

CHAPTER – I

1.1. Object and application of the research work

Physico-chemical Investigation of electrolytes plays a very important role in understanding the solute-solute, solute-solvent and solvent-solvent interactions in solutions. In order to explore the strength and nature of the interactions, transport properties of electrolytes, along with thermodynamic and acoustic studies involving binary and ternary systems of liquid and of one or more solutes in pure and mixed systems of liquid are very useful.

The importance and uses of the Chemistry of electrolytes in non- aqueous and mixed solvents are well organized. The applications and implications of the studies of reactions in non-aqueous and mixed solvents have been summarized by Franks ⁽¹⁾, Meck ⁽²⁾, Popovych ⁽³⁾, Bates ⁽⁴⁻⁵⁾, Parker ⁽⁶⁻⁷⁾, Criss and Salomon ⁽⁸⁾, Mercus ⁽⁹⁾ and others ⁽¹⁰⁻¹²⁾. The solute-solute and solute-solvent interactions have been subject of wide interest as apparent from recent Faraday Trans. of the chemical society ⁽¹³⁾.

The proper understanding of the solute-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent of interaction of ions in solvents and thus pave the way for real understanding of the different phenomena associated with solution chemistry. Estimation of solute-solvent interactions can be obtained thermodynamically and also from the measurement of partial molar volumes, viscosity *B*-coefficient and conductivity studies.

In recent years there have been increasing interests in the behavior of electrolytes in non- aqueous and mixed solvents with a view to investigating solute-solute and solute-solvent

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interactions under varied conditions. However, different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open vistas for physical chemists and interests in these organic solvents transcends the traditional boundaries of inorganic, physical organic analytical and electrochemistry⁽¹⁴⁾.

Fundamental research on non-aqueous electrolyte solutions has catalyzed their wide technical applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ion conductors, especially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents, additives, and electrolytes with widely varying properties. High-energy primary and secondary batteries, wet double-layer capacitors and supercapacitors, electrodeposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions has brought the biggest success⁽¹⁵⁻¹⁶⁾. Other fields where non-aqueous electrolyte solutions are some devices and processes for which the use of non-aqueous electrolyte solutions are broadly used include electro-chromic displays and smart windows, photo-electrochemical cells, electro-machining, etching, polishing, and electro-synthesis. In spite of wide technical applications, our understanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of ion-molecular interactions and their influence on structural and dynamic properties of non-aqueous electrolyte solutions.

Studies of transport properties of electrolytes, along with thermodynamic and compressibility studies, give very valuable information about ion-ion and ion-solvent interactions in solutions⁽¹⁷⁾. The influence of these ion-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation

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have important applications in such diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction⁽¹⁸⁾.

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become increasingly clear that the majority of the solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, like water, is substantially modified by the presence of solutes⁽¹⁹⁾.

1.2. Importance and scope of physico-chemical parameters

The study of physico-chemical properties involves the interpretation of the excess properties as a mean of unraveling the nature of intermolecular interactions among the mixed components. The interactions between molecules can be established from a study of characteristic departure from ideal behaviour of some physical properties such as density, volume, viscosity, compressibility, etc.⁽²⁰⁾

Density of solvent mixtures and related volumetric properties like excess molar volume are essential for theoretical as well as practical aspects. The sign and magnitude of excess molar volume imparts estimate of strength of unlike interactions in the binaries. The negative values of excess molar volume (V^E) suggest specific interactions⁽²¹⁾ between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces⁽²¹⁾ between them. The negative (V^E) values indicate the specific interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components because of the difference in molar volume. The negative (V^E) values may also be due to the difference in the dielectric constants of the liquid components of the binary mixture.⁽²¹⁾

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A knowledge of viscosity of fluids is required in most engineering calculations where fluid flow, mass transport and heat transport are important factors. 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 led to significant improvement towards a successful molecular theory of transport properties in fluids and a proper understanding of molecular motions and interaction patterns in nonelectrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents. The study of physico-chemical behaviours like dissociation or association from acoustic measurements and from the calculation of isentropic compressibility has gained much importance. Excess isentropic compressibility, intermolecular free length etc. impart valuable information about the structure and molecular interactions in pure and mixed solvents. The acoustic measurements can also be used for the test of various solvent theories and statistical models and are quite sensitive to changes in ionic concentrations as well as useful in elucidating the solute-solvent interactions.

Drugs are basically composed of organic molecules and the study of bio-molecules plays a key role in the elucidation of thermodynamic properties of bio-chemical processes in living cells. The process of drug transport, protein binding, anesthesia, etc are few examples where drug and bio-macromolecules appear to interact in an important and vitally significant way. Drug transport across biological cells and membranes is dependent on physico-chemical properties of drugs. But direct study of the physico-chemical properties in physiological media such as blood, intracellular fluids is difficult to accomplish. One of the well-organized approaches is the study of molecular interactions in fluids by thermodynamic methods as thermodynamic parameters are convenient for interpreting intermolecular interactions in solution phase. Also, the study of

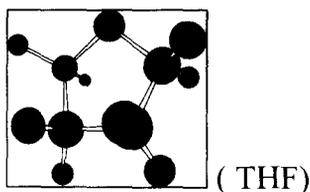
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thermodynamic properties of drug in a suitable medium can be correlated to its therapeutic effects. These facts therefore prompted us to undertake the study of binary or ternary solvent systems with formamide, 1,3-dioxolane, tetrahydrofuran, monoalkanols, monoalkanoic acids as primary solvents with some polar, weakly polar and nonpolar solvents as well as with some solutes. Furthermore, the excess properties derived from experimental density, viscosity and speeds of sound data and subsequent interpretation of the nature and strength of intermolecular interactions help in testing and development of various theories of solution.

1.3. Importance of solvents used

N,N-dimethylformamide, 1,3-dioxolane, tetrahydrofuran, i-amyl alcohol, acrylonitrile, monoalkanols (methanol, ethanol, propanol, iso propanol, butanol, pentanol), monoalkanoic acids (formic acid, acetic acid, propionic acid), aromatic aldehydes (anisaldehyde, cinnamaldehyde, benzaldehyde, 2-chloro benzaldehyde), chlorobenzene have been chosen as main solvents in my research works. The study of these solvents, in general, are of interest because of their wide use as solvents and so in general, is of interest because of their wide use as solvent and solubilizing agent in many industries with interests ranging from pharmaceutical to cosmetic products.

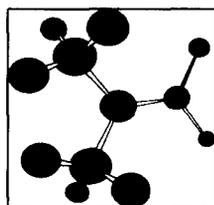
Tetrahydrofuran and its mixtures are the very important solvents widely used in various industries. This is a good industrial solvent and figures prominently in the high-energy battery technologies and has found its application in organic syntheses as manifested from the physico-chemical studies in this medium⁽²²⁾.



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Tetrahydrofuran (Merck, India), was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over lithium aluminium hydride (LiAlH₄). The purified solvent had a boiling point of 66°C, a density of 0.88072 g·cm⁻³, a coefficient of viscosity of 0.46300 mPa.s and a specific conductance of Ca. 0.81 X 10⁻⁶ Ω⁻¹ cm⁻¹ at 25°C⁽¹⁴⁾.

Formamide and its derivatives are good solvents for many organic and inorganic compounds and also used as a plasticizer. It is also chosen for the study as it is a simplest amide that contains a peptide linkage, the fundamental building block of proteins.⁽²³⁾



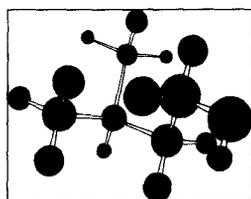
(N, N-DMF)

Benzaldehyde is used- (i) for flavouring purposes, in perfumery; (ii) in the manufacture of dyes; and (iii) as a starting material for the synthesis of several other organic compounds, e.g., cinnamaldehyde, cinnamic acid, benzoyl chloride, etc.⁽²⁴⁾

Alcohols and their aqueous and non-aqueous mixtures are widely used in pharmaceutical industry as excipients in different formulations or as solvents. Alcohols have varied applications in chemical and cosmetic industries. These are useful in enology and as an alternative energy source.⁽²⁵⁾ A knowledge of their physico-chemical characteristics helps to understand their behaviour 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 usually be removed by distillation, or by use of molecular sieves and calcium hydride.

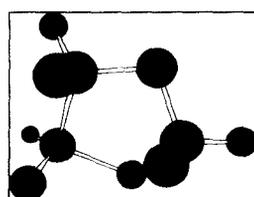
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The importance of iso-amyl alcohol in research field is implied for its usefulness in gas chromatography. It can isolate high quality RNA from even the hardest to isolate samples for immediate use in micro array application and it is also useful in most DNA applications.⁽²⁶⁾



(i Amyl Alcohol)

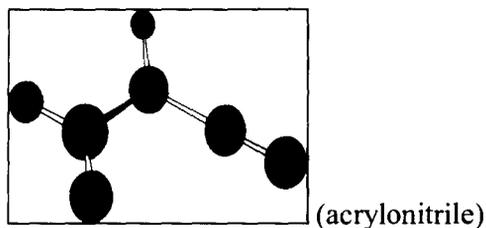
1,3-dioxolane is cyclic diether and it figure prominently in the high energy battery technology⁽²⁷⁾ and have also found application in organic synthesis as manifested from the physico-chemical studies in this media.



(1,3-DO)

The study of mixtures of acrylonitrile in various solvents is of interest because of its wide use as an important industrial monomer for polyacrylonitrile as well as for investigating the effect of the simultaneous presence of the C=C double bond and the polar nitrile C≡N group on the molecular interactions. Further, the properties of liquid mixtures are also very important for polymer solubility, as some of the polymers which are insoluble in a single solvent can be dissolved in a solvent mixture. This behavior depends not only on the interactions between the polymer and each one of the liquids but also on the interactions between the liquids themselves. In fact, these interactions are decisive in determining the solubilization of the polymer and the coiling expansion of the polymer chains in solution.⁽²⁸⁾

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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 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 or ternary mixtures and they can serve different purposes such as increasing water solubility, modifying the viscosity, absorption of the dissolved substance.

Moreover, in recent years, the above-mentioned solvents have drawn much focused in electro-analytical investigation, still more studies on the electrolytic behavior in these non-aqueous medium can be explore.

1.4. Method of Investigations

The interactions and equilibria of ions in aqueous and non-aqueous media in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occur in these systems. The structures and existence of free ions, solvated ions, and ion pairs depend on concentration regions ⁽⁹⁾.

Various techniques ^(5a, 29) have been employed to study the solvation structure, ion-solvent interactions and dynamics of ions in aqueous and non-aqueous media.

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The phenomenon of ion-solvent interactions and solvation is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed five important methods, namely, conductometric, viscometric, densitometry, ultrasonic interferometer and spectrophotometer to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative to Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions.

The change in viscosity by the addition of electrolyte solutions is attributed to interionic and ion-solvent effects. The B -coefficients are also separated into ionic components by the 'reference electrolyte' method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure-breaking or structure-making, polarization, etc. may be given⁽³⁰⁾.

The transport properties in most cases are studied using the conductance data, especially the conductance at infinite dilution. Conductance data obtained as a function of concentration can be used to study the ion-association with the help of appropriate equations.

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1.5. Summary of the works done

The present dissertation has been divided into twelve chapters.

Chapter I: This chapter entails the object and application of the research work. This mainly comprise of the choice of the main solvent used and its applications in different fields, methods of investigation and summary of the work done.

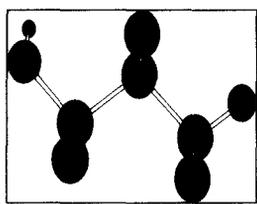
Chapter II: This chapter involves the general introduction (Review of the Earlier Work) of the thesis and the background of the present work. After presenting a brief review of notable works in the field of solute-solvent, solute-solute and solvent-solvent interactions, the discussion centers on the conductance, density, viscosity, spectroscopy and adiabatic compressibility of different electrolytes in different solvent systems at different temperatures. The solution properties of the various electrolytes in different solvents are then elaborated and discussed, stressing the importance of the work associated with the thesis.

Chapter III: This chapter states and explains the experimental section consisting of the sources, and purification of the solvents and electrolytes used and the various techniques of the experiments applied here.

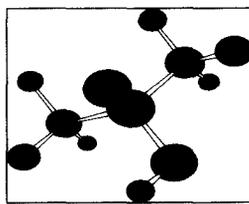
Chapter IV: This chapter describes the study of the densities and viscosities of six ternary mixtures of the water, monoalkanols (1-propanol, 2-propanol) and monoalkanoic acids (formic acid, acetic acid and propionic acid) are determined over the entire range of composition at 298.15, 308.15 and 318.15 K. From the experimental observations the excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) were calculated, and then the viscous synergy and synergy interaction index are derived by the equations developed by Kalentunc-Gencer and Peleg and Howell, respectively. The speeds of sound of these ternary mixtures have been measured over

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the whole composition range at the same temperatures (298.15K) and also, the isentropic compressibilities (K_S) and excess isentropic compressibilities (K_S^E) have been evaluated from the experimental data. The variation of η_{\max} and I_s with the number of carbon atoms are also shown. The results thus obtained indicates that monoalkanoic acids containing up to three carbon atoms mix with water and monoalkanol mixtures in any proportion but the synergic interactions tend to decrease with the increase of C atoms in the chain due to increasing +I-effect and The monoalkanols with the hydroxyl group positioned at the second carbon atom accept more water and acids than those with the terminal hydroxyl group. An example is shown below:



1-propanol



2-propanol

Chapter V: This chapter includes the study on interaction between solvent-solvent occurring in binary mixtures of N, N-dimethylformamide with some aromatic aldehydes by volumetric, viscometric and acoustic measurements. The excess molar volume (V^E) and viscosity deviations ($\Delta\eta$) have been derived from density (ρ) and viscosity (η) data of the binary mixtures of N,N-dimethylformamide (DMF) with anisaldehyde, cinnamaldehyde, benzaldehyde and 2-chloro benzaldehyde measured at 298.15, 308.15, and 318.15K. The data have been correlated with the Grunberg-Nissan equation. Moreover, deviations in isentropic compressibility (ΔK_S) have been calculated from ultrasonic speed measurements of these binary mixtures at 298.15 K. The results have been discussed in terms of molecular interactions and structural effects.

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Chapter VI: This chapter involves the studies of the conductivities of some tetraalkylammonium iodides and bromides, at 298.15 K in chlorobenzene. A minima in the conductometric curves (molar conductance, Λ vs. square root of concentration, \sqrt{c}) was observed for concentrations which were dependant upon both the salt and the solvent. The observed molar conductivities were explained by the formation of ion-pairs ($M^+ + X^- \leftrightarrow MX$) and triple-ions ($2M^+ + X^- \leftrightarrow M_2X^+$; $M^+ + 2X^- \leftrightarrow MX_2^-$). A linear relationship between the triple-ion formation constants [$\log(K_T / K_P)$] and the salt concentrations at the minimum conductivity ($\log C_{min}$) was given for all the salts in chlorobenzene. The formation of triple-ions might be attributed to the ion sizes in solutions in which Coulombic interactions and non-Coulombic interactions act as the main forces between the ions ($R_4N^+ \dots X^-$).

Chapter VII: This chapter involves the studies on the Ion-Solvent, Ion-Ion and Solvent-Solvent interactions. Electrolytic conductivities of sodium salts with different anionic parts NaZ (Z = SCN^- , CH_3COO^- , I^-) have been investigated in 10, 20, and 30 mass% of acrylonitrile + MeOH mixtures at 293.15, 298.15, 303.15 K. The conductance data have been analyzed by the Fuoss-conductance-concentration equation in terms of the limiting molar conductance (Λ_0), the association constant (K_A), and the distance of closest approach of ion (R). The association constant (K_A) tends to increase in the order: 10 mass% > 20 mass% > 30 mass% acrylonitrile + MeOH > pure acrylonitrile, while it decreases with temperature. Thermodynamic parameters ΔH_0 , ΔG_0 , and ΔS_0 are obtained and discussed. Also, Walden products ($\Lambda^0 \eta$) are reported. The results have been interpreted in terms of ion-solvent interactions.

Chapter VIII: This chapter includes the volumetric, viscometric, and ultrasonic studies of some acetate salts [CH_3COONH_4 , CH_3COOLi , CH_3COONa , CH_3COOK] in aqueous binary mixtures of tetrahydrofuran (10, 20 and 30 mass % tetrahydrofuran) at different temperatures (303.15,

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313.15, and 323.15) K. The experimental values of ρ were used to calculate the values of the apparent molar volume (Φ_V). The limiting apparent molar volume (Φ_V^0) and the experimental slope (S_V^*) have been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure making / breaking capacities of the (1:1) electrolytes have been inferred from the sign of $(\delta^2 V_{\Phi^0} / \delta T^2)_p$ and dB/dT . The compressibilities obtained from the data supplemented with their ultrasonic speeds indicate the electrostriction of the solvent-mixture molecule around the ammonium and metal ions.

Chapter IX: This chapter deals with conductance and FTIR spectroscopic study of sodium tetraphenylborate in pure 1,3-dioxolane and isoamyl alcohol and their binary mixtures. Systems of 1,3-dioxolane and isoamyl alcohol complexed with sodium tetraphenylborate (NaBPh_4) are examined using electrical conductance measurements and FTIR spectroscopy at 298.15 K. The conductance data have been analyzed by the Fuoss conductance-concentration equation in terms of the limiting molar conductance (Λ_0), the association constant (K_A) and the distance of closest approach of ions (R). The observed molar conductivities were explained by the formation of ion-pairs ($\text{M}^+ + \text{X}^- \leftrightarrow \text{MX}$). Cation-anion interactions along with the hydrogen bonding interactions are investigated by evaluating the frequency shifts of the solvents in the pure state as well as their binary mixtures upon complexation with the salt.

Chapter X: In this chapter an attempt has been made to reveal the solution properties of some alkali bromides in aqueous binary mixtures of 1,3-dioxolane in view of different models.

Viscosity B -coefficients of lithium, sodium and potassium bromide in 30%, 60% and 90% aqueous 1,3-dioxolane solutions have been determined at 298.15 and 308.15K. from density and viscosity measurements employing Jones-Dole, Breslau-Miller and Vand equations. B -coefficients thus obtained were compared. Furthermore, the applicability of Moulik equation was

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shown by linear plots of relative viscosity and concentration values in their square terms. It has been found that the B -coefficient varies with the size of the cations and suggesting structure promoting tendency for all the salts and for all the concentrations.

Chapter XI : This chapter deals with the study of molar volumes, viscosity, and isentropic compressibility and isentropic compressibility of some primary monoalkanols in aqueous N,N -dimethylformamide solutions. The determination of density, viscosity and speeds of sound is used as a tool to learn about the liquid state of the systems because of the close connection between liquid structure and macroscopic properties. The present work contributes and extends our study of density (ρ), viscosity deviations ($\Delta\eta$), viscous synergy, excess molar volumes (V^E) and isentropic compressibility (K_s^E) to the aqueous mixtures of N,N -dimethylformamide (DMF) with some monoalkanols;

Chapter XII: In this chapter the dissertation ends with some concluding remarks mentioning the methods, various equations, importance and application of the work

REFERENCES

1. F. Franks, Physico-Chemical Processes in Mixed Aqueous Solvents, Ed. F. Franks, Heinemann Educational Books Ltd., 141(1967).
2. D. K. Meck, The Chemistry of Non- Aqueous solvents, Ed., J.J. Logowski, Academic Press, New York, London, Part 1, Chapter 1 (1996).
3. O. Popovych, Crit. Rev. Anal. Chem., 1, 73 (1970).
4. R. G. Bates, Determination of pH Theory and Practice, Second Ed., John Wiley and sons. N.Y., Chapter 8 (1973).

Object and application of the research work

5. (a) R. G. Bates, Solute-solvent Interactions, Ed., J.J. Coetzee and C.D. Ritchie, Marcel Dekker, New York and London, (1969)

(b) R.G. Bates and A.J.Parker, Chemical Physics of Ionic solutions, Ed., B.E. Conway and R.G. Barrades, John Wiley and Sons. Inc., New York, 211 (1966).
6. A.J. Parker and J.H. Sharp, Proceeding of the Royal Australian Chemical Institute, **89** (1972).
7. A.J.Parker, Electrochim. Acta., **21**, 671 (1976).
8. C. M. Criss and M. Salomon, J. Chem. Educ., **53**, 763 (1976).
9. Y. Marcus, Ion solvation, Wiley, Chinchester, (1986)
10. E.J. King, Acid- Base Equilibria, Pergamon Press, Oxford, (1965).
11. O.Ppovych and R.T.P.Tomkins, Non – Aqueous solution Chemistry, John Wiley and Sons, New York, (1981).
12. R.R. Dogonadze, E. Kalman, A.A.Kornyshev, and J. Ulstrup., The Chemical Physics of Salvation, Part C, Elsevier. Amsterdam, (1988).
13. Faraday Discussion of the Chemical Society, **67**, (1977).
14. A.K.Covington and T.Dickenson , Physical Chemistry of Organic solvent Systems, Ed., A.K.Covington and T.Dickenson, Plenum Press, London, New York, (1973).
15. Y. Marcus, Introduction to Liquid State Chemistry, Wiley-Interscience, New York, (1997).
16. G.A.Krestov, Thermodynamics of Solvation, Ellis Horwood, Chichester, (1991).

Object and application of the research work

17. J. Padova, in *Water and Aqueous Solutions*, Ed. R.A.Horne, Wiley- Interscience, New York, chapter 4 (1972).
18. R. Fernandez-Prini, H. Corti and M. Japas, *High Temperatures Aqueous Solutions: Thermodynamic Properties*, C.R.C. Press, Boca Raton, Florida, (1992).
19. R.G. Bates, *J.Electonal. Chem.*, **29**, 1 (1971),
20. E. P. Georgios, I. Z. Ioannis, *J. Chem. Eng. Data*, **37**, 167 (1992).
21. J. N. Nayak, M. I. Aralaguppi, T. J. Aminabhavi, *J. Chem. Eng. Data*, **48**, 1489 (2003).
22. N. Inove, M. Xu, and S. Petrucci, *J.Phys. Chem.*, **91**, 4628 (1984).
23. G. T. Fraser, R. D. Suenram, F. J. Lovas, *J. Mol. Liq.*, **189**, 165 (1988).
24. D. W. A. Sharp, *Dictionary of Chemistry*, 2nd ed., Penguin Books, Great Britain, (1990).
25. J. V. Herraiez, R. Belda, O. Diez, *Phys. Chem. Liq.*, **42**, 467 (2004).
26. J. Verga, E. Rinyu, E. Kevei, B. Toth, Z. Kozakiewicz, *Can. J. Microbiol/ Rev. Can. Microbiol*, **44**, 569 (1998).
27. C. G. Janz, R. P. T. Tomkins, *Non-Aqueous Electrolyte Handbook*, Academic, New York, **2**, (1973).
28. S. L. Oswal, N. B. Patel, *J. Chem. Eng. Data*, **45**, 225 (2000).
29. H.Ohtaki and T. Radnai, *Structure and Dynamics of Hydrated Ions*, *Chem.Rev.* **93**, 1157 (1993).
30. W.M.Cox and J.H.Wolfenden, *Proc. Roy, Soc., London*, **145A**, 475 (1934).