.004)	-0.020 (±0.002)	-0.019 (±0.001)
$\frac{B}{\text{dm}^{3}\cdot\text{mol}^{-1}}$	0.631 (±0.009)	0.543 (±0.011)	0.503 (±0.004)
σ	0.001	0.001	0.001
S_n	2.47 (±0.04)	2.14 (±0.04)	1.99 (±0.02)
		0.60^{a}	
$\frac{A}{\text{dm}^{3/2}\cdot\text{mol}^{-1/2}}$	-0.036 (±0.002)	-0.030 (±0.002)	-0.015 (±0.002)
$\frac{B}{\text{dm}^{3}\cdot\text{mol}^{-1}}$	0.564 (±0.011)	0.522 (±0.014)	0.488 (±0.013)
σ	0.001	0.001	0.001
S_n	2.23 (±0.05)	2.08 (±0.06)	1.95 (±0.05)
		0.40^{a}	
$\frac{A}{\text{dm}^{3/2}\cdot\text{mol}^{-1/2}}$	-0.014 (±0.002)	-0.005 (±0.001)	-0.001 (±0.000)
$\frac{B}{\text{dm}^{3}\cdot\text{mol}^{-1}}$	0.487 (±0.004)	0.461 (±0.016)	0.430 (±0.021)
σ	0.001	0.001	0.001
S_n	1.94 (±0.05)	1.84 (±0.07)	1.72 (±0.09)
		0.20^{a}	
$\frac{A}{\text{dm}^{3/2}\cdot\text{mol}^{-1/2}}$	-0.002 (0.001)	0.0004 (0.0001)	0.031 (0.002)
$\frac{B}{\text{dm}^{3}\cdot\text{mol}^{-1}}$	0.466 (±0.019)	0.440 (±0.028)	0.387 (±0.017)
σ	0.001	0.002	0.001
S_n	1.86 (±0.08)	1.76 (±0.12)	1.56 (±0.07)

[a] Mass fraction of DMSO in the solvent mixtures.
Standard errors are given the parenthesis.

Table 5.5 also shows that viscosity *B*- coefficients are positive and decrease as both the amount of water in the solvent mixture and experimental temperatures increase. A decrease in viscosity *B*-coefficient value shows that the ions cause weaker orientation effects in the solvation layer.[2] In the water rich region the value of viscosity *B*-coefficients change gradually with solvent composition and a smaller viscosity *B*-coefficient values (as compared to those in pure DMSO) are found in aqueous DMSO solutions. DMSO has the "rigidifying" effect on water structure[35] and at higher DMSO mass fractions (w_2) the decreased mobility (i.e., increased viscosity) is due to strong hydrogen bonding interaction between water and DMSO.[24]

A solute with positive viscosity *B*-coefficients is considered to be a long-range structure maker. The present results indicate that in pure DMSO and aqueous DMSO solutions [Cr(salen)(H_2O)$_2$]Cl has positive viscosity *B*-coefficients and behave as structure maker or solvent structure promoter. Again the viscosity *B*-coefficients decrease as the experimental temperature increases and this could be attributed to the fact that as the temperature increases the kinetic energy of the system increases and the solvent molecules attached to the solvation shell of [Cr(salen)(H_2O)$_2$]Cl returns to the bulk solution in order to favor hydrogen bonding interactions between water and DMSO. The sign of $(\partial B/\partial T)$ values also provide important information regarding long-range structure making or structure breaking ability of a solute in solutions. In general the sign of $(\partial B/\partial T)$ is negative for a solvent structure maker and *vice-versa*. $(\partial B/\partial T)$ values can be obtained from the slopes of linear fittings of viscosity *B*-coefficients against temperatures (depicted in figure 5.3) and the negative $(\partial B/\partial T)$ values[36] for studied solutions indicate that [Cr(salen)(H_2O)$_2$]Cl acts as solvent structure maker for studied solutions.

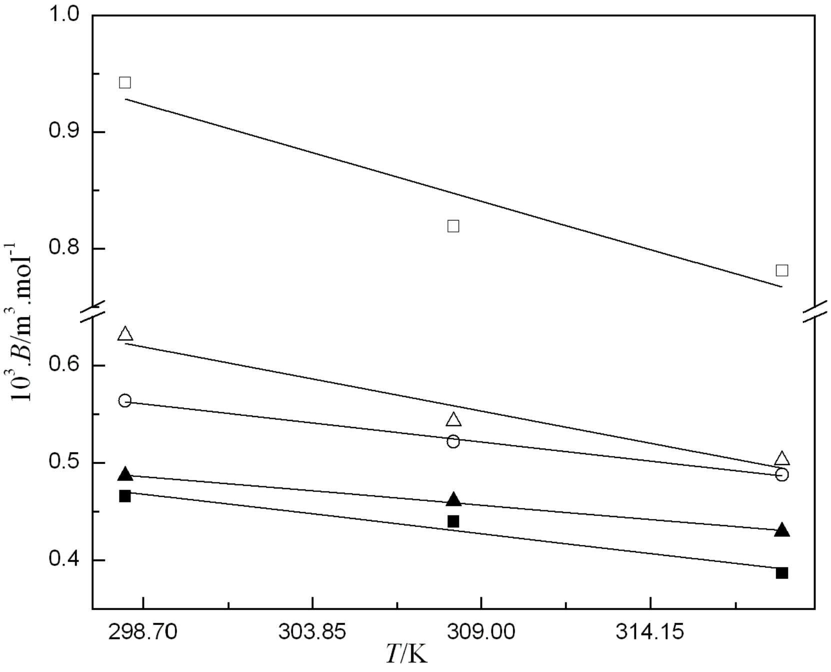

Fig. 5.3. Dependence of viscosity *B*-coefficients of [Cr(salen)(H_2O)$_2$]Cl on experimental temperatures. Symbols: □, w_2 = 1.00; Δ, w_2 = 0.80; ○, w_2 = 0.60; ▲, w_2 = 0.40; ■, w_2 = 0.20.

5.3.4. *Solvation numbers*

Solvation numbers (S_n) for the complex, [Cr(salen)(H_2O)$_2$]Cl, in the solvent media were obtained from the relation:[36]

$$S_n = B / \phi_V^0 \qquad (6)$$

S_n is indicative of the formation of a primary solvation sphere around a solute. The range $S_n \approx 0 - 2.5$ indicates unsolvated solutes in the solution[36] and higher S_n values indicate solvated solutes with primary solvation sphere. So an inspection of S_n values given in table 5.5 indicated that the complex remains solvated with primary solvation spheres in pure DMSO but suffers from desolvation effects with the advent of water and S_n values continue to decrease with further addition of water in the ternary solutions. These results indicate that water promotes the desolvation of [Cr(salen)(H_2O)$_2$]Cl (i.e., release of DMSO molecules from the primary solvation sphere of the complex) and favors the solvent-solvent interactions between water and

DMSO; so solvation of the complex with water seems to be rather meager. However, decrease in S_n values at higher temperatures concurs with our view that thermal effects disrupt the weak interactions between the ions and solvent molecules.

5.3.5. *Ionic B-coefficients*

For a better understanding of ion-solvent interactions splitting of viscosity *B*-coefficients into individual ionic viscosity *B*-coefficients ($B_{[\mathrm{Cr(salen)(H_2O)_2}]^+}$ and $B_{\mathrm{Cl^-}}$) is necessary. A popular method depends on the choice of an electrolyte for which the cation-solvent and anion-solvent interactions can be taken as equal, e.g., electrolytes with large polyatomic ions like tetraalkylammonium and tetraphenyl or borate.[37] We used the principle of additivity of ionic viscosity *B*-coefficients and subtracting literature $B_{\mathrm{Cl^-}}$ values [2, 38] in aqueous DMSO solutions from the viscosity *B*-coefficients, $B_{[\mathrm{Cr(salen)(H_2O)_2}]^+}$ were calculated (except for ternary solutions with $w_2 = 0.80$ for the lack of literature values of $B_{\mathrm{Cl^-}}$). Ionic viscosity *B*-coefficients are given in table 5.6. It shows that $B_{[\mathrm{Cr(salen)(H_2O)_2}]^+}$ values are positive and decrease as the mass fractions (w_2) of DMSO in the ternary solutions decrease; $B_{[\mathrm{Cr(salen)(H_2O)_2}]^+}$ values ultimately become negative in the ternary mixture with $w_2 = 0.20$. $B_{[\mathrm{Cr(salen)(H_2O)_2}]^+}$ values also decrease with an increase in the experimental temperatures. These trends in $B_{[\mathrm{Cr(salen)(H_2O)_2}]^+}$ values with solvent compositions and temperatures are in line with those followed by viscosity *B*-coefficients of the complex. The positive $B_{[\mathrm{Cr(salen)(H_2O)_2}]^+}$ values in the solutions with $w_2 = 0.40$, 0.60, 1.00 indicate long-range structure making ability of the $[\mathrm{Cr(salen)(H_2O)_2}]^+$ ion in these solvent mixtures but the negative $B_{[\mathrm{Cr(salen)(H_2O)_2}]^+}$ values obtained in solutions with $w_2 = 0.20$ are probably partly due to desolvation of $[\mathrm{Cr(salen)(H_2O)_2}]^+$ ion and partly due to water structure breaking ability of DMSO when present in small quantities.[39-41]

Table 5.6. Ionic viscosity *B*-coefficients ($B_{\mathrm{Cl^-}}$), ionic solvation numbers ($S_{n,\mathrm{Cl^-}}$) for $\mathrm{Cl^-}$ and ionic viscosity *B*-coefficients ($B_{\mathrm{[Cr(salen)(H_2O)_2]^+}}$), ionic partial molar volumes ($\phi^0_{V,\mathrm{[Cr(salen)(H_2O)_2]^+}}$) and ionic solvation numbers ($S_{n,\mathrm{[Cr(salen)(H_2O)_2]^+}}$) for $\mathrm{[Cr(salen)(H_2O)_2]^+}$ in aqueous DMSO solutions

w_2 [a]	$B_{\mathrm{Cl^-}}/\mathrm{dm^3\cdot mol^{-1}}$			$B_{\mathrm{[Cr(salen)(H_2O)_2]^+}}/\mathrm{dm^3\cdot mol^{-1}}$			$\frac{\phi^0_{V,\mathrm{[Cr(salen)(H_2O)_2]^+}}\cdot 10^6}{\mathrm{m^3\ mol^{-1}}}$	$S_{n,\mathrm{Cl^-}}$	$S_{n,\mathrm{[Cr(salen)(H_2O)_2]^+}}$
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K			
1.00	0.258 [b]	0.230 [b]	0.216 [b]	0.684	0.589	0.565	232.25 [d]	10.19 [d]	2.94 [d]
0.60	0.163 [c]	0.168 [c]	0.172 [c]	0.401	0.354	0.316	227.68 [d]	6.44 [d]	1.76 [d]
0.40	0.161 [c]	0.165 [c]	0.1705 [c]	0.326	0.296	0.2595	225.87 [d]	6.36 [d]	1.44 [d]
0.20	0.6992 [c]	0.6933 [c]	0.6678 [c]	-0.2332	-0.2533	-0.2808	224.88 [d]	27.64 [d]	-1.04 [d]

[a] Mass fraction of DMSO in the solvent mixtures.

[b] Values from Ref. [39], [c] values from Ref. [2] and [d] values at $T = 298.15$ K.

As literature values of ionic viscosity *B*-coefficients are available, ionic solvation numbers ($S_{n,\pm}$) were calculated by using the equation (6) by using ionic partial molar volumes ($\phi^0_{V,\pm}$) of the ions. For this purpose we have used ϕ^0_{V,Cl^-} = 25.3 cm^3.mol^{-1} at 298.15 K given by Kale and Zana.[42] $S_{n,\pm}$ values are given in table 5.6 and it is evident that $[\mathrm{Cr(salen)(H_2O)_2}]^+$ ion remains slightly solvated in the solutions with w_2 = 0.40, 0.60, 1.00 and its degree of solvation decreases as mass fractions (w_2) of DMSO decrease and becomes negative for solvent mixture with w_2 = 0.20. These results thus concur with the results obtained from S_n values discussed earlier.

5.3.6. *Thermodynamics of viscous flow*

While viscosity *B*-coefficient is very useful, greater insight into viscous flow can be obtained from the thermodynamic activation parameters. According to Eyring and co-workers,[43] the application of statistical thermodynamics to the hole model of viscous flow on the basis on the absolute reaction rate theory yielded the following relation for the free energy of activation for viscous flow per mole of the solvent/solvent mixture, $\Delta\mu_1^{0\neq}$:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_1\phi^0_{V,1}/hN_A) \qquad (7)$$

where N_A , $\phi^0_{V,1}$ are the Avogadro's number and the molar volumes of the solvent, respectively. The other symbols have their usual significances. For the aqueous binary mixtures of DMSO, used as solvents, $\phi^0_{V,1}$ is taken as the mole fraction average of molecular weights of H_2O and DMSO normalized by densities at the experimental temperatures. The above relation can also be expressed as: [44, 45]

$$\ln(\eta_1\phi^0_{V,1}/hN_A) = -\frac{\Delta S_1^{0\neq}}{R} + \left(\frac{\Delta H_1^{0\neq}}{R}\right)\frac{1}{T} \qquad (8)$$

So the values of $\Delta H_1^{0\neq}$ and $\Delta S_1^{0\neq}$ were obtained from a linear regression treatment (with $R^2 \approx 0.96851 - 0.99747$) of equation (8). Plots of $\ln(\eta_1\phi^0_{V,1}/hN_A)$ against ($10^3/T$) is shown in figure 5.4.

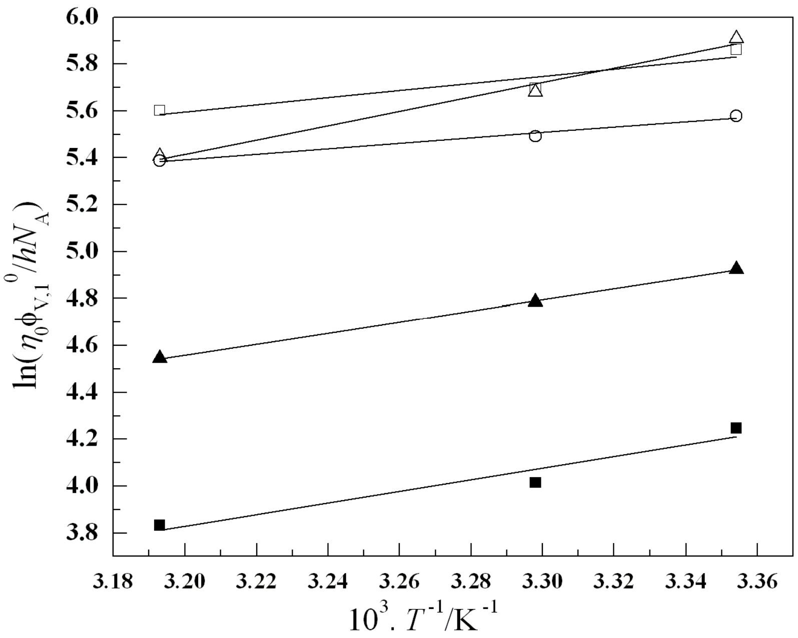

Fig. 5.4. Plots of $\ln(\eta_1\phi_{V,1}^0/hN_A)$ against $10^3 \cdot T^{-1}$ for different solvent mixtures as a function of the mass fractions (w_2) of DMSO. Symbols: □, $w_2 = 1.00$; Δ, $w_2 = 0.80$; ○, $w_2 = 0.60$; ▲, $w_2 = 0.40$; ■, $w_2 = 0.20$.

According to Feakins *et al.*[45] viscosity *B*- coefficients can be expressed as:

$$B = (\nu\phi_{V,1}^0 - \phi_{V,2}^0) + \phi_{V,1}^0\left(\frac{\Delta\mu_2^{0\neq} - \nu\Delta\mu_1^{0\neq}}{RT}\right) \tag{9}$$

where $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ stand for Gibbs free energy of activation of viscous flow per mole of the solvent and Gibbs free energy of activation of viscous flow per mole of the solute, respectively. The coefficient ν in equation (9) is 2 for 1:1 electrolytes. So we have calculated $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values by using the above relation and the *B*- coefficient values obtained from equation (9). Again $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values can also be expressed as:

$$\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT} = -\frac{\Delta S_2^{0\neq} - \Delta S_1^{0\neq}}{R} + \left\{\frac{\Delta H_2^{0\neq} - \Delta H_1^{0\neq}}{R}\right\}\frac{1}{T} \tag{10}$$

where $\Delta S_i^{0\neq}$ and $\Delta H_i^{0\neq}$ are the standard partial molar entropy and enthalpy of activation for viscous flow per mole of i^{th} component in the solution. So a linear regression treatment (with $R^2 \approx 0.94413 - 0.99832$) of equation (10) provided the values of $(\Delta S_2^{0\neq} - \Delta S_1^{0\neq})$ and $(\Delta H_2^{0\neq} - \Delta H_1^{0\neq})$ from the

Table 5.7. Values of $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$ and ($\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}$) for [Cr(salen)(H_2O)$_2$]Cl in aqueous DMSO solutions at T = (298.15 to 318.15) K.

/K	$\frac{\Delta\mu_1^{0\neq}}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{\Delta\mu_2^{0\neq}}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\#})}{\mathrm{kJ \cdot mol^{-1}}}$
		1.00 [a]	
298.15	14.530 (±0.001)	65.806 (±0.025)	51.276 (±0.025)
308.15	14.597 (±0.001)	62.318 (±0.020)	47.720 (±0.020)
318.15	14.818 (±0.001)	62.051 (±0.023)	47.233 (±0.023)
		0.80 [a]	
298.15	14.647 (±0.001)	75.878 (±0.009)	61.230 (±0.009)
308.15	14.554 (±0.001)	71.699 (±0.011)	57.145 (±0.011)
318.15	14.301 (±0.001)	69.791 (±0.004)	55.490 (±0.004)
		0.60 [a]	
298.15	13.830 (±0.001)	88.242 (±0.011)	74.411 (±0.011)
308.15	14.070 (±0.001)	86.526 (±0.014)	72.456 (±0.015)
318.15	14.251 (±0.001)	85.326 (±0.013)	71.075 (±0.014)
		0.40 [a]	
298.15	12.204 (±0.001)	93.466 (±0.012)	81.262 (±0.013)
308.15	12.263 (±0.001)	92.561 (±0.016)	80.298 (±0.017)
318.15	12.020 (±0.001)	90.400 (±0.022)	78.380 (±0.022)
		0.20 [a]	
298.15	10.528 (±0.001)	101.540 (±0.020)	91.012 (±0.019)
308.15	10.286 (±0.001)	99.704 (±0.029)	89.417 (±0.029)
318.15	10.137 (±0.001)	92.293 (±0.017)	82.156 (±0.017)

[a] Mass fraction of DMSO in the solvent mixtures. Standard errors are given the parenthesis.

corresponding slopes and intercept. The parameters $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$ and $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ are reported in table 5.7. $\Delta H_1^{0\neq}, \Delta H_2^{0\neq}$, $\Delta S_1^{0\neq}$ and $\Delta S_2^{0\neq}$ are reported in table 5.8. Plots of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}) / RT$ against $(10^3 / T)$ are shown in figure 5.5.Table 5.7 shows that $\Delta\mu_1^{0\neq}$ is almost invariant of the experimental temperatures but decreases with increase in water-content in the mixed solvents. This implies that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity *B*-coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms for a solvent composition. The values $\Delta\mu_2^{0\neq}$ contain the change in the free energy of activation of solute molecules in presence of solvent as well as the contribution from the movement of solute molecules. $\Delta\mu_2^{0\neq}$ values were positive and greater than $\Delta\mu_1^{0\neq}$ at all the experimental temperatures suggesting that the interactions between [Cr(salen)(H_2O)$_2$]Cl and solvent molecules in the ground state are stronger than in the transition state. Hence in the transition state solvation of [Cr(salen)(H$_2$O)$_2$]Cl is less favored in free energy terms. Also $\Delta\mu_2^{0\neq}$ values decrease as the temperature increases but increase gradually as the water content in ternary solutions increases. Such a trend of $\Delta\mu_2^{0\neq}$ values suggests that the viscous flow becomes easier at higher temperatures but more hindered when water content in the ternary solutions increases probably due to stronger solvent-solvent interactions (between water and DMSO [6, 7, 23, 24]) that plays also crucial role in determining solution viscosities.

According to Feakins *et al.*[44] the quantity $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ is the change in the activation energy per mole of solute on replacing one mole of solvent by one mole of solute in an infinite dilution. The values of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ obtained are positive for all the solvent mixtures and increase further with the addition

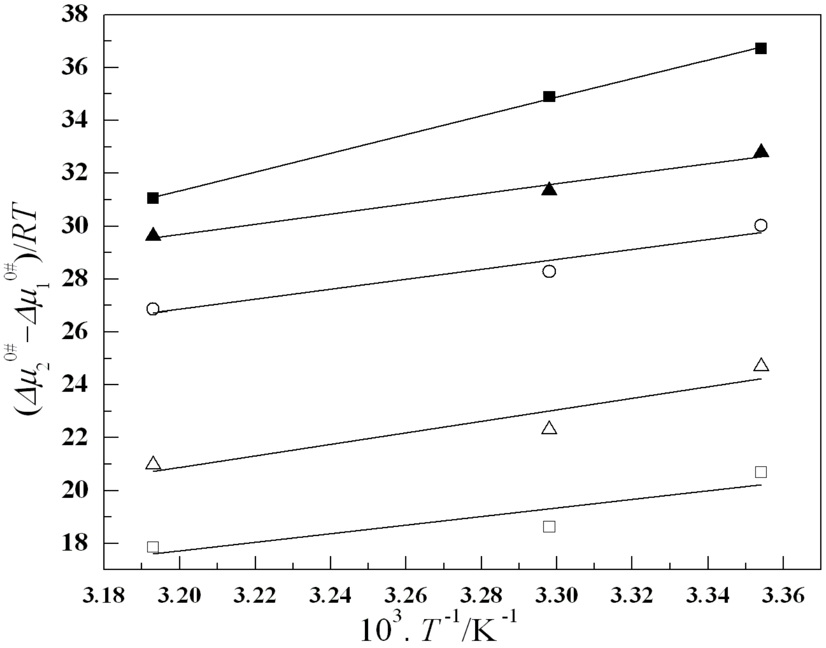

Fig. 5.5. Plots of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/RT$ against $10^3 \cdot T^{-1}$ for different solvent mixtures as a function of the mass fractions (w_2) of DMSO. Symbols: □, w_2 = 1.00; Δ, w_2 = 0.80; ○, w_2 = 0.60; ▲, w_2 = 0.40; ■, w_2 = 0.20.

Table 5.8. Values of $\Delta H_1^{0\neq}$, $\Delta H_2^{0\neq}$, $\Delta S_1^{0\neq}$ and $\Delta S_2^{0\neq}$ for [Cr(salen)(H_2O)$_2$]Cl in aqueous DMSO solutions.

Solvent	$\frac{\Delta H_1^{0\neq}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta H_2^{0\neq}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta S_1^{0\neq}}{\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\frac{\Delta S_2^{0\neq}}{\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$
1.00 [a]	10.255	122.314	-14.257	191.214
	(±0.094)	(±1.987)	(±0.306)	(±6.456)
0.80 [a]	19.788	166.990	17.159	306.780
	(±0.098)	(±1.597)	(±0.319)	(±5.189)
0.60 [a]	7.552	131.801	-21.090	146.368
	(±0.036)	(±0.391)	(±0.118)	(±1.270)
0.40 [a]	14.892	138.961	8.858	151.932
	(±0.186)	(±0.775)	(±0.606)	(±2.516)
0.20 [a]	16.373	238.462	19.653	456.323
	(±0.002)	(±3.552)	(±0.186)	(±11.540)

[a] Mass fraction of DMSO in the solvent mixtures. Standard errors are given the parenthesis.

of water in the ternary solutions. The positive $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values and their negative temperature dependence as well as similar trends in viscosity *B*-coefficients indicate the structure making ability of the solute. Again table 5.8 shows that the $\Delta H_2^{0\neq}$ values are positive for almost all the solvent systems and increase as the amount of water in the ternary solutions increases (except for solvent composition with w_2 = 0.60 characterized by maximum non-ideality[15]). This indicates that the viscous process involves breaking and distortion of the solvation bonds or intermolecular bonds between the competing molecules in the activated state of viscous flow and that the viscous process is endothermic. Thus the viscous flow should be accompanied by a decrease in order and thus positive $\Delta S_2^{0\neq}$ values are obtained.

5.3.7. *Refractometric results*

The dimensionless optical property refractive index, n_D, is very sensitive to changes in molecular organization of pure liquids, solutions and mixtures. The apparent molar refractivity, R_D of a solute can be expressed as:[46]

$$R_D = \frac{1000}{c}\left[\frac{n_D^2-1}{n_D^2+2} - \frac{1}{\rho_1}\left(\rho - \frac{cM}{1000}\right)\frac{n_{D,1}^2-1}{n_{D,1}^2+2}\right] \qquad (11)$$

where n_D and $n_{D,1}$ are the refractive indices of the solution and solvent/solvent mixture, respectively at 298.15 K and other symbols have their usual meanings. R_D values, given in table 5.9, increases linearly as the concentration of [Cr(salen)(H_2O)$_2$]Cl in all the solvent/solvent mixtures but decreases as the mass fraction (w_2) of DMSO decreases in the studied solutions. This indicated that refractive indices are directly related to ion-solvent interactions in the solutions. As R_D is directly proportional to the molecular polarizability,[47] the increasing trend in R_D values indicates an overall increase in the molecular polarizabilities ($\alpha_{\mathrm{P}} = 3R_{\mathrm{M}} / 4\pi N_A$).[46] The molar refractivities (R_{M}) were estimated by using Lorentz-Lorenz equation.[48]

Table 5.9. Refractive indices (n_D), molar refractivities (R_{M}), apparent molar refractivities (R_D) and molar polarizabilities (α_{P}) as a function of molarities (c) of [Cr(salen)(H_2O)$_2$]Cl in aqueous DMSO solutions

$\frac{c}{\mathrm{mol \cdot dm^{-3}}}$	n_D	$\frac{R_{\mathrm{M}} \cdot 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$	$\frac{R_{\mathrm{D}} \cdot 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$	$\frac{\alpha_{\mathrm{P}} \cdot 10^{-30}}{\mathrm{m^3 \cdot mol^{-1}}}$
1.00 [a]				
0.0120	1.4773	20.88 (±0.01)	90.97 (±3.90)	8.28 (±0.01)
0.0160	1.4777	21.13 (±0.01)	99.57 (±2.98)	8.38 (±0.01)
0.0199	1.4781	21.38 (±0.01)	105.01 (±2.42)	8.48 (±0.01)
0.0240	1.4785	21.64 (±0.01)	108.49 (±2.02)	8.58 (±0.01)
0.0300	1.4790	22.01 (±0.01)	110.34 (±1.63)	8.72 (±0.01)
0.0360	1.4793	22.36 (±0.01)	108.84 (±1.35)	8.87 (±0.01)
0.80 [a]				
0.0120	1.4528	11.98 (±0.01)	86.59 (±3.73)	4.75 (±0.01)
0.0160	1.4532	12.14 (±0.01)	95.80 (±2.85)	4.81 (±0.01)
0.0199	1.4536	12.31 (±0.01)	101.32 (±2.31)	4.88 (±0.01)
0.0240	1.4540	12.46 (±0.01)	105.00 (±1.94)	4.94 (±0.01)
0.0300	1.4545	12.70 (±0.01)	107.08 (±1.56)	5.04 (±0.01)
0.0360	1.4551	12.94 (±0.01)	109.89 (±1.31)	5.13 (±0.01)
0.60 [a]				
0.0120	1.4237	8.21 (±0.01)	83.79 (±3.55)	3.25 (±0.01)
0.0160	1.4240	8.32 (±0.01)	89.48 (±2.70)	3.30 (±0.01)
0.0199	1.4244	8.43 (±0.01)	95.63 (±2.19)	3.34 (±0.01)
0.0240	1.4249	8.55 (±0.01)	102.03 (±1.85)	3.39 (±0.01)
0.0300	1.4253	8.72 (±0.01)	102.28 (±1.48)	3.46 (±0.01)
0.0360	1.4258	8.89 (±0.01)	103.97 (±1.24)	3.52 (±0.01)
0.40 [a]				
0.0120	1.3919	6.13 (±0.01)	79.63 (±3.36)	2.43 (±0.01)
0.0161	1.3923	6.22 (±0.01)	88.69 (±2.56)	2.47 (±0.01)

Contd…

0.0199	1.3927	6.30 (±0.01)	94.48 (±2.04)	2.50 (±0.01)
0.0240	1.3932	6.39 (±0.01)	100.57 (±1.76)	2.53 (±0.01)
0.0300	1.3936	6.52 (±0.01)	100.34 (±1.41)	2.59 (±0.01)
0.0360	1.3941	6.65 (±0.01)	101.87 (±1.18)	2.64 (±0.01)
		0.20 [a]		
0.0120	1.3609	4.79 (±0.01)	75.30 (±3.16)	1.90 (±0.01)
0.0160	1.3613	4.86 (±0.01)	84.78 (±2.43)	1.93 (±0.01)
0.0199	1.3617	4.93 (±0.01)	90.58 (±1.97)	1.96 (±0.01)
0.0240	1.3622	5.00 (±0.01)	96.73 (±1.67)	1.98 (±0.01)
0.0300	1.3627	5.11 (±0.01)	98.40 (±1.34)	2.03 (±0.01)
0.0360	1.3633	5.21 (±0.01)	101.10 (±1.12)	2.07 (±0.01)

[a] Mass fraction of DMSO in the solvent mixtures.
Standard errors are given the parenthesis.

Thus an inspection of table 5.9 reveals that the studied solutions are characterized by structural changes due ion-solvent and solvent-solvent interactions.

5.4. Conclusion

In summary, different derived parameters like ϕ_V^0 and viscosity *B*-coefficients, S_n, $S_{n,\pm}$, etc., for [Cr(salen)(H_2O)$_2$]Cl in pure DMSO and aqueous DMSO indicate that the solutions are predominantly characterized by strong solvent-solvent interactions and ion-solvent interactions rather than by ion-ion interactions and the complex, [Cr(salen)(H_2O)$_2$]Cl, acts as a net structure promoter for the studied solutions.

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CHAPTER VI

Partial molar volumes and viscosity *B*-coefficients of N, N$^{/}$-ethylenebis-(salicylideneiminato)cobalt(II) in binary mixtures of 1,4-Dioxane + Methanol at *T* = (298.15, 303.15, 308.15 and 313.15) K[*]

6.1. Introduction

Mixed solvents are characterized by the variation of properties such as dielectric constant or viscosity, etc., enabling better studies on solute-solute and solute-solvent interactions. Furthermore, different properties strongly influenced by solvent properties can be derived in terms of concentration dependence of a solute. Alcohols in non-polar solvents associate by means of hydrogen bonds into a series of *n*-mers.[1,2] In dilute solutions the predominant species are the unassociated molecules-while in concentrated solutions both linear and n-mers coexist. In solvents such as 1,4-dioxane that can form hydrogen bonds with methanol, the self-association of alcohols may be reduced/perturbed in favour of hydrogen bonded structures when mixed together leading to intermolecular association between methanol and 1,4-dioxane molecules.[3] Papanastasiou *et al.*[4] suggested that the binary mixtures of 1,4-dioxane and methanol is characterized by the formation of two intermolecular complexes (1,4-dioxane: methanol) of the types 1:1 and 1:2 and that 1,4- dioxane can associate through hydrogen bonds by either of its two oxygen atoms.

It is well known that naturally occurring oxygen carriers and storage proteins contain transition metal ions to reversibly bind dioxygen. Since cobalt-Schiff base complexes were reported to be synthetic reversible oxygen carriers by Tsumaki,[5, 6] many investigators have conducted extensive studies on the oxygen-carrying property of these complexes.[7-11] Among the cobalt-Schiff base complexes, the best known is N, N$^{/}$-ethylenebis(salicylideneiminato)cobalt(II), abbreviated as Co(salen), has a low-spin configuration with a square planar donor atom (ONNO) symmetry and it can exist in different crystalline forms depending on the solvent used in its preparation. These crystalline forms have varying capacity for oxygenation in the solid state and only few solvents that can promote the oxygenation of Co(salen) were found to be ligated to the cobalt in the final oxygenated inactive form.[12] Hence solvent composition has a major role to play.

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Ochiai *et al.*[13,14] indicated that oxygenation of Co(II)L complex (where L is a solvent base ligand) forms either O_2:CoL (1:1 adduct) or LCo:O_2:CoL (2:1 adduct) and 2:1 adduct is thermodynamically favoured. Hence the solution behavior of Co(salen) in mixed solvent media like 1,4-dioxane + methanol will be quite intriguing and interesting. However, such studies on the solute-solute and solute-solvent interactions prevailing in solutions of Co(salen) in various pure and mixed solvents are rare in the literature. Again standard partial molar volumes ϕ_V^0 and viscosity *B*-coefficients in solution phase provide valuable information about solute-solvent and solvent-solvent interactions[15-17] and thus are of fundamental importance for a proper understanding of the solution behavior of the solute under investigation. Hence in this chapter an attempt has been undertaken to reveal the various interactions prevailing in the ternary mixtures of Co(salen) + 1,4-dioxane + methanol at 298.15, 303.15, 308.15 and 313.15 K under ambient pressure.

6.2. Experimental section

6.2.1. *Materials*

A. R. grade cobalt acetate, $Co(OAc)_2.4H_2O$; 1,2-ethylenediamine and salicylaldehyde, each of purity > 99%, were procured from Thomas Baker, India. These chemicals were used without further purification. Spectroscopic grade methanol and 1,4-dioxane were procured Merck, India and used as received. Both of these liquids have purity (minimum assay, GC) > 99.8% with 0.05% of water. The various binary solvent mixtures were prepared by mass and necessary adjustments were done to achieve exact mass % ($w_1 = 0.10, 0.20, 0.30$ and 0.40) of 1,4- dioxane in the binary solvent mixtures with methanol at 298.15 K. The physical properties of these solvent mixtures as given in table 6.1 showed that the experimental densities and viscosities were more or less comparable to the values obtained by the least squares fitting of the literature data[4] with necessary conversion of mole fractions into mass fractions or *vice-versa* up to 308.15 K. A comparison of literature data[4, 18-22] for the densities and viscosities of the pure liquids were also made in table 6.1 with the experimentally determined values whenever available.

Table 6.1. Density (ρ), and viscosity (η) for different mixtures of 1,4-dioxane (1) + methanol (2) at T = (298.15 to 313.15) K

Solvent mixture	T/K	$\frac{\rho \cdot 10^{-3}}{\mathrm{kg \cdot m^{-3}}}$		$\frac{\eta}{\mathrm{mPa \cdot s}}$	
		Expt.	Lit.	Expt.	Lit.
$w_1 = 0.00$	298.15	0.7866	0.78645[4]	0.547	0.542[4]
	303.15	0.7818	0.7819[18]	0.508	0.510[18]
	308.15	0.7769	0.77710[4]	0.471	0.469[4]
	313.15	0.7728	0.7720[19]	0.449	0.4470[19]
$w_1 = 0.10$	298.15	0.8112	0.8068[a]	0.550	0.544[a]
	303.15	0.8064	0.8005[a]	0.511	0.505[a]
	308.15	0.8017	0.7975[a]	0.473	0.472[a]
	313.15	0.7969	0.7365[a]	0.432	0.429[a]
$w_1 = 0.20$	298.15	0.8344	0.8278[a]	0.554	0.554[a]
	303.15	0.8288	0.8217[a]	0.517	0.514[a]
	308.15	0.8234	0.8184[a]	0.482	0.479[a]
	313.15	0.8184	0.7663[a]	0.448	0.436[a]
$w_1 = 0.30$	298.15	0.8525	0.8497[a]	0.565	0.568[a]
	303.15	0.8474	0.8438[a]	0.527	0.526[a]
	308.15	0.8426	0.8402[a]	0.489	0.491[a]
	313.15	0.8380	0.7973[a]	0.452	0.447[a]
$w_1 = 0.40$	298.15	0.8751		0.587	
	303.15	0.8702		0.548	
	308.15	0.8655		0.508	
	313.15	0.8606		0.467	
$w_1 = 1.00$	298.15	1.0273	1.0278[20]	1.196	1.196[20]
	303.15	1.0223	1.0222[21]	1.093	1.0937[21]
	308.15	1.0178	1.01689[4]	1.011	1.0112[4]
	313.15	1.0143	1.0144[22]	0.978	0.9785[22]

[a] Least square fitted values of density and viscosity data from Ref 4.

Co(salen) was prepared by a slight modification of a known method[5, 23] from equimolar quantities of cobalt acetate and the Schiff base, SalenH$_2$ in methanol. The molecular structures of the ligand, SalenH$_2$ and the complex, Co(salen) were depicted in figure 6.1. Before use Co(salen) was kept in a vacuum desiccator over anhydrous CaCl$_2$ for several hrs. Then stock solutions of Co(salen) in different solvent mixtures ($w_1 = 0.00, 0.10, 0.20, 0.30$ and 0.40) were prepared by mass and the working solutions were prepared by mass dilution. The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The conversion of molality into molarity was accomplished by using experimental density values. All solutions were prepared afresh before use. The uncertainty in molarity of the Co(salen) solutions was evaluated to ± 0.0001 $\mathrm{mol \cdot dm^{-3}}$.

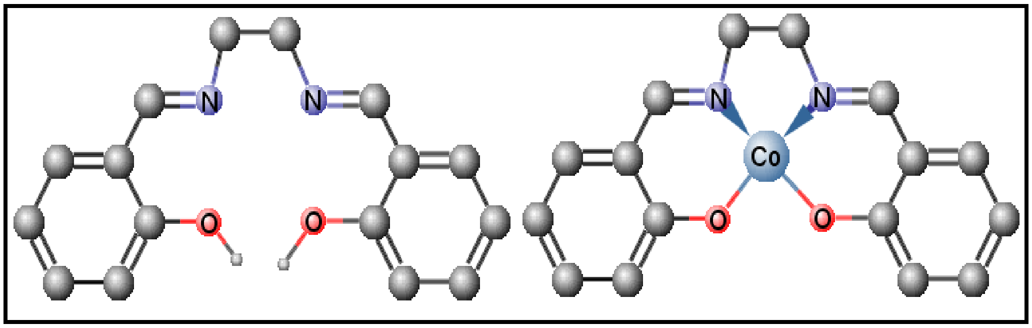

Fig. 6.1. Molecular structure of SalenH$_2$ and Co(salen).

6.2.2. *Apparatus and procedure*

The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M), maintained at ± 0.01 K of the desired temperatures and calibrated at the experimental temperatures with doubly distilled water and dry air. The viscosity was measured by means of a suspended Ubbelohde type viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled water and purified methanol.[24-26] It was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a digital stopwatch correct to ± 0.01s. In all determinations, an average of triplicate measurements was taken into account and adequate precautions were taken to minimize evaporation loses during the actual measurements. The uncertainty in viscosity measurements was within ± 0.003 $\mathrm{mPa \cdot s}$. Refractive indices were measured with an Abbe refractometer at 298.15 K. Water was circulated through the refractometer from a water bath maintained to ± 0.01 K of 298.15 K. The refractometer was calibrated with doubly distilled, degassed water before each series of measurements. The uncertainty in refractive indices was within ± 0.0002. Details of density, viscosity and refractive index measurements have been described in chapter III.

The absorption spectra of Co(salen) in different mixtures of 1,4-dioxane and methanol at a concentration of 5.0×10^{-5} $\mathrm{mol \cdot dm^{-3}}$ were recorded on Jasco V-530 double beam UV-VIS Spectrophotometer coupled with thermostatic arrangement (model TB-85, Japan) at ambient temperature by using a quartz cell of 1 cm path length and spectroscopic grade methanol as the reference solvent.

6.3. Results and discussion

The experimental values of molalities (*m*), densities (ρ), viscosities (η) and derived parameters for the experimental solutions of Co(salen) in different mass % of 1,4-dioxane + methanol mixtures at various temperatures are reported in table 6.2.

Table 6.2. Molalities (*m*), densities (ρ), viscosities (η), apparent molar volumes (ϕ_V) for Co(salen) in different mixtures of 1,4-dioxane (1) + methanol (2) at $T = (298.15 - 313.15)$ K

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{\rho\cdot 10^{-3}}{\text{kg}\cdot\text{m}^{-3}}$	$\frac{\eta}{\text{mPa}\cdot\text{s}}$	$\frac{\phi_V\cdot 10^{6}}{\text{m}^3\cdot\text{mol}^{-1}}$
$w_1 = 0.00$			
T/K= 298.15			
0.0036	0.7871	0.551	188.92
0.0046	0.7873	0.555	167.42
0.0061	0.7876	0.561	148.38
0.0087	0.7882	0.572	116.05
0.0107	0.7886	0.582	111.14
0.0127	0.7890	0.593	107.76
T/K = 303.15			
0.0036	0.7823	0.512	188.69
0.0046	0.7825	0.516	166.93
0.0061	0.7828	0.521	147.65
0.0087	0.7834	0.533	114.93
0.0107	0.7838	0.540	109.96
0.0127	0.7842	0.552	106.54
T/K = 308.15			
0.0036	0.7774	0.473	188.44
0.0046	0.7776	0.478	166.40
0.0061	0.7779	0.483	146.88
0.0087	0.7785	0.495	113.74
0.0107	0.7789	0.502	108.71
0.0127	0.7793	0.515	105.25
T/K = 313.15			
0.0036	0.7733	0.453	188.22
0.0046	0.7735	0.457	165.94
0.0061	0.7738	0.463	146.21
0.0087	0.7744	0.474	112.72
0.0107	0.7748	0.481	107.64
0.0127	0.7752	0.494	104.15
$w_1 = 0.10$			
T/K = 298.15			
0.0035	0.8117	0.556	183.77

Contd…

0.0044	0.8119	0.559	162.53
0.0059	0.8122	0.565	140.40
0.0084	0.8128	0.575	113.83
0.0104	0.8132	0.585	108.46
0.0123	0.8136	0.594	104.15
T/K = 303.15			
0.0035	0.8069	0.516	183.56
0.0044	0.8071	0.520	158.57
0.0059	0.8074	0.526	142.54
0.0084	0.8080	0.536	110.23
0.0104	0.8084	0.545	107.36
0.0123	0.8088	0.556	102.99
T/K = 308.15			
0.0035	0.8022	0.478	183.34
0.0044	0.8024	0.482	158.06
0.0059	0.8027	0.487	141.84
0.0084	0.8033	0.497	109.15
0.0104	0.8037	0.505	106.25
0.0123	0.8041	0.516	101.83
T/K = 313.15			
0.0035	0.7974	0.437	183.10
0.0044	0.7976	0.441	157.51
0.0059	0.7979	0.447	141.10
0.0084	0.7985	0.457	108.01
0.0104	0.7989	0.464	105.08
0.0123	0.7993	0.475	100.61
$w_1 = 0.20$			
T/K = 298.15			
0.0034	0.8349	0.558	178.49
0.0043	0.8351	0.562	155.87
0.0058	0.8354	0.568	142.01
0.0082	0.8360	0.576	109.36
0.0101	0.8364	0.586	105.15
0.0120	0.8368	0.593	102.27
T/K = 303.15			
0.0034	0.8293	0.521	178.26
0.0043	0.8295	0.525	155.34
0.0058	0.8298	0.531	141.29
0.0082	0.8304	0.541	108.19
0.0101	0.8308	0.549	103.93
0.0120	0.8312	0.555	101.01
T/K = 308.15			
0.0034	0.8239	0.487	178.02
0.0043	0.8241	0.491	156.85
0.0058	0.8244	0.497	140.56
0.0082	0.8250	0.505	107.03
0.0101	0.8254	0.513	102.71
0.0120	0.8258	0.521	99.75
T/K = 313.15			
0.0034	0.8189	0.453	177.77

Contd…

0.0043	0.8191	0.457	155.99
0.0058	0.8194	0.464	139.86
0.0082	0.8200	0.471	105.92
0.0101	0.8204	0.479	101.55
0.0120	0.8208	0.487	98.55
$w_1 = 0.30$			
T/K = 298.15			
0.0033	0.8530	0.569	172.96
0.0042	0.8532	0.573	152.09
0.0056	0.8535	0.578	135.68
0.0080	0.8541	0.587	106.15
0.0099	0.8545	0.595	103.33
0.0117	0.8549	0.603	99.02
T/K = 303.15			
0.0033	0.8479	0.531	172.74
0.0042	0.8481	0.535	151.62
0.0056	0.8484	0.541	135.01
0.0080	0.8490	0.549	105.13
0.0099	0.8494	0.557	102.27
0.0117	0.8498	0.566	97.91
T/K = 308.15			
0.0033	0.8431	0.494	172.52
0.0042	0.8433	0.498	151.15
0.0056	0.8436	0.504	134.35
0.0080	0.8442	0.513	104.13
0.0099	0.8446	0.521	101.24
0.0117	0.8450	0.528	96.83
T/K = 313.15			
0.0033	0.8385	0.456	172.29
0.0042	0.8387	0.461	150.69
0.0056	0.8390	0.468	133.70
0.0080	0.8396	0.476	103.15
0.0099	0.8400	0.484	100.23
0.0117	0.8404	0.491	95.77
$w_1 = 0.40$			
T/K = 298.15			
0.0032	0.8756	0.591	167.56
0.0041	0.8758	0.594	148.63
0.0055	0.8761	0.598	134.12
0.0078	0.8767	0.607	103.64
0.0096	0.8771	0.612	99.42
0.0114	0.8775	0.621	96.52
T/K = 303.15			
0.0032	0.8707	0.551	167.35
0.0041	0.8709	0.555	148.20
0.0055	0.8712	0.561	133.53
0.0078	0.8718	0.567	102.71
0.0096	0.8722	0.575	98.44
0.0114	0.8726	0.582	95.51

Contd…

T/K = 308.15			
0.0032	0.8660	0.514	167.13
0.0041	0.8662	0.518	147.77
0.0055	0.8665	0.524	132.94
0.0078	0.8671	0.532	101.79
0.0096	0.8675	0.540	97.48
0.0114	0.8679	0.546	94.51
T/K = 313.15			
0.0032	0.8611	0.472	166.89
0.0041	0.8613	0.476	147.31
0.0055	0.8616	0.481	132.31
0.0078	0.8622	0.491	100.81
0.0096	0.8626	0.497	96.44
0.0114	0.8630	0.503	93.44

6.3.1. *Standard partial molar volume*

For the analysis of solvation state of a solute in solution phase and its interaction with solvent components, data of partial molar volumes are important. For this purpose, the apparent molar volumes (ϕ_V) were determined from the solution densities using the following relation:

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_1)}{m\rho\rho_1} \qquad (1)$$

where M is the molar mass of Co(salen), m is the molality of the solution, ρ_1 and ρ are the densities of the solvent and solution, respectively. Uncertainties in ϕ_V values were within the range $0.02 - 0.05 \times 10^{-6}\,\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$. As the plots of ϕ_V against square root of molar concentration ($\sqrt{m}$) were not linear, ϕ_V values were fitted to the following equation:[27]

$$\phi_V = \phi_V^0 + A_V\sqrt{m} + B_V m \qquad (2)$$

where ϕ_V^0 is the partial molar volume at infinite dilution, A_V and B_V are two adjustable parameters. The ϕ_V^0 values were determined by fitting the dilute data ($m <$ 0.1) to equation (2) by using a least squares regression method and the coefficient of regression (R^2) values were within the range 0.9991-0.9999. The values of ϕ_V^0 at each temperature are reported in Table 6.3. The estimated uncertainties in ϕ_V^0 were equal to standard deviation (σ), the root mean square of the deviations between the experimental and calculated ϕ_V values for each data point. ϕ_V^0 values were further optimized from the linear variation of the parameter ($\phi_V - A_V\sqrt{m}$) against the molalities (m) of the experimental solutions in different solvent systems at different experimental temperatures (Figures 6.2-6.6).

Table 6.3 shows that ϕ_V^0 values are positive and increase with a rise in the temperature but decreases as the amount of 1,4- dioxane in the mixtures increases. This indicates the presence of strong solute-solvent interactions and these interactions

Table 6.3. Standard partial molar volumes (ϕ_V^0), adjustable parameters A_V and B_V for Co(salen) in mixtures of 1,4-dioxane (1) + methanol (2) with standard deviations (σ) at T = (298.15 to 313.15) K

T/K	$\frac{\phi_V^0\cdot10^6}{\mathrm{m^3\cdot mol^{-1}}}$	$\frac{A_V\cdot10^6}{\mathrm{m^3\cdot mol^{-1.5}}}$	$\frac{B_V\cdot10^6}{\mathrm{m^3\cdot mol^{-2}}}$	$\frac{\sigma\cdot10^6}{\mathrm{m^3\cdot mol^{-1}}}$
		$w_1 = 0.00$		
298.15	467.11 (±0.02)	-6248.36 (±2.18)	27089.97 (±2.06)	0.33
303.15	470.30 (±0.02)	-6325.42 (±2.02)	27425.22 (±2.09)	0.34
308.15	473.66 (±0.02)	-6406.48 (±2.20)	27778.05 (±2.10)	0.35
313.15	476.56 (±0.02)	-6476.98 (±2.14)	28087.82 (±2.17)	0.36
		$w_1 = 0.10$		
298.15	466.58 (±0.03)	-6518.85 (±0.16)	29348.60 (±1.67)	0.11
303.15	467.72 (±0.03)	-6571.78 (±0.45)	29618.04 (±1.83)	0.02
308.15	470.85 (±0.03)	-6649.28 (±0.49)	29968.32 (±1.81)	0.02
313.15	474.12 (±0.03)	-6730.53 (±0.60)	30336.27 (±1.90)	0.02
		$w_1 = 0.20$		
298.15	431.38 (±0.06)	-5854.27 (±1.24)	25934.18 (±3.61)	0.55
303.15	434.59 (±0.06)	-5933.79 (±1.34)	26286.64 (±3.67)	0.56
308.15	439.20 (±0.06)	-6020.67 (±1.96)	26576.76 (±3.85)	0.76
313.15	441.83 (±0.06)	-6091.25 (±1.96)	26903.17 (±3.87)	0.75
		$w_1 = 0.30$		
298.15	425.81(±0.12)	-5965.73 (±1.01)	27221.04 (±11.45)	0.01
303.15	428.62 (±0.12)	-6037.18 (±0.98)	27546.49 (±11.59)	0.01
308.15	431.38 (±0.12)	-6107.75 (±1.17)	27870.69 (±11.70)	0.01
313.15	433.99 (±0.13)	-6174.86 (±1.01)	28177.05 (±11.87)	0.01
		$w_1 = 0.40$		
298.15	396.00 (±0.03)	-5387.12 (±3.07)	24085.03 (±2.01)	0.75
303.15	398.38 (±0.03)	-5448.31 (±3.15)	24359.82 (±2.01)	0.77
308.15	400.66 (±0.03)	-5507.29 (±2.98)	24623.87 (±2.03)	0.77
313.15	403.06 (±0.03)	-5569.35 (±3.11)	24899.72 (±2.07)	0.80

Standard errors are given the parenthesis

are further strengthened at higher temperatures but weakened with higher content of the cyclic diether. In this study, Co(salen) was actually taken in its oxygenated form and methanol being a protic solvent may interact with the dioxygen coordinated to sixth position of Co(salen), resulting in the rapid breakdown of the dioxygen complex with oxidation of Co(II) to Co(III). It may also interact with Co(salen) via hydrogen bond formation with ONNO sites of the complex. It is also reported that 1,4-dioxane forms extensive hydrogen bonding with methanol. Hence with increasing amount of 1,4-dioxane in the solvent mixtures, interaction between methanol and Co(salen) decreases owing to favourable hydrogen bond interaction between 1,4-dioxane and methanol molecules. Thus the addition of 1,4-dioxane decreases ϕ_V as well as ϕ_V^0 values for the ternary systems under investigation. A schematic representation of such probable molecular interactions has been depicted in figure 6.7.

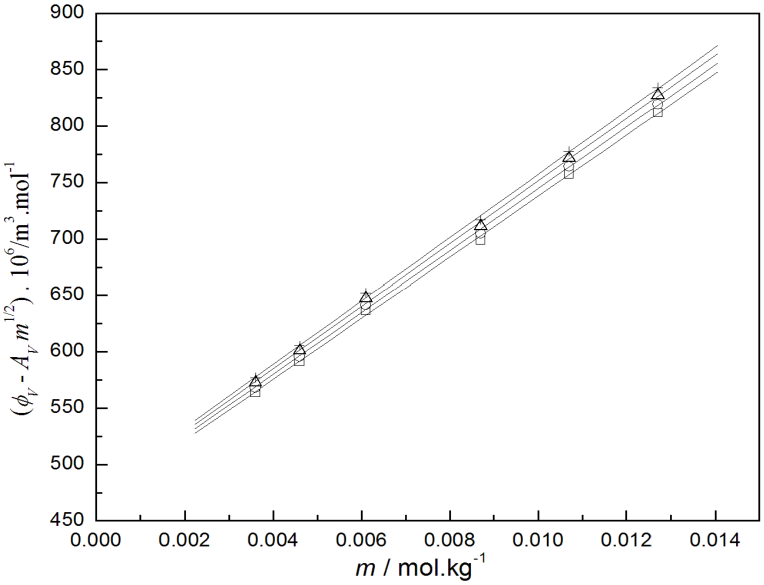

Fig. 6.2. Variation of the parameter ($\phi_V - A_V\sqrt{m}$) as a function of molality (m) of Co(salen) in methanol at T = (298.15 to 313.15) K: □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; and +, 313.15 K.

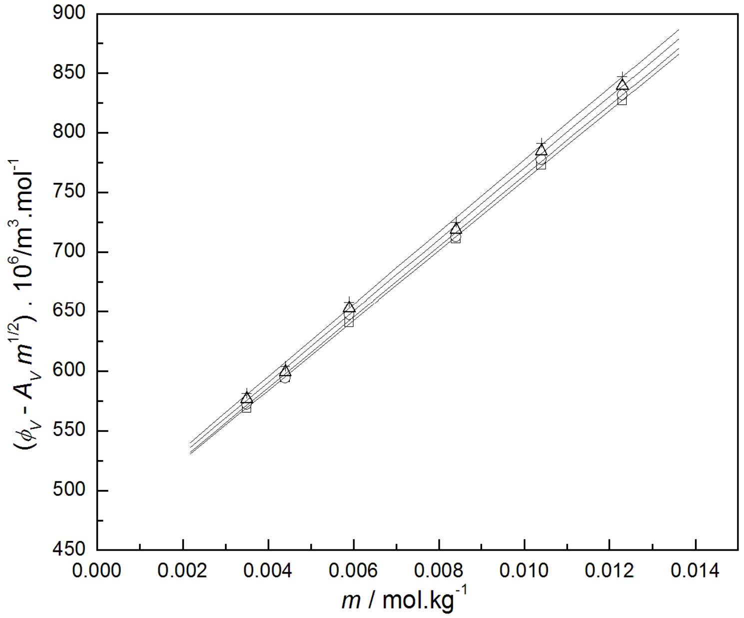

Fig. 6.3. Variation of the parameter ($\phi_V - A_V\sqrt{m}$) as a function of molality (m) of Co(salen) in in 1,4-dioxane (1) + methanol (2) mixture with $w_1 = 0.10$ at T = (298.15 to 313.15) K: □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; and +, 313.15 K.

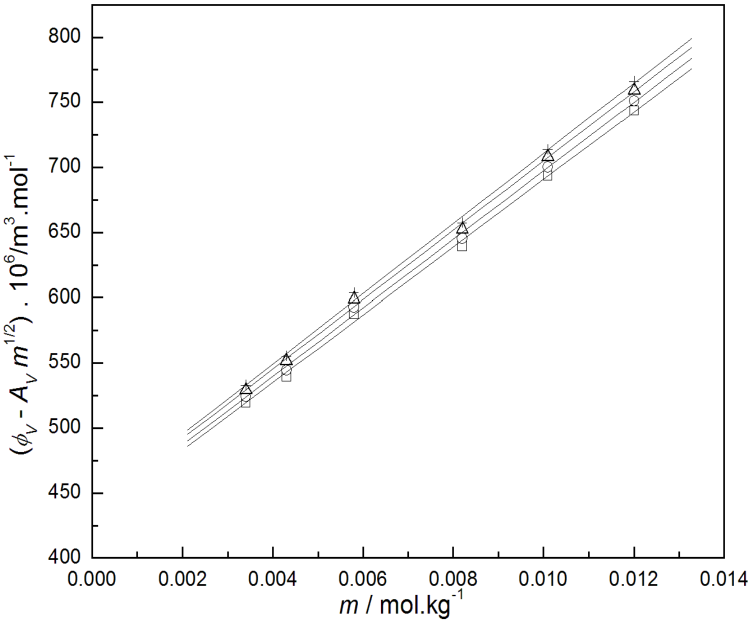

Fig. 6.4. Variation of the parameter ($\phi_V - A_V\sqrt{m}$) as a function of molality (m) of Co(salen) in in 1,4-dioxane (1) + methanol (2) mixture with $w_1 = 0.20$ at T = (298.15 to 313.15) K: □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; and +, 313.15 K.

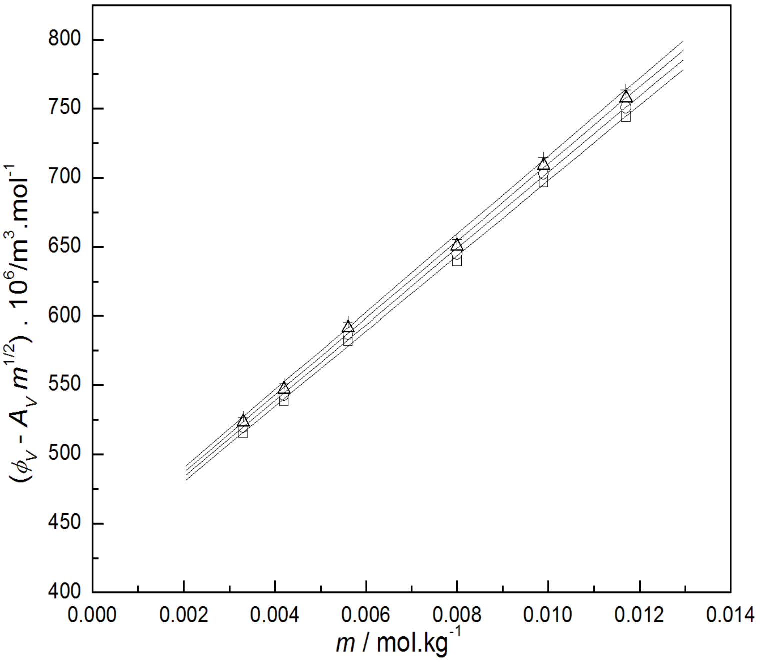

Fig. 6.5. Variation of the parameter ($\phi_V - A_V\sqrt{m}$) as a function of molality (m) of Co(salen) in in 1,4-dioxane (1) + methanol (2) mixture with $w_1 = 0.30$ at T = (298.15 to 313.15) K: □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; and +, 313.15 K.

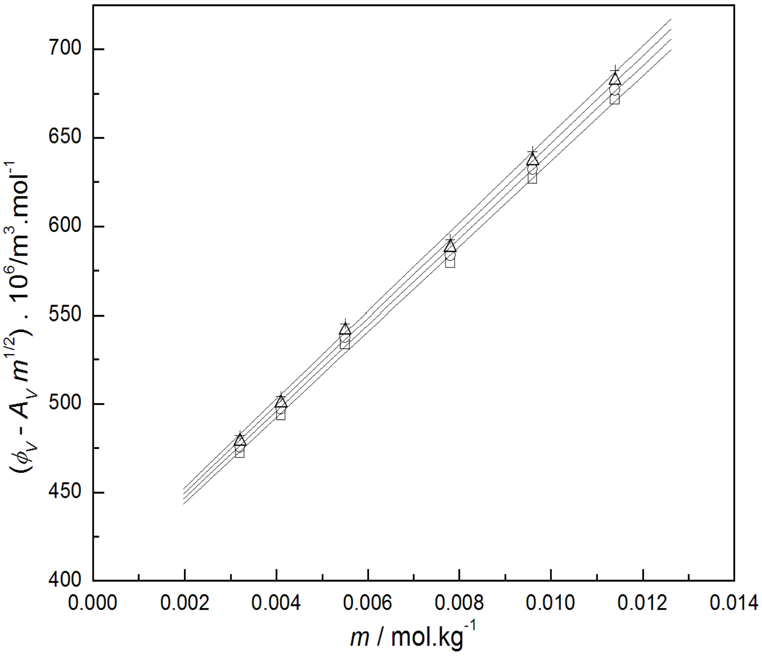

Fig. 6.6. Variation of the parameter ($\phi_V - A_V\sqrt{m}$) as a function of molality (m) of Co(salen) in in 1,4-dioxane (1) + methanol (2) mixture with $w_1 = 0.40$ at T = (298.15 to 313.15) K: □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; and +, 313.15 K.

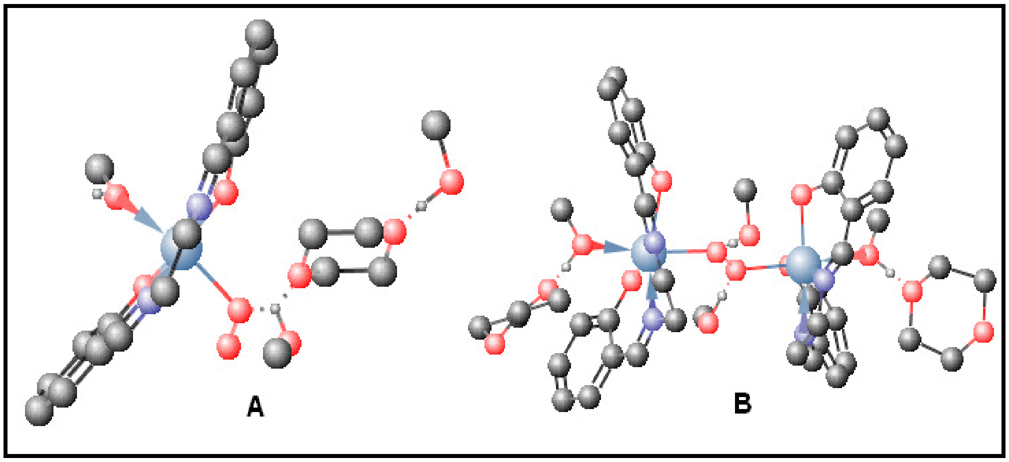

Fig. 6.7. Schematic representation of different hydrogen bond interactions in the ternary solutions of Co(salen) + 1,4-dioxane + Methanol: A, interactions with 1:1 oxygen adduct of Co(salen); B: interactions with 2:1 oxygen adduct of Co(salen).

Although ϕ_V values decrease slightly as the temperature increases, ϕ_V^0 values increase appreciably. This is probably due to greater solvation of Co(salen) with methanol and 1,4-dioxane molecules owing to more molecular collisions at elevated temperatures, thus the effect of B_V predominates over A_V in characterizing resultant ϕ_V^0 values. Having two oxygen atoms in its structure 1,4-dioxane may form 2:1 complex with Co(salen) like dioxygen but our results indicate that such complex formation is hindered due to more bulkier size of 1,4-dioxane compared to methanol.

These results are also reflected in the UV-VIS absorption spectra of the studied solutions. Figure 6.8 shows the absorption spectra of the Schiff base, SalenH$_2$ in methanol and various mixed solvents at 298.15 K. The spectra in methanol is characterized by the presence of two strong peaks at 254, 316 nm and a weak peak at 404 nm; assigned to $\pi \to \pi^*$ transitions, $\mathrm{n} \to \pi^*$ transitions involving the molecular orbitals of $\mathrm{C} = \ddot{\mathrm{N}}$ chromophore and benzene ring and $\mathrm{n} \to \pi^*$ transitions of $\mathrm{C} = \ddot{\mathrm{N}}$ chromophore, respectively.

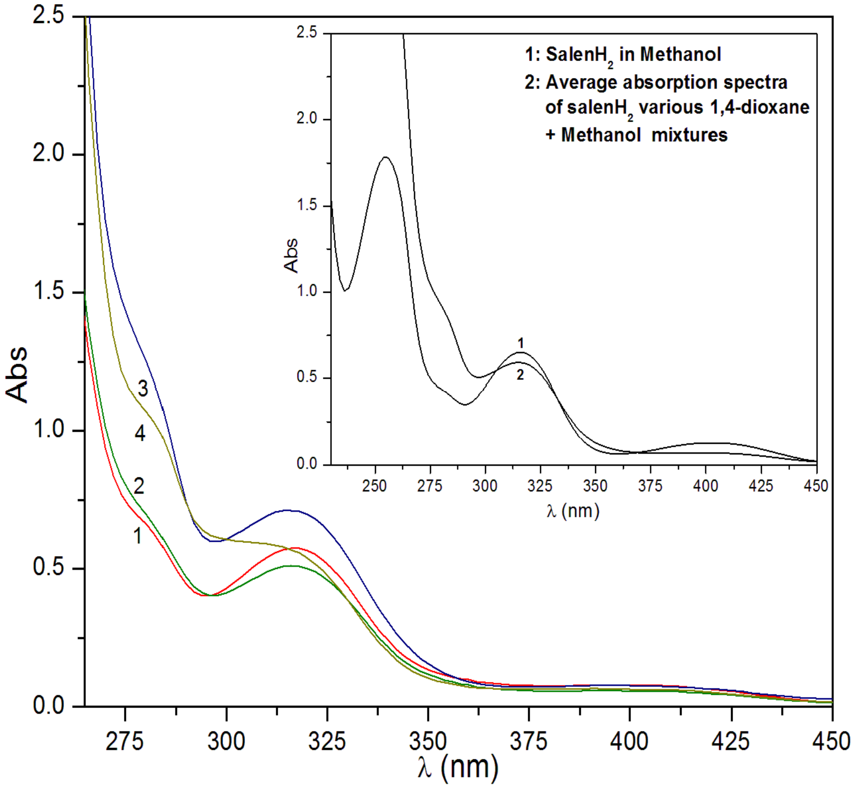

Fig. 6.8. Changes in the UV-Visible absorption spectra of SalenH$_2$ solutions in different 1,4-dioxane (1) + methanol (2) mixtures at 298.15 K: 1, in mixture with $w_1 = 0.10$; 2, in mixture with $w_1 = 0.20$; 3, in mixture with $w_1 = 0.30$; 4, in mixture with $w_1 = 0.40$. Inset: 1, SalenH$_2$ in methanol; 2: average absorption spectra in different 1,4-dioxane + methanol mixtures at 298.15 K.

The appearance of the weak peak at 404 nm indicates that the keto-enol tautomeric equilibrium between an –OH (enol-imine) and –NH (keto-enamine) forms of the Schiff base[28] exists to some extent in methanol. But when 1,4-dioxane is introduced the 404 nm peak gradually disappears and forms a valley as the concentration of 1,4-dioxane increases in the ternary solutions. Thus the position of the weak peak varies with the polarity of the solvent. Also the 316 nm peak suffers from hypochromic shifts on addition of 1,4-dioxane. The absorption spectra of Co(salen) in methanol and various mixed solvents at 298.15 K is depicted in figure 6.9. It shows that the 404 nm peak of the Schiff base is blue shifted to 388 nm in the methanol due to coordination to Co(II). In the mixed solvents this peak is further blue shifted to 382 nm and suffers

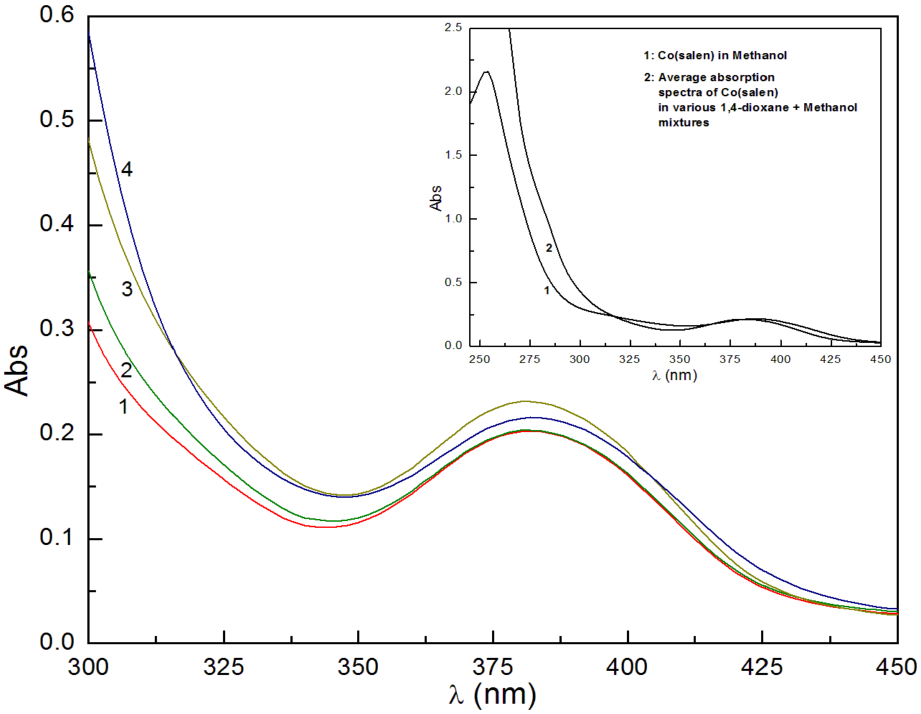

Fig. 6.9. Changes in the UV-Visible absorption spectra of Co(salen) solutions in different 1,4-dioxane (1) + methanol (2) mixtures at 298.15 K: 1, in mixture with $w_1 = 0.10$; 2, in mixture with $w_1 = 0.20$; 3, in mixture with $w_1 = 0.30$; 4, in mixture with $w_1 = 0.40$. Inset: 1, Co(salen) in methanol; 2: average absorption spectrum in different 1,4-dioxane + methanol mixtures at 298.15 K.

from hyperchromic shifts probably due to decrease in polarity of the solvent mixture with further addition of 1,4-dioxane.

6.3.2. Partial molar expansibilities

Apparent molar volumes (ϕ_V) and density (ρ) data at the experimental temperatures were used to calculate the apparent molar expansibilities (ϕ_E) of Co(salen) solutions using the relation:[29]

$$\phi_E = \alpha\phi_V + \frac{1000(\alpha - \alpha_1)}{m\rho_1} \tag{3}$$

where α and α_1 are the coefficients of isobaric thermal expansion of the solvent and solution, respectively and other symbols have their usual significance. α and α_1 are defined as: $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$ and $\alpha_1 = -\rho_1^{-1}(\partial\rho_1/\partial T)_P$; the corresponding uncertainty was $\pm 5\times10^{-6}\,\mathrm{K}^{-1}$. The uncertainty in apparent molar expansibilities (ϕ_E)

was within $\pm 0.001\times10^{-6}\mathrm{m}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$. The partial molar expansibilities (ϕ_E^0) were then determined from the relation:[29]

$$\phi_E = \phi_E^0 + S_E\sqrt{m} \tag{4}$$

$(\partial\phi_E^0/\partial T)_P$ values were obtained from the slope of a linear fit of ϕ_E^0 values against experimental temperature T with the coefficient of regression (R^2) values within the range 0.9991-0.9999. The ϕ_E^0 values for different experimental solutions at different temperatures are given in Table 6.4. It reveals that ϕ_E^0 values are negative and further decreases gradually as the temperature increases for all the solutions. This may be attributed to structural perturbation caused by the addition of the cyclic diether or to the appearance of caging/packing effect[30 ,31] and Co(salen) seemed to behave more or less like common electrolytes[27] in binary mixtures of 1,4-dioxane with methanol. However, such gradual decrease in ϕ_E^0 values with increasing temperature suggests gradual disappearance of such effects leading to release of CH_3OH molecules in favour of hydrogen bond interactions with 1,4-dioxane molecules and thus decreases volumes and increases densities of the solutions (Table 6.2). According to Hepler[32] the sign of $(\partial\phi_E^0/\partial T)_P$ is a better criterion in characterizing the long-range structure making or breaking ability of a solute in solution phase. If the term $(\partial\phi_E^0/\partial T)_P$ is small negative or positive, the solute is a structure maker, otherwise it is a structure breaker. The $(\partial\phi_E^0/\partial T)_P$ values for different ternary solutions are given in table 6.4 and Co(salen) was found to act as a net structure promoter in presence of 1,4-dioxane.

Table 6.4. Partial molar expansibility (ϕ_E^0), its temperature dependence $(\partial\phi_E^0/\partial T)_P$ and the slope (S_E) of equation (4) for Co(salen) in different mixtures of 1,4-dioxane (1) + methanol (2) at *T* = (298.15 to 313.15) K

Solvent mixture	$\frac{\phi_E^0 \cdot 10^{-6}}{\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}}$				$\frac{S_E \cdot 10^{-6}}{\mathrm{m^3 \cdot kg^{1/2} \cdot mol^{-1} \cdot K^{-1}}}$				$\frac{\left(\frac{\partial \phi_E^0}{\partial T}\right)_p \cdot 10^{-6}}{\mathrm{m^3 \cdot mol^{-1} \cdot K^{-2}}}$
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K	
$w_1 = 0.00$	-1.636 (±0.062)	-1.666 (±0.063)	-1.698 (±0.064)	-1.726 (±0.064)	-18.867 (±0.711)	-19.215 (±0.718)	-19.579 (±0.724)	-19.891 (±0.730)	-0.601 (±0.001)
$w_1 = 0.10$	-1.614 (±0.064)	-1.643 (±0.065)	-1.672 (±0.065)	-1.703 (±0.066)	-17.727 (±0.742)	-18.045 (±0.748)	-18.362 (±0.755)	-18.694 (±0.762)	-0.591 (±0.001)
$w_1 = 0.20$	-1.691 (±0.064)	-1.725 (±0.065)	-1.759 (±0.066)	-1.792 (±0.066)	-19.139 (±0.752)	-19.530 (±0.760)	-19.915 (±0.768)	-20.282 (±0.755)	-0.676 (±0.001)
$w_1 = 0.30$	-1.508 (±0.059)	-1.535 (±0.059)	-1.562 (±0.060)	-1.587 (±0.060)	-16.445 (±0.699)	-16.743 (±0.705)	-17.029 (±0.712)	-17.311 (±0.717)	-0.532 (±0.001)
$w_1 = 0.40$	-1.416 (±0.056)	-1.439 (±0.056)	-1.463 (±0.057)	-1.488 (±0.057)	-15.918 (±0.669)	-16.189 (±0.675)	-16.453 (±0.680)	-16.735 (±0.686)	-0.485 (±0.001)

Standard errors are given the parenthesis

6.3.3. *Viscosity B-coefficients*

The viscosity data for the solutions of Co(salen) in different mass % ($w_1 = 0.00, 0.10, 0.20, 0.30$ and 0.40) of 1,4-dioxane + methanol mixtures were analyzed using the Jones-Dole equation:[33]

$$(\eta/\eta_1 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (5)$$

where $\eta_r = \eta/\eta_1$, η_1 and η are the viscosities of solvent and solution, respectively. *A* and *B* are the coefficients estimated by a least squares regression method and the coefficient of regression (R^2) values were within the range 0.9882-0.9993; these coefficients reported in Table 6.5. The viscosity *B*-coefficient[34, 35] reflects the effects of solute-solvent interactions on the solution viscosity similar to ϕ_V^0. Table 6.5 shows that the viscosity *B*-coefficients for Co(salen) in the studied solvent systems are positive and the trend is in line with the ϕ_V^0 values supporting the results discussed earlier on the basis of ϕ_V^0 values. However, the *A*-coefficients are negative indicating the presence of weak solute-solute interactions in the ternary solutions and supports the results obtained on the basis of the viscosity *B*-coefficients for all the studied solutions.

6.3.4. *Thermodynamics of viscous flow*

According to transition state theory of relative viscosity as suggested by Feakings *et al.*[34] the free energy of activation of viscous flow per mole of the solute, $\Delta\mu_2^{0\neq}$, is related to the viscosity *B*-coefficients by the following relation:

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + RT(1000B + \phi_{V,2}^0 - \phi_{V,1}^0)/\phi_{V,1}^0 \qquad (6)$$

where $\phi_{V,1}^0$ and $\phi_{V,2}^0$ are the partial molar volumes of the solvent and solute, respectively. The free energy of activation of viscous flow for the solvent/solvent mixture per mole, $\Delta\mu_1^{0\neq}$, is given by the relation:[34, 35]

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_0\phi_{V,1}^0/hN_A) \qquad (7)$$

where N_A is the Avogadro's number and the other symbols have their usual significance.

Table 6.5. Values of *A* and *B*-coefficients for Co(salen) in different mixtures of 1,4-dioxane (1) + methanol (2) with standard deviations σ at T = (298.15 to 313.15) K

Viscosity coefficients	Solvent mixtures			
	$w_1 = 0.00$			
	298.15 K	303.15 K	308.15 K	313.15 K
$A \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	-0.644 (±0.001)	-0.647 (±0.001)	-0.827 (±0.001)	-0.752 (±0.001)
$B \cdot 10^6/\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	14.702 (±0.012)	14.954 (±0.013)	17.471 (±0.002)	17.440 (±0.003)
$\sigma \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	0.001	0.004	0.003	0.001
	$w_1 = 0.10$			
$A \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	-0.486 (±0.001)	-0.569 (±0.001)	-0.577 (±0.001)	-0.619 (±0.001)
$B \cdot 10^6/\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	12.782 (±0.008)	14.341 (±0.006)	14.789 (±0.002)	16.163 (±0.004)
$\sigma \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	0.001	0.001	0.001	0.002
	$w_1 = 0.20$			
$A \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	-0.482 (±0.001)	-0.515 (±0.001)	-0.458 (±0.006)	-0.480 (±0.001)
$B \cdot 10^6/\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	11.944 (±0.008)	12.854 (±0.008)	12.801 (±0.002)	13.730 (±0.004)
$\sigma \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	0.001	0.001	0.001	0.001
	$w_1 = 0.30$			
$A \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	-0.448 (±0.001)	-0.487 (±0.001)	-0.469 (±0.001)	-0.541 (±0.001)
$B \cdot 10^6/\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	11.209 (±0.008)	12.249 (±0.005)	13.010 (±0.004)	14.509 (±0.005)
$\sigma \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	0.001	0.001	0.001	0.002
	$w_1 = 0.40$			
$A \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	-0.364 (±0.000)	-0.438 (±0.001)	-0.343 (±0.001)	-0.422 (±0.001)
$B \cdot 10^6/\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	9.282 (±0.006)	10.697 (±0.002)	11.214 (±0.003)	12.390 (±0.004)
$\sigma \cdot 10^6/\mathrm{m}^{3/2} \cdot \mathrm{mol}^{-1/2}$	0.001	0.001	0.002	0.003

Standard errors are given the parenthesis

Table 6.6. Values of $(\phi^0_{V,2} - \phi^0_{V,1})$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $T\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ for Co(salen) in different mixtures of 1,4-dioxane (1) + methanol (2) at T = (298.15 to 313.15) K

Parameters	298.15 K	303.15 K	308.15 K	313.15 K
	$w_1 = 0.00$			
$(\phi^0_{V,2} - \phi^0_{V,1}) \cdot 10^6 \ / \mathrm{m^3 \cdot mol^{-1}}$	426.38	429.32	432.42	435.10
$\Delta\mu_1^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	9.97	9.97	9.95	10.00
$\Delta\mu_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	931.72	955.97	1122.15	1132.50
$T\Delta S_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-4582.62	-4659.47	-4736.32	-4813.17
$\Delta H_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-3650.89	-3703.50	-3614.17	-3680.67
	$w_1 = 0.10$			
$(\phi^0_{V,2} - \phi^0_{V,1}) \cdot 10^6 \ / \mathrm{m^3 \cdot mol^{-1}}$	424.39	425.28	428.16	431.17
$\Delta\mu_1^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	10.07	10.07	10.05	9.99
$\Delta\mu_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	786.10	887.09	923.40	1016.10
$T\Delta S_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-4331.00	-4403.63	-4476.26	-4548.89
$\Delta H_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-3544.90	-3516.54	-3552.86	-3532.79
	$w_1 = 0.20$			
$(\phi^0_{V,2} - \phi^0_{V,1}) \cdot 10^6 \ / \mathrm{m^3 \cdot mol^{-1}}$	387.38	390.30	394.62	396.97
$\Delta\mu_1^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	10.19	10.21	10.21	10.20
$\Delta\mu_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	704.97	763.84	768.49	830.16
$T\Delta S_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-2267.27	-2305.29	-2343.31	-2381.34
$\Delta H_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-1562.30	-1541.45	-1574.82	-1551.17
	$w_1 = 0.30$			
$(\phi^0_{V,2} - \phi^0_{V,1}) \cdot 10^6 \ / \mathrm{m^3 \cdot mol^{-1}}$	379.36	381.89	384.38	386.73
$\Delta\mu_1^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	10.38	10.39	10.38	10.36
$\Delta\mu_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	628.77	691.51	740.55	831.04
$T\Delta S_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-3910.81	-3976.39	-4041.98	-4107.56
$\Delta H_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-3282.04	-3284.88	-3301.43	-3276.52
	$w_1 = 0.40$			
$(\phi^0_{V,2} - \phi^0_{V,1}) \cdot 10^6 \ / \mathrm{m^3 \cdot mol^{-1}}$	346.88	348.98	351.01	353.12
$\Delta\mu_1^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	10.61	10.63	10.62	10.59
$\Delta\mu_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	496.58	574.30	607.27	674.90
$T\Delta S_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-3386.64	-3443.44	-3500.23	-3557.03
$\Delta H_2^{0\neq} \ / \mathrm{kJ \cdot mol^{-1}}$	-2890.06	-2869.14	-2892.96	-2882.12

The entropy of activation for ternary solutions $\Delta S_2^{0\neq}$ were obtained from the negative slope of the plots of $\Delta\mu_2^{0\neq}$ against T ,

$$\Delta S_2^{0\#} = -d(\Delta\mu_2^{0\#})/dT \tag{8}$$

and the activation enthalpy ($\Delta H_2^{0\neq}$) has been calculated using the relation,[34]

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \tag{9}$$

The parameters $(\phi_{V,2}^0 - \phi_{V,1}^0)$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $\Delta H_2^{0\neq}$ and $T\Delta S_2^{0\neq}$ are reported in table 6.6. The values $\Delta\mu_2^{0\neq}$ contain the change in the free energy of activation of solvent molecules in presence of solute as well as the contribution from the movement of solute molecules. Table 6.6 shows that $\Delta\mu_1^{0\neq}$ is almost invariant of the solvent compositions and temperatures, implying that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity *B*-coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms. $\Delta\mu_2^{0\neq}$ values were positive at all the experimental temperatures suggesting that the process of viscous flow becomes difficult as the temperature increases but becomes easier to some extent as the content of 1,4-dioxane in ternary solutions increases, i.e., the formation of the transition state becomes less favourable as temperature increases but 1,4-dioxane fovours its formation.[34] The quantity $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ is the change in the activation energy per mole of solute on replacing one mole of solvent by one mole of solute in an infinite dilution, hence according to Feakings *et al.*[34] $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$, for solutes with positive viscosity *B*-coefficients, indicates stronger solute-solvent interactions; thereby suggesting the formation of transition state to be accompanied by the rupture and distortion of the intermolecular forces in solvent structure.[34] The greater the value of $\Delta\mu_2^{0\neq}$, the greater is the structure-promoting tendency of a solute and the positive values of $\Delta\mu_2^{0\neq}$ for Co(salen) in the different ternary solutions suggest it to be a net tructure promoter in the studied ternaries. The negative values of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ for all the experimental solutions and temperatures suggest that the transition state is associated with bond formation and increase in order.

6.3.5. *Refractometric results*

The dimensionless optical property refractive index (n_D) is very sensitive to changes in molecular organization of pure liquids, solutions and mixtures. The molar refractivity (R_M) of the ternary solutions were also calculated from the refractive indices of the solutions (n_D) by using Lorentz-Lorenz equation:[36]

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} \sum_{i=1}^{3} (x_i M_i)/\rho \qquad (11)$$

where x_i and M_i are the mole fraction and molecular weight of the i^{th} component, respectively. R_M values are given in table 6.7. It shows that R_M values increases linearly with the amount of Co(salen) and 1,4-dioxane for all the experimental solutions. As R_M is directly proportional to the molecular polarizability ($\alpha_{\mathrm{P}} = 3R_{\mathrm{M}}/4\pi N_A$),[37] the increasing trend in R_M values indicates an overall increase in the molecular polarizabilities and thus reveals that the ternary solutions are characterized by structural changes and strong solute-solvent interactions.

Table 6.7. Refractive indices (n_D), molar refractivities (R_{M}) molar polarizabilities (α_{P}) as a function of molarities (c) of Co(salen) in different mixtures of 1,4-dioxane (1) + methanol (2) at T = 298.15 K

$\frac{c}{\mathrm{mol \cdot dm^{-3}}}$	n_D	$\frac{R_{\mathrm{M}} \cdot 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$	$\frac{\alpha_{\mathrm{P}} \cdot 10^{-30}}{\mathrm{m^3 \cdot mol^{-1}}}$
		$w_1 = 0.00$	
0.0028	1.3340	8.46 (±0.01)	3.36 (±0.01)
0.0036	1.3345	8.49 (±0.01)	3.37 (±0.01)
0.0048	1.3352	8.54 (±0.01)	3.38 (±0.01)
0.0068	1.3360	8.60 (±0.01)	3.41 (±0.01)
0.0084	1.3371	8.66 (±0.01)	3.43 (±0.01)
0.0100	1.3380	8.71 (±0.01)	3.45 (±0.01)
		$w_1 = 0.10$	
0.0028	1.3345	8.78 (±0.01)	3.48 (±0.01)
0.0036	1.3351	8.81 (±0.01)	3.49 (±0.01)
0.0048	1.3360	8.86 (±0.01)	3.51 (±0.01)
0.0068	1.3371	8.93 (±0.01)	3.54 (±0.01)
0.0084	1.3380	8.99 (±0.01)	3.56 (±0.01)
0.0100	1.3385	9.01 (±0.01)	3.58 (±0.01)
		$w_1 = 0.20$	
0.0028	1.3381	9.24 (±0.01)	3.66 (±0.01)
0.0036	1.3385	9.27 (±0.01)	3.68 (±0.01)
0.0048	1.3394	9.32 (±0.01)	3.70 (±0.01)
0.0068	1.3401	9.39 (±0.01)	3.72 (±0.01)
0.0084	1.3410	9.45 (±0.01)	3.75 (±0.01)
0.0100	1.3420	9.51 (±0.01)	3.77 (±0.01)

Contd…

		$w_1 = 0.30$	
0.0028	1.3480	10.02 (±0.01)	3.97 (±0.01)
0.0036	1.3485	10.05 (±0.01)	3.98 (±0.01)
0.0048	1.3492	10.10 (±0.01)	4.00 (±0.01)
0.0068	1.3502	10.17 (±0.01)	4.03 (±0.01)
0.0084	1.3514	10.25 (±0.01)	4.06 (±0.01)
0.0100	1.3521	10.31 (±0.01)	4.09 (±0.01)
		$w_1 = 0.40$	
0.0028	1.3610	10.95 (±0.01)	4.34 (±0.01)
0.0036	1.3621	11.00 (±0.01)	4.36 (±0.01)
0.0048	1.3632	11.06 (±0.01)	4.39 (±0.01)
0.0068	1.3640	11.14 (±0.01)	4.42 (±0.01)
0.0084	1.3651	11.21 (±0.01)	4.44 (±0.01)
0.0100	1.3663	11.29 (±0.01)	4.48 (±0.01)

Standard errors are given the parenthesis.

6.4. Conclusion

In summary, ϕ_V^0 and viscosity *B*-coefficient values for Co(salen) indicate the presence of strong solute-solvent interactions and these interactions are further strengthened at higher temperatures but decreases for higher content of 1,4-dioxane in the ternaries. Also, Co(salen) acts as a net methanol structure promoter in the ternary solutions.

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Chapter VI

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CHAPTER VII

Solution behavior of iron(III)-N, N/-ethylene-bis(salicylideneiminato)-chloride in aqueous methanol at T = (298.15, 303.15 and 313.15) K[*]

7.1. Introduction

Many natural products contain structural units similar to metal heterocyclic compounds that can be used as targets for synthetic, methodological, and biological applications.[1] Amongst many potential materials, Schiff base metal complexes belong to the class of the many potential materials that deserves extensive studies and amongst the traditional metal complexes salen-type Schiff base ligands or their derivatives are of great importance in coordination chemistry and homogeneous catalysis.[2] They can also be regarded as models of reaction centers for metalloenzymes[3] and nonlinear optical materials.[4] According to Groves *et al.*[5-7] simple iron(III) porphyrins can be used as models for the reaction site of cytochrome P-450. In this regard metal complexes of salen ligand are also of great interest to synthetic chemists, since they share features in common with metalloporphyrins as far as their electronic structure and catalytic activities are concerned. Interestingly, Fe^{III}(salen)Cl and Fe^{III} porphyrins have some structural and chemical similarities.[8,9] Like Fe^{III} porphyrins, the iron atom of Fe^{III}(salen)Cl has a penta-coordinated pyramidal geometry wherein the tetradentate salen ligand is in a square planar coordination and the chloride ligand is attached at an epical position and the complex has an open sixth coordination site and salen forms some complexes that mimic porphyrin chemistry.[10] Moreover, Fe^{III}(salen)Cl has the affinity for the oxygen molecule and is capable of forming oxo-species like Fe^{III} porphyrin derivatives;[8,9] Amongst the conventional solvents, methanol is used in numerous chemical processes and it is has a structure analogous to water but with a CH_3-group in place of a proton. This substitution affects the liquid structure and causes significant differences between methanol and water. Hence it is important to understand how solutes like Fe^{III}(salen)Cl behave in these mixed solvents, because an understanding of such behaviour can through light on the effects of solute concentration on hydrogen-bonded network, solvation structure and solute dynamics, etc.[11]

However, such studies on Fe^{III}(salen)Cl in various pure and mixed solvents are still rare in the literature. To the best of our knowledge, only one report on the

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solvent effects on the electrochemical behavior of Fe^{III}(salen)Cl is available in literature.[12] Hence in this work we studied solution behaviour of Fe^{III}(salen)Cl in different aqueous methanol solutions at 298.15, 303.15 and 313.15 K under ambient pressure and discussed the results in terms of solute-solute and solute-solvent interactions.

7.2. Experimental section

7.2.1. *Materials*

Analytical reagent (AR) grade ferric chloride, $FeCl_3.6H_2O$, 1,2-ethylenediamine, and salicylaldehyde, each of purity > 99 %, were purchased from Merck, India. These chemicals were used as received. Spectroscopic grade methanol (minimum assay, GC, purity > 99.8%) with 0.05% of water was purchased from Merck, India and used as received. Doubly distilled de-ionized water with a specific conductance of $1\times10^{-6}\ \mathrm{S\,cm^{-1}}$ at 298.15 K was used for preparing the mixed solvents and the various binary solvents were prepared by mass with necessary adjustments by volume make up were done to achieve exact mass fraction of methanol (w_1 = 0.60, 0.70, 0.80 and 0.90) at 298.15 K. The relative error in solvent composition was estimated to be about 1%. The physical properties of different solvent/solvent mixtures at the experimental temperatures are reported in table 7.1 and compared against available literature values.[13-16]

Fe^{III}(salen)Cl was prepared by a known method[17] and the details of the synthesis and physicochemical characterization of Fe^{III}(salen)Cl is described in chapter III. Molecular structure of the ligand and the complex is depicted in figure 7.1. Stock solutions of the complex in different aqueous methanol solutions were prepared by mass and the working solutions were prepared by mass dilution. Solute molalities (m) were converted into molarities (c) by using experimental density values. All solutions were prepared afresh and degassed with dry nitrogen before use. The uncertainty in molarity of Fe^{III}(salen)Cl solutions was evaluated to be ±0.0001 $mol.dm^{-3}$.

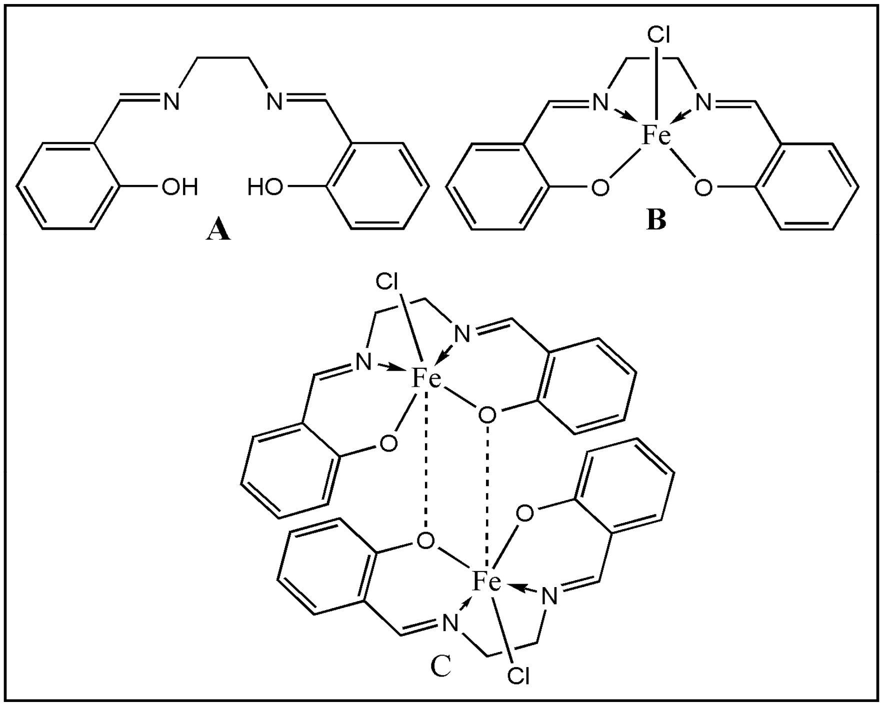

Fig. 7.1. Molecular structures of A) SalenH$_2$, B) Fe^{III}(salen)Cl and C) [Fe^{III}(salen)Cl]$_2$.

Table 7.1. Densities (ρ) and viscosities (η) of different aqueous methanol solutions at different temperatures.

w_1[a]	T/K	$\rho \cdot 10^{-3}/\mathrm{kg \cdot m^{-3}}$		$\eta/\mathrm{mPa \cdot s}$	
		Expt.	Lit.	Expt.	Lit.
1.00	298.15	0.78662	0.78645[13]	0.5469	0.542[13]
	303.15	0.78188	0.7819[15]	0.5092	0.510[15]
	313.15	0.77280	0.7720[16]	0.4488	0.4470[16]
0.90	298.15	0.81582	0.8158[14]	0.7619	0.7885[14]
	303.15	0.81084	0.8108[14]	0.7112	-
	313.15	0.80236	0.8023[14]	0.6344	-
0.80	298.15	0.84237	0.8424[14]	1.0036	1.0241[14]
	303.15	0.83769	0.8378[14]	0.9634	-
	313.15	0.82961	0.8294[14]	0.8871	-
0.70	298.15	0.86761	0.8675[14]	1.1849	1.2335[14]
	303.15	0.86310	0.8630[14]	1.1430	-
	313.15	0.85532	0.8550[14]	1.0620	-
0.60	298.15	0.89113	0.8910[14]	1.4091	1.4264[14]
	303.15	0.88649	0.8864[14]	1.3689	-
	313.15	0.87885	0.8787[14]	1.3017	-

[a] Mass fraction of methanol in the solvent mixtures.

7.2.2. *Apparatus and procedure*

The mass measurements were done on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with a precision of ±0.01 mg. The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M). It was calibrated at the experimental temperatures with doubly distilled, degassed water and dry air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $\pm 1\times10^{-2}\,\mathrm{K}$ using a built–in Peltier technique. The estimated uncertainty of the density measurements for most of the solutions was found to be better than $\pm 2\times10^{-5}\,\mathrm{g\cdot cm^{-3}}$. The viscosity was measured by means of a suspended Ubbelohde (Canon-type) viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled, degassed water and purified methanol.[19-21] It was filled with experimental solution and placed vertically in a glass sided thermostat (maintained constant to ± 0.01 K) with the aid of wooden clumps. Sufficient time was allowed for the attainment of thermal equilibrium and the flow times of solutions were recorded with a digital stopwatch (correct to ± 0.01s). In all determinations, adequate precautions were taken to minimize evaporation losses and at least three repetitions of each data were taken to average the flow times. The uncertainty in viscosity measurements was estimated to be within $\pm 4\times10^{-4}\,\mathrm{mPa\cdot s}$. Details of density and viscosity measurements have been described in chapter III. The absorption spectra of $\mathrm{Fe^{III}}$(salen)Cl ($5.0\times10^{-5}\,\mathrm{mol\cdot dm^{-3}}$) in different aqueous methanol solutions at 298.15 K were recorded on Jasco V-530 double beam UV-VIS Spectrophotometer (coupled with a thermostatic arrangement). A quartz cell with a path length of 1 cm was used and the reference solvent was spectroscopic grade methanol for all the spectroscopic measurements.

7.3. Results and discussion

Molalities (m), densities (ρ) viscosities (η) and the apparent molar volumes (ϕ_V) for the experimental solutions of $\mathrm{Fe^{III}}$(salen)Cl in different aqueous methanol solutions at various temperatures are given in table 7.2.

7.3.1. *Standard partial molar volumes*

The apparent molar volumes (ϕ_V) of Fe^{III}(salen)Cl in different aqueous methanol solutions were determined from the solution densities by using the following equation:

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_1)}{m\rho\rho_1} \qquad (1)$$

where *M* is the molar mass of Fe^{III}(salen)Cl, *m* is the molality of the solution, ρ_1 and ρ are the densities of the solvent and solution, respectively. When ϕ_V values were plotted against square root of molal concentrations ($\sqrt{m}$), linear dependence was observed. Hence the partial molar volumes (ϕ_V^0) at infinite dilution and the slopes (S_V^*) were determined by using least squares fitting of ϕ_V values to the Masson equation: [22]

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \qquad (2)$$

The ϕ_V^0 and S_V^* values are reported in table 7.3. It shows that ϕ_V^0 values are positive and increase as the amount of water increases in the mixtures but decreases with a rise in the temperature. This indicates the presence of strong solute-solvent interactions[21,23] and these interactions are further strengthened at higher content of water but weakened at higher temperatures. The dependence of ϕ_V^0 values on the solvent composition and temperature is shown in figure 7.2. Fe^{III}(salen)Cl can exist in the solid state either as dimer or monomer. Its behavior in the solid state depends on the nature of the solvent used in its recrystalization. However, the two forms can be distinguished by their magnetic moments and IR spectra (shown in figure 7.3). For monomeric complex the range of magnetic moment is 5.29-6.06 BM. We obtained a value of 5.31 BM for the complex Fe^{III}(salen)Cl and IR spectra are devoid of any band near 850 cm^{-1}. Thus the complex was in monomeric form[24] rather than in the dimeric form and it contains a d^5 high spin electronic configuration[25, 26] with a square planar geometry around Fe^{3+} at the center and a apical chlorine atom as coordinated to the fifth coordination site. So solvent molecules can coordinate to the unoccupied sixth position of the coordination site. In this regard donor power of individual solvents plays a crucial role.

Table 7.2. Molalities (m), densities (ρ), viscosities (η), and apparent molar volumes (ϕ_V) of Fe^{III}(salen)Cl in different aqueous methanol solutions at different temperatures.

$m/\mathrm{mol\cdot kg^{-1}}$	$\rho\cdot10^{-3}/\mathrm{kg\cdot m^{-3}}$	$\eta/\mathrm{mPa\cdot s}$	$\phi_V\cdot10^{6}/\mathrm{m^3\cdot mol^{-1}}$
$w_1 = 1.00$ [a]			
T/K= 298.15			
0.0025	0.78706	0.5539	170.12
0.0036	0.78728	0.5575	158.24
0.0056	0.78774	0.5638	131.25
0.0076	0.78825	0.5710	107.82
0.0097	0.78876	0.5781	97.84
0.0117	0.78931	0.5879	82.80
T/K = 303.15			
0.0025	0.78234	0.5164	156.34
0.0036	0.78256	0.5209	148.30
0.0056	0.78302	0.5272	124.24
0.0076	0.78353	0.5327	102.06
0.0097	0.78405	0.5399	91.22
0.0117	0.78459	0.5472	78.26
T/K = 313.15			
0.0025	0.77327	0.4551	147.90
0.0036	0.77349	0.4595	141.73
0.0056	0.77397	0.4650	112.78
0.0076	0.77446	0.4705	96.85
0.0097	0.77498	0.4761	86.23
0.0117	0.77552	0.4815	73.26
$w_1 = 0.90$ [a]			
T/K = 298.15			
0.0025	0.81625	0.7659	179.86
0.0034	0.81646	0.7697	155.44
0.0054	0.81692	0.7772	132.14
0.0074	0.81741	0.7884	115.32
0.0093	0.81794	0.7961	95.63
0.0113	0.81849	0.8055	83.10
T/K = 303.15			
0.0025	0.81129	0.7151	167.20
0.0034	0.81149	0.7189	150.17
0.0054	0.81195	0.7246	128.25
0.0074	0.81244	0.7321	111.99
0.0093	0.81298	0.7415	90.84
0.0113	0.81353	0.7509	78.73
T/K = 313.15			
0.0025	0.80282	0.6383	159.83
0.0034	0.80303	0.6428	139.52
0.0054	0.80350	0.6494	117.64
0.0074	0.80399	0.6559	103.37
0.0093	0.80453	0.6625	83.07
0.0113	0.80508	0.6692	71.60

Contd…

$w_1 = 0.80$ [a]			
T/K = 298.15			
0.0024	0.84279	1.0096	177.85
0.0033	0.84300	1.0126	155.41
0.0052	0.84346	1.0251	128.99
0.0071	0.84395	1.0377	110.74
0.0090	0.84448	1.0503	93.93
0.0109	0.84507	1.0639	75.24
T/K = 303.15			
0.0024	0.83812	0.9693	171.52
0.0033	0.83833	0.9732	150.45
0.0052	0.83879	0.9820	125.32
0.0071	0.83928	0.9926	107.60
0.0090	0.83981	1.0051	91.02
0.0109	0.84041	1.0178	71.09
T/K = 313.15			
0.0024	0.83005	0.8948	164.63
0.0033	0.83025	0.8987	149.19
0.0052	0.83072	0.9064	120.78
0.0071	0.83121	0.9169	103.47
0.0090	0.83175	0.9266	85.39
0.0109	0.83230	0.9381	72.29
$w_1 = 0.70$ [a]			
T/K = 298.15			
0.0023	0.86802	1.1921	175.32
0.0032	0.86822	1.1961	158.86
0.0051	0.86869	1.2081	130.73
0.0069	0.86919	1.2240	107.82
0.0088	0.86971	1.2389	94.96
0.0106	0.87032	1.2597	72.35
T/K = 303.15			
0.0023	0.86352	1.1470	169.15
0.0032	0.86371	1.1536	158.36
0.0051	0.86419	1.1667	127.30
0.0069	0.86468	1.1799	106.78
0.0088	0.86521	1.1930	92.27
0.0106	0.86582	1.2054	69.69
T/K = 313.15			
0.0023	0.85574	1.0651	168.44
0.0032	0.85593	1.0708	157.45
0.0051	0.85642	1.0820	123.15
0.0069	0.85691	1.0938	102.96
0.0088	0.85745	1.1066	87.06
0.0106	0.85802	1.1176	69.74
$w_1 = 0.60$ [a]			
T/K = 298.15			
0.0022	0.89153	1.4105	172.30
0.0031	0.89172	1.4197	161.56
0.0049	0.89219	1.4321	128.77
0.0067	0.89270	1.4523	106.06

Contd…

0.0085	0.89321	1.4707	92.97
0.0103	0.89386	1.4912	67.36
T/K = 303.15			
0.0022	0.88688	1.3734	177.78
0.0031	0.88711	1.3795	148.83
0.0049	0.88756	1.3938	125.41
0.0067	0.88808	1.4091	101.27
0.0085	0.88863	1.4263	82.87
0.0103	0.88918	1.4477	70.89
T/K = 313.15			
0.0022	0.87925	1.3061	171.46
0.0031	0.87945	1.3121	156.25
0.0049	0.87992	1.3243	124.07
0.0067	0.88045	1.3385	97.58
0.0085	0.88097	1.3537	83.82
0.0103	0.88154	1.3736	68.60

[a] Mass fraction of methanol in the solvent mixtures.

The aqueous methanol solutions are characterized by hydrophobic and hydrophilic interactions. Both computer simulation[27] and experimental studies[28-33] revealed that water strongly interacts with methanol to form complexes. Recent spectroscopic and high performance liquid chromatographic studies revealed that methanol forms a number of complexes with a number of water molecules at low methanol but at high methanol content, it forms 1:1 complex.[28-33] According to Wu *et al.*[34] two critical solvent compositions are H_2O:CH_3OH ≈ 5:1 and ≈ 1:1. Thus as the methanol concentration decreases more water molecules becomes free in the bulk solvent mixtures. Hence methanol and water molecules may coordinate for the sixth vacant coordination site of Fe^{III}(salen)Cl via $O\cdots Fe$ interaction. Moreover, methanol/water may also interact with Fe^{III}(salen)Cl via hydrogen bond interactions with ONNO sites of the complex and thereby affecting its spin-equilibrium in solution. No doubt, H_2O will have comparatively more such hydrogen bond interaction than CH_3OH and because of the fact that methanol (with effective hard sphere diameter 0.364 nm[35]) is more bulky than water (with effective hard sphere diameter 0.284 nm[35]), the increase in ϕ_V values as well as concomitant increase in ϕ_V^0 values with the increase of water content in the mixtures may be attributed to preferential coordination of the unoccupied sixth position of Fe^{III}(salen)Cl by water molecules or preferential solvation of Fe^{III}(salen)Cl by water molecules due to stronger electrostatic interaction and comparatively more donor strength of water than methanol.[36]

Table 7.3. Standard partial molar volumes (ϕ_V^0) and the slopes (S_V^*) of equation (2) for $\mathrm{Fe^{III}(Salen)Cl}$ in different aqueous methanol solutions with corresponding standard deviations (σ) at different temperatures.

T/K	$\frac{\phi_V^0 \cdot 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$	$\frac{S_V^* \cdot 10^6}{\mathrm{m^3 \cdot kg^{1/.2} \cdot mol^{-3/2}}}$	$\frac{\sigma \cdot 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$
		$w_1 = 1.00$ [a]	
298.15	247.37 (±4.65)	-1537.95 (±56.44)	3.10
303.15	228.45 (±4.26)	-1400.29 (±51.76)	2.84
313.15	216.30 (±5.18)	-1335.03 (±62.88)	3.45
		$w_1 = 0.90$ [a]	
298.15	257.09 (±5.83)	-1659.90 (±72.09)	3.86
303.15	243.14 (±3.17)	-1554.86 (±39.15)	2.10
313.15	232.10 (±4.65)	-1524.93 (±57.44)	3.08
		$w_1 = 0.80$ [a]	
298.15	260.72 (±4.47)	-1779.20 (±56.26)	2.96
303.15	253.03 (±0.02)	-1734.17 (±50.46)	2.66
313.15	244.78 (±3.02)	-1672.77 (±38.05)	2.00
		$w_1 = 0.70$ [a]	
298.15	262.39(±3.59)	-1830.54 (±45.76)	2.39
303.15	257.29 (±3.95)	-1799.56 (±50.35)	2.63
313.15	256.91 (±3.95)	-1826.92 (±50.39)	2.63
		$w_1 = 0.60$ [a]	
298.15	264.36 (±5.07)	-1912.71 (±65.74)	3.40
303.15	261.07 (±6.86)	-1917.72 (±88.93)	4.60
313.15	261.20 (±4.89)	-1931.27 (±63.41)	3.28

[a] Mass fraction of methanol in the solvent mixtures .
Standard errors are given the parenthesis.

Again, as ϕ_V^0 values for the ternary systems increase with more water or polarity of the solvent mixture (the order of relative permittivity of the solvent mixtures: [23] 31.5, 35.7, 40.1, 45.0 and 50.1 for w_1 = 1.00, 0.90, 0.80, 0.70 and 0.60, respectively), the complex most probably remains in monomeric form in solution phase, because Fe-atom is comparatively more available to the solvent molecules for $\mathrm{O \cdots Fe}$ interaction in monomeric form[18] than in dimeric form. However, the decrease in ϕ_V^0 values with a rise in temperature indicates disruption of hydrogen bond and $\mathrm{O \cdots Fe}$ interactions at elevated temperatures and slight increase in ϕ_V^0 values at 303.15 and 313.15 K for solvent mixtures for w_1 = 0.60 may probably arises from a delicate balance between the loosely bound dimmer and the monomer in this solvent compositions.[24,26]

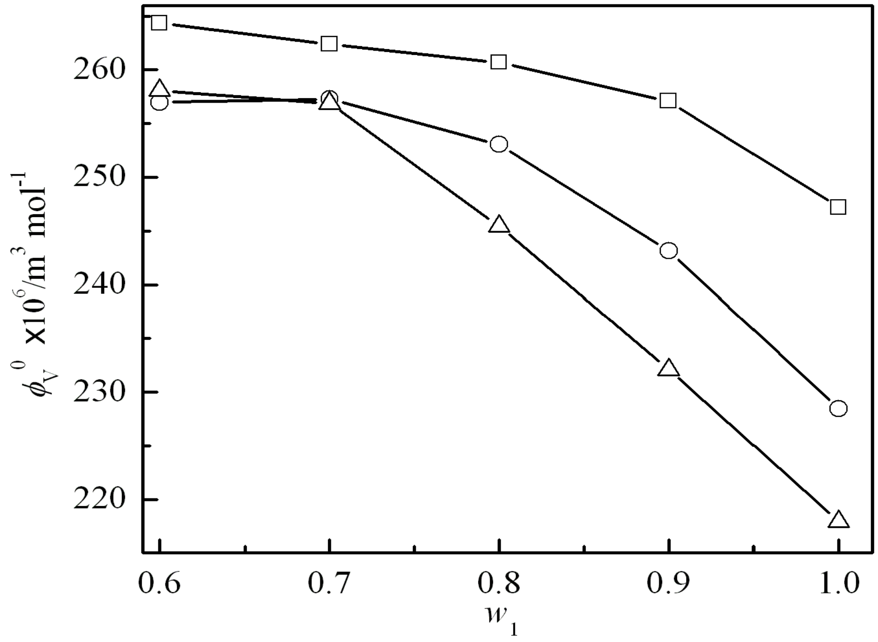

Fig. 7.2. Dependence of standard partial molar volume (ϕ_V^0) on mass fraction of methanol (w_1) in the aqueous methanol solutions at different temperatures. Symbols: T = 298.15 K, □; T = 303.15 K, ○; T = 313.15 K, Δ.

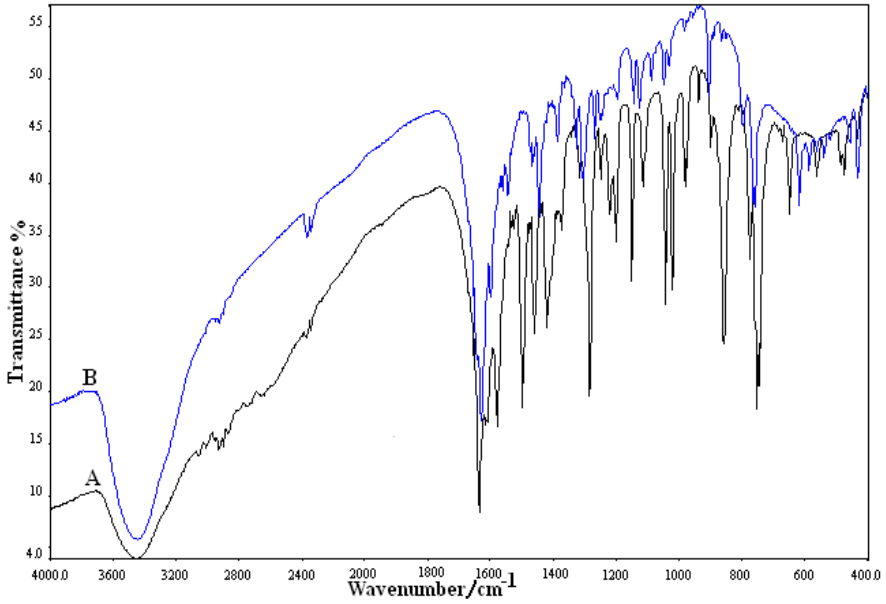

Fig. 7.3. IR spectra of A) SalenH$_2$ and B) Fe^{III}(salen)Cl in KBr pallet.

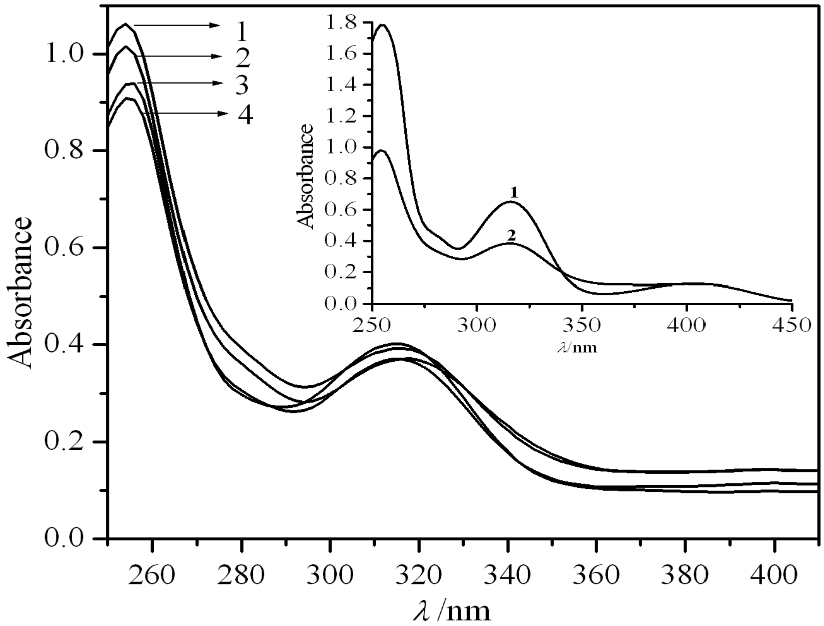

Fig. 7.4. Changes in the UV-Visible absorption spectra of SalenH$_2$ solutions in different aqueous methanol solutions at 298.15 K: 1, $w_1 = 0.70$; 2, $w_1 = 0.60$; 3, $w_1 = 0.90$; 4, $w_1 = 0.80$. Inset: 1, SalenH$_2$ in methanol; 2: average absorption spectra in aqueous methanol mixtures at 298.15 K.

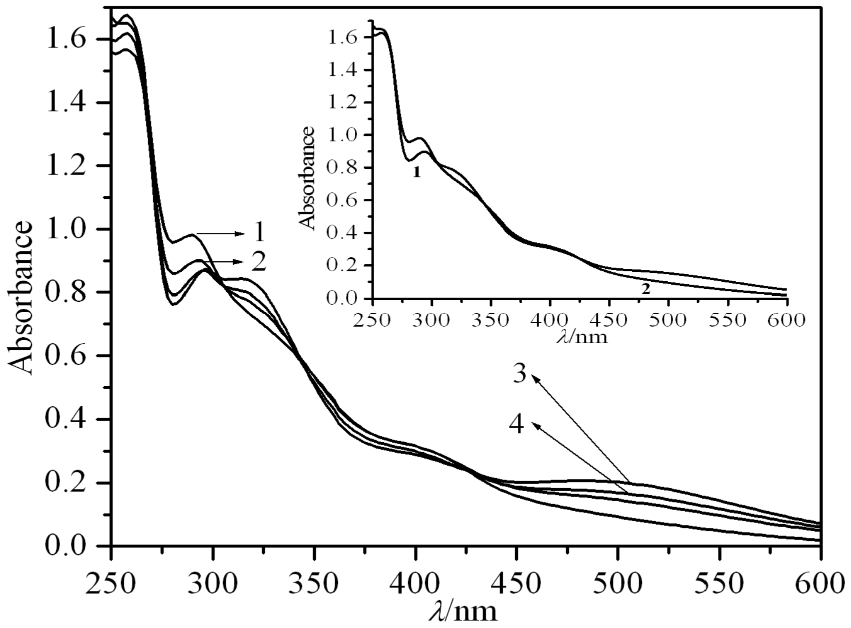

Fig. 7.5. Changes in the UV-Visible absorption spectra of Fe^{III}(salen)Cl solutions different aqueous methanol solutions at 298.15 K: 1, $w_1 = 1.00$; 2, $w_1 = 0.90$; 3, $w_1 = 0.70$; 4, $w_1 = 0.80$. Inset: 1, Fe^{III}(salen)Cl in methanol; 2: average absorption spectrum in aqueous methanol mixtures at 298.15 K.

The parameter S_V^* is a volumetric viral coefficient and characterizes the pair-wise interactions between the solvated species[37, 38] in the solution. Its sign is determined by the interactions between solute species (solute-solute interactions). Negative values of S_V^* and its trend opposite to the trend in ϕ_V^0 values indicate weak solute-solute interactions for Fe^{III}(salen)Cl in the experimental aqueous methanol solutions studied.

These results are also reflected in the UV-VIS absorption spectra of the studied solutions**.** Figure 7.4 shows the absorption spectra of the Schiff base, $SalenH_2$ in methanol and various aqueous methanol solutions at 298.15 K. The spectra of $SalenH_2$ in methanol is characterized by the presence of two strong peaks at 254, 316 nm and a weak peak at 404 nm and discussed earlier.[21] Interestingly, when water was introduced the peak at 404 nm of $SalenH_2$ gradually disappears and forms a valley as the concentration of water increases in the ternary solutions and thus the position of the weak peak at 404 nm varies with the polarity of the aqueous methanol solutions. Also the 316 nm peak suffers from hypochromic shifts on addition of water. The absorption spectra of Fe^{III}(salen)Cl in methanol and various aqueous methanol solutions at 298.15 K is shown in figure 7.5 and it shows that the 404 nm peak of the Schiff base disappeared in methanol as well as in all the aqueous methanol solutions due to coordination of solvent molecules to Fe(III). Instead, an additional a peak around 500 nm appeared and suffers hypsochromic effect indicating coordination or solvation by solvent molecules.[39] The peak at 258 nm does not change appreciably but a new peak around 320 nm also appeared as the amount of water in the ternary systems increased.[26]

7.3.2. *Apparent molar expansibilities*

Apparent molar volumes (ϕ_V) and densities (ρ) were used to derive the apparent molar expansibilities (ϕ_E) of Fe^{III}(salen)Cl solutions by using the relation:[23]

$$\phi_E = \alpha\phi_V + \frac{1000(\alpha - \alpha_1)}{m\rho_1} \tag{3}$$

where α and α_1 are the coefficients of isobaric thermal expansion of the solvent and solution, respectively and other symbols have their usual significance. α and α_1 are defined as: $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$ and $\alpha_1 = -\rho_1^{-1}(\partial\rho_1/\partial T)_P$, respectively and other symbols have their usual significances. The uncertainty of α and α_1 values was $\pm 6\times10^{-6}\,\mathrm{K}^{-1}$ and the uncertainty in ϕ_E values was within $\pm 0.006-0.061\times10^{-6}\,\mathrm{m}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$, respectively. The partial molar expansibilities (ϕ_E^0) were determined from the relation:[23]

$$\phi_E = \phi_E^0 + S_E\sqrt{m} \qquad (4)$$

The ϕ_E^0 values for different experimental solutions at different temperatures are listed in table 7.4. It reveals that ϕ_E^0 values are negative and decrease further as the temperature increases but increase as H_2O content increases for all the solutions. These facts may be attributed to structural perturbation influenced by the gradual appearance or disappearance of caging/packing effect[40] as the water content increases in the ternary solutions or as the temperature of the solutions increases, respectively.

According to Hepler[41] the sign of $(\partial\phi_E^0/\partial T)_P$ is a better criterion in characterizing the long-range structure making or breaking ability of a solute in solution phase. If the $(\partial\phi_E^0/\partial T)_P$ values are small negative or positive, the solute acts as a structure maker, otherwise it acts as a structure breaker. $(\partial\phi_E^0/\partial T)_P$ values were obtained from the slope of a linear fit of ϕ_E^0 values against experimental temperatures (T) with the correlation coefficient (R^2) values within the range (0.97210-0.99552). The $(\partial\phi_E^0/\partial T)_P$ values for different ternary solutions are given in table 7.4 and $\mathrm{Fe^{III}}$(salen)Cl was found to act as a net structure promoter in the aqueous methanol solutions.

Table 7.4. Limiting partial molar expansibility (ϕ_E^0), its temperature dependence $(\partial\phi_E^0 / \partial T)_P$ and the slope (S_E) of equation (4) for Fe^{III}(Salen)Cl in aqueous methanol solutions at different temperatures.

w_1 [a]	$\frac{\phi_E^0 \cdot 10^{-6}}{m^3 \cdot mol^{-1} \cdot K^{-1}}$			$\frac{S_E \cdot 10^{-6}}{m^3 \cdot kg^{1/2} \cdot mol^{-1} \cdot K^{-1}}$			$\frac{\left(\frac{\partial \phi_E^0}{\partial T}\right)_p \cdot 10^{-6}}{m^3 \cdot mol^{-1} \cdot K^{-2}}$
	298.15 K	303.15 K	313.15 K	298.15 K	303.15 K	313.15 K	
1.00	-2.158 (±0.203)	-2.208 (±0.206)	-2.278 (±0.214)	13.809 (±2.468)	14.152 (±2.502)	14.584 (±2.600)	-0.785 (±0.044)
0.90	-1.804 (±0.085)	-1.844 (±0.091)	-1.898 (±0.091)	9.623 (±1.060)	9.868 (±1.121)	10.130 (±1.120)	-0.612 (±0.035)
0.80	-1.252 (±0.262)	-1.277 (±0.265)	-1.313 (±0.274)	8.491 (±1.299)	8.641 (±1.33)	8.890 (±1.449)	-0.389 (±0.015)
0.70	-0.550 (±0.261)	-0.562 (±0.265)	-0.575 (±0.272)	1.504 (±0.326)	1.558 (±0.379)	1.576 (±0.347)	-0.160 (±0.015)
0.60	-0.409 (±0.319)	-0.418 (±0.329)	-0.427 (±0.334)	0.496 (±0.146)	0.506 (±0.265)	0.518 (±0.333)	-0.115 (±0.011)

[a] Mass fraction of methanol in the solvent mixtures. Standard errors are given the parenthesis.

7.3.3. *Viscometric results*

It is reported[42] that Fe^{III}(salen)Cl can produce stable $[Fe^{III}(salen)]^+$ cation but the experimental solutions did not respond to $AgNO_3$ test for free Cl^- anion, hence we analyzed solution viscosities (η) with the modified Jones-Dole equation:[43]

$$\eta/\eta_1 = \eta_r = 1 + Bc \tag{5}$$

where $\eta_r = \eta/\eta_1$ is the relative viscosity; η_1 and η are the viscosities of solvent and solution, respectively. The adjustable parameter *B,* referred to as viscosity *B*-coefficient, was obtained by a least squares analysis and are reported in table 7.5. The viscosity *B*-coefficient[44, 45] provides another avenue into the effects of solute-solvent interactions on the solution viscosity similar to ϕ_V^0. Table 7.5 shows that the viscosity *B*-coefficients for Fe^{III}(salen)Cl in the studied solvent systems are positive but their temperature dependence is negative. A solute that has a positive viscosity *B*-coefficients with a negative dependence on temperature is generally considered as a structure maker. Accordingly Fe^{III}(salen)Cl can be considered as a structure maker for the present solvent systems studied. However, the viscosity *B*-coefficients decreased on the introduction of water (from w_1 = 1.00 to w_1 = 0.90), but after that the viscosity *B*-coefficients increase monotonically with further addition of water in the ternary solutions. This is probably due to the sudden perturbation of the arrangement of methanol molecules in bulk methanol structure arising from the strong solvent-solvent interaction in the solvent mixture with w_1 = 0.90 and for the remaining solvent compositions, solute-solvent interaction seems to dominate in characterizing solution viscosities and the viscosity *B*-coefficients.

7.3.4. *Thermodynamics of viscous flow*

According to Eyring and co-workers,[45] the application of statistical thermodynamics to the hole model of viscous flow on the basis on the absolute reaction rate theory yielded the following relation for the free energy of activation for viscous flow per mole of the solvent/solvent mixture ($\Delta\mu_1^{0\neq}$):

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_1\phi_{V,1}^0/hN_A) \tag{6}$$

where N_A , $\phi_{V,1}^0$ are the Avogadro's number and the molar volume of the solvent, respectively. Other symbols have their usual significances.[44]

Table 7.5. Viscosity *B*-coefficients for $\mathrm{Fe^{III}}$(salen)Cl in different aqueous methanol solutions with standard deviations (σ) for linear regression of equation (5) at different temperatures.

Parameters	T = 298.15 K	T = 303.15 K	T = 313.15 K
	w_1 = 1.00 [a]		
$\frac{B\cdot 10^{6}}{\mathrm{m^{3}\cdot mol^{-1}}}$	8.424 (±0.254)	8.255 (±0.161)	8.124 (±0.143)
R^2	0.99459	0.99772	0.99815
$\frac{\sigma\cdot 10^{6}}{\mathrm{mPa\cdot s}}$	0.002	0.001	0.001
	w_1 = 0.90 [a]		
$\frac{B\cdot 10^{6}}{\mathrm{m^{3}\cdot mol^{-1}}}$	7.295 (±0.156)	6.941 (±0.265)	6.706 (±0.124)
R^2	0.99725	0.99131	0.99794
$\frac{\sigma\cdot 10^{6}}{\mathrm{mPa\cdot s}}$	0.001	0.002	0.001
	w_1 = 0.80 [a]		
$\frac{B\cdot 10^{6}}{\mathrm{m^{3}\cdot mol^{-1}}}$	7.649(±0.180)	7.123 (±0.244)	6.887 (±0.199)
R^2	0.99667	0.99302	0.99502
$\frac{\sigma\cdot 10^{6}}{\mathrm{mPa\cdot s}}$	0.001	0.002	0.001
	w_1 = 0.70 [a]		
$\frac{B\cdot 10^{6}}{\mathrm{m^{3}\cdot mol^{-1}}}$	7.883 (±0.364)	7.193 (±0.004)	6.991 (±0.079)
R^2	0.98738	0.99999	0.99922
$\frac{\sigma\cdot 10^{6}}{\mathrm{mPa\cdot s}}$	0.002	0.001	0.001
	w_1 = 0.60 [a]		
$\frac{B\cdot 10^{6}}{\mathrm{m^{3}\cdot mol^{-1}}}$	7.891 (±0.231)	7.439 (±0.261)	7.133 (±0.298)
R^2	0.99490	0.99265	0.98962
$\frac{\sigma\cdot 10^{6}}{\mathrm{mPa\cdot s}}$	0.002	0.002	0.002

[a] Mass fraction of methanol in the solvent mixtures.
Standard errors are given the parenthesis

The above relation was also used for liquid mixtures[44, 45] and when rearranged this relation can be expressed as:

$$\ln(\eta_1 \phi_{V,1}^0 / hN_A) = -\frac{\Delta S_1^{0\neq}}{R} + \left(\frac{\Delta H_1^{0\neq}}{R}\right)\frac{1}{T} \tag{7}$$

So the values of $\Delta H_1^{0\neq}$ and $\Delta S_1^{0\neq}$ were obtained from a linear regression treatment of equation (7) with the correlation coefficient (R^2) values within the range (0.99866-0.99961). Plots of $\ln(\eta_1 \phi_{V,1}^0 / hN_A)$ against ($10^3/T$) are shown in figure 7.6. A correlation between viscosity *B*-coefficients and the deviation between the contribution per mole of a solute to the free energy of activation for viscous flow of the solution ($\Delta\mu_2^{0\neq}$) and the free energy of activation of viscous flow per mole of the pure solvent or solvent mixture ($\Delta\mu_1^{0\neq}$) has been suggested by Feakins *et al.*[46] in the form of the following relation:

$$B = (\nu\phi_{V,1}^0 - \phi_{V,2}^0) + \phi_{V,1}^0\left(\frac{\Delta\mu_2^{0\neq} - \nu\Delta\mu_1^{0\neq}}{RT}\right) \tag{8}$$

where the coefficient ν is 1 for undissociated uncharged solute and $\phi_{V,2}^0$ is the standard partial molar volume of the solute. So we have calculated $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values by using the above relation and the *B*-coefficient values obtained from equation (5). Again $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values can also be expressed as:

$$\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT} = -\frac{\Delta S_2^{0\neq} - \Delta S_1^{0\neq}}{R} + \left\{\frac{\Delta H_2^{0\neq} - \Delta H_1^{0\neq}}{R}\right\}\frac{1}{T} \tag{9}$$

where $\Delta S_i^{0\neq}$ and $\Delta H_i^{0\neq}$ are the standard partial molar entropy and enthalpy of activation for viscous flow per mole of ith component in the solution. So a linear regression treatment of equation (9) with the correlation coefficient (R^2) values within the range (0.81698-0.96863) provided the values of $(\Delta S_2^{0\neq} - \Delta S_1^{0\neq})$ and $(\Delta H_2^{0\neq} - \Delta H_1^{0\neq})$ from the corresponding slopes and intercept. The parameters $\Delta\mu_1^{0\neq}$ and $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ are reported in table 7.6. $\Delta H_1^{0\neq}$, $(\Delta H_2^{0\neq} - \Delta H_1^{0\neq})$, $\Delta S_1^{0\neq}$ and $(\Delta S_2^{0\neq} - \Delta S_1^{0\neq})$ are reported in table 7.7. Plots of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/RT$ against ($10^3/T$) are shown in figure 7.7.

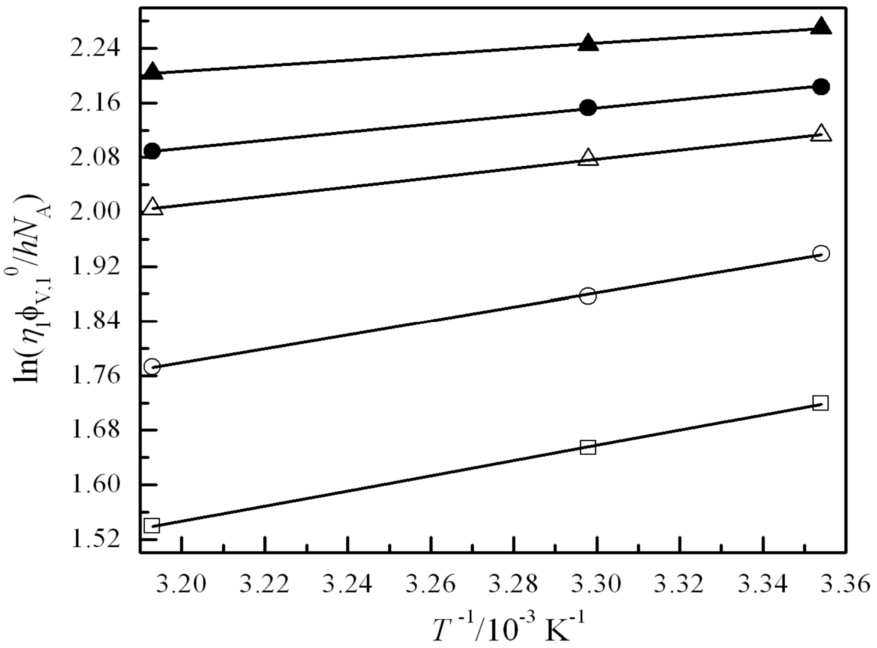

Fig. 7.6. Plots of $\ln(\eta_1 \phi_{V,1}^0 / hN_A)$ against $10^3 \times T^{-1}$ for Fe^{III}(salen)Cl in aqueous methanol mixtures. Symbols: w_1 = 1.00, □; w_1 = 0.90, ○; w_1 = 0.80, Δ; w_1 = 0.70, ●; w_1 = 0.60, ▲.

Table 7.6 shows that $\Delta\mu_1^{0\neq}$ is almost invariant of the solvent compositions and temperatures, implying that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity *B*-coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms. The values $\Delta\mu_2^{0\neq}$ contain the change in the free energy of activation of solute molecules in presence of solvent as well as the contribution from the movement of solute molecules. $\Delta\mu_2^{0\neq}$ values were positive at all the experimental temperatures but decrease as the temperature increases and increase as the content of water in ternary solutions (except for those with w_1= 0.90) increases. Such a trend of $\Delta\mu_2^{0\neq}$ values suggests that the viscous flow becomes easier at higher temperature but becomes difficult with increased amount of water in the ternary solutions, i.e., the formation of the transition state becomes less favorable at increased amount of water but higher temperature favors its formation.[44]

Table 7.6. Values of $\Delta\mu_1^{0\neq}$ and $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ for Fe$^{\text{III}}$(salen)Cl in different aqueous methanol solutions at different temperatures.

T/K	$\dfrac{\Delta\mu_1^{0\neq}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\dfrac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\#}}{\text{kJ}\cdot\text{mol}^{-1}}$
	$w_1 = 1.00$ [a]	
298.15	9.97 (±0.01)	525.22 (±0.26)
303.15	9.97 (±0.01)	519.26 (±0.17)
313.15	10.00 (±0.01)	521.15 (±0.15)
	$w_1 = 0.90$ [a]	
298.15	10.52 (±0.01)	511.29 (±0.16)
303.15	10.53 (±0.01)	491.39 (±0.27)
313.15	10.61 (±0.01)	484.95 (±0.13)
	$w_1 = 0.80$ [a]	
298.15	10.95 (±0.01)	593.23 (±0.18)
303.15	11.04 (±0.01)	559.14 (±0.25)
313.15	11.22 (±0.01)	553.04 (±0.20)
	$w_1 = 0.70$ [a]	
298.15	11.12 (±0.01)	671.90 (±0.37)
303.15	11.23 (±0.01)	621.36 (±0.01)
313.15	11.43 (±0.01)	618.75 (±0.08)
	$w_1 = 0.60$ [a]	
298.15	11.33 (±0.01)	734.73 (±0.24)
303.15	11.47 (±0.01)	701.61 (±0.27)
313.15	11.73 (±0.01)	689.83 (±0.30)

[a] Mass fraction of methanol in the solvent mixtures.
Standard errors are given the parenthesis

Table 7.7. Values of $\Delta H_1^{0\neq}$, $(\Delta H_2^{0\neq} - \Delta H_1^{0\neq})$, $\Delta S_1^{0\neq}$ and $(\Delta S_2^{0\neq} - \Delta S_1^{0\neq})$ for Fe$^{\text{III}}$(salen)Cl in different aqueous methanol solutions.

w_1 [a]	$\dfrac{\Delta H_1^{0\neq}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\dfrac{\Delta H_2^{0\neq} - \Delta H_1^{0\neq}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\dfrac{\Delta S_1^{0\neq}}{\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$	$\dfrac{\Delta S_2^{0\neq} - \Delta S_1^{0\neq}}{\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}}$
1.00	9.28 (±0.01)	587.17 (±7.34)	-2.31 (±0.04)	214.20 (±4.09)
0.90	8.56 (±0.02)	988.83 (±7.72)	-6.54 (±0.07)	1617.19 (±6.17)
0.80	5.62 (±0.01)	1307.11 (±4.45)	-17.89 (±0.03)	2423.24 (±8.32)
0.70	4.95 (±0.01)	1592.97 (±3.39)	-20.72 (±0.03)	3135.12 (±6.59)
0.60	3.37 (±0.01)	1552.35 (±4.52)	-26.70 (±0.02)	2767.67 (±7.28)

[a] Mass fraction of methanol in the solvent mixtures.

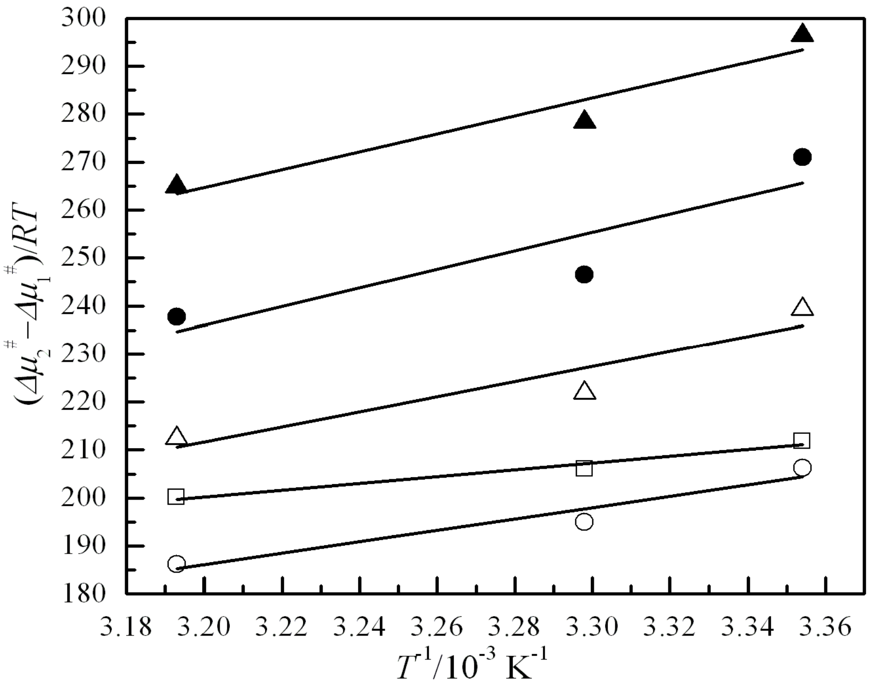

Fig. 7.7. Plots of $(\Delta\mu_2^{0\neq}-\Delta\mu_1^{0\neq})/RT$ against $10^3\cdot T^{-1}$ for Fe^{III}(salen)Cl in aqueous methanol mixtures. Symbols: w_1 = 1.00, □; w_1 = 0.90, ○; w_1 = 0.80, Δ; w_1 = 0.70, ●; w_1 = 0.60, ▲.

According to Feakins *et al.*[46] a solute molecule interacts with every solvent molecules and sum of these interactions for all solute and solvent molecules is collectively defined as solute-solvent interaction. A solute molecule interacts with all the solvent molecules in solution including any solvent molecule in its transition state. Thus the effect of the solute on the activation free energy of the solvent molecule is the difference between the solvation energies of the solute in the ground state solvent and the transition state solvent or free energy of transfer, $\Delta G_2^{0\neq}(1\rightarrow1')$ between them. The second contribution to $\Delta\mu_2^{0\neq}$ comes from the movement of the solute through its own viscous transition state, $\Delta G_2^{0\neq}(2\rightarrow2')$. So the term $\Delta\mu_2^{0\neq}$ can also expressed as:

$$\Delta\mu_2^{0\neq}=\Delta G_2^{0\neq}(1\rightarrow1')+\Delta G_2^{0\neq}(2\rightarrow2') \qquad (10)$$

The values $\Delta G_2^{0\neq}(2\rightarrow2')$ can be approximated with the $\Delta\mu_1^{0\neq}$ values and the values $\Delta G_2^{0\neq}(1\rightarrow1')$ simply become equal to $(\Delta\mu_2^{0\neq}-\Delta\mu_1^{0\neq})$ values.

Thus, the quantity $(\Delta\mu_2^{0\neq}-\Delta\mu_1^{0\neq})$ is the change in the activation energy per mole of solute on replacing one mole of solvent by one mole of solute in an infinite dilution. The values of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ obtained are positive for all the solvent mixtures and the values decrease almost linearly as the temperature increases for all the solvent mixtures, but they increase with further addition of water in the ternary solutions (except for those with $w_1 = 0.90$). The positive $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values and their negative temperature dependence with a similar trends in viscosity *B*-coefficients for $\mathrm{Fe^{III}}$(salen)Cl indicated the structure making ability of the solute and the transfer of the solute molecules from the ground state solvent to the transition state solvent is thermodynamically hindered.

Table 7.7 shows that the $\Delta H_2^{0\neq}$ values are positive for all the solvent systems and thus indicate rupture and distortion of the solvation bonds or intermolecular forces in the activated state of viscous flow and that the viscous process is endothermic. Thus the viscous flow will be accompanied by a decrease in order and thus positive $\Delta S_2^{0\neq}$ values were obtained for all the studied solutions. However, negative $\Delta S_1^{0\neq}$ values for all the solvent mixtures may be attributed to negative entropy of mixing solutions over the entire range of concentration for aqueous methanol; such negative entropy of mixing originates from the strong association between solvent molecules at low methanol contents[34] and the tendency of the solvent molecules to segregate and form clusters[49-51] in aqueous methanol solutions dominating the thermodynamics of aqueous methanol solutions.[47, 48]

7.6. Conclusion

In the present study derived parameters like standard partial molar volumes (ϕ_V^0), partial molar expansibilities (ϕ_E^0), viscosity *B*-coefficients and various activation parameters for viscous flow for $\mathrm{Fe^{III}}$(salen)Cl under investigation indicate the presence of strong solute-solvent interactions and these interactions are further strengthened for higher content of water in the ternaries but decrease at higher temperatures. The results further shows that $\mathrm{Fe^{III}}$(salen)Cl is preferentially more solvated by water rather than methanol and it acts as a net structure promoter in the ternary solutions studied. UV-VIS absorption spectra of the ternary solutions also stand in support of the results obtained. The transition state theory treatment of viscosity *B*-coefficients revealed that the transfer of the solute molecules from the ground state solvent to the transition state solvent is thermodynamically hindered and the viscous process is endothermic.

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CHAPTER VIII

Solution thermodynamics of iron(III)-N, N$^{/}$-ethylene-bis(salicylideneiminato)-chloride in binary mixtures of N, N-dimethylformamide and acetonitrile at T = (298.15, 303.15, 308.15 and 313.15) K

8.1. Introduction

The rate of a chemical reaction often depends on the nature of solvent or solvent mixture used as reaction media and simply by changing the reaction medium the rate can be changed by factors in powers of 10.[1] Also solvents can influence the mode of crystallization for several transition metal complexes[2] and modify the molecular structures and charge distributions in solution.[3] Solvent effects can be explained qualitatively with the aid of experimental physical and chemical data of solvents and intermolecular forces[4] operating therein a solution. Molecular interaction such as the short and long range solute-solute and solute-solvent interactions affect the thermodynamic and transport properties of a solute in solution phase and depend on the molecular details such as size, shape, dipole moment, steric hindrance, polarizability, donor number or donor strength, etc., of the solvents. Specifically in mixed solvents, specific solvent-solvent interaction can alter the structural properties of the solutes and thereby influence the solute-solvent interaction. Among the many potential materials, Schiff base metal complexes are worthy of extensive studies and metal complexes with salen-type ligands or their derivatives have been one of the highlights in coordination chemistry and homogeneous catalysis for organic reactions[5] as well as models of reaction centers for metalloenzymes[6] and nonlinear optical material.[7]

N, N-dimethylformamide (DMF) is an aprotic, proton-acceptor, non-hydrogen bonded solvent. Acetonitrile (ACN), because of its polarity, is a good solvent for both electrolytes and non-electrolytes and its molecules do not form hydrogen bonds as a proton-donor or as a proton acceptor. Although they have nearly the same dielectric constants ($\varepsilon_{r,\mathrm{DMF}} = 37.6$ and $\varepsilon_{r,\mathrm{ACN}} = 36.0$[8]), they differ in their solvating capabilities (Gutmann numbers[9]). Therefore their binary mixture is a good choice for studying the solvation behaviour of a complex. That is why several authors[10-12] have extensively studied the binary system of DMF and ACN. Gill *et al.*[13, 14] studied the solvation of Na^+, Cu^+ and ClO_4^- in DMF + ACN mixtures wherein results indicated that the extent of solvation of a particular depends on the solvent composition. Also as an industrial solvent, both ACN and DMF play significant roles in numerous chemical processes and their dipoles are oriented in different fashions.[15] Their binary mixture is characterized by mutual destruction of dipolar structures and strong dipole-dipole interactions and while DMF preferably solvates the cations, ACN solvates both the cations and anions.[13, 14] Hence it is important to understand how solutes behave in these mixed solvents, because an understanding of such behaviour can through light on the effects of solute concentration on hydrogen-bonded network, solvation structure and solute dynamics, etc.[16]

Interestingly some structural and chemical similarities between Fe^{III}(salen)Cl and Fe^{III} porphyrins exist.[17,18] As in Fe^{III} porphyrins, the iron atom of Fe^{III}(salen)Cl is penta-coordinated in a pyramidal geometry with the tetradentate salen ligand in a square planar coordination; the chloride ligand is in the fifth apical coordination site and the sixth coordination site is unoccupied. Although N, N/-ethylenebis(salicylideneamine), $salenH_2$ consists of one pair of each N and O-atoms, rather than two pairs of N-atoms, $salenH_2$ forms complexes that mimic porphyrin chemistry.[19] Moreover, the affinity of Fe^{III}(salen)Cl for the oxygen molecule and the capability to form oxo-complexes is similar to that of Fe^{III} porphyrin derivatives;[17,18] it is also reported to be an efficient catalyst for many organic transformations.[20-24] Standard partial molar volumes (ϕ_V^0) and viscosity *B*- coefficients of a solute in solution phase provide valuable information about solute-solvent and solvent-solvent interactions[25-27] and thus are of fundamental importance for a proper understanding of the solution behavior of a solute like Fe^{III}(salen)Cl. But such studies on the solute-solute and solute-solvent interactions involving Fe^{III}(salen)Cl in various pure and mixed solvents are rare in the literature. To the best of our knowledge, only one report on the solvent effects on the electrochermical behavior of Fe^{III}(salen)Cl is available in literature.[28] Hence in this chapter an attempt has been undertaken to reveal the various interactions prevailing in the ternary mixtures of Fe^{III}(salen)Cl + DMF + ACN (with DMF mass fractions: w_1 = 0.25, 0.50, 0.75 and 1.00) at 298.15, 303.15, 308.15 and 313.15 K under ambient pressure.

8.2. Experimental section

8.2.1. *Materials*

A. R. grade ferric chloride, $FeCl_3.6H_2O$; 1,2-ethylenediamine and salicylaldehyde, each of purity > 99%, were procured from Thomas Baker, India. These chemicals were used without further purification. Spectroscopic grade ACN and DMF (minimum assay, GC > 99.8%) was procured from Merck, India and used as received. The various binary solvent mixtures were prepared by mass and necessary adjustments were done to achieve exact mass fractions (w_1 = 0.25, 0.50, and 0.75) of DMF in the binary solvent mixtures at 298.15 K. The relative error in solvent composition was about 1%. The physical properties of these solvent/solvent mixtures are given in table 8.1 and compared to the literature values[8, 13, 29-32] whenever available.

Fe^{III}(salen)Cl was prepared by a slight modification of a known method[33] and the details of synthesis and physicochemical characterization[34] of Fe^{III}(salen)Cl have been described in chapter III. Molecular structure of the ligand and the complex is depicted in figure 8.1. Stock solutions of the complex in different solvent mixtures were prepared by mass and the working solutions were prepared by mass dilution. The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The conversion of molality into molarity was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in molarity of Fe^{III}(salen)Cl solutions was evaluated to $\pm 0.0001\ \text{mol}\,\text{dm}^{-3}$.

8.2.2. *Apparatus and procedure*

The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M). The densitometer was calibrated at the experimental temperatures with doubly distilled and degassed water and dry air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $\pm 1\times10^{-2}$ K by using the built–in Peltier technique. The estimated uncertainty of the density measurements for most of the solutions was found to be better than $\pm 2\times10^{-5}\ \text{g}\,\text{cm}^{-3}$.

Table 8.1. Densities (ρ) and viscosities (η) of different mixtures of DMF (1) + ACN (2) at T = (298.15 to 313.15) K

w_1[a]	T (K)	$\rho \cdot 10^{-3}$ / kg · mol^{-3}		η / mPa · s	
		Expt.	Lit.	Expt.	Lit.
0.00	298.15	0.77647	0.77649 [8] 0.7762 [29] 0.7768 [30]	0.3420	0.341 [8] 0.342 [29]
	303.15	0.77156	0.77125 [8] 0.77080 [29] 0.7715 [30]	0.3269	0.324 [8] 0.326 [29]
	308.15	0.76526	0.76586 [8] 0.76518 [29] 0.7663 [30]	0.3092	0.314 [8] 0.306 [29]
	313.15	0.75955	0.76047 [8] 0.75942 [29] 0.7610 [30]	0.2929	0.2974 [8] 0.291 [29]
0.25	298.15	0.81675	0.81565 [b]	0.3959	0.4079 [c]
	303.15	0.81182	0.81055 [b]	0.3598	
	308.15	0.80658	0.80557 [b]	0.3417	
	313.15	0.80183	0.80055 [b]	0.3262	
0.50	298.15	0.85692	0.85780 [b]	0.5214	0.5260 [c]
	303.15	0.85267	0.85290 [b]	0.4600	
	308.15	0.84738	0.84815 [b]	0.4340	
	313.15	0.84257	0.84330 [b]	0.4038	
0.75	298.15	0.90014	0.89995 [b]	0.6465	0.6441 [c]
	303.15	0.89546	0.89525 [b]	0.6145	
	308.15	0.89088	0.89072 [b]	0.5816	
	313.15	0.88623	0.88605 [b]	0.5524	
1.00	298.15	0.94465	0.9445 [30] 0.9446 [31] 0.94421 [32]	0.7986	0.803 [31] 0.808 [32]
	303.15	0.94005	0.9401 [30] 0.9398 [31] 0.93945 [32]	0.7550	0.756 [31] 0.760 [32]
	308.15	0.93571	0.9357 [30]	0.7069	
	313.15	0.92991	0.9312 [30] 0.9302 [31] 0.92986 [32]	0.6716	0.673 [31] 0.675 [32]

[a] Mass fraction of DMF in the solvent mixtures.

[b, c] Obtained from linear interpolation of literature data in Ref. [30] and Ref. [13], respectively.

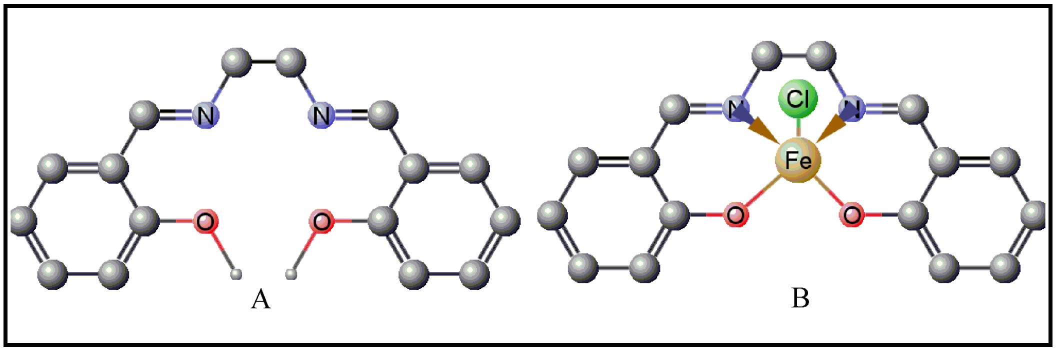

Fig. 8.1. Molecular structures of A) SalenH$_2$, B) Fe^{III}(salen)Cl.

The viscosity was measured by means of a suspended Ubbelohde (Canon-type) viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled, degassed water and purified methanol.[35-37] It was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a digital stopwatch correct to ± 0.01s. In all determinations, an average of triplicate measurements was taken into account and adequate precautions were taken to minimize evaporation loses during the actual measurements. The uncertainty in viscosity measurements, based on our work on several pure liquids, was within $\pm 4\times10^{-4}\,\text{mPa s}$. Details of density and viscosity measurements have been described in chapter III.

The absorption spectra of Fe^{III}(salen)Cl in different binary mixtures at a concentration of $5\times10^{-5}\,\text{mol dm}^{-3}$ were recorded on JascoV-530 double beam UV-VIS spectrophotometer coupled with thermostatic arrangement at 298.15 K using a quartz cell of 1 cm path length and spectroscopic grade ACN as the reference solvent.

8.3. Results and discussion

The experimental values of molalities m, densities ρ, viscosities η, and derived parameters for the experimental solutions of Fe^{III}(salen)Cl in different mixed solvents at various temperatures are reported in table 8.2.

8.3.1. *Standard partial molar volumes*

The apparent molar volumes ϕ_V were determined from the solution densities using the following relation:

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_1)}{m\rho\rho_1} \qquad (1)$$

where M is the molar mass of $\mathrm{Fe^{III}(salen)Cl}$, m is the molality of the solution, ρ_1 and ρ are the densities of the solvent and solution, respectively. As the plots of ϕ_V against square root of molar concentration ($\sqrt{m}$) were linear, ϕ_V values were fitted to Masson equation:[38]

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \qquad (2)$$

where ϕ_V^0 and S_V^* are the partial molar volume at infinite dilution and the experimental slope, respectively. The ϕ_V^0 and S_V^* values were determined by fitting the dilute data ($m < 0.1\ \mathrm{mol\,kg^{-1}}$) to equation (2) by using a least squares regression method with the correlation coefficient values (R^2) falling within the range (0.98669-0.99932). The ϕ_V^0 and S_V^* values at each temperature are reported in table 8.3. Standard errors in ϕ_V^0 and S_V^* values were evaluated by following the rules of error propagation[39] and are given in table 8.3 along with the standard deviations (σ) of linear fit with equal weight to all data points. Table 8.3 shows that ϕ_V^0 values are positive and increase as the amount of DMF increases in the mixtures but decrease as the temperature increases. Such a trend in ϕ_V^0 values indicates strong solute-solvent interactions[37, 38] in the solutions studied; also these interactions increase further at higher content of DMF and highest ϕ_V^0 values for $\mathrm{Fe^{III}(salen)Cl}$ were observed in pure DMF. However, gradual decrease in ϕ_V^0 values as the temperature increases for solutions studied indicate that increase in experimental temperatures hampers or weakens the solute-solvent interactions. The dependence of ϕ_V^0 values on the solvent composition and temperature is depicted in figure 8.2.

Table 8.2. Molalities (m), densities (ρ), viscosities (η), and apparent molar volumes (ϕ_V) of Fe^{III}(salen)Cl in different mixtures of DMF (1) + ACN (2) at T = (298.15 to 313.15) K

m/mol·kg^{-1}	$\rho\cdot10^{-3}$ / kg·mol^{-3}	η / mPa·s	$\phi_V\cdot10^{6}$ / m^3·mol^{-1}
$w_1{}^a = 0.00$			
T/K= 298.15			
0.0015	0.77669	0.3464	217.21
0.0026	0.77686	0.3497	211.63
0.0046	0.77717	0.3542	207.94
0.0067	0.77750	0.3597	205.28
0.0088	0.77785	0.3642	200.07
0.0103	0.77810	0.3686	197.64
T/K = 303.15			
0.0015	0.77178	0.3335	217.03
0.0026	0.77195	0.3368	211.39
0.0046	0.77226	0.3401	207.65
0.0067	0.77259	0.3446	204.95
0.0088	0.77293	0.3490	201.59
0.0103	0.77318	0.3534	198.84
T/K = 308.15			
0.0015	0.76548	0.3179	216.77
0.0026	0.76565	0.3212	211.03
0.0046	0.76596	0.3245	207.24
0.0067	0.76629	0.3279	204.49
0.0088	0.76663	0.3323	201.08
0.0103	0.76687	0.3367	199.94
T/K = 313.15			
0.0015	0.75977	0.3016	216.50
0.0026	0.75994	0.3049	210.68
0.0046	0.76025	0.3093	206.83
0.0067	0.76058	0.3127	204.04
0.0088	0.76091	0.3160	202.55
0.0103	0.76116	0.3182	199.43
$w_1{}^a = 0.25$			
T/K = 298.15			
0.0015	0.81697	0.4005	217.90
0.0024	0.81711	0.4051	212.87
0.0044	0.81742	0.4097	209.38
0.0064	0.81774	0.4166	205.68
0.0083	0.81805	0.4223	202.70
0.0098	0.81831	0.4292	198.81
T/K = 303.15			
0.0015	0.81204	0.3644	217.88
0.0024	0.81218	0.3679	212.79
0.0044	0.81249	0.3736	209.26
0.0064	0.81281	0.3783	205.52
0.0083	0.81311	0.3829	204.33
0.0098	0.81337	0.3887	200.11

[a] Mass fraction of DMF in the solvent mixtures

Contd…

T/K = 308.15			
0.0015	0.80680	0.3509	217.84
0.0024	0.80694	0.3543	212.68
0.0044	0.80725	0.3578	209.11
0.0064	0.80756	0.3635	207.72
0.0083	0.80787	0.3682	204.11
0.0098	0.80812	0.3728	201.41
T/K = 313.15			
0.0015	0.80205	0.3342	217.79
0.0024	0.80219	0.3365	212.57
0.0044	0.80250	0.3400	209.95
0.0064	0.80281	0.3446	207.55
0.0083	0.80312	0.3493	203.90
0.0098	0.80336	0.3527	202.75
$w_1{}^a = 0.50$			
T/K = 298.15			
0.0014	0.85712	0.5238	222.70
0.0023	0.85726	0.5286	215.90
0.0042	0.85755	0.5345	212.87
0.0061	0.85785	0.5439	209.45
0.0079	0.85815	0.5533	204.97
0.0093	0.85839	0.5627	201.70
T/K = 303.15			
0.0014	0.85287	0.4636	222.83
0.0023	0.85301	0.4671	215.97
0.0042	0.85330	0.4731	212.91
0.0061	0.85360	0.4802	209.45
0.0079	0.85389	0.4873	206.67
0.0093	0.85413	0.4944	203.10
T/K = 308.15			
0.0014	0.84758	0.4376	222.99
0.0023	0.84772	0.4423	216.04
0.0042	0.84801	0.4471	212.94
0.0061	0.84831	0.4530	209.44
0.0079	0.84859	0.4601	208.39
0.0093	0.84884	0.4660	203.01
T/K = 313.15			
0.0014	0.84277	0.4108	223.12
0.0023	0.84291	0.4155	216.09
0.0042	0.84320	0.4203	212.95
0.0061	0.84349	0.4251	211.73
0.0079	0.84378	0.4310	208.36
0.0093	0.84402	0.4357	204.43
$w_1{}^a = 0.75$			
T/K = 298.15			
0.0013	0.90032	0.6502	226.33
0.0022	0.90045	0.6551	223.28
0.0040	0.90072	0.6613	218.16
0.0058	0.90100	0.6747	214.06
0.0076	0.90129	0.6869	210.24

[a] Mass fraction of DMF in the solvent mixtures

Contd…

0.0089	0.90150	0.6990	208.35
T/K = 303.15			
0.0013	0.89564	0.6194	226.61
0.0022	0.89577	0.6243	223.53
0.0040	0.89604	0.6316	218.36
0.0058	0.89632	0.6426	214.21
0.0076	0.89660	0.6523	212.00
0.0089	0.89681	0.6632	209.85
T/K = 308.15			
0.0013	0.89106	0.5853	226.89
0.0022	0.89119	0.5901	223.77
0.0040	0.89146	0.5963	218.55
0.0058	0.89173	0.6048	216.53
0.0076	0.89201	0.6157	213.78
0.0089	0.89221	0.6218	212.78
T/K = 313.15			
0.0013	0.88641	0.5584	227.16
0.0022	0.88654	0.5621	224.01
0.0040	0.88680	0.5670	221.92
0.0058	0.88707	0.5755	218.89
0.0076	0.88735	0.5840	215.59
0.0089	0.88755	0.5925	214.34
$w_1^{\,a} = 1.00$			
T/K = 298.15			
0.0013	0.94482	0.8050	231.96
0.0021	0.94493	0.8101	229.06
0.0038	0.94518	0.8190	222.12
0.0055	0.94544	0.8330	217.40
0.0072	0.94570	0.8481	214.88
0.0085	0.94592	0.8583	210.83
T/K = 303.15			
0.0013	0.94022	0.7601	232.37
0.0021	0.94033	0.7639	229.44
0.0038	0.94058	0.7716	222.44
0.0055	0.94084	0.7842	217.67
0.0072	0.94109	0.7944	216.70
0.0085	0.94130	0.8045	213.70
T/K = 308.15			
0.0013	0.93588	0.7120	232.76
0.0021	0.93599	0.7183	229.81
0.0038	0.93624	0.7247	222.74
0.0055	0.93649	0.7335	220.00
0.0072	0.93675	0.7437	216.94
0.0085	0.93695	0.7538	215.26
T/K = 313.15			
0.0013	0.93008	0.6779	233.27
0.0021	0.93019	0.6817	230.28
0.0038	0.93043	0.6893	226.17
0.0055	0.93068	0.6981	222.46
0.0072	0.93093	0.7070	220.47
0.0085	0.93113	0.7145	218.27

Again S_V^* values are negative for all the solvent/solvent mixtures and follow a trend opposite to that followed by ϕ_V^0 values and S_V^* values are minimum for pure DMF; thus the trends in S_V^* values indicate weak solute-solute interactions[37, 38] in the solvents/solvent mixtures studied. Fe^{III}(salen)Cl can exist in the solid state either in dimeric or monomeric form depending on the nature of the solvent used in its recrystalization and it has been reported that the two forms can be distinguished by their magnetic moments at ambient temperature: for monomeric complex the range fall within 5.29-6.06 BM.

Table 8.3. Standard partial molar volumes (ϕ_V^0), the slopes (S_V^*) and corresponding standard deviations (σ) for Fe^{III}(Salen)Cl in different mixtures of DMF (1) + ACN (2) at T = (298.15 To 313.15) K

T/K	$\frac{\phi_V^0 \cdot 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$	$\frac{S_V^* \cdot 10^6}{\mathrm{m^3 \cdot kg^{1/2} \cdot mol^{-3/2}}}$	$\frac{\sigma \cdot 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$
	$w_1{}^a = 0.00$		
298.15	227.93 (±1.19)	-293.99 (±2.66)	0.94
303.15	226.35 (±1.07)	-268.39 (±2.14)	0.85
308.15	225.36 (±1.18)	-256.76 (±2.50)	0.93
313.15	224.54 (±1.42)	-246.59 (±3.72)	1.12
	$w_1{}^a = 0.25$		
298.15	228.42 (±1.12)	-290.37 (±2.13)	0.88
303.15	227.05 (±1.34)	-265.07 (±2.06)	1.05
308.15	226.12 (±1.38)	-244.78 (±2.60)	1.08
313.15	225.30 (±1.38)	-231.70 (±2.53)	1.08
	$w_1{}^a = 0.50$		
298.15	233.56 (±1.61)	-323.41 (±2.32)	1.27
303.15	232.40 (±1.62)	-298.57 (±2.44)	1.27
308.15	232.07 (±2.07)	-289.20 (±2.61)	1.63
313.15	231.33 (±2.09)	-269.11 (±2.45)	1.65
	$w_1{}^a = 0.75$		
298.15	237.82 (±0.23)	-313.18 (±2.33)	0.18
303.15	236.91 (±0.47)	-289.47 (±2.71)	0.37
308.15	235.09 (±0.81)	-243.19 (±1.53)	0.65
313.15	234.84 (±0.69)	-215.72 (±2.74)	0.54
	$w_1{}^a = 1.00$		
298.15	245.59 (±0.78)	-373.09 (±1.35)	0.61
303.15	244.12 (±1.33)	-335.47 (±1.28)	1.04
308.15	243.76 (±1.04)	-316.81 (±1.05)	0.81
313.15	242.52 (±0.39)	-263.92 (±4.66)	0.31

[a] Mass fraction of DMF in the solvent mixtures.
Standard errors are given in parentheses.

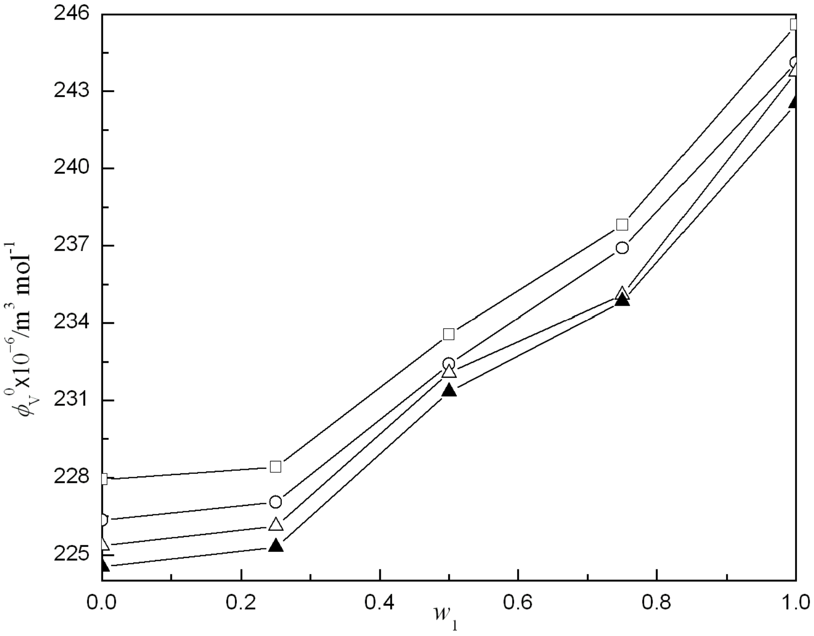

Fig. 8.2. Dependence of standard partial molar volume (ϕ_V^0) of the complex Fe^{III}(salen)Cl on mass fractions (w_1) of DMF in different solvent mixtures at different temperatures. Symbols: T = 298.15 K, □; T = 303.15 K, ○; T = 308.15 K, Δ; T = 313.15 K, ▲.

We obtained a value of 5.31 BM for the complex Fe^{III}(salen)Cl indicating that it contains a d^5 high spin electronic configuration[40, 41] with a square planar geometry around the metallic center and a apical chlorine atom as the fifth ligand; many solvents can act as a ligand for the unoccupied sixth position in the coordination sphere of iron. Although Fe^{III}(salen)Cl can also produce stable [Fe^{III}(salen)]$^+$ cation, the solutions of the complex in the solvent systems studied did not respond to $AgNO_3$ test for free Cl$^-$ anion. So the complex was treated as a non-electrolyte in these solvent systems. Anyway, regarding coordination of the unoccupied sixth position in the coordination sphere of iron in Fe^{III}(salen)Cl donor power of individual solvents has an important role to play by reducing Fe(III) to Fe(II) reversibly. IR spectra (as shown in figure 7.3 of chapter VII) are devoid of the characteristic Fe-O-Fe band[42] near 850 cm^{-1} and thus signify that our complex was in monomeric form. Hence DMF and ACN molecules may coordinate for the sixth vacant coordination site of iron in Fe^{III}(salen)Cl either via O···Fe or N···Fe interactions. Increase in ϕ_V^0 values with increase in mass fraction (w_1) of DMF in the studied solutions may be attributed to the solvent-solvent interactions and molecular nature as well as orientations of the solvent molecules in solution. The binary mixture of DMF and ACN is characterized by mutual destruction of dipolar structures and strong dipole-dipole interactions[12] that lead to molecular association between DMF and ACN[11]and also release of free dipoles when DMF is mixed with ACN.[12] Due to two CH_3-groups at N-atom of DMF, coordination of DMF to the unoccupied sixth position in the coordination sphere of iron of Fe^{III}(salen)Cl seems sterically hindered. But no such steric hindrance is viable in case of ACN. But experimental results indicate that Fe^{III}(salen)Cl is preferentially solvated by DMF rather than ACN. Actually DMF has a strong electron pair donor and accepting ability and is a resonance hybrid of two resonating structures (shown in figure 8.3): one neutral molecule and another zwitter ionic form with negative O-pole and positive N-pole.

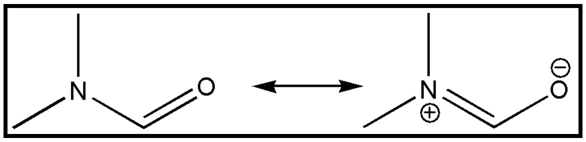

Fig. 8.3. Resonance structures of DMF.

The negative O-pole is positioned out of the rest of the molecule and its unshared electron pair is exposed enough for strong solvation. The positive N-pole is buried within the molecule and two electron repelling CH_3-groups further make its lone pair electrons more perceptible for donation.[43, 44] Also due to the positive charge on N-pole, CH_3-groups become more polar. Thus all these factors probably impart higher solvating power to DMF and it interacts preferably more with Fe^{III}(salen)Cl through $O\cdots Fe$ interaction as far as the present solutions studied are concerned. Again as polarity of the solvent mixtures increase with more DMF,[14] concomitant increase in ϕ_V^0 values indicate that some interactions probably exist among the polar segments of the complex and the solvents as well as electrostatic interactions between local charges of the complex and the solvent dipoles. However, the decrease in ϕ_V^0 values with a rise in temperature indicates disruption of these interactions at elevated temperatures.

These results are also qualitatively reflected in the UV-VIS absorption spectra of the studied solutions (shown in figure 8.4). The absorption spectrum of Fe^{III}(salen)Cl in ACN shows a weak peak around 468 nm that may be assigned to

$n \rightarrow \pi^*$ transitions involving the molecular orbitals of $C=\ddot{N}$ chromophore and indicates coordination of ACN to Fe^{III}(salen)Cl but on successive addition of DMF this peak is gradually blue shifted to 448 nm in DMF and suffers from hypchromic effects indicating coordination or preferential solvation by DMF molecules[45] through the negative O-pole. Such coordination creates changes in the solvation sphere of Fe^{III}(salen)Cl and ultimately increases the intensity of the peal at 448 nm in DMF. However, intensity of the peak at 448 nm in DMF increases compared to those in mixed solvents.

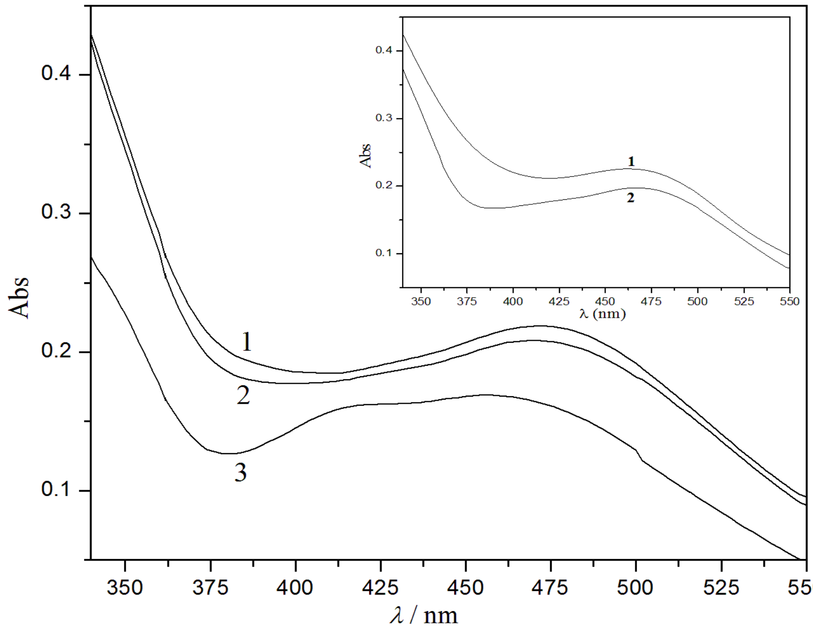

Fig. 8.4. Changes in the UV-Visible absorption spectra of Fe^{III}(salen)Cl in different DMF (1) + ACN (2) mixtures at 298.15 K: 1, w_1 = 0.20; 2, w_1 = 0.40; 3, w_1 = 0.80; 4. Inset: 1, Fe^{III}(salen)Cl in ACN; 2: average absorption spectra in w_1 = 0.20, 0.40 and 0.80 solvent mixtures at 298.15 K.

8.3.2. *Apparent molar expansibilities*

The temperature dependence of partial molar volumes (ϕ_V^0) can be described by the following relation:

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \tag{3}$$

where a_0, a_1, and a_2 are regression coefficients and are listed in table 8.4 along with standard deviations of polynomial fitting of (ϕ_V^0, T) data with correlation coefficient

(R^2) values falling within the range (0.95044-0.99899). The partial molar expansibilities ϕ_E^0 can be obtained by using the relation:

$$\phi_E^0 = (\partial \phi_V^0 / \partial T)_P = a_1 + 2a_2 T \qquad (4)$$

The ϕ_E^0 values for the studied ternary solutions at different temperatures are shown in table 8.5. It shows that ϕ_E^0 values are negative and increase as the temperature as well as mass fractions (w_1) of DMF in the solvent mixtures (except for solvent mixture with w_1 = 0.75) increase. These facts are probably due to structural perturbation influenced by the gradual disappearance of caging/packing effect[46, 47] as the DMF content in the ternary solutions and the temperature of the solutions increases. According to Hepler[48] the sign of $(\partial \phi_E^0 / \partial T)_P$ is a better criterion in characterizing the long-range structure making or breaking ability of a solute in solution phase. The general thermodynamic expression is as follows:

$$(\partial \phi_E^0 / \partial T)_P = (\partial^2 \phi_V^0 / \partial T^2)_P = 2a_2 \qquad (5)$$

If the sign of $(\partial \phi_E^0 / \partial T)_P$ is positive, the solute is a structure-maker; otherwise it is a structure breaker. It is seen from table 8.5 that Fe^{III}(salen)Cl predominantly acts as a structure maker and its structure-making ability generally decreases with an increase in DMF content in the ternary solutions.

Table 8.4. Regression coefficients of equation (3) and corresponding standard deviations for Fe^{III}(salen)Cl in different mixtures of DMF (1) + ACN (2).

$w_1{}^a$	$a_0 \cdot 10^{-6}$ /($\mathrm{m^3 \cdot mol^{-1}}$)	$a_1 \cdot 10^{-6}$ /($\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$)	$a_2 \cdot 10^{-6}$ /($\mathrm{m^3 \cdot mol^{-1} \cdot K^{-2}}$)	$\sigma \cdot 10^{-6}$ /($\mathrm{m^3 \cdot mol^{-1}}$)
0.00	1004.035	-4.869	0.008	0.001
0.25	803.274	-3.568	0.005	0.001
0.50	667.494	-2.708	0.004	0.004
0.75	918.319	-4.249	0.007	0.015
1.00	517.297	-1.597	0.002	0.010

[a] Mass fraction of DMF in the solvent mixtures.

Table 8.5. Partial molar expansibility (ϕ_E^0) and its temperature dependence $(\partial \phi_E^0 / \partial T)_P$ for Fe$^{\text{III}}$(salen)Cl in different mixtures of DMF (1) + ACN (2) at T = (298.15 to 313.15) K.

$w_1{}^a$	$\phi_E^0 \cdot 10^{-6} / (\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}})$				$\left(\frac{\partial \phi_E^0}{\partial T}\right)_p \cdot 10^{-6}$ $/(\mathrm{m^3 \cdot mol^{-1} \cdot K^{-2}})$
	T /K= 298.15	T/K = 303.15	T/K = 308.15	T/K = 318.15	
0.00	-0.337 (±0.002)	-0.261 (±0.003)	-0.185 (±0.005)	-0.109 (±0.004)	0.015 (±0.004)
0.25	-0.288 (±0.005)	-0.233 (±0.004)	-0.178 (±0.002)	-0.123 (±0.001)	0.011 (±0.002)
0.50	-0.203 (±0.007)	-0.161 (±0.004)	-0.119 (±0.004)	-0.077 (±0.005)	0.008 (±0.001)
0.75	-0.314 (±0.003)	-0.248 (±0.002)	-0.182 (±0.004)	-0.116 (±0.002)	0.013 (±0.002)
1.00	-0.225 (±0.004)	-0.202 (±0.003)	-0.179 (±0.005)	-0.156 (±0.002)	0.005 (±0.001)

[a] Mass fraction of DMF in the solvent mixtures.

8.3.3. *Viscometric results*

Solution viscosities (η) were analyzed with the modified Jones-Dole equation:[49]

$$\eta_r = 1 + Bc \qquad (6)$$

where $\eta_r = \eta / \eta_1$; η_1, η and c are viscosities of the solvents, viscosities of the solutions and molar concentration of the solute in the studied solutions, respectively. Viscosity *B*-coefficient depends on solute-solvent interaction and structural factors; it gives a measure of structural modification induced by the solute-solvent interactions and viscosity *B*-coefficients for solutions studied were estimated by least squares linear regression analysis with correlation coefficient (R^2) values falling with the range (0.98260-0.99746). Table 8.6 shows that the viscosity *B*-coefficients for Fe$^{\text{III}}$(salen)Cl in the studied solvent systems are positive but their temperature dependence is negative. A solute with positive viscosity *B*-coefficients and a negative dependence of viscosity *B*-coefficients on temperature $(\partial B / \partial T)$ is generally considered as a structure maker. Accordingly Fe$^{\text{III}}$(salen)Cl can be considered as a structure maker for the present solvent systems studied. Interestingly, although the viscosity *B*-coefficients generally increase on the introduction of DMF from pure ACN (w_1 = 0.00) up to w_1 = 0.75 in the binary solvent mixtures, such values decrease in pure DMF. This fact may be attributed partly to the strong solvent-solvent interactions between DMF and ACN with maximum non-ideality near to this solvent composition[12] rather than in pure solvents and partly to the strong solute-solvent interaction in the ternary mixtures affecting the overall viscous process.

8.3.4. *Solvation numbers*

Solvation numbers S_n for the complex Fe^{III}(salen)Cl in the solvent media were calculated from the relation:[50]

$$S_n = B/\phi_V^0 \tag{7}$$

S_n is indicative of the formation of a primary solvation sphere around a solute and the range 0-2.5 for S_n indicates unsolvated solutes in the solution.[50] So an inspection of S_n values given in table 8.6 indicated that the complex remains highly solvated and its solvation further increases in the mixed solvents up to $w_1 = 0.50$ and then decreases to be minimum in pure DMF. S_n values also decrease at higher temperatures; thus it can be concluded that solvent molecules are loosely bound in the primary solvation sphere of the complex Fe^{III}(salen)Cl and thermal agitation at higher temperatures hampers solute-solvent interactions and thus solvated solvent molecules are released in favor of bulk structure more easily at higher temperatures.

8.3.5. *Thermodynamics of viscous flow*

While viscosity *B*-coefficient is very useful, greater insight into viscous flow can be obtained from the thermodynamic activation parameters. According to Eyring and co-workers,[51] the application of statistical thermodynamics to the hole model of viscous flow on the basis on the absolute reaction rate theory yielded the following relation for the free energy of activation for viscous flow per mole of the solvent/solvent mixture, $\Delta\mu_1^{0\neq}$:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_1\phi_{V,1}^0 / hN_A) \tag{8}$$

where N_A , $\phi_{V,1}^0$ are the Avogadro's number and the molar volumes of the solvent, respectively. The other symbols have their usual significances. The above relation was also used for liquid mixtures[51, 52] and when rearranged this relation can be expressed as:

$$\ln(\eta_1\phi_{V,1}^0 / hN_A) = -\frac{\Delta S_1^{0\neq}}{R} + \left(\frac{\Delta H_1^{0\neq}}{R}\right)\frac{1}{T} \tag{9}$$

Table 8.6. Viscosity *B*-coefficients for Fe^{III}(salen)Cl in Different Mixtures of DMF (1) + ACN (2) with Standard Deviations σ for Linear Regression of equation (6) at T = (298.15 to 313.15) K.

Parameters	298.15 K	303.15 K	308.15 K	313.15 K
	$w_1{}^a = 0.00$			
$B \cdot 10^{-6} / \mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	9.333 (±0.147)	8.627 (±0.278)	8.470 (±0.305)	8.267 (±0.364)
$\sigma \cdot 10^{-6} / \mathrm{mPa} \cdot \mathrm{s}$	0.001	0.002	0.002	0.002
S_n	40.95 (±0.86)	38.11 (±1.19)	37.58 (±1.55)	36.82 (±1.85)
	$w_1{}^a = 0.25$			
$B \cdot 10^{-6} / \mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	10.401 (±0.354)	9.560 (±0.292)	9.223 (±0.265)	8.525 (±0.175)
$\sigma \cdot 10^{-6} / \mathrm{mPa} \cdot \mathrm{s}$	0.002	0.002	0.002	0.001
S_n	45.53 (±0.18)	42.10 (±1.53)	40.789 (±1.42)	37.84 (±1.01)
	$w_1{}^a = 0.50$			
$B \cdot 10^{-6} / \mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	11.389 (±0.472)	9.799 (±0.281)	9.317 (±0.351)	8.876 (±0.301)
$\sigma \cdot 10^{-6} / \mathrm{mPa} \cdot \mathrm{s}$	0.003	0.002	0.002	0.002
S_n	48.76 (±2.36)	42.16 (±1.50)	40.15 (±1.87)	38.37 (±1.65)
	$w_1{}^a = 0.75$			
$B \cdot 10^{-6} / \mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	10.935 (±0.594)	10.218 (±0.386)	9.304 (±0.313)	8.952 (±0.417)
$\sigma \cdot 10^{-6} / \mathrm{mPa} \cdot \mathrm{s}$	0.004	0.002	0.002	0.003
S_n	45.98 (±2.54)	43.13 (±1.71)	39.58 (±1.47)	38.12 (±1.89)
	$w_1{}^a = 1.00$			
$B \cdot 10^{-6} / \mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	9.911 (±0.372)	8.662 (±0.317)	8.449 (±0.346)	8.111 (±0.122)
$\sigma \cdot 10^{-6} / \mathrm{mPa} \cdot \mathrm{s}$	0.002	0.002	0.002	0.001
S_n	40.36 (±1.64)	35.48 (±1.49)	34.66 (±1.57)	33.44 (±0.56)

[a] Mass fraction of DMF in the solvent mixtures.

So the values of $\Delta H_1^{0\neq}$ and $\Delta S_1^{0\neq}$ were obtained from a linear regression (with $R^2 \approx$ 0.96512-0.99939) treatment of equation (9). Plots of $\ln(\eta_1 \phi_{V,1}^0 / hN_A)$ against $(10^3 / T)$ is shown in figure 8.5.

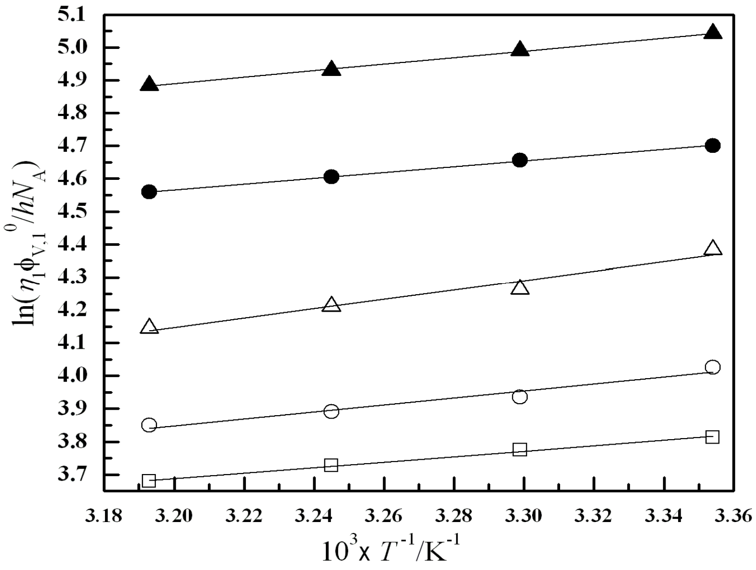

Fig. 8.5. Plots of $\ln(\eta_1\phi_{V,1}^{0}/hN_A)$ against $10^3 \times T^{-1}$ for Fe$^{\mathrm{III}}$(salen)Cl in different DMF (1) + ACN (2) mixtures. Symbol: $w_1 = 0.00$, □; $w_1 = 0.25$, ○; $w_1 = 0.50$, Δ; $w_1 = 0.75$, ●; $w_1 = 1.0$, ▲.

A correlation between viscosity *B*- coefficients and the deviation function, $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ has been suggested by Feakins *et al.*[53] in the form of the following relation:

$$B = (\nu\phi_{V,1}^{0} - \phi_{V,2}^{0}) + \phi_{V,1}^{0}\left(\frac{\Delta\mu_2^{0\neq} - \nu\Delta\mu_1^{0\neq}}{RT}\right) \tag{10}$$

where the coefficient ν is 1 for undissociated uncharged solute. So we have calculated $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values by using the above relation and the *B*- coefficient values obtained from equation (6). Again $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values can also be expressed as:

$$\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT} = -\frac{\Delta S_2^{0\neq} - \Delta S_1^{0\neq}}{R} + \left\{\frac{\Delta H_2^{0\neq} - \Delta H_1^{0\neq}}{R}\right\}\frac{1}{T} \tag{11}$$

where $\Delta S_i^{0\neq}$ and $\Delta H_i^{0\neq}$ are the standard partial molar entropy and enthalpy of activation for viscous flow per mole of i^{th} component in the solution. So a linear regression (with $R^2 \approx 0.87801$-0.98176) treatment of equation (11) provided the values of $(\Delta S_2^{0\neq} - \Delta S_1^{0\neq})$ and $(\Delta H_2^{0\neq} - \Delta H_1^{0\neq})$ from the corresponding slopes and intercept. The parameters $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$ and $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ are reported in table 8.7.

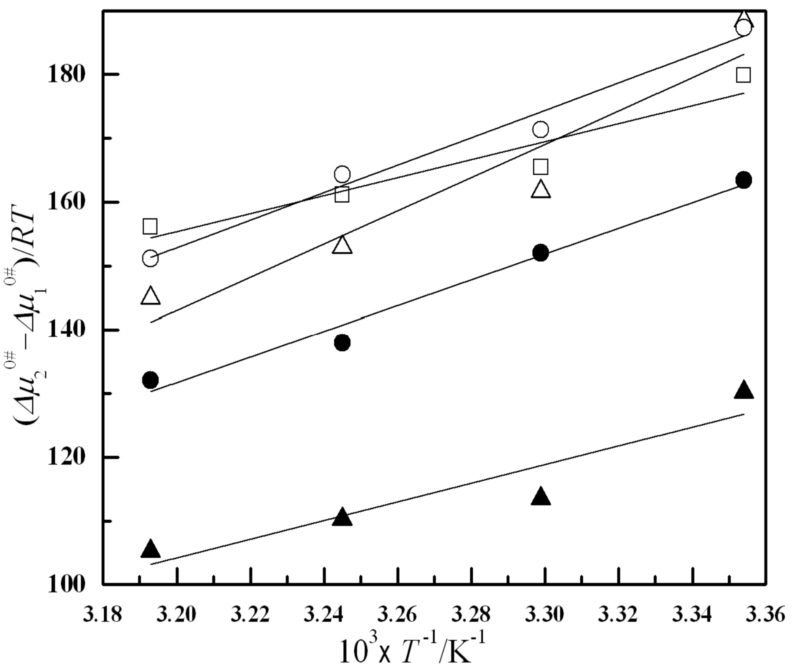

Fig. 8.6. Plots of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/RT$ against $10^3 \cdot T^{-1}$ for Fe$^{\mathrm{III}}$(salen)Cl in different DMF (1) + ACN (2) mixtures. Symbol: w_1 = 0.00, □; w_1 = 0.25, ○; w_1 = 0.50, Δ; w_1 = 0.75, ●; w_1 = 1.0, ▲.

$\Delta H_1^{0\neq}, \Delta H_2^{0\neq}, \Delta S_1^{0\neq}$ and $\Delta S_2^{0\neq}$ are reported in table 8.8. Plots of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/RT$ against ($10^3/T$) is shown in figure 8.6. Table 8.7 shows that $\Delta\mu_1^{0\neq}$ values are almost invariant of temperatures for a solvent composition and are mainly dependent on the viscosity *B*-coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms. The $\Delta\mu_2^{0\neq}$ values contain the change in the free energy of activation of solute molecules in presence of solvent as well as the contribution from the movement of solute molecules. $\Delta\mu_2^{0\neq}$ values are positive and decrease as the temperature increases but increase as the mass fractions (w_1) of DMF in ternary solutions increase up to w_1 = 0.50. Thereafter $\Delta\mu_2^{0\neq}$ values decrease for solvent mixture with w_1 = 0.75 and pure DMF. Such a trend of $\Delta\mu_2^{0\neq}$ values suggests that the viscous flow becomes easier at higher temperature but becomes difficult with increased amount of DMF in the ternary solutions, i.e., the formation of the transition state becomes less favorable at increased mass fraction (w_1) of DMF up to w_1 = 0.50 but higher temperature favors its formation.[51] According to Feakins *et al.*[53] the quantity $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ is the change in the activation energy per mole of solute on replacing one mole of solvent by one mole of solute in an infinite dilution.

Table 8.7. Values of $\Delta\mu_1^{0\neq}$ and ($\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}$) for Fe^{III}(salen)Cl in different mixtures of DMF (1) + ACN (2) at T = (298.15 to 313.15) K

T/K	$\Delta\mu_1^{0\neq}$ / kJ mol^{-1}	$\Delta\mu_2^{0\neq}$ / kJ mol^{-1}	$(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\#})$ / kJ mol^{-1}
	$w_1{}^a = 0.00$		
298.15	9.453 (±0.001)	455.261 (±0.148)	445.809 (±0.148)
303.15	9.513 (±0.001)	426.396 (±0.229)	416.883 (±0.229)
308.15	9.549 (±0.001)	422.281 (±0.306)	412.732 (±0.306)
313.15	9.582 (±0.001)	416.043 (±0.365)	406.461 (±0.366)
	$w_1{}^a = 0.25$		
298.15	9.978 (±0.001)	474.287 (±0.355)	464.309 (±0.355)
303.15	9.920 (±0.001)	441.765 (±0.293)	431.845 (±0.294)
308.15	9.968 (±0.001)	430.939 (±0.266)	420.971 (±0.267)
313.15	10.024 (±0.001)	403.647 (±0.174)	393.624 (±0.177)
	$w_1{}^a = 0.50$		
298.15	10.867 (±0.001)	477.983 (±0.474)	467.116 (±0.474)
303.15	10.746 (±0.001)	418.285 (±0.283)	407.539 (±0.283)
308.15	10.790 (±0.001)	402.548 (±0.353)	391.758 (±0.353)
313.15	10.792 (±0.001)	388.200 (±0.303)	377.408 (±0.303)
	$w_1{}^a = 0.75$		
298.15	11.653 (±0.001)	416.812 (±0.594)	405.159 (±0.595)
303.15	11.734 (±0.001)	395.038 (±0.386)	383.305 (±0.387)
308.15	11.799 (±0.001)	365.241 (±0.314)	353.442 (±0.314)
313.15	11.870 (±0.001)	355.869 (±0.418)	343.999 (±0.418)
	$w_1{}^a = 1.00$		
298.15	12.499 (±0.001)	305.410 (±0.373)	322.911 (±0.373)
303.15	12.579 (±0.001)	298.761 (±0.318)	286.181 (±0.319)
308.15	12.630 (±0.001)	295.179 (±0.347)	282.549 (±0.347)
313.15	12.718 (±0.001)	286.818 (±0.122)	274.100 (±0.123)

[a] Mass fraction of DMF in the solvent mixtures.

Table 8.8. Values of $\Delta H_1^{0\neq}$, $\Delta H_2^{0\neq}$, $\Delta S_1^{0\neq}$ and $\Delta S_2^{0\neq}$ for Fe^{III}(salen)Cl in different mixtures of DMF (1) + ACN (2)

$w_1{}^a$	$\Delta H_1^{0\neq}$ / kJ mol^{-1}	$\Delta H_2^{0\neq}$ / kJ mol^{-1}	$\Delta S_1^{0\neq}$ /J mol^{-1} K^{-1}	$\Delta S_2^{0\neq}$ /J mol^{-1} K^{-1}
0.00	6.924 (±0.024)	1183.499 (±21.289)	-8.508 (±0.079)	2465.253 (±69.685)
0.25	8.885 (±0.102)	1801.514 (±14.794)	-3.557 (±0.333)	4462.147 (±48.427)
0.50	11.950 (±0.128)	2182.762 (±40.728)	3.767 (±0.419)	5761.527 (±32.319)
0.75	7.374 (±0.011)	1687.892 (±14.448)	-14.363 (±0.036)	4268.454 (±47.292)
1.00	8.286 (±0.025)	1228.487 (±27.378)	-14.136 (±0.082)	3024.530 (±89.617)

[a] Mass fraction of Methanol in the solvent mixtures.

The positive $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values and their negative temperature dependence as well as similar trends in viscosity *B*-coefficients (i.e., negative $\partial B/\partial T$) indicated the structure making ability of the solute and the transfer of the solute molecules from the ground state solvent to the transition state solvent is hindered [54]. Table 8.8 shows that the $\Delta H_2^{0\neq}$ values are positive for all the solvent systems and thus indicate rupture and distortion of the solvation bonds or intermolecular forces in the activated state of viscous flow and that the viscous process is endothermic. Thus the viscous flow will be accompanied by a decrease in order and thus positive $\Delta S_2^{0\neq}$ values were obtained.

8.4. Conclusion

In summary, ϕ_V^0 and viscosity *B*-coefficient values for Fe^{III}(salen)Cl in various solvent/solvent mixtures indicate the presence of strong solute-solvent interactions and these interactions are further strengthened with higher mass fractions (w_1) of DMF up to $w_1 = 0.75$ in the ternaries but decrease at higher temperatures. The overall results indicate preferential solvation of Fe^{III}(salen)Cl with DMF rather than with ACN in the ternary solutions and Fe^{III}(salen)Cl acts as a net structure promoter in the ternary solutions.

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CHAPTER IX

Effect of tetrabutylammonium bromide on solution behavior of salicylaldehyde anil zinc (II) in methanol at T = (298.15, 308.15 and 318.15) K*

9.1. Introduction

The rate of a chemical reaction often depends on the nature of solvent or solvent mixture used as reaction media and simply by changing the reaction medium the rate can be changed by factors in powers of 10.[1] Solvents can also influence the mode of crystallization for several transition metal complexes[2] and modify the molecular structures and charge distributions in solution.[3] Such solvent effects can be explained qualitatively with the aid of experimental physical and chemical data of solvents concerned and intermolecular forces[4] operating therein a solution. In solution phase the short and long range solute-solute, solute-cosolute and solute-solvent interactions affect the thermodynamic and transport properties of a solute and these interactions depend on the molecular details of solutes, cosolutes and solvents such as size, shape, dipole moment, steric hindrance, polarizability, donor number or donor strength, etc. Specifically when salt solutions are used as solvent medium, specific solvent-solvent interaction can alter the structural properties of the solutes and thereby influence the solute-solvent interaction; solutions of tetraalkylammonium salts often involve unusual structural effects caused by these organic electrolytes on solvent structure. Tetraalkylammonium halides are bulky in nature and can orient polar molecules around them depending on their alkyl chain. Thus organic electrolytes like tetrabutylammonium bromide (Bu_4NBr) can provide a better insight into the effect of electrostatic and solvophobic interactions in solution phase, because these salts are known to influence macromolecular conformations by weakening attraction or repulsion inter and intra charge-charge interactions and by affecting solvophobic interactions through the side chain of the alkyl groups.

Schiff bases are nitrogen analogs of aldehydes or ketones with their carbonyl groups (C=O) replaced by imine or azomethine (C=N) groups.[5] They find many applications as anti-microbial, anti-fungal, anti-viral, anti-tumor and dying agents, *etc*. They can also be used to obtain optical materials, conducting polymers and pH sensors, etc. Schiff base metal complexes are also of great importance in coordination

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chemistry and homogeneous catalysis.[6] They are often regarded as models of reaction centers for metalloenzymes[7] and nonlinear optical materials.[8] Salicylidene-aniline originating from the condensation of salicylaldehyde with aniline is an interesting Schiff base regarding its uses for constructing optical switches and optical memory devices. Liu *et al.* [9] studied optical properties of SAZ as a new electro-luminescent material in films and ethanol and also characterized its structure and thermal stability by IR-spectra and DTA-TG-analysis. Although information about solute-solvent and solvent-solvent interactions[10-12] for a solute in solution phase are important for a proper understanding of the solution behavior of a solute, to the best of our knowledge such studies on the solute-solute and solute-solvent interactions involving SAZ in various pure and mixed solvents are not available in the literature. Hence in this chapter an attempt has been undertaken to study the nature and degree of the various possible solution phase interactions characterizing the ternary mixtures of SAZ + Bu_4NBr + MeOH as functions of concentrations of SAZ, Bu_4NBr and temperature under ambient pressure.

9.2. Experimental section

9.2.1. *Materials*

A. R. grade zinc acetate ($Zn(O_2CCH_3)_2.2H_2O$), aniline and salicylaldehyde, each of purity > 99% were procured from S. D. Fine Chemicals, India. These chemicals were used without further purification. Spectroscopic grade MeOH (minimum assay, GC > 99.8% with 0.05% of water) was procured from Merck, India and used as received. Bu_4NBr (A. R. grade, Merck, India, purity > 98%) was dissolved in mixed alcohol medium and recrystallised from solvent ether medium[13] and was dried in a vacuum desiccator for few hours. The various binary solvent mixtures were prepared by mass and necessary adjustments were done to achieve exact molar solution (0.00, 0.02, 0.04 and 0.05 $\text{mol}\cdot\text{dm}^{-3}$) of Bu_4NBr in the binary solvent mixtures at 298.15 K. The relative error in solvent composition was about 1%. The physical properties of these binary solvent mixtures are given in table 9.1 and are compared to the literature values whenever available.[12, 14-16]

SA, $C_{13}H_{11}NO$ and SAZ, $C_{26}H_{24}N_2O_4Zn$ were prepared by following literature method[17] with slight modifications and the details of the syntheses and physicochemical characterization of SA and complex SAZ have been described in chapter III. The molecular structures of the ligand SA and the complex SAZ are depicted in figure 9.1. Stock solutions of the complex in different solvent mixtures were prepared by mass and the working solutions were prepared by mass dilution. The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The conversion of molality into molarity was accomplished using experimental density values whenever needed. All working solutions were prepared afresh before use. The uncertainty in molarity of SAZ solutions was evaluated to $\pm 0.0001\,\text{mol}\cdot\text{dm}^{-3}$.

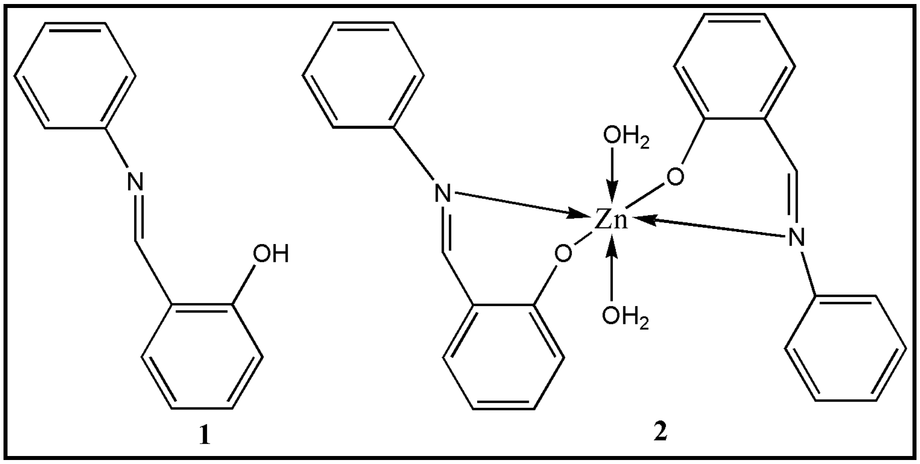

Fig 9.1. Molecular structure of 1) SA and 2) SAZ.

9.2.2. *Apparatus and procedure*

The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M). The densitometer was calibrated at the experimental temperatures with doubly distilled and degassed water and dry air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $\pm 1\times10^{-2}$ K by using the built–in Peltier technique. The estimated uncertainty of the density measurements for most of the solutions was found to be better than $\pm 2\times10^{-5}\,\text{g}\cdot\text{cm}^{-3}$.

The viscosity was measured by means of a suspended Canon-type Ubbelohde viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled, degassed water and purified methanol.[12, 18, 19] It was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow

Table 9.1. Densities (ρ) and viscosities (η) of different mixtures of methanol (1) + Bu_4NBr (2) at T = (298.15 to 318.15) K.

Solvent	T/K	$\rho \cdot 10^{-3}$/kg · m^{-3}		η/mPa·s	
		Expt.	Lit.	Expt.	Lit.
0.00 [a]	298.15	0.78662	0.7866 [12] 0.78645 [14] 0.78659 [15] 0.78656 [16]	0.5451	0.547 [12] 0.542 [14] 0.5446 [15] 0.5422 [16]
	308.15	0.77718	0.7769 [12] 0.77710 [14] 0.77728 [15] 0.77720 [16]	0.476	0.471 [12] 0.469 [14] 0.4747 [15] 0.4742 [16]
	318.15	0.76774	0.76774 [15] 0.76770 [16]	0.4183	0.4185 [15] 0.4174 [16]
0.02 [a]	298.15	0.79069	-	0.5542	-
	308.15	0.78094	-	0.4951	-
	318.15	0.77106	-	0.4390	-
0.04 [a]	298.15	0.79274	-	0.5810	-
	308.15	0.78343	-	0.5135	-
	318.15	0.77392	-	0.4469	-
0.05 [a]	298.15	0.79489	-	0.5973	-
	308.15	0.78533	-	0.5274	-
	318.15	0.77568	-	0.4584	-

[a] Molarity of Bu_4NBr in methanol.

of liquids were recorded with a digital stopwatch correct to ± 0.01s. In all determinations, an average of triplicate measurements was taken into account and adequate precautions were taken to minimize evaporation loses during the actual measurements. The uncertainty in viscosity measurements, based on our work on several pure liquids, was within $\pm 4\times10^{-4}\,\mathrm{mPa\cdot s}$. Details of density and viscosity measurements have been described in chapter III.

The absorption spectra of SAZ in different binary mixtures of Bu_4NBr + MeOH at 298.15 K were recorded on a Jasco V-530 double beam UV-VIS Spectrophotometer. It was coupled with thermostatic arrangement and maintained at 298.15 K. A quartz cell of 1 cm path length was used and spectroscopic grade methanol was used as the reference solvent for all the absorption measurements. Concentrations of Bu_4NBr in different binary mixtures of Bu_4NBr in MeOH were in the range $5.73\text{-}6.54\times10^{-6}\,\mathrm{mol\cdot dm^{-3}}$ and the concentration of SAZ was kept constant at $5\times10^{-5}\,\mathrm{mol\cdot dm^{-3}}$ during the absorption measurements.

9.3. Results and discussion

The experimental molalities (m), densities (ρ), viscosities (η) and derived parameters for the experimental solutions of SAZ in different mixed solvents at various temperatures are reported in table 9.2.

9.3.1. *Standard partial molar volumes*

The apparent molar volumes ϕ_V were obtained from the following relation:

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_1)}{m\rho\rho_1} \tag{1}$$

where M is the molar mass of SAZ, m is the molality of the solution, ρ_1 and ρ are the densities of the solvent and solution, respectively. Uncertainties in ϕ_V values were within the range $0.15 - 0.25 \times 10^{-6}\,\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$. As the plots of ϕ_V against square root of molar concentration ($\sqrt{m}$) were linear, ϕ_V values were fitted to Masson equation:[20]

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \tag{2}$$

where ϕ_V^0 is the partial molar volume at infinite dilution and S_V^* is the experimental slope. The ϕ_V^0 values were determined by fitting the dilute data ($m < 0.1$) to equation (2) by using a least squares regression method and the correlation coefficient (R^2) values were within the range 0.99274-0.99815. The values of ϕ_V^0 and S_V^* at each temperature are reported in table 10.3. Standard errors in ϕ_V^0 and S_V^* values were evaluated by following the rules of error propagation [21] and are given in table 10.3 along with the standard deviations (σ) of linear fit with equal weight to all data points. A perusal of table 10.3 shows that ϕ_V^0 values are positive and increase as both the amount of Bu_4NBr in the ternary mixtures and experimental temperatures increase. This indicates the presence of strong solute-solvent interactions[12, 22] and these interactions are further strengthened at higher temperatures and at enhanced molarities of Bu_4NBr in the ternary mixtures. As partial molar volumes of a solute reflects cumulative effects of different solute-solute, solute-cosolute and solute-solvent interactions in solution, positive ϕ_V^0 values for all the studied solutions may

Table 9.2. Molalities (m), densities (ρ), viscosities (η), and apparent molar volumes (ϕ_V) of SAZ in different mixtures of methanol (1) + Bu$_4$NBr (2) at T = (298.15 to 318.15) K.

$m / \mathrm{kg \cdot mol^{-1}}$	$\rho \cdot 10^{-3} / \mathrm{kg \cdot m^{-3}}$	η/mPa·s	$\phi_V \cdot 10^6 / \mathrm{m^3 \cdot mol^{-1}}$
0.00 ^{a}			
T/K = 298.15			
0.0025	0.78731	0.5497	181.63
0.0041	0.78780	0.5543	162.47
0.0051	0.78813	0.5587	149.06
0.0066	0.78863	0.5633	135.31
0.0081	0.78914	0.5689	124.65
0.0102	0.78987	0.5768	112.44
T/K = 308.15			
0.0025	0.77787	0.4806	178.36
0.0041	0.77836	0.4862	158.73
0.0051	0.77869	0.4895	144.99
0.0066	0.77919	0.4940	130.92
0.0081	0.77970	0.4996	119.99
0.0102	0.78045	0.5063	104.26
T/K = 318.15			
0.0025	0.76843	0.4230	174.87
0.0041	0.76891	0.4273	158.89
0.0051	0.76923	0.4306	147.33
0.0066	0.76974	0.4356	128.83
0.0081	0.77025	0.4396	117.17
0.0102	0.77100	0.4462	100.61
0.02 ^{a}			
T/K = 298.15			
0.0025	0.79137	0.5589	189.37
0.0040	0.79183	0.5634	168.50
0.0051	0.79218	0.5679	157.00
0.0066	0.79267	0.5735	144.39
0.0081	0.79317	0.5792	134.46
0.0101	0.79386	0.5881	122.09
T/K = 308.15			
0.0025	0.78162	0.4998	186.24
0.0040	0.78207	0.5042	168.94
0.0051	0.78241	0.5088	159.48
0.0066	0.78289	0.5132	147.57
0.0081	0.78340	0.5187	133.99
0.0101	0.78411	0.5266	117.28
T/K = 318.15			
0.0025	0.77173	0.4435	189.56
0.0040	0.77218	0.4480	169.30
0.0051	0.77252	0.4523	158.69
0.0066	0.77300	0.4568	145.74
0.0081	0.77349	0.4613	135.48
0.0101	0.77419	0.4690	118.77

Contd…

0.04 [a]			
T/K = 298.15			
0.0025	0.79342	0.5857	190.01
0.0040	0.79388	0.5902	169.24
0.0050	0.79420	0.5947	158.06
0.0066	0.79472	0.6004	145.25
0.0081	0.79523	0.6081	133.41
0.0101	0.79592	0.6171	121.50
T/K = 308.15			
0.0025	0.78411	0.5182	187.06
0.0040	0.78456	0.5227	169.87
0.0050	0.78488	0.5271	157.61
0.0066	0.78539	0.5327	146.18
0.0081	0.78591	0.5383	131.13
0.0101	0.78661	0.5482	116.93
T/K = 318.15			
0.0025	0.77459	0.4522	190.53
0.0040	0.77504	0.4574	170.41
0.0050	0.77536	0.4610	157.01
0.0066	0.77587	0.4660	144.49
0.0081	0.77637	0.4715	132.72
0.0101	0.77706	0.4787	118.60
0.05 [a]			
T/K = 298.15			
0.0025	0.79557	0.6010	190.66
0.0040	0.79603	0.6066	170.01
0.0050	0.79635	0.6111	158.88
0.0065	0.79684	0.6178	146.15
0.0081	0.79738	0.6246	134.37
0.0101	0.79808	0.6357	120.95
T/K = 308.15			
0.0025	0.78600	0.5320	194.16
0.0040	0.78645	0.5365	174.62
0.0050	0.78677	0.5420	161.60
0.0065	0.78726	0.5476	147.07
0.0081	0.78778	0.5553	138.01
0.0101	0.78847	0.5642	124.29
T/K = 318.15			
0.0025	0.77635	0.4630	191.11
0.0040	0.77679	0.4685	175.23
0.0050	0.77710	0.4729	164.38
0.0065	0.77757	0.4784	153.06
0.0081	0.77813	0.4850	133.56
0.0101	0.77881	0.4938	121.14

[a] Molarity of Bu_4NBr in methanol.

originate from different possible interaction like: electrostatic interactions between the local charge on the complex and the dipoles of MeOH as well as hydrogen bond interaction between MeOH and SAZ molecules leading to solvation of the complex SAZ, interlocking packing interactions of the complex with MeOH leading to interstitial packing or caging and other polar-ionic group and polar-polar interactions between different polar and non-polar groups of Bu_4NBr and SAZ. These polar-ionic group and polar-polar interactions plausible for these ternary solutions increase with increasing amount of Bu_4NBr in the solutions and at enhanced experimental temperatures due to more thermal agitation.

The parameter S_V^* is a volumetric viral coefficient and characterizes the pair-wise interactions between the solvated species in the solution. Its sign is determined by the interactions between solute species (solute-solute interactions). Negative values of S_V^* and its trend opposite to the trend in ϕ_V^0 values indicate weak solute-solute interactions[12, 22] in the concentration range of SAZ studied in the ternary solutions and such interactions further decrease at higher temperatures but slightly increase with the advent of Bu_4NBr ($0.02\ \text{mol}\cdot\text{dm}^{-3}$) in MeOH; probably due to sudden perturbation of MeOH structure in presence of Bu_4NBr and dissociation of Bu_4NBr into its ions that distort the hydrogen bonds in MeOH. According to Criss *et al.*[23] the hydrogen bonds between MeOH molecules decrease in comparison to those between MeOH and Br^- ion; this shifts the equilibrium from solvent-solvent to solvent-solute hydrogen bonds and Br^- ion competes more for solvent hydrogen bonds. Although Bu_4N^+ ion enhances the water structure through hydrophobic solvation, [23, 24] structure enhancement is not significant in MeOH in presence of Bu_4NBr[23, 24] and Kustov *et al.*[25] reported that solvophobic solvation effects weaken MeOH bulk structure in presence of Bu_4NBr and thereby promotes solvation of SAZ; thus the trends in ϕ_V^0 values as functions of Bu_4NBr content and temperature for the studied solutions are attributable to increase in solvation of SAZ. Increase in ϕ_V^0 values at enhanced temperatures is probably due to release of solvent molecules from the secondary solvation spheres of SAZ to the bulk solvent structure resulting into the expansion of the solutions.[26, 27] However, regarding this, knowledge of solvation numbers is helpful.

Table 9.3. Standard partial molar volumes (ϕ_V^0), the slopes (S_V^*) and standard deviations (σ) of linear regression of equation (3) for SAZ in different mixtures of methanol (1) + Bu_4NBr (2) at T = (298.15 To 318.15) K.

T/K	$\phi_V^0 \cdot 10^6 / \mathrm{m^3 \cdot mol^{-1}}$	$S_V^* \cdot 10^6 / \mathrm{m^3 \cdot kg^{1/2} \cdot mol^{-3/2}}$	$\sigma \cdot 10^6 / \mathrm{m^3 \cdot mol^{-1}}$
		0.00 [a]	
298.15	249.43 (±0.19)	-1378.99 (±0.88)	1.84
308.15	250.87 (±0.13)	-1459.87 (±0.73)	1.23
318.15	252.03 (±0.16)	-1495.87 (±0.37)	1.99
		0.02 [a]	
298.15	253.12 (±0.17)	-1320.98 (±0.44)	1.71
308.15	254.67 (±0.11)	-1346.39 (±0.45)	1.57
318.15	257.16 (±0.17)	-1370.27 (±0.46)	1.87
		0.04 [a]	
298.15	255.48 (±0.17)	-1350.53 (±0.63)	1.56
308.15	257.11 (±0.17)	-1390.99 (±0.47)	1.20
318.15	259.70 (±0.15)	-1414.20 (±0.56)	1.47
		0.05 [a]	
298.15	257.29 (±0.17)	-1368.34 (±0.72)	1.31
308.15	261.51 (±0.12)	-1382.90 (±0.64)	2.04
318.15	263.77 (±0.14)	-1415.44 (±0.61)	2.22

[a] Molarity of Bu_4NBr in methanol.

The absorption spectra of SAZ in MeOH and various mixed solvents at 298.15 K are depicted in figure 9.2. The absorption spectrum of SAZ in MeOH, which is very much similar to that measured in ethanol reported earlier,[9] has three peaks at 226, 296 and 382 nm. These peaks are due to $\pi \rightarrow \pi^*$ transitions of the phenyl ring, $\pi \rightarrow \pi^*$ transitions of azomethine group (C=N) and charge transfer between phenyl ring and azomethine (C=N) group, respectively. The blue shift of the absorption peaks when compared to those of SAZ films were attributed by Liu *et al.*[9] to hydrogen bond interactions between alcohol and SAZ molecules in the mixtures. Hydrogen bond interactions stabilize the ground state of SAZ in MeOH but due to electron delocalization the excited state becomes less stable and such interactions become weakened. Thus SAZ molecules are asymmetric and polar[9] in nature. Figure 9.2 shows that as the molarity of Bu_4NBr in the ternary solutions increase all the three peaks of SAZ suffered hypochromic shifts and the peak at 382 nm (originated from the charge transfer between phenyl ring and azomethine (C=N) group) becomes very weak for higher concentrations of Bu_4NBr in MeOH used during the absorption measurements and becomes almost a shoulder. Such variation of the spectra measured

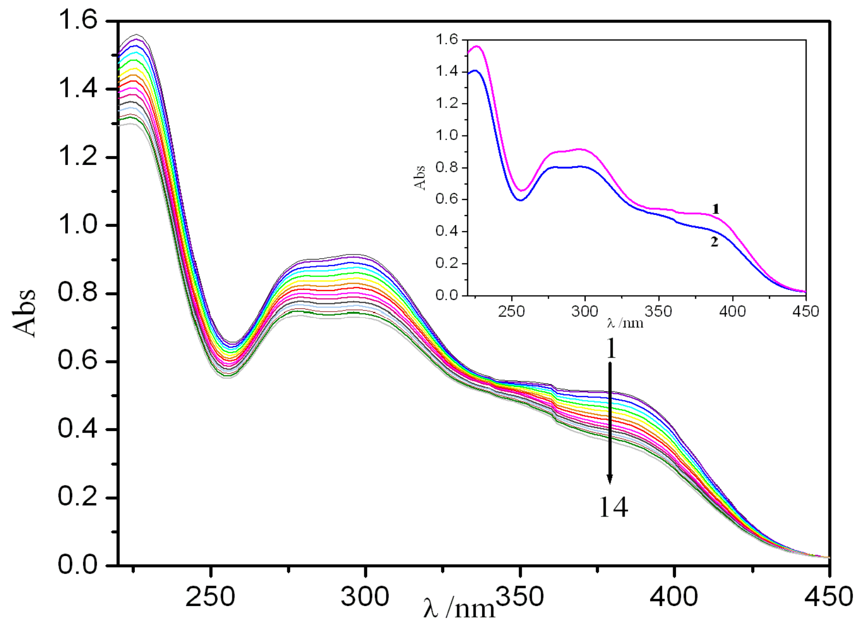

Figure 9.2. Changes in the UV-Visible absorption spectra of SAZ solutions in different mixtures of Bu_4NBr with MeOH at 298.15 K: SAZ in pure MeOH, 1; SAZ in different mixtures of Bu_4NBr + MeOH with Bu_4NBr concentrations ($\text{mol}\cdot\text{dm}^{-3}$): 2, 6.40×10^{-6}; 3, 6.34×10^{-6}; 4, 6.28×10^{-6}; 5, 6.22×10^{-6}; 6, 6.16×10^{-6}; 7, 6.10×10^{-6}; 8, 6.04×10^{-6}; 9, 5.99×10^{-6}; 10, 5.94×10^{-6}; 11, 5.88×10^{-6}; 12, 5.83×10^{-6}; 13, 5.77×10^{-6}; 14, 5.73×10^{-6}. Inset: 1, SAZ in pure MeOH; 2: average absorption spectra of SAZ in different mixtures of Bu_4NBr with MeOH at 298.15 K.

for SAZ in different mixtures of Bu_4NBr and MeOH reflects changes in the solvation sphere of the SAZ[28] in the ternary mixtures.

9.3.2. *Partial molar volume of transfer*

To understand the nature of solute-cosolute interactions (SAZ-Bu_4NBr interactions) we have calculated the partial molar volume of transfer ($\Delta_t\phi_V^0$) from the following relation:

$$\Delta_t\phi_V^0 = \phi_V^0(\text{SAZ} + \text{Bu}_4\text{NBr} + \text{MeOH}) - \phi_V^0(\text{SAZ} + \text{MeOH}) \quad (3)$$

$\Delta_t\phi_V^0$ values (as depicted in figure 9.3 as a function molarity of Bu_4NBr) are positive and increase as both the molarity of Bu_4NBr and experimental temperatures increase for the ternary solutions.

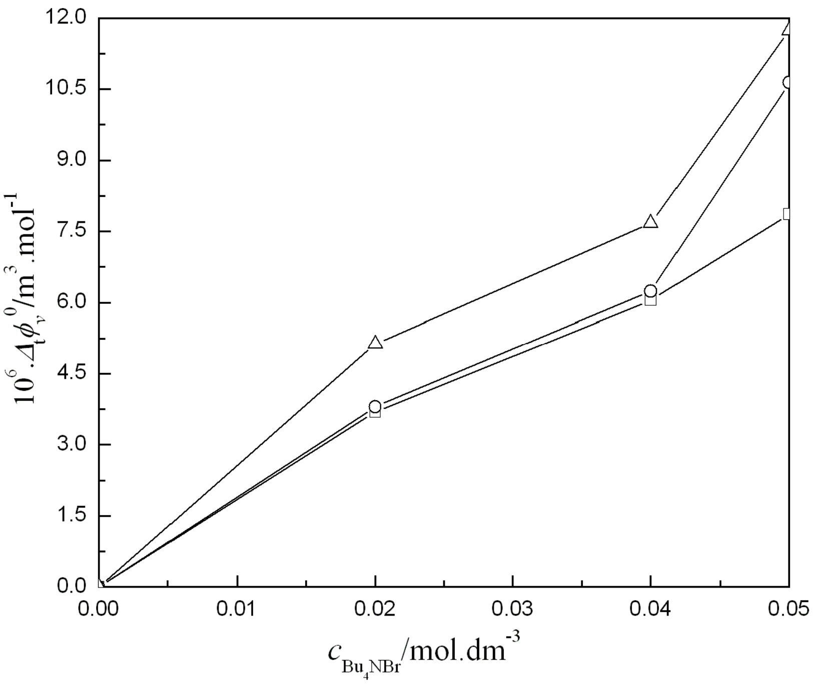

Fig 9.3. Plots of the partial molar volume of transfer ($\Delta_t\phi_V^0$) for SAZ solutions against molarities of Bu4NBr ($c_{\mathrm{Bu_4NBr}}$) in MeOH. Symbols *T*/K: 298.15 (□); 308.15 (○); 318.15 (Δ).

$\Delta_t\phi_V^0$, by definition, is free from solute-solute interactions (SAZ-SAZ interactions) and provides some information about solute-cosolute interactions. According to the cosphere overlap model[29] interactions between SAZ and Bu4NBr molecules can be categorized as follows: (i) the polar–ionic group interactions, (ii) polar-polar group interactions, (iii) polar-non-polar group interactions and (iv) nonpolar-nonpolar group interactions between SAZ and Bu4NBr. While interactions of types (iii) and (iv) lead to negative $\Delta_t\phi_V^0$ values, interactions of types (i) and (ii) lead to positive $\Delta_t\phi_V^0$ values. Thus the positive $\Delta_t\phi_V^0$ values for the ternary solutions studied indicate the dominance of polar–ionic group and polar-polar interactions over polar-non-polar and non-polar-non-polar group interactions between SAZ and MeOH. Positive $\Delta_t\phi_V^0$ values also stand in support of fact the presence of Bu4NBr promotes solvation of SAZ by weakening MeOH bulk structure;[25] thus decrease solvent-solvent interactions in favor of solute-solvent interactions.

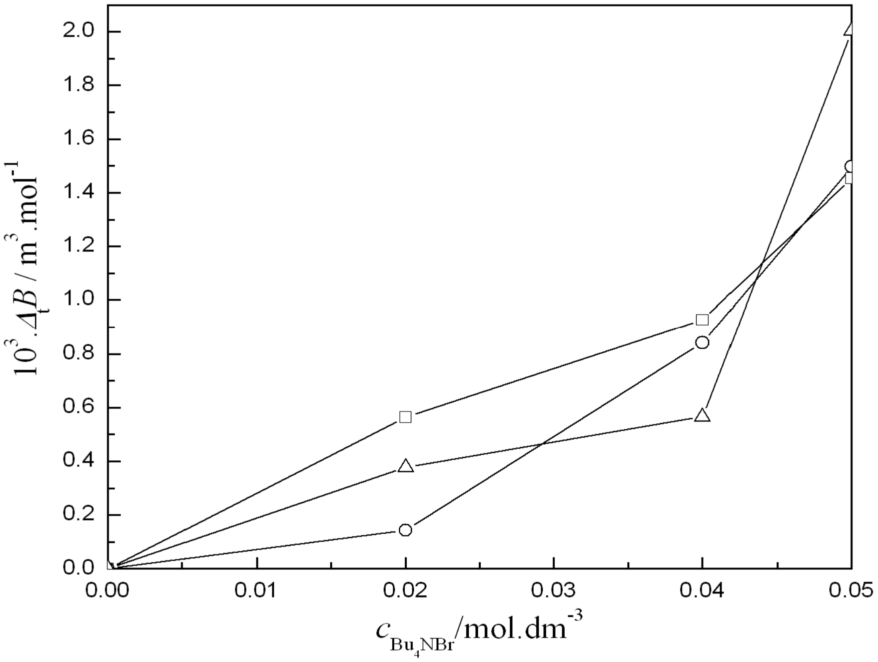

Figure 9.4. Plots of viscosity *B*-coefficient of transfer ($\Delta_t B$) for SAZ solutions against molarities of Bu4NBr ($c_{\mathrm{Bu_4NBr}}$) in MeOH. Symbols *T*/K: 298.15 (□); 308.15 (○); 318.15 (Δ).

9.3.3. *Partial molar expansibilities*

The apparent molar expansibilities (ϕ_E) of SAZ solutions were determined by using the relation:[30]

$$\phi_E = \alpha\phi_V + \frac{1000(\alpha - \alpha_1)}{m\rho_1} \tag{4}$$

where α and α_1 are the coefficients of isobaric thermal expansion of the solvent and solution, respectively and other symbols have their usual significance. α and α_1 are defined as: $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$ and $\alpha_1 = -\rho_1^{-1}(\partial\rho_1/\partial T)_P$; The uncertainty in the coefficients of isobaric thermal expansion was $\pm 5\times10^{-6}\,\mathrm{K}^{-1}$ and the uncertainty in ϕ_E values was within $\pm 0.003\times10^{-6}\,\mathrm{m}^3\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$, respectively. The partial molar expansibilities (ϕ_E^0) were determined from the relation: [30]

$$\phi_E = \phi_E^0 + S_E\sqrt{m} \tag{5}$$

$(\partial\phi_E^0/\partial T)_P$ values were obtained from the slope of a linear fit of ϕ_E^0 values against experimental temperature (T) with the correlation coefficient (R^2) values within the range (0.96338-0.99999). The ϕ_E^0 values for different experimental solutions at different temperatures are listed in table 9.4. It reveals that ϕ_E^0 values are negative and decrease further as the temperature increases but increase as Bu_4NBr content increases for all the solutions. These facts may be attributed to structural perturbation influenced by the gradual appearance or disappearance of caging/packing effect[31, 32] as the Bu_4NBr content increases in the ternary solutions or as the temperature of the solutions increases, respectively.

According to Hepler[33] the sign of $(\partial\phi_E^0/\partial T)_P$ is a better criterion in characterizing the long-range structure making or breaking ability of a solute in solution phase. If the $(\partial\phi_E^0/\partial T)_P$ values are negative the solute acts as a structure breaker, otherwise it acts as a structure maker. The $(\partial\phi_E^0/\partial T)_P$ values (given in table 9.4) for different ternary solutions are negative. As the overall structure of the solvents is controlled not only by the solute (SAZ) but also by the cosolute (Bu_4NBr), the negative $(\partial\phi_E^0/\partial T)_P$ values obtained for 0.00, 0.02 and 0.04 $\mathrm{mol\cdot dm^{-3}}$ Bu_4NBr solutions indicate SAZ to be a net structure breaker due to distortion of hydrogen bonds in MeOH bulk structure and its solvation by MeOH. However, the small positive $(\partial\phi_E^0/\partial T)_P$ value obtained for 0.05 $\mathrm{mol\cdot dm^{-3}}$ Bu_4NBr solutions may probably arises from the overall structure making effect[31] of Bu_4NBr at this concentration.

9.3.4. *Viscometric results*

The viscosity values (η) for the solutions can be analyzed with the Jones-Dole equation[34] for dilute solutions:

$$\eta/\eta_1 = \eta_r = 1 + A\sqrt{c} + Bc \qquad (6)$$

where $\eta_r = \eta/\eta_1$; η_1, η and $\sqrt{c}$ are the viscosities of solvents and solutions and square root of molar concentration of the solute in the studied solutions, respectively. The constants *A* and *B* are referred to as the viscosity *A*- and *B*- coefficients generally estimated by a least squares regression method. According to Falkenhagen,[35] *A*-coefficient values for uncharged solutes are zero. Actually the values of *A*-coefficients were found to be zero or very close to zero within the experimental errors when equation (6) was fitted to the experimental viscosities.

Table 9.4. Partial molar expansibility (ϕ_E^0), its temperature dependence $(\partial\phi_E^0/\partial T)_P$, the slope ($S_E$) of equation (5) for SAZ in different mixtures of methanol (1) + Bu_4NBr (2) at T = (298.15 to 318.15) K.

Solvent	$\phi_E^0 \cdot 10^{-4}$ $/\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$			$S_E \cdot 10^{-4}$ $/\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$			$\left(\frac{\partial \phi_E^0}{\partial T}\right)_p \cdot 10^{-6}$ $/\mathrm{m^3 \cdot mol^{-1} \cdot K^{-2}}$
	T/K = 298.15	T/K = 308.15	T/K = 318.15	T/K = 298.15	T/K = 308.15	T/K = 318.15	
0.00 [a]	-1.687 (±0.001)	-1.749 (±0.001)	-1.816 (±0.001)	-39.368 (±0.003)	-41.097 (±0.003)	-42.332 (±0.003)	-0.642 (±0.010)
0.02 [a]	-1.141 (±0.001)	-1.189 (±0.001)	-1.230 (±0.001)	-7.432 (±0.002)	-7.729 (±0.002)	-8.013 (±0.002)	-0.448 (±0.014)
0.04 [a]	-0.948 (±0.001)	-0.988 (±0.001)	-1.019 (±0.002)	-14.671 (±0.001)	-15.312 (±0.001)	-15.765 (±0.002)	-0.355 (±0.014)
0.05 [a]	0.055 (±0.001)	0.070 (±0.002)	0.060 (±0.001)	-6.287 (±0.003)	-6.416 (±0.003)	-6.765 (±0.004)	0.021 (±0.013)

[a] Molarity of Bu_4NBr in methanol. Standard errors are given the parenthesis.

Hence the experimental viscosities were fitted to the following linear regression relation (with $R^2 \approx 0.99436 - 0.99972$) giving equal weights to all the viscosities:[36]

$$\eta = C^{/} + B^{/} c \qquad (7)$$

where $B^{/}$ and $C^{/}$ are constants; $C^{/}$ values were found to agree with the observed η_1 values within the experimental error limit and $B^{/}$ is related to *B*- coefficients by the following relation: [36]

$$B = B^{/} / C^{/} \qquad (8)$$

The viscosity *B*-coefficient[37, 38] provides another avenue into the effects of solute-solvent interactions on the solution viscosity similar to ϕ_V^0. Table 9.5 shows that viscosity *B*-coefficients are positive and increase as the amount of Bu_4NBr in the ternary mixtures increase. Also such values in a particular solvent mixture increase with a rise in experimental temperatures (positive $\partial B / \partial T$). These results thus reflect the long-range restriction of the motion of the solvent molecules through ion-dipole interactions and the ternary solutions are characterized by strong solute-solvent interaction and SAZ can be considered as a structure breaker for the solutions[39] as previously indicated by $(\partial \phi_E^0 / \partial T)_P$ values.

9.3.5. *Solvation numbers*

Solvation numbers S_n for the complex SAZ in the solvent media were calculated from the relation:[39]

$$S_n = B / \phi_V^0 \qquad (9)$$

S_n is indicative of the formation of a primary solvation sphere around a solute. The range $S_n \approx 0 - 2.5$ indicates unsolvated solutes in the solution[39] but higher values of S_n indictes solvated solutes with primary solvation sphere. So an inspection of S_n values given in table 9.6 indicated that the complex remains highly solvated with primary solvation spheres and its solvation further increases with an increase in Bu_4NBr-content in the ternary solutions and experimental temperatures. Thus it can be concluded that Bu_4NBr promotes the solvation of SAZ and also weakens the hydrogen bonded bulk structure of MeOH and thus favors concomitant increase in ϕ_V^0 values.

Table 9.5. Values of $C^{/}/\eta_1$ and viscosity *B*-coefficients for SAZ in different mixtures of methanol (1) + Bu_4NBr (2) with standard deviations σ for linear regression of equation (7) at T = (298.15 to 318.15) K.

Parameters	T/K = 298.15	T/K = 308.15	T/K = 318.15
		0.00^{a}	
$B\cdot10^3/\mathrm{m}^3\cdot\mathrm{mol}^{-1}$	8.353 (±0.015)	9.081 (±0.064)	9.509 (±0.090)
$C^{/}/\eta_1$	0.99119	0.99244	0.99283
$\sigma\cdot10^4/\mathrm{mPa\cdot s}$	4.26	1.54	1.87
		0.02^{a}	
$B\cdot10^3/\mathrm{m}^3\cdot\mathrm{mol}^{-1}$	8.917 (±0.202)	9.224 (±0.170)	9.886 (±0.183)
$C^{/}/\eta_1$	0.98953	0.99051	0.99112
$\sigma\cdot10^4/\mathrm{mPa\cdot s}$	5.69	4.57	4.04
		0.04^{a}	
$B\cdot10^3/\mathrm{m}^3\cdot\mathrm{mol}^{-1}$	9.280 (±0.298)	9.923 (±0.308)	10.075 (±0.103)
$C^{/}/\eta_1$	0.98761	0.98812	0.99239
$\sigma\cdot10^4/\mathrm{mPa\cdot s}$	8.78	7.90	2.32
		0.05^{a}	
$B\cdot10^3/\mathrm{m}^3\cdot\mathrm{mol}^{-1}$	9.806 (±0.279)	10.579 (±0.243)	11.512 (±0.184)
$C^{/}/\eta_1$	0.98510	0.98635	0.98735
$\sigma\cdot10^4/\mathrm{mPa\cdot s}$	8.39	6.41	4.17

[a] Molarity of Bu_4NBr in methanol. Standard errors are given the parenthesis.

Also increase in ϕ_V^0 values at higher temperatures is due to release of solvent molecules from the secondary solvation spheres of SAZ to the bulk solvent structure resulting into the expansion of the solutions[26, 27] as well as expansion of the primary solvation sphere; although such expansion may be reduced to some extent by electrostriction of the solvent by Bu_4NBr.

9.3.6. *Viscosity B-coefficient of transfer*

Similar to $\Delta_t\phi_V^0$, viscosity *B*-coefficient of transfer ($\Delta_t B$) is free from solute-solute interactions and provides information about solute-cosolute interactions. $\Delta_t B$ values can be calculated from the following relation:

$$\Delta_t B = B(\mathrm{SAZ}+\mathrm{Bu_4NBr}+\mathrm{MeOH}) - B(\mathrm{SAZ}+\mathrm{MeOH}) \qquad (10)$$

$\Delta_t B$ values for the ternary solutions studied were depicted a function molarity of Bu_4NBr in figure 9.4. Positive $\Delta_t B$ values indicate that SAZ molecules are in more structural environment in presence of Bu_4NBr than in MeOH; which is attributable to structure making characteristics of Bu_4NBr.

Table 9.6. Values of $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$ and solvation numbers (S_n) for SAZ in different mixtures of methanol (1) + Bu$_4$NBr (2) at T = (298.15 to 318.15) K.

Parameters	T/K = 298.15	T/K = 308.15	T/K = 318.15
		0.00 [a]	
$\Delta\mu_1^{0\neq}$ / kJ·mol^{-1}	9.962 (±0.006)	9.980 (±0.007)	9.994 (±0.008)
$\Delta\mu_2^{0\neq}$ / kJ·mol^{-1}	531.012 (±0.018)	587.343 (±0.066)	626.022 (±0.093)
S_n	33.48 (±0.48)	36.19 (±0.56)	37.72 (±0.87)
		0.02 [a]	
$\Delta\mu_1^{0\neq}$ / kJ·mol^{-1}	10.008 (±0.006)	10.087 (±0.007)	10.130 (±0.008)
$\Delta\mu_2^{0\neq}$ / kJ·mol^{-1}	564.405 (±0.205)	595.109 (±0.173)	648.452 (±0.185)
S_n	35.23 (±1.21)	36.22 (±1.05)	38.44 (±0.99)
		0.04 [a]	
$\Delta\mu_1^{0\neq}$ / kJ·mol^{-1}	10.137 (±0.006)	10.191 (±0.007)	10.186 (±0.008)
$\Delta\mu_2^{0\neq}$ / kJ·mol^{-1}	584.053 (±0.301)	636.160 (±0.310)	658.326 (±0.106)
S_n	36.32 (±1.55)	38.59 (±1.51)	38.79 (±0.78)
		0.05 [a]	
$\Delta\mu_1^{0\neq}$ / kJ·mol^{-1}	10.207 (±0.006)	10.262 (±0.007)	10.257 (±0.008)
$\Delta\mu_2^{0\neq}$ / kJ·mol^{-1}	615.521 (±0.281)	676.256 (±0.246)	748.201 (±0.188)
S_n	38.11 (±1.42)	40.45 (±1.47)	43.64 (±1.33)

[a] Molarity of Bu$_4$NBr in methanol. Standard errors are given the parenthesis.

Regarding solute-cosolute interactions $\Delta_t B$ values originate from interactions of Bu$_4$NBr with polar/non-polar groups of SAZ. The overall results obtained on the basis of $\Delta_t B$ values depend on the modification of solvent structure by the cosolute as well as size, shape and orientation of solute molecules in solution and the decrease in $\Delta_t B$ values for solutions with 0.04 $\mathrm{mol \cdot dm^{-3}}$ of Bu$_4$NBr at 308.15 and 318.15 K is probably due to solvophobic solvation of SAZ.

9.3.7. *Thermodynamics of viscous flow*

The viscosity values were also used for calculating the Gibbs free energy of activation per mole of solute ($\Delta\mu_2^{0\neq}$) and Gibbs free energy of activation per mole of solvent ($\Delta\mu_1^{0\neq}$) according to transition sate theory proposed by Feakins *et al.*[37, 40] According to this theory viscosity *B*- coefficient is given by the relation,

$$B = (\nu\phi_{V,1}^0 - \phi_{V,2}^0) + \phi_{V,1}^0\left(\frac{\Delta\mu_2^{0\neq} - \nu\Delta\mu_1^{0\neq}}{RT}\right) \tag{11}$$

where the coefficient ν is 1 for undissociated uncharged solute and other symbols have their usual meanings. Equation (11) rearranges to give the Gibbs free energy of activation per mole of the solute, $\Delta\mu_2^{0\neq}$

$$\Delta\mu_2^{0\neq} = \nu\Delta\mu_1^{0\neq} + [B - (\nu\phi_{V,1}^0 - \phi_{V,2}^0)](\phi_{V,1}^0 / RT) \tag{12}$$

The Gibbs free energy of activation per mole of the solvent ($\Delta\mu_1^{0\neq}$) has been calculated by using Eyring viscosity relation, [38]

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_1\phi_{V,1}^0 / hN_A) \tag{13}$$

where N_A , $\phi_{V,1}^0$ are the Avogadro's number and the molar volumes of the solvent, respectively. The other symbols have their usual significances. For the binary mixtures of Bu_4NBr + MeOH, used as solvents, $\phi_{V,1}^0$ is taken as the mole fraction average of molecular weights of Bu_4NBr and MeOH normalized by densities at the experimental temperatures. So we have calculated $\Delta\mu_2^{0\neq}$ values by using equation (12) and the *B*- coefficient values obtained from equation (8). The parameters $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ are given in table 9.6. Table 9.6. shows that $\Delta\mu_1^{0\neq}$ is almost invariant of the solvent compositions and temperatures, implying that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity *B*-coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms. The values $\Delta\mu_2^{0\neq}$ contain the change in the free energy of activation of solute molecules in presence of solvent as well as the contribution from the movement of solute molecules. $\Delta\mu_2^{0\neq}$ values are positive and much greater than $\Delta\mu_1^{0\neq}$ for all the solvent mixtures at all the experimental temperatures suggesting that the interactions between SAZ and MeOH molecules in the ground state are stronger than in the transition state. Hence in the transition state solvation of SAZ is less favored in free energy terms. Also $\Delta\mu_2^{0\neq}$ values increase as the temperature and Bu_4NBr-content in ternary solutions increase. Such a trend of $\Delta\mu_2^{0\neq}$ values suggests that the viscous flow becomes more difficult due to increase in solute-solvent interactions with increased amount of Bu_4NBr at higher temperatures.[38]

Also the positive $\Delta\mu_2^{0\neq}$ values and their positive temperature dependence as well as similar trends in viscosity *B*-coefficients (positive $\partial B/\partial T$) indicate the structure breaking ability of the solute[39] and the transfer of the solute molecules from the ground state solvent to the transition state solvent is hindered.

9.4. Conclusion

In summary, ϕ_V^0 and viscosity *B*-coefficient values for SAZ indicate the presence of strong solute-solvent interactions and these interactions are further strengthened at higher temperatures for higher content of Bu_4NBr in the ternaries. Also, SAZ acts as a net structure breaker in the ternary solutions with Bu_4NBr concentrations up to 0.05 $\mathrm{mol \cdot dm^{-3}}$.

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CHAPTER X

Non-covalent interactions between {N, N$^/$-bis[(2-pyridinyl)methylene]-1, 2-benzenediamine]-bis(nitrato)}Cu(II) with pyridoxine hydrochloride in methanol at *T* = (298.15, 308.15 and 318.15) K

10.1. Introduction

The non-covalent interactions in condensed phase greatly influence various physical, chemical and biological processes.[1]Among all non-covalent interactions hydrogen bond interaction deserves a special place[2] and plays a significant role in substrate–enzyme binding[3] and determines the specificity of DNA molecule.[4] Such non-covalent interactions regulate the structure and reactivity of supramolecular assemblies[5] and control association of molecules in condensed phase.[6] Pyridoxine (vitamin B_6) is a constituent of the enzyme system concerned with transamination and decarboxylation of amino acids and it has been paid special attention in clinical and pharmaceutical lines because of its extensive and essential applications in bio-metabolisms. It is reported that vitamin B_6 and its derivatives have major influence in gene modulation, sexual behavior, cancer research, and immune modulation in HIV-1 infection[7-10] and its deficiency leads to neurological and neuromuscular disorders.[11] On the other hand Schiff bases are considered as "privileged ligands" for their very simple preparative procedure and wide variety of biological actions such as antibacterial, antifungal, herbicidal, clinical and analytical activities by virtue of azomethine linkage.[12-13] Among many potential materials, Schiff base metal complexes and their activities are under the subject of extensive and continuous studies. These complexes are important for their involvement in a diverse range of fields such as organic synthesis[14-17], liquid crystals[18], and heterogeneous catalysis.[19] Copper, as an essential element for human with its bio-essential activity and oxidative nature, has attracted numerous inorganic chemists to address Cu(II) complexes with the aim of medical applications.[20] Copper complexes were extensively studied in recent years due to their flexibility, facile preparation and capacity of stabilizing unusual oxidation states.[21-22] Again pyridine derivatives play important roles in many bio-chemical reactions and one such compound is 2-pyridinecarboxaldehyde involved in enzyme reactions[23-24] and it has received much attention[25] during the last decade.

Thus exploration and designing novel molecules capable of interacting with nucleic acids and triggering apoptosis is currently one of the most promising strategies for the discovery of novel DNA-targeted anticancer drugs.[26-27] Among the various non-aqueous solvents methanol is the simplest amphiphilic hydrogen bonding solvent like water but possessing methyl group and can mimic solvophobic/hydrophobic interactions with special relevance to biophysical chemistry[28-30] It is one of the best examples of self-associated liquids by hydrogen bonds. Solute molecules can remain completely H-bonded in methanol environment and their reactivity is many-a-time largely determined by the thermodynamic parameters that are affected by H-bonding.

Hence in the present chapter we selected pyridoxine hydrochloride, {N, $N^{/}$-bis[(2-pyridinyl)methylene]-1, 2-benzenediamine]-bis(nitrato)}Cu(II), abbreviated as $CuL(NO_3)_2$ as solutes and MeOH as the solvent to study their mutual interaction in solution phase by a combination of volumetric, viscometric and spectrophotometric methods at 298.15, 308.15 and 318.15 K under ambient pressure. It is because information about solute-solvent, solute-cosolute and solvent-solvent interactions in solution phase are of fundamental importance regarding the solution behavior and may be crucial factors in improving varied activities of a solute/cosolute like catalytic, optical, anti-microbial, anti-fungal, anti-viral, anti-tumor and dying, etc. However, no study on the solute-solute and solute-solvent interactions involving the complex $CuL(NO_3)_2$ with pyridoxine hydrochloride in various pure and mixed solvents is available in the literature.

10.2. Experimental section

10.2.1. *Materials*

A. R. grade Copper nitrate trihydrate $Cu(NO_3)_2.3H_2O$, 1,2-phenylenediamine and 2-pyridinecarboxaldehyde and pyridoxine hydrochloride, each of purity > 99% were procured from S. D. Fine Chemicals, India. These chemicals, except pyridoxine hydrochloride, were used as received from the vendors without further purification. Pyridoxine hydrochloride was taken in a darkened glass bottle and kept in a vacuum desiccator over fused $CaCl_2$ for several hrs before use. Spectroscopic grade MeOH (minimum assay, GC > 99.8% with 0.05% of water) was procured from Merck, India and used as received. The various binary solvent mixtures were prepared by mass and necessary adjustments were done to achieve exact molar solution (0.01, 0.02 and 0.03

$mol \cdot dm^{-3}$) of pyridoxine hydrochloride in the binary solvent mixtures at 298.15 K. The relative error in solvent composition was about 1%. The physical properties of these binary solvent mixtures are given in table 10.1 and are comparable to the literature values whenever available.[31-34]

The Cu(II) complex was prepared by following a literature method[35] and the details of the synthesis and physicochemical characterization of Cu(II) complex has been described in chapter III. The molecular structures of the complex and pyridoxine hydrochloride are depicted in figure 10.1. Stock solutions of the complex in different solvent mixtures were prepared by mass and the working solutions were prepared by mass dilution. The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The conversion of molality into molarity was accomplished using experimental density values whenever needed. All solutions were prepared afresh before use. The uncertainty in molarity of $CuL(NO_3)_2$ solutions was evaluated to $\pm 0.0001 \ mol \cdot dm^{-3}$.

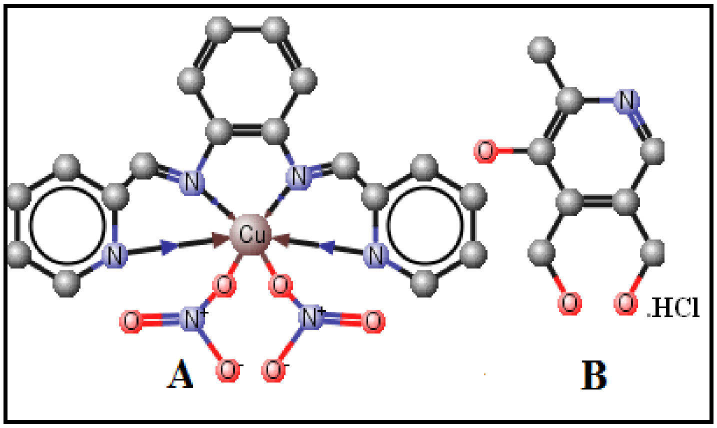

Fig. 10.1. Molecular structure of A) $CuL(NO_3)_2$ and B) pyridoxine hydrochloride.

10.2.2. *Apparatus and procedure*

The densities were measured with a vibrating-tube density meter (Anton Paar, DMA 4500M). The densitometer was calibrated at the experimental temperatures with doubly distilled, degassed water and dry air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $\pm 1 \times 10^{-2}$ K by using the built–in Peltier technique. The estimated uncertainty of the density measurements for most of the solutions was found to be better than $\pm 2\times10^{-5}\,\mathrm{g\cdot cm^{-3}}$.

The viscosity was measured by means of a suspended Canon-type Ubbelohde viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled, degassed water and purified methanol.[36-38] It was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a digital stopwatch correct to ± 0.01s. In all determinations, an average of triplicate measurements was taken into account and adequate precautions were taken to minimize evaporation loses during the actual measurements. The uncertainty in viscosity measurements, based on our work on several pure liquids, was within $\pm 4\times10^{-4}\,\mathrm{mPa\cdot s}$. Details of density and viscosity measurements have been described in chapter III.

Table 10.1. Densities (ρ) and viscosities (η) of different mixtures of methanol (1) + pyridoxine hydrochloride (2) at T = (298.15 to 318.15) K

$w_2{}^a$	T/K	$\frac{\rho\cdot10^{-3}}{\mathrm{kg\cdot m^{-3}}}$		$\frac{\eta}{\mathrm{mPa\cdot s}}$	
		Expt.	Lit.	Expt.	Lit.
0.00	298.15	0.78667	0.78645 [31] 0.7866 [32] 0.78659 [33] 0.78656 [34]	0.5430	0.542 [31] 0.547 [32] 0.5446 [33] 0.5422 [34]
	308.15	0.77718	0.77710 [31] 0.7769 [31] 0.77728 [32] 0.77720 [33]	0.4708	0.469 [31] 0.471 [32] 0.4747 [33] 0.4742 [34]
	318.15	0.76775	0.76774 [33] 0.76770 [34]	0.4194	0.4185 [33] 0.4174 [34]
0.01	298.15	0.78907		0.5562	
	308.15	0.77865		0.4853	
	318.15	0.76925		0.4275	
0.02	298.15	0.78994		0.5621	
	308.15	0.77985		0.4955	
	318.15	0.77018		0.4468	
0.03	298.15	0.79086		0.5712	
	308.15	0.78083		0.5034	
	318.15	0.77113		0.4640	

[a]Molarity of pyridoxine hydrochloride in methanol.

The absorption spectra of $CuL(NO_3)_2$ in presence of pyridoxine hydrochloride in MeOH were recorded on Jasco V-530 double beam UV-VIS Spectrophotometer. It was coupled with thermostatic arrangement and maintained at 298.15 K. A quartz cell of 1 cm path length was used and spectroscopic grade methanol was used as the reference solvent for all the absorption measurements. During spectrophotometric titration, 2.0 mL of $CuL(NO_3)_2$ solution ($5.0\times10^{-5}\,\text{mol}\cdot\text{L}^{-1}$) was placed in the quartz cell and the absorbance of the solution was measured. Then 10 μL of a methanolic solution of pyridoxine hydrochloride ($1.3\times10^{-3}\,\text{mol}\cdot\text{L}^{-1}$) was added in a stepwise fashion through a 10μL pre-calibrated Hamilton syringe. The absorbance of the solution was measured at each step. The stoichiometry of the resulting species was examined by the mole ratio method.

10.3. Results and discussion

The experimental molalities *m*, densities ρ, viscosities η, and derived parameters for the experimental solutions of $CuL(NO_3)_2$ in different mixed solvents at various temperatures are reported in table 10.2.

10.3.1. *Standard partial molar volumes*

The apparent molar volumes ϕ_V were obtained from the following relation:

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho-\rho_1)}{m\rho\rho_1} \tag{1}$$

where *M* is the molar mass of $CuL(NO_3)_2$, *m* is the molality of the solution, ρ_1 and ρ are the densities of the solvent and solution, respectively. As apparent molar volumes (ϕ_V) follow a linear correlation with the square roots of molalities ($\sqrt{m}$) of $CuL(NO_3)_2$ at each investigated temperature the limiting apparent molar volumes or standard partial molar volume (ϕ_V^0) and the slopes (S_V^*) were obtained from the Masson equation:[39]

$$\phi_V = \phi_V^0 + S_V^*\sqrt{m} \tag{2}$$

by fitting the ($\sqrt{m}, \phi_V$) data by using least square linear regression with the correlation coefficient (R^2) values lying in the range 0.98895-0.99974.

Table 10.2. Molalities (m), densities (ρ), viscosities (η), and apparent molar volumes (ϕ_V) of $\mathrm{CuL(NO_3)_2}$ in mixtures of methanol (1) + pyridoxine hydrochloride (2) at T = (298.15 to 318.15) K

$\frac{m}{\mathrm{mol\cdot kg^{-1}}}$	$\frac{\rho\cdot 10^{-3}}{\mathrm{kg\cdot m^{-3}}}$	$\frac{\eta}{\mathrm{mPa\cdot s}}$	$\frac{\phi_V\cdot 10^{6}}{\mathrm{m^{3}\cdot mol^{-1}}}$
0.00^{a}			
T/K = 298.15			
0.0051	0.78754	0.5478	326.35
0.0071	0.78790	0.5522	321.92
0.0102	0.78847	0.5590	316.48
0.0133	0.78906	0.5667	311.04
0.0163	0.78964	0.5755	306.77
0.0204	0.79047	0.5856	299.91
T/K = 308.15			
0.0051	0.77806	0.4755	323.68
0.0071	0.77842	0.4789	320.06
0.0102	0.77899	0.4855	315.19
0.0133	0.77957	0.4901	311.25
0.0163	0.78015	0.4967	306.88
0.0204	0.78095	0.5035	302.29
T/K = 318.15			
0.0051	0.76864	0.4282	320.77
0.0071	0.76900	0.4316	318.00
0.0102	0.76957	0.4360	313.75
0.0133	0.77015	0.4395	310.10
0.0163	0.77073	0.4440	305.86
0.0204	0.77153	0.4497	301.37
0.01^{a}			
T/K = 298.15			
0.0051	0.78994	0.5610	326.19
0.0071	0.79029	0.5666	324.05
0.0102	0.79087	0.5743	316.38
0.0132	0.79144	0.5821	311.23
0.0163	0.79204	0.5910	306.73
0.0204	0.79287	0.6011	299.91
T/K = 308.15			
0.0051	0.77953	0.4922	323.60
0.0071	0.77989	0.4955	320.00
0.0102	0.78046	0.5011	315.15
0.0132	0.78103	0.5078	310.23
0.0163	0.78164	0.5144	304.84
0.0204	0.78243	0.5212	301.49
T/K = 318.15			
0.0051	0.77013	0.4385	324.04
0.0071	0.77049	0.4428	320.35
0.0102	0.77106	0.4473	315.38
0.0132	0.77162	0.4518	311.63
0.0163	0.77221	0.4563	307.94
0.0204	0.77300	0.4610	303.87

Contd…

0.02[a]			
T/K = 298.15			
0.0051	0.79081	0.5690	326.13
0.0071	0.79116	0.5746	324.00
0.0102	0.79174	0.5823	316.34
0.0132	0.79232	0.5912	309.99
0.0163	0.79294	0.6011	303.77
0.0204	0.79375	0.6102	299.13
T/K = 308.15			
0.0051	0.78073	0.5044	323.54
0.0071	0.78109	0.5089	319.95
0.0102	0.78166	0.5165	315.12
0.0132	0.78223	0.5222	310.21
0.0163	0.78285	0.5278	303.83
0.0204	0.78365	0.5357	299.88
T/K = 318.15			
0.0051	0.77106	0.4577	324.00
0.0071	0.77142	0.4621	320.32
0.0102	0.77200	0.4666	313.71
0.0132	0.77256	0.4722	310.34
0.0163	0.77316	0.4767	305.87
0.0204	0.77396	0.4824	301.40
0.03[a]			
T/K = 298.15			
0.0051	0.79173	0.5771	326.07
0.0071	0.79208	0.5826	323.94
0.0101	0.79265	0.5914	315.10
0.0132	0.79325	0.6014	308.75
0.0162	0.79385	0.6092	302.93
0.0203	0.79469	0.6225	296.09
T/K = 308.15			
0.0051	0.78171	0.5113	323.49
0.0071	0.78207	0.5179	319.91
0.0101	0.78263	0.5235	313.84
0.0132	0.78323	0.5302	307.71
0.0162	0.78382	0.5368	302.99
0.0203	0.78462	0.5468	299.20
T/K = 318.15			
0.0051	0.77201	0.4708	323.96
0.0071	0.77238	0.4752	317.91
0.0101	0.77294	0.4797	312.40
0.0132	0.77353	0.4863	307.78
0.0162	0.77412	0.4929	302.94
0.0203	0.77492	0.4986	299.06

[a] Molarity of pyridoxine hydrochloride in methanol

In equation (2) ϕ_V^0 stands for the partial molar volume at infinite dilution or standard partial molar volume and is, by definition, free from solute-solute interactions and provides a measure of solute-solvent and solute-cosolute interactions; the experimental slope S_V^* provides information regarding solute-solute interaction. The values of ϕ_V^0 and S_V^* along with their standard errors at each temperature are reported in table 10.3. Standard errors were evaluated by following the rules of error propagation.[40]

Table 10.3. Standard partial molar volumes (ϕ_V^0), the slopes (S_V^*) and corresponding standard deviations (σ) for $CuL(NO_3)_2$ in different mixtures of methanol (1) + pyridoxine hydrochloride (2) at T = (298.15 To 318.15) K

T/K	$\phi_V^0 \cdot 10^6$ / $m^3 \cdot mol^{-1}$	$S_V^* \cdot 10^6$ / $m^3 \cdot kg^{1/2} \cdot mol^{-3/2}$	$\sigma \cdot 10^6$ / $m^3 \cdot mol^{-1}$
		0.00[a]	
298.15	352.81 (±0.90)	-364.76 (±8.23)	0.54
308.15	345.31(±0.47)	-299.65 (±4.23)	0.28
318.15	340.88 (±0.88)	-273.05 (±7.98)	0.52
		0.01[a]	
298.15	354.40 (±1.55)	-376.75 (±14.15)	0.93
308.15	346.88 (±1.06)	-320.76 (±9.62)	0.63
318.15	344.15 (±0.20)	-282.98 (±1.85)	0.12
		0.02[a]	
298.15	356.39 (±1.91)	-403.40 (±17.40)	1.14
308.15	348.65 (±1.41)	-341.67 (±12.85)	0.84
318.15	346.74 (±0.75)	-318.96 (±6.81)	0.45
		0.03[a]	
298.15	359.17 (±1.91)	-440.28 (±17.41)	1.14
308.15	349.39 (±1.17)	-357.72 (±10.64)	0.69
318.15	347.91 (±1.20)	-348.60 (±10.91)	0.71

[a]Molarity of pyridoxine hydrochloride in methanol.
Standard errors are given the parenthesis

Table 10.3 shows that ϕ_V^0 values are positive and increases as the amount of pyridoxine hydrochloride in the ternary mixtures increase. Also ϕ_V^0 values for a particular solvent mixture decreases with a rise in experimental temperatures. These trends in ϕ_V^0 values indicate that strong solute-solvent interactions[36, 41] characterize the systems under study and these interactions are further strengthened at higher molarities of pyridoxine hydrochloride but decreases with a rise in experimental temperatures. Such trends in ϕ_V^0 values is probably due to the solvation behavior of solute, $CuL(NO_3)_2$ and cosolute (pyridoxine hydrochloride) molecules due to different types of interactions like: (a) different probable hydrogen bond interactions between solute/cosolute and the solvent molecules, (b) the overlap of solvation co-spheres of $CuL(NO_3)_2$ and pyridoxine hydrochloride resulting in volume change. Such overlap of the solvation cospheres of the solute and cosolute in the present study results in enhancement of ϕ_V^0 values and justifies the presence of strong solute-solvent and solute-cosolute interactions. Such overlap also releases some solvated methanol molecules and thus favors hydrogen bond associated methanol bulk structure. However, the decrease in ϕ_V^0 values at higher temperatures for $CuL(NO_3)_2$ in (methanol + pyridoxine hydrochloride) solution indicates the rupturing of the hydrogen bond interactions between the solutes and solvent molecules due to thermal effects. The dependence of ϕ_V^0 values on the solvent composition and temperature is shown in figure 10.2. The negative S_V^* values and their reversed trend in comparison to those followed by ϕ_V^0 values indicate weak solute-solute and cosolute-cosolute interactions[36-42] at the studied concentration range of solute, cosolute in solution phase.

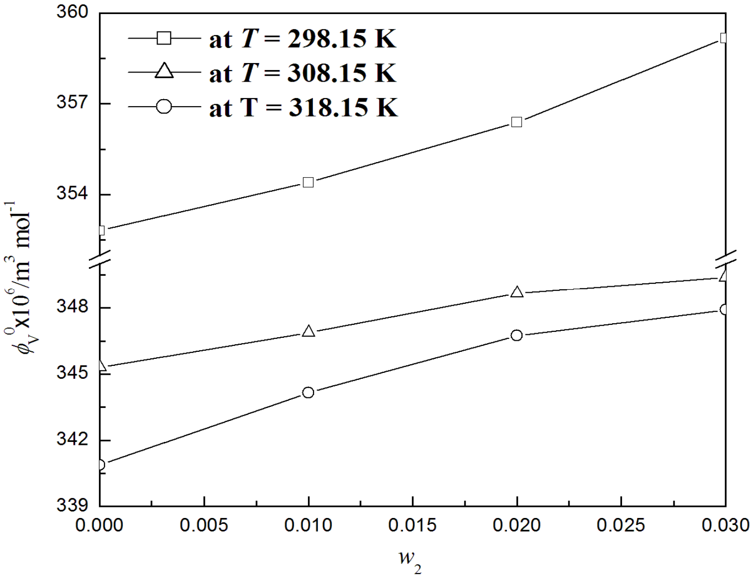

Fig. 10.2. Dependence of standard partial molar volumes (ϕ_V^0) on the solvent composition (w_2) at T = (298.15-318.15) K.

The absorption spectra of $CuL(NO_3)_2$ and pyridoxine hydrochloride in methanol at 298.15 K is shown in figure 10.3. The $CuL(NO_3)_2$ in methanol showed a maximum absorption at 330 nm and this may be attributed to $n \longrightarrow \pi^*$ transition between the phenyl ring and the azomethanine moiety. The UV absorption of the complex, $CuL(NO_3)_2$ suffered a blue shift on successive addition of pyridoxine hydrochloride. The shift in absorbance of complex is indicative of interaction with pyridoxine hydrochloride. Also the pyridoxine hydrochloride showed a maximum absorption λ_{max} at 286 nm and this absorption maxima is red shifted to around 290 nm on interaction with $CuL(NO_3)_2$. The stoichiometry of the probable hydrogen bond complex between $CuL(NO_3)_2$ and pyridoxine hydrochloride was examined by mole ratio method at λ_{max} = 328 nm (shown in figure 10.4).

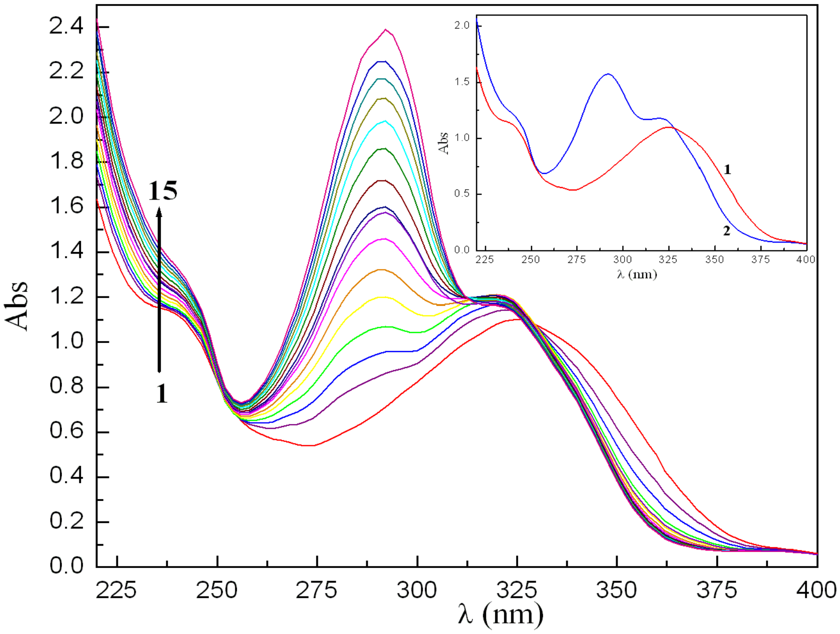

Fig. 10.3. Changes in the UV-Visible absorption spectra of $CuL(NO_3)_2$ solutions in different MeOH (1) + pyridoxine hydrochloride (2) mixtures at 298.15 K.: $CuL(NO_3)_2$ in pure MeOH, 1; $CuL(NO_3)_2$ in different MeOH (1) + pyridoxine hydrochloride (2) mixtures with pyridoxine hydrochloride concentrations ($mol \cdot dm^{-3}$): 2, 5.62×10^{-5}; 3, 6.24×10^{-5}; 4, 6.85×10^{-5}; 5, 7.45×10^{-5}; 6, 8.05×10^{-5}; 7, 8.64×10^{-5}; 8, 9.23×10^{-5}; 9, 9.81×10^{-5}; 10, 10.38×10^{-5}; 11, 10.95×10^{-5}; 12, 11.51×10^{-5}; 13, 12.07×10^{-5}; 14, 12.36×10^{-5}; 15, 13.18×10^{-5}; 15, 13.72×10^{-5}. Inset: 1, $CuL(NO_3)_2$ in pure MeOH; 2: average of absorption spectra (1 to 15) at 298.15 K.

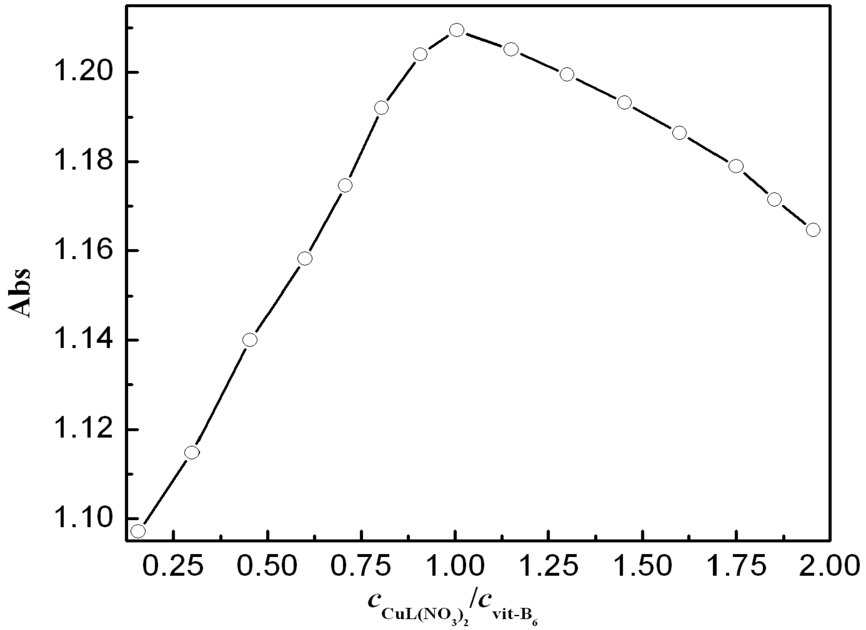

Fig. 10.4. Absorption versus mole-ratio plot showing 1:1 hydrogen bonded association of $CuL(NO_3)_2$ and pyridoxine hydrochloride in MeOH.

It is evident from figure 10.4 that 1:1 type of interaction occurs between $CuL(NO_3)_2$ and pyridoxine hydrochloride. The absorbance-mole ratio data were fitted to Benesi-Hildebrand equation,[43] which further supports the 1:1 type interaction between the studied solutes by specific interaction, i.e., hydrogen bond interaction and the formation constant ($\log k_f$) was calculated to be 5.83 at 298.15 K. however, from the absorbance-mole ratio plot (figure 10.4) it is evident that the H-bond complex species dissociates after reaching the 1:1 stoichiometry upon successive addition of pyridoxine hydrochloride and this indicates that the H-bond complex species is rather weak. Figure 10.5 depicts a schematic representation of 1:1 hydrogen bonding interactions between the solutes studied in methanol.

10.3.2. *Partial molar volume of transfer*

$\Delta_t\phi_V^0$, by definition, is free from solute-solute interactions and provides some information about solute-cosolute interactions. Hence we have calculated the partial molar volume of transfer ($\Delta_t\phi_V^0$) from the following relation:

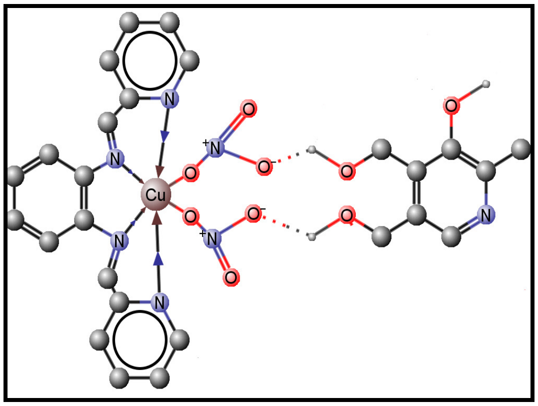

Fig. 10.5. Schematic representation of 1:1 hydrogen bond interactions between the complex $CuL(NO_3)_2$ and pyridoxine hydrochloride.in methanol.

$$\begin{aligned}\Delta_t\phi_V^0 = {} & \phi_V^0[\mathrm{CuL(NO_3)_2} + \text{Pyridoxine hydrochloride} + \mathrm{MeOH}] \\ & - \phi_V^0[\mathrm{CuL(NO_3)_2} + \mathrm{MeOH}] \qquad (3)\end{aligned}$$

$\Delta_t\phi_V^0$ values (depicted in figure 10.6 as a function molarity of pyridoxine hydrochloride) are positive and increase as both the molarity of pyridoxine hydrochloride and experimental temperatures for the ternary solutions. The interactions between $CuL(NO_3)_2$ and pyridoxine hydrochloride molecules can be categorized as follows: (i) the polar–ionic group interactions, (ii) polar-polar group interactions, (iii) polar-non-polar group interactions and (iv) non-polar-non-polar group interactions between $CuL(NO_3)_2$ and pyridoxine hydrochloride. According to the cosphere overlap model[44] while interactions of types (iii) and (iv) lead to negative $\Delta_t\phi_V^0$ values, interactions of types (i) and (ii) lead to positive $\Delta_t\phi_V^0$ values. Thus the positive $\Delta_t\phi_V^0$ values for the ternary solutions studied indicate the dominance of polar–ionic group and polar-polar interactions over polar-non-polar and non-polar-non-polar group interactions between $CuL(NO_3)_2$ and pyridoxine hydrochloride. Also the concomitant increase in the transfer volumes ($\Delta_t\phi_V^0$) at higher concentrations of pyridoxine hydrochloride arises from greater polar-ionic groups and polar-polar group interactions with increased concentrations of pyridoxine hydrochloride. Although $\Delta_t\phi_V^0$ values decrease little bit at 308.15 K for all the solvent compositions studied, these values increased much sharply at 318.15 K indicating that polar-ionic group and polar-polar group interactions superceded temperature effects in characterizing the ternary solutions.

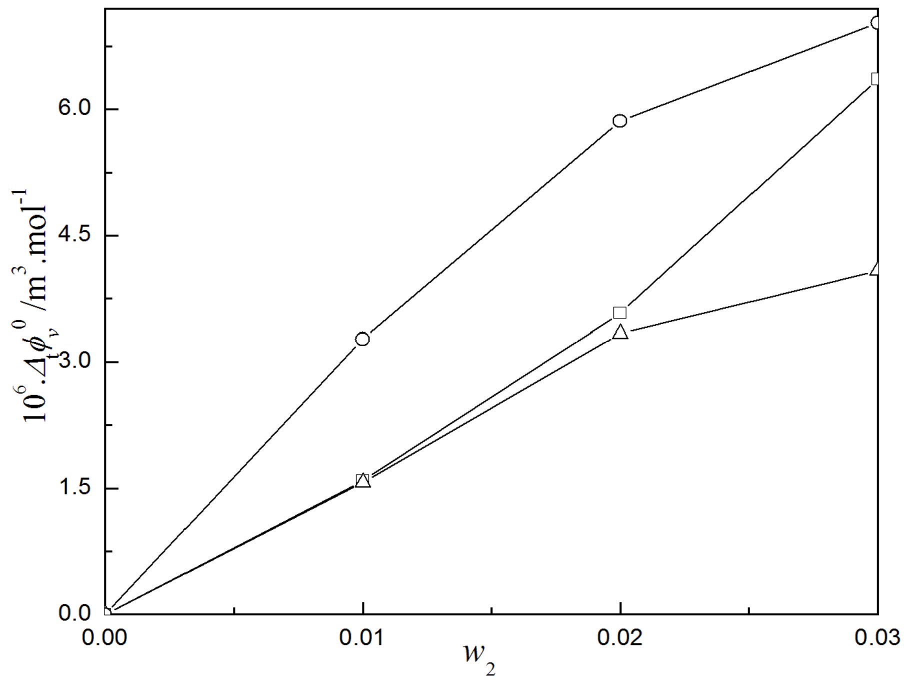

Fig. 10.6. Plots of partial molar volumes of transfer ($\Delta_t\phi_V^0$) from MeOH to (MeOH + pyridoxine hydrochloride) solutions for $CuL(NO_3)_2$ at different temperatures. Symbols: □, 298.15 K; Δ, 308.15 K; ○, 318.15 K.

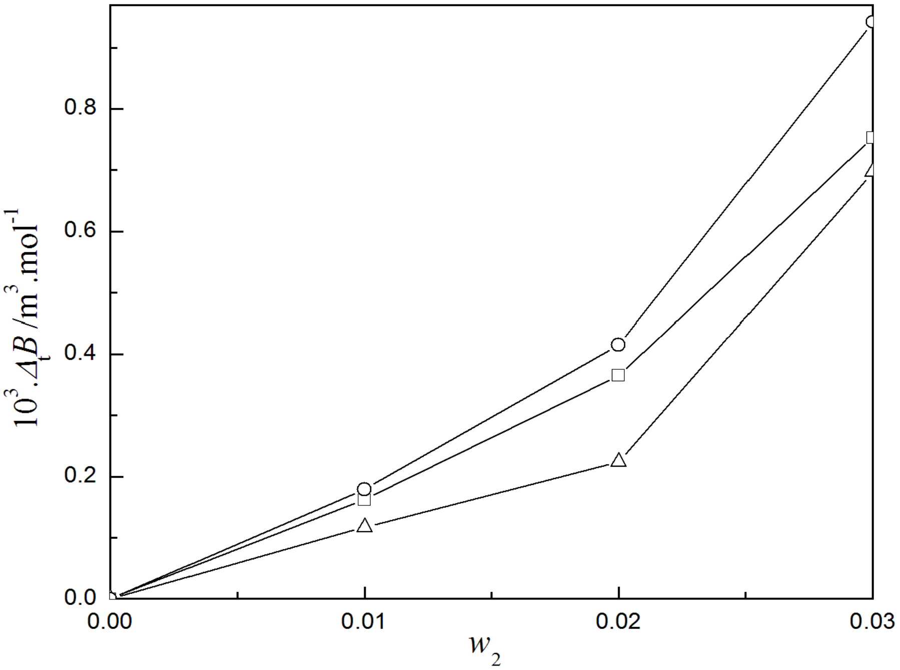

Fig. 10.7. Plots of viscosity *B*-coefficients of transfer ($\Delta_t B$) from MeOH to (MeOH + pyridoxine hydrochloride) solutions for $CuL(NO_3)_2$ at different temperatures. Symbols: □, 298.15 K; Δ, 308.15 K; ○, 318.15 K.

However, standard partial molar volume of a solute reflects a overall result of several solute-solute and solute-solvent interactions prevailing in solutions like: electrostatic interactions between the local charge on the complex and the dipole moment of MeOH, interlocking packing interactions of the complex with MeOH leading to interstitial packing or caging as well as solvation, and other polar-ionic group (H-bonding) interactions between different polar and non-polar groups of $CuL(NO_3)_2$ and pyridoxine hydrochloride; all these interactions can characterize the overall state of the solutions studied.

10.3.3. *Partial molar expansibilities*

The apparent molar expansibilities (ϕ_E) of $CuL(NO_3)_2$ solutions were determined by using the relation: [39]

$$\phi_E = \alpha\phi_V + \frac{1000(\alpha - \alpha_1)}{m\rho_1} \qquad (4)$$

where α and α_1 are the coefficients of isobaric thermal expansion of the solvent and solution, respectively and other symbols have their usual significance. α and α_1 are defined as: $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$ and $\alpha_1 = -\rho_1^{-1}(\partial\rho_1/\partial T)_P$; The uncertainty in the coefficients of isobaric thermal expansion was $\pm 5\times10^{-6}\,\mathrm{K}^{-1}$ and the uncertainty in ϕ_E values was within $\pm 0.002\text{-}0.022\times10^{-6}\,\mathrm{m}^3\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$, respectively. The partial molar expansibilities (ϕ_E^0) were determined from the relation: [45]

$$\phi_E = \phi_E^0 + S_E\sqrt{m} \qquad (5)$$

$(\partial\phi_E^0/\partial T)_P$ values were obtained from the slope of a linear fit of ϕ_E^0 values against experimental temperature T with the coefficient of regression (R^2) values within the range (0.99428-0.99961). The ϕ_E^0 values for different experimental solutions at different temperatures are listed in table 10.4. It reveals that ϕ_E^0 values are negative and increases as the content of pyridoxine hydrochloride increases for all the solutions except those with 0.03 $\mathrm{mol\cdot dm^{-3}}$ of pyridoxine hydrochloride. However, such values decrease as the experimental temperatures increase. These facts may be attributed to structural perturbation influenced by the gradual disappearance or appearance of caging/packing

Table 10.4. Partial molar expansibilities (ϕ_E^0) for $CuL(NO_3)_2$ in mixtures of methanol (1) + pyridoxine hydrochloride (2) at T = (298.15 to 318.15) K

Solvent	$\frac{\phi_E^0 \cdot 10^{-3}}{m^3 \cdot mol^{-1} \cdot K^{-1}}$			$\frac{S_E \cdot 10^{-3}}{m^3 \cdot kg^{1/2} \cdot mol^{-1} \cdot K^{-1}}$			$\frac{\left(\frac{\partial \phi_E^0}{\partial T}\right)_p \cdot 10^{-5}}{m^3 \cdot mol^{-1} \cdot K^{-2}}$
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	
0.00[a]	-0.981 (±0.033)	-1.020 (±0.035)	-1.056 (±0.036)	4.804 (±0.303)	5.006 (±0.317)	5.168 (±0.325)	-0.372 (±0.004)
0.01[a]	-0.920 (±0.079)	-0.960 (±0.084)	-0.992 (±0.086)	4.920 (±0.724)	5.131 (±0.762)	5.310 (±0.782)	-0.365 (±0.013)
0.02[a]	-0.893 (±0.095)	-0.932 (±0.098)	-0.963 (±0.102)	4.510 (±0.865)	4.713 (±0.896)	4.867 (±0.933)	-0.352 (±0.012)
0.03[a]	-0.971 (±0.140)	-1.014 (±0.145)	-1.048 (±0.151)	4.898 (±1.28)	5.136 (±1.33)	5.284 (±1.38)	-0.382 (±0.017)

[a] Molarity of pyridoxine hydrochloride in methanol. Standard errors are given the parenthesis

effect[46, 47] as the pyridoxine hydrochloride content increases in the ternary solutions or as the experimental temperatures increase, respectively.

According to Helper[48] the sign of $\left(\partial \phi_E^0 / \partial T\right)_P$ is a better criterion in characterizing the long-range structure making or breaking ability of a solute in solution phase. If the $\left(\partial \phi_E^0 / \partial T\right)_P$ values are small negative or positive, the solute acts as a structure maker, otherwise it acts as a structure breaker. The $\left(\partial \phi_E^0 / \partial T\right)_P$ values (given in table 10.4) for different ternary solutions are small negative; thus $CuL(NO_3)_2$ acts as a net structure maker for the solutions by favoring hydrogen bonded bulk structure of MeOH in presence of pyridoxine hydrochloride.

10.3.4. *Viscometric results*

As the complex $CuL(NO_3)_2$ behaves as a non-eletrolyte,[35] solution viscosities (η) were analyzed with the modified Jones-Dole equation:[49]

$$\eta_r = 1 + Bc \qquad (6)$$

where $\eta_r = \eta / \eta_1$; η_1, η and c are viscosities of the solvents, viscosities of the solutions and molar concentration of the solute in the studied solutions, respectively. The viscosity *B*- coefficients were estimated by least squares linear regression analysis.

The viscosity *B*-coefficient [50, 51] provides another avenue into the effects of solute-solvent interactions on the solution viscosity similar to ϕ_V^0 and *B*-coefficients give a measure of structural modification induced by the solute-solvent interactions. Table 10.5 shows that viscosity *B*-coefficients are positive and increase as the amount of pyridoxine hydrochloride in the ternary mixtures increase but decrease with a rise in the experimental temperatures. These results thus reflect strong solute–cosolute and solute-solvent interactions in the ternary solutions. The $\left(\partial B / \partial T\right)$ values are also negative and indicate that the complex acts as a structure maker for the solutions as previously indicated by small negative $\left(\partial \phi_E^0 / \partial T\right)_P$ values.

Table 10.5. Viscosity *B*-coefficients for $CuL(NO_3)_2$ with the correlation coefficients (R^2), standard deviations (σ) for linear regression of equation (6) along with the solvation number (S_n) in different mixtures of methanol (1) + pyridoxine hydrochloride (2) at T = (298.15-318.15) K

Parameters	298.15 K	308.15 K	318.15 K
		0.00^a	
$\frac{B\cdot 10^3}{m^3\cdot mol^{-1}}$	5.861 (±0.106)	5.078 (±0.093)	4.292 (±0.076)
R^2	0.98805	0.99801	0.99813
σ	0.001	0.001	0.001
S_n	16.61 (±0.34)	14.71 (±0.29)	12.59 (±0.25)
		0.01^a	
$\frac{B\cdot 10^3}{m^3\cdot mol^{-1}}$	6.023 (±0.049)	5.195 (±0.103)	4.471 (±0.145)
R^2	0.99960	0.99766	0.99374
σ	0.001	0.001	0.002
S_n	16.99 (±0.21)	14.98 (±0.34)	12.99 (±0.43)
		0.02^a	
$\frac{B\cdot 10^3}{m^3\cdot mol^{-1}}$	6.226 (±0.121)	5.302 (±0.126)	4.707 (±0.117)
R^2	0.99773	0.99664	0.99627
σ	0.001	0.001	0.001
S_n	17.47 (±0.39)	15.21 (±0.42)	13.57 (±0.39)
		0.03^a	
$\frac{B\cdot 10^3}{m^3\cdot mol^{-1}}$	6.614 (±0.084)	5.775 (±0.140)	5.234 (±0.157)
R^2	0.99904	0.99647	0.99465
σ	0.001	0.001	0.002
S_n	18.42 (±0.33)	16.53 (±0.46)	15.04 (±0.50)

[a] Molarity of pyridoxine hydrochloride in methanol.
Standard errors are given the parenthesis

Similar to $\Delta_t \phi_V^0$, $\Delta_t B$ is free from solute-solute interactions and is another avenue for solute-cosolute interactions. $\Delta_t B$ values can be had from the following relation:

$$\Delta_t B = B[\mathrm{CuL(NO_3)_2} + \mathrm{Pyridoxine\ \ hydrochloride} + \mathrm{MeOH}] \\ - B[\mathrm{CuL(NO_3)_2} + \mathrm{MeOH}] \qquad (7)$$

$\Delta_t B$ values for the ternary solution studied have been depicted in figure 10.7 as a function molarity of pyridoxine hydrochloride and simply reinforces the trends in $\Delta_t \phi_V^0$ values discussed earlier.

10.3.5. *Thermodynamics of viscous flow*

According to Eyring and co-workers,[51] the application of statistical thermodynamics to the hole model of viscous flow on the basis on the absolute reaction rate theory yielded the following relation for the free energy of activation for viscous flow per mole of the solvent/solvent mixture, $\Delta\mu_1^{0\neq}$:

$$\Delta\mu_1^{0\neq} = RT\ln(\eta_1 \phi_{V,1}^0 / hN_A) \tag{8}$$

where N_A , $\phi_{V,1}^0$ are the Avogadro's number and the molar volumes of the solvent, respectively. The other symbols have their usual significances. For the binary mixtures of pyridoxine hydrochloride + MeOH (used as solvents), $\phi_{V,1}^0$ is taken as the mole fraction average of molecular weights of pyridoxine hydrochloride and MeOH normalized by densities at the experimental temperatures. When rearranged for solvent mixtures the above relation can also be expressed as: [50, 51]

$$\ln(\eta_1 \phi_{V,1}^0 / hN_A) = -\frac{\Delta S_1^{0\neq}}{R} + \left(\frac{\Delta H_1^{0\neq}}{R}\right)\frac{1}{T} \tag{9}$$

So the values of $\Delta H_1^{0\neq}$ and $\Delta S_1^{0\neq}$ were obtained from a linear regression treatment (with $R^2 \approx 0.99768\text{-}0.99999$) of equation (9). Plots of $\ln(\eta_1 \phi_{V,1}^0 / hN_A)$ against $(10^3/T)$ are shown in figure 10.8. A correlation between *B*- coefficients and the deviation function, $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ has been suggested by Feakins *et al.* [52] in the form of the following relation:

$$B = (\nu\phi_{V,1}^0 - \phi_{V,2}^0) + \phi_{V,1}^0\left(\frac{\Delta\mu_2^{0\neq} - \nu\Delta\mu_1^{0\neq}}{RT}\right) \tag{10}$$

where the coefficient ν is 1 for undissociated uncharged solute. So we have calculated $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values by using the above relation and the *B*- coefficient values obtained from equation (6). Again $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ values can also be expressed as:

$$\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT} = -\frac{\Delta S_2^{0\neq} - \Delta S_1^{0\neq}}{R} + \left\{\frac{\Delta H_2^{0\neq} - \Delta H_1^{0\neq}}{R}\right\}\frac{1}{T} \tag{11}$$

where $\Delta S_i^{0\neq}$ and $\Delta H_i^{0\neq}$ are the standard partial molar entropy and enthalpy of activation for viscous flow per mole of i^{th} component in the solution.

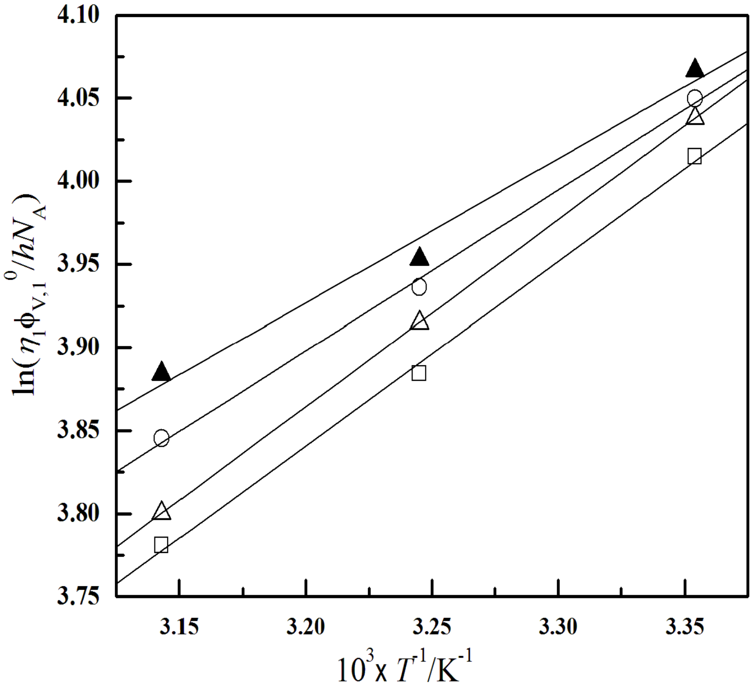

Fig. 10.8. Plots of $\ln(\eta_1\phi_{V,1}^0/hN_A)$ against $10^3 \times T^{-1}$ for CuL(NO$_3$)$_2$ in different MeOH (1) + pyridoxine hydrochloride (2). Symbol: w_1=0.00, □; w_1=0.01, Δ; w_1=0.02, ○; w_1=0.03, ▲.

So a linear regression treatment (with $R^2 \approx$ 0.95501-0.99561) of equation (11) provided the values of $(\Delta S_2^{0\neq} - \Delta S_1^{0\neq})$ and $(\Delta H_2^{0\neq} - \Delta H_1^{0\neq})$ from the corresponding slopes and intercept. The parameters $\Delta\mu_1^{0\neq}$ and $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})$ are reported in table 10.6. $\Delta H_1^{0\neq}$, $(\Delta H_2^{0\neq} - \Delta H_1^{0\neq})$, $\Delta S_1^{0\neq}$ and $(\Delta S_2^{0\neq} - \Delta S_1^{0\neq})$ are reported in table 10.7. Plots of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/RT$ against $(10^3/T)$ are shown in figure 10.9.

Table 10.6 shows that $\Delta\mu_1^{0\neq}$ are almost invariant of the solvent compositions and temperatures, implying that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity *B*-coefficients and $(\phi_{V,2}^0 - \phi_{V,1}^0)$ terms. The values $\Delta\mu_2^{0\neq}$ contain the change in the free energy of activation of solute molecules in presence of solvent as well as the contribution from the movement of solute molecules.

Table 10. 6. Values of $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$ and ($\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}$) for $CuL(NO_3)_2$ in different mixtures of methanol (1) + pyridoxine hydrochloride (2) at T = (298.15 to 318.15) K

T/K	$\frac{\Delta\mu_1^{0\neq}}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta\mu_2^{0\neq}}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\#}}{\mathrm{kJ\cdot mol^{-1}}}$
0.00 [a]			
298.15	9.952 (±0.001)	385.633 (±0.107)	375.681 (±0.107)
308.15	9.951 (±0.001)	344.442 (±0.093)	334.491 (±0.093)
318.15	10.001 (±0.001)	300.999 (±0.077)	290.998 (±0.077)
0.01 [a]			
298.15	10.010 (±0.001)	395.982 (±0.051)	385.973 (±0.051)
308.15	10.030 (±0.001)	351.765 (±0.104)	341.735 (±0.104)
318.15	10.052 (±0.001)	312.554 (±0.145)	302.502 (±0.145)
0.02 [a]			
298.15	10.038 (±0.001)	408.064 (±0.122)	398.025 (±0.123)
308.15	10.085 (±0.001)	358.375 (±0.127)	348.291 (±0.127)
318.15	10.172 (±0.001)	327.429 (±0.118)	317.257 (±0.119)
0.03 [a]			
298.15	10.081 (±0.001)	431.493 (±0.085)	421.412 (±0.086)
308.15	10.128 (±0.001)	387.476 (±0.141)	377.348 (±0.142)
318.15	10.274 (±0.001)	360.666 (±0.157)	350.392 (±0.158)

[a] Molarity of pyridoxine hydrochloride in methanol.

Table 10.7. Values of $\Delta H_1^{0\neq}$, ($\Delta H_2^{0\neq} - \Delta H_1^{0\neq}$), $\Delta S_1^{0\neq}$ and ($\Delta S_2^{0\neq} - \Delta S_1^{0\neq}$) for $CuL(NO_3)_2$ in different mixtures of methanol (1) + pyridoxine hydrochloride (2)

Solvent	$\frac{\Delta H_1^{0\neq}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta H_2^{0\neq}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta S_1^{0\neq}}{\mathrm{J\,mol^{-1}\,K^{-1}}}$	$\frac{\Delta S_2^{0\neq}}{\mathrm{J\,mol^{-1}\,K^{-1}}}$
0.00 [a]	9.233 (±0.031)	1646.931 (±1.451)	-2.386 (±0.100)	4229.237 (±4.714)
0.01 [a]	9.375 (±0.001)	1640.528 (±3.089)	-2.129 (±0.004)	4176.844 (±10.033)
0.02 [a]	8.060 (±0.025)	1613.254 (±11.561)	-6.614 (±0.080)	4052.031 (±37.557)
0.03 [a]	7.216 (±0.061)	1490.201 (±10.615)	-9.555 (±0.199)	3559.926 (±34.483)

[a] Molarity of pyridoxine hydrochloride in methanol.

$\Delta\mu_2^{0\neq}$ values were positive and greater than $\Delta\mu_1^{0\neq}$ at all the experimental temperatures (positive $\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}$ values) suggesting that the interaction between the solute/cosolute and the solvent molecules is stronger in the ground state than in the transition state, i.e., the formation of transition state is less favored or the transfer of the solute molecules from the ground state solvent to the transition state solvent is hindered. Also $\Delta\mu_2^{0\neq}$ values increase as the content of pyridoxine hydrochloride in ternary solutions increase. Such a trend in $\Delta\mu_2^{0\neq}$ values suggests that the viscous flow becomes hindered with increased amount of pyridoxine hydrochloride for the ternary solutions but becomes little bit easier at higher temperatures.[39] Again table 10.7 shows that the $\Delta H_2^{0\neq}$ values are positive for almost all the solvent systems indicating that the viscous process is endothermic and involves breaking/distortion of intermolecular bonds between the competing molecules in the ternary solutions resulting in positive $\Delta S_2^{0\neq}$ values.

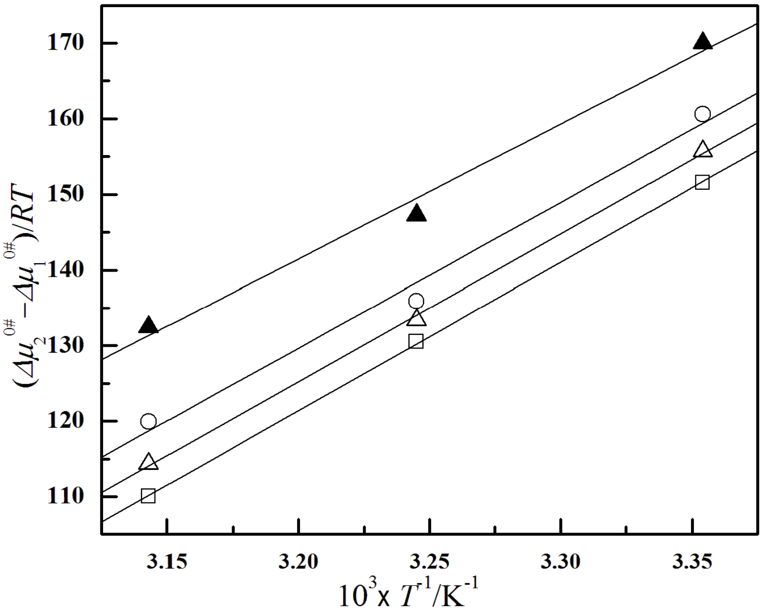

Fig. 10.9. Plots of $(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/RT$ against $10^3 \cdot T^{-1}$ for CuL(NO$_3$)$_2$ in different MeOH (1) + pyridoxine hydrochloride (2). Symbol: w_1=0.00, □; w_1=0.01, Δ; w_1=0.02, ○; w_1=0.03, ▲.

10.4. Conclusion

In summary, partial molar volumes ϕ_V^0 and viscosity *B*-coefficients for $CuL(NO_3)_2$ in the ternary solutions indicate the presence of strong solute-solvent and solute-cosolute interactions; these interactions strengthens at higher content of pyridoxine hydrochloride but decreases as the experimental temperature increases. Spectrophotometric titration indicated a weak 1:1 association between $CuL(NO_3)_2$ and pyridoxine hydrochloride by specific interactions, *i.e.*, hydrogen bond and $CuL(NO_3)_2$ acts as a net structure maker for the solutions by favoring hydrogen bonded bulk structure of MeOH in presence of pyridoxine hydrochloride.

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CHAPTER XI

Concluding Remarks

The aim of the research works embodied in this thesis was to investigate to solution behavior of some Schiff base metal complexes in different pure and mixed solvent systems in terms of various thermodynamics properties.

The study of partial molar volumes and viscosity *B*-coefficients for $[Cr(salen)(H_2O)_2]Cl$ in methanolic solutions of 1- butyl- 2, 3-dimethylimidazolium tetrafluoroborate ($[bdmim]BF_4$) at 298.15, 308.15 and 318.15 K revealed that the ternary solutions are characterized by the presence of strong ion-solvent interactions which further increase with increasing temperatures due to favorable (stronger) solvation of solute or caging effect at higher temperatures but increasing concentration of $[bdmim]BF_4$ causes desolvation of the complex and both the complex and $[bdmim]BF_4$ behave as strong electrolytes in the studied solutions. An inspection of solvation numbers (S_n) indicated that the complex remains solvated and its solvation decreases at higher concentration of $[bdmim]BF_4$ in the studied solutions but increases at higher temperatures. Such trends in S_n values are due to the fact that $[bdmim]BF_4$ itself interacts with MeOH and thus decreases solvation of the complex or its ions and the complex $[Cr(salen)(H_2O)_2]Cl$ acts as a net structure breaker for the studied solutions.

The study on ion-solvent and ion-ion interactions in solutions of $[Cr(salen)(H_2O)_2]Cl$ in aqueous dimethylsulphoxide at 298.15, 308.15 and 318.15 K revealed the presence of strong ion-solvent interactions in these systems. However, such interactions gradually decrease with the advent of more water in solvent mixtures when compared to those values in pure DMSO and thus indicate that the loosely bound DMSO molecules around the complex return to the bulk solution in order to promote hydrogen bonded structures with water molecules. Also the solutions experience ion-ion interactions and these interactions further strengthen in water rich solvent mixtures, because dielectric constants of the solvent mixtures increase with more water and the more ions are dispersed in solutions due to dissociation of the complex $[Cr(salen)(H_2O)_2]Cl$ into its constituent ions. However, in all the studied solutions the ion-solvent interaction plays a dominant role than the ion-ion interactions in characterizing the volumetric properties of studied systems. An inspection of solvation numbers (S_n) indicated that the complex remains solvated with primary solvation spheres in pure DMSO but suffers from desolvation effects with the advent of water. These results indicate that water promotes the desolvation of $[Cr(salen)(H_2O)_2]Cl$ and favors the solvent-solvent interactions between water and DMSO; so solvation of the complex with water seems to be rather meager and $[Cr(salen)(H_2O)_2]Cl$ acts as a net structure maker in aqueous DMSO solutions.

The study of partial molar volumes and viscosity *B*-coefficients of N, N$^{/}$-ethylenebis-(salicylideneiminato)cobalt(II) in binary mixtures of 1,4-Dioxane + Methanol at 298.15, 303.15, 308.15 and 313.15 K indicated the presence of strong solute-solvent interactions and these interactions are further strengthened at higher temperatures but weakened with higher content of the cyclic diether. It is due to the fact that interaction between methanol and Co(salen) decreases owing to favorable hydrogen bond interaction between 1,4-dioxane and methanol molecules. Again refractometric results revealed that the ternary solutions are characterized by structural changes and strong solute-solvent interactions and Co(salen) acts as a net structure promoter for the ternary solutions.

The study on solution behavior of iron(III)-N, N$^{/}$-ethylene-bis(salicylideneiminato)-chloride in aqueous methanol at 298.15, 303.15 and 313.15 K indicated the presence of strong solute-solvent interactions and weak solute-solute interactions in the ternary solutions. Solute-solvent interactions further strengthen at higher content of water and weaken at higher temperatures. Increase in solute-solvent interaction at higher water content in the mixtures was attributed to preferential coordination of the unoccupied sixth position of Fe^{III}(salen)Cl by water molecules or preferential solvation of Fe^{III}(salen)Cl by water molecules due to stronger electrostatic interaction and comparatively more donor strength of water than methanol and Fe^{III}(salen)Cl acts as a net structure promoter in the ternary solutions studied. UV-VIS absorption spectra of the ternary solutions also stand in support of the results obtained. The transition state theory treatment of viscosity *B*-coefficients revealed that the transfer of the solute molecules from the ground state solvent to the transition state solvent is thermodynamically hindered and the viscous process is endothermic.

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The study on solution thermodynamics of iron(III)-N, N$^{/}$-ethylene-bis(salicylideneiminato)-chloride in binary mixtures of N, N-dimethylformamide and acetonitrile at 298.15, 303.15, 308.15 and 313.15 K indicate the presence of strong solute-solvent interactions and these interactions are further strengthened with higher mass fractions (w_1) of DMF up to $w_1 = 0.75$ in the ternaries but decrease at higher temperatures, i.e., Fe^{III}(salen)Cl is preferentially solvated by DMF rather than ACN. Actually solute-solvent interactions depend on molecular nature as well as orientations of the solvent molecules in solution. DMF has a strong electron pair donor and accepting ability and is a resonance hybrid of two resonating structures: one neutral molecule and another zwitter ionic form with negative O-pole and positive N-pole. The negative O-pole is positioned out of the rest of the molecule and its unshared electron pair is exposed enough for strong solvation. The positive N-pole is buried within the molecule and two electron repelling CH$_3$-groups further make its lone pair electrons more perceptible for donation. Also due to the positive charge on N-pole, CH$_3$-groups become more polar. Thus all these factors probably impart higher solvating power to DMF and it interacts preferably more with Fe^{III}(salen)Cl through $\mathrm{O}\cdots\mathrm{Fe}$ interaction as far as the present solutions studied are concerned. Again as polarity of the solvent mixtures increase with more DMF, concomitant increase in solute-solvent interactions indicate that interactions exist among the polar segments of the complex and the solvents as well as electrostatic interactions between local charges of the complex and the solvent dipoles. From the values of $(\partial \phi_E^0 / \partial T)_P$ and $(\partial B/\partial T)$ it is evident that Fe^{III}(salen)Cl predominantly acts as a structure maker and its structure-making ability generally decreases with an increase in DMF content in the ternary solutions. Also an inspection of solvation numbers (S_n) reveals that the complex remains highly solvated and its solvation increases in the mixed solvents but decreases to be minimum in pure DMF.

The study of the effect of tetrabutylammonium bromide on solution behavior of salicylaldehyde anil zinc (II) in methanol at T = (298.15, 308.15 and 318.15) K reveals that the ternary solutions studied are characterized by the presence of strong solute-solvent interactions and weak solute-solute interactions. The trends in solute-solvent interactions as functions of Bu$_4$NBr content and temperature are attributable to increase in solvation of SAZ and dissociation of Bu$_4$NBr into its ions that distort the hydrogen bonds in MeOH. Actually the dominance of polar–ionic group and polar-polar interactions over polar-non-polar and non-polar-non-polar group interactions between SAZ and MeOH characterizes the overall nature of the ternary solutions. An inspection of solvation numbers (S_n) indicated that the complex remains highly solvated with primary solvation spheres and its solvation further increases with an increase in Bu_4NBr-content in the ternary solutions and experimental temperatures. Thus it can be concluded that Bu_4NBr promotes the solvation of SAZ and also weakens the hydrogen bonded bulk structure of MeOH and thus favors concomitant increase in solute-solvent interactions and SAZ acts as a net structure breaker.

The study of non-covalent interactions in solutions comprising of pyridoxine hydrochloride, {N, N$^/$-bis[(2-pyridinyl)methylene]-1, 2-benzenediamine]-bis(nitrato)}Cu(II) in MeOH in terms of partial molar volumes ϕ_V^0 and viscosity *B*-coefficients indicate the presence of strong solute-solvent and solute-cosolute interactions in the ternary solutions; these interactions further strengthens at higher content of pyridoxine hydrochloride but decreases as the experimental temperature increases. Spectrophotometric titration indicated a weak 1:1 association between the complex $CuL(NO_3)_2$ and pyridoxine hydrochloride by specific interactions, *i.e.*, hydrogen bond. The $(\partial B/\partial T)$ and $(\partial \phi_E^0/\partial T)_P$ values indicate that the complex acts as a structure maker for the solutions. Also trends in $\Delta\mu_2^{0\neq}$ values suggest that the viscous flow becomes hindered with increased amount of pyridoxine hydrochloride for the ternary solutions but becomes little bit easier at higher temperatures and the viscous process is endothermic (positive $\Delta H_2^{0\neq}$ values) and involves breaking/distortion of intermolecular bonds between the competing molecules in the ternary solutions resulting in positive $\Delta S_2^{0\neq}$ values.

Anyway, it is necessary to keep in mind that molecular interactions are very complex in nature and quite difficult to explore and interpret. Numerous forces may operate between the molecules in a solvent mixture and it is really hard to separate and assign them all. Nevertheless, if careful experimental technique and methodology are used, important conclusions may be obtained regarding the nature of structure and order of the systems in solution phase. The knowledge of the type and structure of the complex species in solution is essential for the optimal choice of solvents for varied applications and proper understanding of the various interactions may constitute the basis of explaining quantitatively the influence of the solvents and ions in solution and thus pave the way for real understanding of different phenomena associated with solution chemistry and still a lot of systems comprising of Schiff base transition metal complexes dissolved in different solvent systems remains to be explored.

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CHAPTER II

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APPENDIX I

List of Publications

[1] Partial molar volumes and viscosity *B*-coefficients of N, N$'$-Ethylene-bis(salicylideneiminato)cobalt(II) in Binary Mixtures of 1,4-dioxane + methanol at T = (298.15, 303.15, 308.15, and 313.15) K, **J. Chem. Eng. Data, 56 (2011) 3073-3082**.

[2] Effect of tetrabutylammonium bromide on solution behavior of salicylaldehyde anil zinc (II) in methanol at T = (298.15, 308.15 and 318.15) K, **J. Chem. Thermodynamics, 67 (2013) 13-20**.

[3] Solution behavior of iron(III)-N, N$'$-ethylene-bis- (salicylideneiminato) chloride in aqueous methanol at 298.15, 303.15 and 313.15 K, In Press: **J. Serb. Chem. Soc. (2013), doi: 10.2298/JSC170413082B**

[4] Partial molar volumes and viscosity *B*-coefficients for N, N$'$-ethylene-bis(salicylideneiminato)-diaquochromium(III) chloride in methanolic solutions of 1- butyl- 2, 3-dimethylimidazolium tetrafluoroborate at T = (298.15, 308.15 and 318.15), **J. Chem. Thermodynamics 68 (2014) 260–269.**

APPENDIX II

List of Communicated Articles

[1] Solution Thermodynamics of iron(III)-N, N$^{/}$-ethylene bis(salicylideneiminato)-chloride in binary mixtures of N, N-dimethylformamide and acetonitrile at T = (298.15, 303.15,308.15 and 313.15) K, **Communicated**.

[2] Non covalent interactions between {N, N$^{/}$-bis[(2-pyridinyl)methylene]-1, 2-benzenediamine]-bis(nitrato)}Cu(II) with pyridoxine hydrochloride in methanol at T = (298.15, 308.15 and 318.15) K probed by physico-chemical methods, **Communicated**.

[3] Ion-solvent and ion-ion interactions in solutions of N, N$^{/}$-ethylenebis-(salicylideneiminato)-diaquochromium(III) chloride in aqueous dimethylsulphoxide at T = (298.15, 308.15 and 318.15) K, **Communicated.**

APPENDIX III

List of Other Publications

[1] Apparent molar volumes and viscosity *B*-coefficients of caffeine in aqueous thorium nitrate solutions at *T* = (298.15, 308.15, and 318.15) K, **J. Chem. Thermodynamics 42 (2010) 380-386.**

[2] Physicochemical properties of L-alanine in aqueous silver sulphate solutions at (298.15, 308.15, and 318.15) K, **Int. J. Thermophys 32 (2011) 2062-2078**.

[3] Thermophysical properties of binary mixtures of N, N- dimethylformamide with three cyclic ethers, **J. Serb. Chem. Soc. 78 (2013) 1443-1460**.

[4] Thermodynamics of the complexation between salicylaldehyde thiosemicarbazone with Cu^{2+} ion in methanol-1,4-dioxane binary solutions, **J. Serb. Chem. Soc., (2013) doi: 10.2298/JSC130730137B.**

APPENDIX IV

Seminar, Symposium & Convention Attended

- **Sixth CRSI, National Symposium (Kolkata Chapter)**, organized by Department of Chemistry, University of North Bengal, Darjeeling, India on August 2, 2008 as Delegate.

- **National Workshop on ADVANCES IN INSTRUMENTAL TECHIQUES (NWAIT)** organized by Department of Chemistry, Shri Shivaji Science College, Amravati (Maharashtra), India on October 14th -16th, 2010 as Delegate.

- **National Seminar on Frontiers in Chemistry 2011 & Celebration of The International Year of Chemistry 2011** sponsored by University Grants Commission, New Delhi, India & University of North Bengal, Organized by Department of Chemistry, University of North Bengal, Darjeeling, India on March 14-16, 2011 as Delegate.

- **Science Academies' Lecture Workshop on Recent Trends In Chemistry**, organized by Department of Chemistry, University of North Bengal, Darjeeling, India on November 11-12, 2011 as Delegate.

- **Science Academies' Lecture Workshop on Modern Trends In Chemistry and Chemistry Education**, organized by Department of Chemistry, University of North Bengal, Darjeeling, India on November 22-23, 2012 as Delegate.

- **15th CRSI National Symposium in Chemistry**, organized by Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, India on February 1-3, 2013 as Delegate.

- **Workshop on Diversities and Frontiers in Chemistry,** jointly organized by Department of Chemistry, Jadavpur University, Kolkata & Department of Chemistry, University of North Bengal, India on August 7-8, 2013 as delegate.

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