Biointerface Research in Applied Chemistry

Original Review Article

Open Access Journal

A review on conductometric studies of electrolytes in mixed solvent systems to understand ion-ion and ion-solvent interactions

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ABSTRACT

The study of ion- solvent interaction is of much importance to investigate the nature of different solutions. Measurement of electrical conductivity and evaluation of physico-chemical properties, such as molar conductance, limiting molar conductance, ion-pair association, Walden product etc. shade light on different intermolecular interactions present in electrolyte solutions. Solvation properties can be varied by mixing two or more solvents. An extensive literature survey on conductometric studies has been carried out on different electrolytes dissolved in a wide range of mixed solvent systems. The reported results show that strong solute-solute, solute-solvent and solvent-solvent interactions are responsible for the physico- chemical behavior of a solution in mixed solvents.

Keywords:*Solvation; association; conductance; electrolytes; physico-chemical properties; molecular interactions.*

1. INTRODUCTION

An insight into the ion-solvent, ion-ion and solvent-solvent interactions has a significant role in understanding and interpreting the behavior of multicharge electrolytes in different mixed solvents [1-8]. Solvent properties like dielectric constant, structure, basicity, viscosity, thermodynamic properties etc. can be varied by varying the composition of the mixed solvents [9-12]. The study of Conductometric, densimetric, viscometric and acoustic behaviors of electrolytes expands over a large area of research in industry and laboratory, particularly in drug delivery system [13, 14]. Various other physico-chemical and thermodynamic parameters can also be derived from the experimentally obtained data of the above mentioned studies. Conductometric studies of electrolytes in different solvent systems and at different temperatures have been carried out by several researchers over years. They have reported and analysed their experimental findings in the light of solvation and transport properties of the electrolyte solutions. Molar conductance (Λ_m), limiting molar conductance (Λ_m^0), ion association constant (K_A), activation energy (E_a) and Walden product $(\Lambda_m^0\eta^0)$ can be calculated from the experimentally obtained conductance values. The thermodynamic parameters for the process of ion-association can also be determined from the conductance measurements. In this review article an attempt is made to consolidate the work of a large number of researchers studying the solvation behavior, transportation process, formation of ion-pairs and triple ions, structure making/breaking properties of solutes, the temperature dependence of electrical conductivity and influence of the solvents on these properties.

2. CONDUCTOMETRIC STUDIES

Conductometric studies have been proved to be an important tool to analyze the solvation and association of ions in solutions. A number of researchers have been working on solutions of a wide range of electrolytes and solvents to understand the solvation phenomenon and conductometricbehaviour of electrolytes in different mixed solvent systems and their findings are reported in the literature.

Adam Bald and his co-workers [15] have worked on conductance of triisoamylbutylammonium iodide, i-Am₃BuNi (TABI) and sodium tetraphenylborde, NaBPH₄ in different compositions of water + N,N-dimethylformamide at 298.15K. They discussed their results in terms of structure making and structure breaking properties of the solutes. Adam Bald *et al.* [16] also studied conductance behavior of uni-univalent electrolytes, such as NaBPH₄, NaBuI₄, NaI, NaCl, NaBr, and NaClO₄ in aqueous propan-1-ol solution at 298.15K and the values of limiting conductance, association constant, ionic Walden product and other related parameters were calculated by using the well known Fuoss conductance-concentration equation [17]. It was noticed that ionic Walden products decrease as water molecules are replaced with alcohol in the solvation shells. For larger ions such as NBu₄⁺ and BPh₄⁻, the Walden product values are different because of their different sizes and the extent of their solvation in water. It was also seen that mobility of ions in solutions with different propanol content, except 30 mole percent of propanol, is in the order of $ClO_4^->I^->Br^->Cl^-$ which is reverse to that in water.

Adam Bald and his coworkers [18] further worked on the conductance measurements of NaCl, KCl, NaBr, KBr, Bu₄NBr and NaBPH₄ inaqueous 2-methoxyethanol solutions at 298.15K. It was reported that because of greater solvation of smaller ions like chloride and bromide with a higher content of 2-methoxyethanol in solutions, the solvation shell of smaller ions become almost same size to those of larger organic ions like Bu₄N⁺ and BPH₄⁻ which undergo very small solvation in varied compositions of 2-methoxyethanol in mixed solvents. As an extension to their previous work on conductivity studies of electrolyte solutions in

mixed water-organic solvents systems, another report on electrical conductivities of KI, LiBr, LiNO₃, AgNO₃ and Et₄NI in aqueous propanol solutions of different composition have been presented by Adam Bald and his team [19]. Limiting molar conductance, association constant and distances of closest approach of ions in the mixed solvents have been calculated by using the conductance data in low concentration chemical model (lcCM) [20]. Ionic conductivity values for K^+, Li^+, Ag^+, Et_4N^+, and NO_3^- were calculated. Ion–solvent interactions in the electrolyte solutions have been analysed by understanding the correlation between the effective size of the ions, composition of the mixed solvent and ioninc Walden products. It was found that effective size and ionic walden product values for larger organic cations practically do not depend on the percentage of propane-1-ol in the mixed solvent.

Conductance values of alkali metal chlorides, such asLiCl, KCl and NaCl in aqueous ascorbic acid solutions at different temperatures in the range of 303.15- 318.15K are reported by Sunil Kumar et al. [21]. It was observed that limiting molar conductance values increase with increasing temperature which may be attributed to the increasing ionic mobility at higher temperatures. The activation energy values calculated from conductance data are found to be in the order KCl>NaCl>LiCl. From the values of Limiting apparent molar volume (ϕ_v^0), Jones-Dole coefficient (B) and limiting molar conductance (Λ_m^0), the solute–solvent interactions in the solutions have been analysed. The negative sign of temperature coefficients of these data explains structure breaking behavior of LiCl, NaCl and KCl in 0.01 m aqueous ascorbic acid solution.

Conductance values of lanthanum chloride in aqueous and in 1%, 2.5%, 5% and 10% aqueous maltose solutions at 303.15K are reported by M. Chakraborty et al. [22]. They discussed the structural effect of the solvent systems in light of ion-ion and ion-solvent interactions. In their paper it is noted that limiting molar conductance and Walden product values decrease as concentration of maltose increases in the mixed solvent because size of the solvated ions and ion-solvent interactions are more in maltose +water solution than in water alone.

G. Ravichandran et al. [23] studied the equivalent conductance of bile salts in water and in solutions of water + 10% (v/v) of aprotic solvents. It was observed that equivalent conductance varies inversely with bile salt concentration. At low concentration dissociation of bile salt into Na^+ ions and cholate/deoxycholate ions results in an increase in conductivity. The situation is reversed due to the formation of micelles at higher concentration of bile salt.

A study on conductance measurement on tetraalkylammonium halides in THF and CCl₄ mixtures has been reported by Roy et al. [24]. According to their report ion size determines the formation of ion pairs or triple ions. A larger number of triple ions is formed from Otc₄NCl in THF and CCl₄ mixed solvents of different composition in comparison to other smaller halides.

A report on conductance studies of sodium tetraphenylborate and tetrabutylammoniumtetraphenylborate in pure nitrobenzene and nitromethane and their mixtures has been produced by Roy et al. [25]. The study showed that conductance values of both the salts are higher in nitromethane because association of these salts is higher in nitrobenzene. Fuoss relation

was used to evaluate limiting molar conductance (Λ_0), association constants (K_A), and co-sphere diameter (R) for ion-pair formation in the mixed solvent systems. The measurements of electrical conductance of sodium per chlorate (NaClO₄), sodium tetrafluoroborate (NaBF₄) and sodium tetraphenyl borate (NaBPh₄) in 1,2-dimethoxythane by Pitchi J Victor et al. [26] reveals that ClO_4^- ions are solvated to greater extent as compared to BF_4^- and BPh_4^- ions in the solvent. Though both ion-pairs and triple ions form, formation of ion pairs dominates over the formation of triple ions. Solvation of the ClO_4^- ions is significantly higher than the solvation of BF_4^- and BPh_4^- in DME solution.

The investigation and discussion on conductance for alkali metals and tetraalkylammonium halides and perchlorates in propylene carbonate and solvent nature of propylene have been made by Murray L. Jansen et al. [27].

The equivalent conductance of multivalent electrolytes has been measured by S. Mahiuddin et al. [28] at temperature ranging from -20⁰ Cto 70⁰ C over the total concentration range upto a saturation point at -20⁰ C. They observed that the values of specific conductance, activation energies for conductance process and viscous flows and Walden product vary with the concentration along with the structural effect.

Theoretical and experimental investigation have been carried out by Alexander Apleblat [29] on electrical conductance of strong electrolytes, such as alkali metal halides and perchlorates and tetraalkylammonium halides in 2-alkoxyethanol-water mixtures. At a given temperature and composition limiting conductance, association constant, ion size parameter and walden product have been calculated from the experimental conductivity data. Electrical conductance of electrolytes isinterpreted in terms of size, structure making/breaking properties, charge densities, polarizability, ion-pair formation, hydration and salvation of ions. Dash et al. [30] have analysed their conductance data of trans-[Co(en)₂Cl₂]Cl and trans-[Co(en)₂Br₂]Br in water and alcohol mixtures by Shedlovsky [31] and Frouss Kraus[32] extrapolation technique. Limiting molar conductance values obtained from both the methods are similar. Association constant values were determined from the conductance data and are found to increase with temperature, alcohol content and the number of $-CH_2-$ group in alcohol. They also stated that ion association for trans-[Co(en)₂Cl₂]Cl is higher than that of trans--[Co(en)₂Br₂]Br in all composition of alcohol mixtures. In their study, Farid I. El-Dossoki [33] has used different compositions of n-butanol-water and iso-butanol-water mixtures as solvents for dilute hydrochloric acid. In order to understand the effect of water and time on the transfer process of the hydronium ion and on the solute–solvent interactions, he has analysed the conductance data of the solutions using Lee-Wheaton conductivity equation [34] and has reported the values of molar conductance, limiting molar conductance, dissociation constant and the standard free energy of dissociation.

It was seen that the values of dissociation constant, (K_d), and the limiting molar conductance, (Λ_m^0), decrease as the relative permittivity of the solvent decreases in order of methanol, ethanol, n-propanol, n-butanol and iso-butanol. He has discussed the results with reference to the water content of the alcohol solutions.

Molar conductance and association constant of potassium, sodium and ammonium halides in different composition of water +

Dextran mixtures at temperatures 298.15- 313.15K were analysedby Dash *et al.* [35] by using Shedlovsky extrapolation technique. Ion- solvent interactions are discussed with varying concentration of the halides, compositons of the mixed solvent and temperature. It was found that limiting molar conductance values for all the halides increase with temperature indicating towards higher bondbreaking, low solvation and higher mobility of ions at a higher temperature. However, the limiting molar conductance values for KCl decrease with increasing concentration of dextran in the mixture because of the lowering of dissociation of solute to ions. Decreasing values of Walden products are in support ofweak solvation of ions in solutions with increasing dextran content. Ion–solvent and solvent–solvent interactions may be analysed with reference to association constant, K_A resulted from varying degree of exothermic ion-pair association in solutions with varied dextran content.

Dash *et al.* [36] further reported conductance measurements of solutions of octahedral Co(III) complexes in water + 5% mannitol and water + %5 sorbitol at different temperatures. They suggested that different association values are attributed to octahedral distortion of the complex. It was reported that the Co(III) complexes with higher ion-ion interactions exhibit low ion-solvent interaction and vice versa. Ion association of Co(III) complexes in water + alcohol mixtures have been evaluated at different temperatures from the conductance data by Dash *et al.* [37]. The results shade light on ion-ion and ion-solvent interactions and structural effects of the solvent in solutions. Guha *et al.* [38] have measured electrical conductivity and discussed limiting molar conductance, association constants and association diameters of ammonium and potassium thiocyanates in 2-ethoxyethanol + water mixtures in terms of varying solvodynamic size of the ions with respect to the composition of the mixed solvent system and temperature. They suggested that non-coulombic interaction plays a major role in ion- association. Ion-association constants for divalent symmetric electrolytes, such as $CoSO_4$, $NiSO_4$, $CuSO_4$ and $ZnSO_4$ in water were evaluated by Bester- Rogac *et al.* [39] from conductivity data using low concentration chemical model (lcCM). They have noted that the values of limiting molar conductance and association constant and other parameters derived from lcCM resemble closely with the values reported earlier in the literature. Thermodynamic functions for the ion pairing process have been calculated and the effects of ion pairing on structural changes of the solvent and the size of the cations have also been discussed. Experimental values of conductance of magnesium solutions in different compositions of water + 1,4-dioxan at different temperatures ranging from 5 -35^{0}C were determined by Bester- Rogac *et al.* [40].

As solubility of magnesium sulphate decreases rapidly in a higher concentration of dioxane in the mixed solvent, concentration of dioxine was restricted to 50% in the mixture. Ion-association values and thermodynamic functions of magnesium sulphate were calculated from ion pairing process using a low concentration chemical model (lcCM). Oleg N Kalugin *et al.* [41] have worked on ion association and solvation process of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Ni^{2+} perchlorates in acetonitrile. They have discussed the temperature dependence of ion association constant for the solvent separated ion- pairs and the effect of non-coulombic forces on the cation solvation. Molar conductance of

potassium ferrocyanide and ferricyanide in aqueous and 5, 10 and 15% aqueous d-fructose solutions has been measured by Sujit K Dehury *et al.* (42) at different temperatures (298.15-313.15K). According to their report conductance values increase with increasing temperature and with charge and total number of ions, as in the case of ferrocyanide. They also found that conductance values decrease with increasing weight percent of d-fructose in the binary solvent system. This may be due to lower mobility of ions as more d-fructose molecules are present in the solvent cage than in water. The process of solvation of the ions in binary mixtures has been discussed to interpret the ion association and thermodynamic properties for the transfer process. Sujit K Dehury and his coworkers (43) also measured the molar conductance of potassium dichromate and pyrophosphate in aqueous and 5, 10 and 15% aqueous d-Mannitol mixtures at different temperatures.

The results are very similar to those of their previous work with potassium ferricyanide and ferrocyanide in aqueous d-fructose solutions. They discussed their experimental results in terms of solvation and mobility of ions in water and in d-mannitol + water mixtures. Electrical conductivities of dilute aqueous solutions of caffeic acid, sodium caffeinate and potassium caffeinate were determined by Apleblat *et al.* [44] in the temperature range from 278.15 K to 313.15 K. The experimental data were analyzed by using the Kohlrausch and Onsager conductivity equation to get the limiting conductances of caffeinate anion, their diffusion coefficients at infinite dilution, and the Stokes radii. They have evaluated the equilibrium constant for dissociation of caffeic acid by applying the Quint-Viallard conductivity equations and activity coefficients by using the Debye-Hückel expression. They have reported the temperature dependence of the equilibrium constant and standard thermodynamic functions of the dissociation process.

Borun *et al.* have performed conductivity studies on various ionic liquids in a wide range of water + organic solvent systems at different temperatures. As an extension of their previous work [45, 46] electrical conductance of 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF4] and 1-butyl-3-methylimidazolium [bmim][BF4] in N, N'-dimethylformamide were measured at 218.15- 318.15K [47]. They have discussed the effect of temperature, solvent structure and properties, the cation and anion of the ionic liquid on the limiting molar conductivity and the ionic association, as well as ion transport processes and thermodynamic properties of ionic association. A Borun and his coworkers have also studied the conductance behavior of the above mentioned imidazolium ions in dichloromethane [48], 1-Butanol [49], N,N-dimethyl acetamide [50], propan 2-ol [51] at a wide range of temperatures.

Their work Further extended to the measurement of conductance of sodium tetraphenylborate ($NaBPh_4$), tetrabutylammonium bromide (Bu_4NBr) and sodium tetrafluoroborate ($NaBF_4$) in N,N-dimethylformamide solutions [52] and of KI, LiBr, $LiNO_3$, $AgNO_3$ and Et_4NI in mixtures of propan-1-ol with water in a whole range of composition of mixtures at 298.15 K [53]. For all the systems they have analysed their experimental conductance data by following low concentration Chemical Model (lcCM). The limiting ionic conductivities of individual ions were determined using the

Fuoss–Hirsch assumption. The limiting molar conductances $\Lambda_m{}^0$, Walden products $\Lambda_m^0 \eta^0$, association constant K_A and distance parameter R were obtained by Fuoss- Justice equation. The thermodynamic parameters for the ion-pair formation were also calculated. An analysis of temperature dependence of ion association process was helpful to understand the ion-solvent interactions.

Borun has recently published a review article on his research on conductance and ion association of imidazoliun ionic solutions in various solvent systems [54].

Their recent works comprise the conductance studies of aqueous solutions of sodium salts of cinnamic acid [55] and benzoic acid derivatives [56] at different temperatures.

In 2017 introduction of Lithium-ion rechargeable batteries completed 25 years [57]. Since then lithium hexafluorophosphate ($LiPF_6$) has been used as the electrolyte in Li battery. Makoto Ue and coworkers have worked on lithium hexafluorophosphate ($LiPF_6$) salt dissolved in ethylene carbonate, propylene carbonate, dimethyl carbonate, ethyl methyl carbonate, and diethyl carbonate [58]. Another electrolyte Lithium bis(fluorosulfonyl)imide (LiFSI) has taken over the market because of its higher elctrical conductivity in organic solvents [59]. In order to study its physicochemical properties in different organic solvents Johannes Neuhaus and coworkersmeasured the electrical conductivity of solutions of LiFSI in dimethyl carbonate (DMC), ethylene carbonate (EC) and propylene carbonate (PC) [60] and in their binary and ternary mixtures [61]. Optimization of performance and cost of the battery was proposed based on the correlation of electrical conductivity with Li salt concentration, solvent composition and temperature. Alkyl carbonate and γ-butyrolactone (GBL) are other organic electrolytes for LIBs thatare stable over a wide range of operating voltages [62].

Recent work on household batteries is concentrating on producing biodegradable batteries to meet the environmental issues related to disposal of these objects. The choice of electrolytes for Li-battery opens a horizon of research. Two categories of electrolytes have been cited in the report presented by M. Kameche and his team [63]. The use of organic solvents to make Li-salt electrolytes is in practice for a couple of decades. However, in an attempt to minimize the toxicity of the Li-salt electrolytes and remain in the framework of green chemistry gel-polymer electrolyte is gathering interest among researchers [64].

3. CONCLUSIONS AND FUTURE SCOPE

Conductometry is one of the most reliable and widely used techniques to investigate electrolyte solutions. Ion association constant can be determined most accurately by conductometric measurements. Ionic mobility, hence electrical conductivity increases when the ions are less solvated. In a mixture of organic solvent + water, with an increasing percentage of organic solvents ionic mobility decreases as water molecules are replaced from the salvation cage by heavier organic molecules.

It was found that smaller ions are more solvated and the solvation shells around them are thicker compared to the larger ions. Weaker solvation of ions is indicated by the higher values of Walden products. Ion-pair association was found to be low in solvents with higher relative permittivity due to the independent solvation of ions. As temperature increases, higher thermal energy leads to greater bond breaking of the molecules, hence higher mobility of ions results in higher limiting molar conductivity.

In an attempt of gaining a greater insight into these phenomenons rigorous research work must be carried out with different electrolytes in different solvent systems and at different working temperatures.

Lithium ion batteries are becoming more and more popular because of their better performance and low cost. It is expected that LIB will be in greater demand in the coming years and research will continue to improve their cost, safety and energy and power capability.

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6. ACKNOWLEDGEMENTS