

ABSTRACT

In 'Solution Chemistry' broadly three types of approaches have been made to estimate the extent of solvation. The approaches involves the studies of viscosity, conductance, etc., of electrolytic solutions and the derivation of various factors associated with ionic solvation, the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated, and the third is spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature.

Studies of thermodynamic properties of electrolytes, along with transport and acoustic studies, give very valuable information about ion-ion and ion-solvent interactions in solutions. The influence of these interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction.

Using mixed solvents in these studies enable the variation of properties such as dielectric constant or viscosity, and therefore the ion-ion and ion-solvent interactions could be better studied. Consequently, a number of conductometric and related studies of different electrolytes in non-aqueous solvents, especially mixed organic solvents, have been made for their optimal use in high-energy batteries and for understanding organic reaction mechanisms. Thus, extensive studies on electrical conductance in mixed organic solvents have been performed to examine the nature and magnitude of ion-ion and ion-solvent interactions.

CHOICE OF SOLVENTS AND SOLUTES

Solvents such as Nitromethane, 1,3-Dioxolane, Nitrobenzene, Methanol, Ethylene glycol, n-Hexanol, o-Toluidine, Aniline, Acetonitrile, N,N-Dimethylformamide, N,N-Dimethylacetamide and Dimethylsulphoxide have been used in the research work because these solvents are industrially very important and by mixing these solvents we could obtain a wide variation of viscosities and

dielectric constants giving us an optimum environment for the study. The electrolytes used in the research work are Sodium Tetrphenylborate, Tetrabutylammonium Tetrphenylborate, Lithium Hexafluoroarsenate, Tetraalkylammonium Iodides, 1-Ethyl-3-methylimidazolium Bromide and Tetrabutylammonium Hexafluorophosphate. These electrolytes are used as reference and supporting electrolytes and are used as non-aqueous electrolytes in electrochemical applications.

METHODS OF INVESTIGATION

Different experimental techniques are employed to get a better insight into the phenomena of solvation and different interactions prevailing in solution. The techniques used to study various interactions in solution are: Densitometry, Viscometric, Conductometry, Ultrasonic Interferometry and Refractometry.

PHYSICO-CHEMICAL PARAMETERS AND THEIR SIGNIFICANCE

Limiting molar conductance (Λ_0) gives an idea about the ion-solvent interaction in the solution. Association constant (K_A) obtained from the conductance study gives an idea about the solvation of the ions. Partial molar volume (ϕ_v^0) and Viscosity B-coefficient obtained from the density and viscosity values respectively indicates the extent of ion-solvent interaction in a solution. From experimental speed of sound values, limiting apparent molar adiabatic compressibility (ϕ_K°) and the experimental slope (S_k^*) can be estimated. These parameters also give an idea about the ion-solvent and ion-ion interaction in the solution.

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SUMMARY OF WORKS DONE

CHAPTER I

This chapter contains the objective and applications of the research work.

CHAPTER II

This chapter contains the general introduction of the thesis and forms the background of the present work. A brief review of notable works in the field of ion-solvent interaction has been given.

CHAPTER III

This chapter contains the experimental section which mainly involves the structure, source, purification and application of the solvents and solutes used in the research work and the details of the instruments used for the study.

CHAPTER IV

In this chapter precise measurements on electrical conductance of sodium tetraphenylborate and tetrabutylammonium tetraphenylborate in different mass fraction (0.00–1.00) of nitromethane in nitrobenzene at 298.15K have been represented. Limiting molar conductances (Λ_0), association constants (K_A) and co-sphere diameter (R) for ion-pair formation in the mixed solvent systems were evaluated using the Fuoss conductance-concentration equation. FT-IR measurements for the solvents and solutions have been undertaken.

CHAPTER V

This chapter includes the study of electrolytic conductivities (Λ), densities (ρ), viscosities (η), refractive indices (n_D) and speed of sound (u) of tetrabutylammonium hexafluorophosphate in nitromethane, 1,3-dioxolane and nitrobenzene at 298.15 K. The limiting molar conductivities (Λ_0), association constants (K_A), and the distance of closest approach of the ion (R) have been evaluated using the Fuoss conductance equation. Triple ion formation in 1,3-

dioxolane has been analyzed by Fuoss-Kraus theory of triple-ions. The limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) derived from the Masson equation, and viscosity A and B coefficients using the Jones-Dole equation have been interpreted in terms of ion-ion and ion-solvent interactions, respectively. Molar refraction (R_M) have been calculated using the Lorentz-Lorenz equation. The adiabatic compressibility (β_s) have been evaluated using the u values. The limiting apparent molar adiabatic compressibility (ϕ_K^0) have been calculated and discussed.

CHAPTER VI

This chapter includes the study of electrolytic conductivities of tetraalkylammonium iodides, R_4NI ($R =$ butyl to heptyl) in (0.00, 0.25, 0.50 and 0.75) mass fraction of *o*-toluidine in *n*-hexanol at 298.15 K. Limiting molar conductances (Λ_0), association constants (K_A) and the co-sphere diameter R for ion-pair formation in 0.00 and 0.25 mass fraction of solvent mixture have been evaluated using the Fuoss-Equation. Triple-ion formation in 0.50 and 0.75 mass fraction of *o*-toluidine in *n*-hexanol has been analyzed by the Fuoss-Kraus theory of triple ions.

CHAPTER VII

Conductometric studies of 1-ethyl-3-methylimidazolium bromide in acetonitrile, methanol, *N,N*-dimethylformamide, *N,N*-dimethylacetamide and dimethylsulphoxide were undertaken at 298.15K. FT-IR measurements were supplemented to explain the ion-dipole interaction in the solution. The extent of interaction is expressed in terms of the association constant (K_A) and shows the ion-dipole interaction to be a function of viscosity.

CHAPTER VIII

In this chapter, conductivities of some tetraalkylammonium iodides were measured at 298.15 K aniline. The observed molar conductivities were analyzed by Fuoss-Kraus theory of triple-ions. A linear relationship between the triple-ion

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formation constants [$\log (K_T / K_p)$] and the salt concentrations at the minimum conductivity ($\log C_{min}$) have been given for all salts in aniline. The formation of triple-ions has been explained on the basis of coulombic interactions and covalent bonding forces operative between the ions.

CHAPTER IX

In this chapter, the electrolytic conductivities, densities and viscosities of lithium hexafluoroarsenate have been studied in different mass fraction of ethylene glycol in methanol at 298.15 K. The limiting molar conductivities (Λ_0), association constants (K_A) and the distance of closest approach of the ion (R) have been evaluated using the Fuoss conductance equation. The limiting apparent molar volumes (ϕ_{V^0}), experimental slopes (S_V^*) derived from the Masson equation and viscosity A and B -coefficients using the Jones-Dole equation have been interpreted in terms of ion-ion and ion-solvent interactions respectively.

CHAPTER X

This chapter contains the concluding remarks of the works related to the thesis.