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Conductivity is a contrivance to explore ion-pair and triple-ion structure of ethanoates in tetrahydrofuran, dimethyl sulfoxide and their binaries

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ABSTRACT

Precise electrical conductance measurements are reported for some ethanoates, viz. ammonium, lithium, sodium and potassium in pure tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) and their binary mixtures at 298.15 K. The conductance data have been analyzed by the Fuoss conductance–concentration equation to evaluate the limiting molar conductance (Λ^o), the thermodynamic association constant (K_A) and the association diameter (R) for ion-pair formation. The limiting ionic conductances have been estimated from the appropriate division of the limiting molar conductivity value of the "reference electrolyte" Bu_4NBPh_4. Furthermore, the conductance data for pure THF have been analyzed by the Fuoss–Kraus theory of triple ions and the values of the ion-pair and triple-ion formation constants (K_P and K_T) were made and the results have been discussed in terms of molecular scale model.

1. Introduction

Studies of the transport properties of electrolytes in different solvent media are of considerable importance for the information they provide on the behavior of ions in solution.

Mixed solvents enable the variation of properties such as dielectric constant or viscosity and therefore the ion–ion and ion–solvent interactions can be better studied. Usually a mixture is repeatedly tested by electrolytes with a common ion (anion or cation) to confirm the trend of changes and to reveal the influences of the co-ion on the quantities derived. In such a direction, binary mixtures of organic solvents with a varying range of composition are most frequently investigated solvent media. A number of conductometric methods are well-suited to investigate the ion–solvent and ion–ion interactions in electrolyte solutions [1–6]. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions, which in its turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent–solvent interactions.

Tetrahydrofuran (THF) is an important liquid which find a variety of applications in pharmaceuticals, cosmetics, etc. Dimethylsulfoxide (DMSO) is a powerful broad spectrum solvent for a wide variety of inorganic and organic reactants. Having low toxicity, DMSO can be used in biology and medicine, especially for low-temperature preservation. We have taken pure THF ($\varepsilon = 7.58$), DMSO ($\varepsilon = 46.7$) and their mixture for this study because we prefer non aqueous solvent which are nonprotic polar solvent and hydrogen bonding can be avoided. The experimental acetate salts are chosen as their charge densities are high and they form solvent-separated ion pairs. Such studies have been assumed important because of their applications in modern technology [7]. This type of solvent mixture have applications in high energy batteries especially lithium batteries, in organic syntheses and cosmetics technology as manifested from the physicochemical studies in these media [8–10].

In this paper, an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of some ethanoates in pure tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) and their binary mixtures by using precise conductivity measurements at 298.15 K.

2. Experimental

Tetrahydrofuran, C_4H_8O (Merck, India) containing 0.1% water and 0.005% peroxide, was kept for several days over KOH, refluxed for 24 h, and distilled over $LiAlH_4$ [8,11–13].

Dimethyl sulfoxide (SRL Extra pure) was kept for several days over anhydrous $CaSO_4$ and refluxed for 4 h over CaO. Then, it was distilled according to the procedure described earlier [14]. Finally the density and viscosity values were compared with the literature

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Nomenclature

ρ	solution density
ρ_0	solvent density
η	solution viscosity
η_0	solvent viscosity
ε	relative permittivity
c	molarity
m	molality
Λ	molar conductance
Λ^o	limiting molar conductance
K_A	association constant
K_S	association constant of contact-pairs
K_R	association constant of solvent-separated pairs
$f_\pm$	mean activity coefficient
R_X	relaxation field effect
E_L	electrophoretic counter current
K_P	ion-pair formation constants
K_T	triple-ion formation constants
C_P	ion-pair concentrations
C_T	triple-ion concentrations
γ	fraction of solute present as unpaired ion
β	twice the Bjerrum distance
κ^{-1}	radius of ionic atmosphere
e	electric charge
k_B	Boltzmann constant
R	association distance or co-sphere diameter
r_s	Stoke's hydrodynamic radii
ΔG^0	Gibbs energy of ion-association reaction
σ	standard deviation

[15,16] and the purity of these chemicals, checked by gas–liquid chromatography.

The experimental ethanoates CH_3COOLi, CH_3COOK, CH_3COONH_4 and CH_3COONa are 99% pure (Merck) and they were purified by recrystallization twice from conductivity water. The samples were dried in vacuum and stored over P_2O_5 under vacuum [17]. Tetrabutylammonium acetate (Bu_4NOAc) was purified by recrystallization from acetone, and the crystallized salt was dried in vacuum for 48 h. Sodium tetraphenylborate ($NaBPh_4$) was recrystallized three times from acetone and then dried under vacuum for 72 h [18]. Deionizer water was used after further distillation having specific conductivity $1.99 \times 10^{-6}\,\Omega^{-1}\,cm^{-1}$ at 298.15 K. The materials finally obtained were found to be >99.5% pure.

Binary solvent mixtures were prepared by mixing a required volume of THF and DMSO with earlier conversion of required mass of each liquid into volume at 298.15 K using experimental densities. A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molality into molarity was accomplished using density values. The uncertainty of molarity of different salt solutions is evaluated to $\pm 0.0001\,mol\,dm^{-3}$.

The value of the relative permittivity (ε) of the solvent mixtures was assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner [19]. The density (ρ) was measured by means of vibrating-tube density-meter (Anton Paar, DMA 4500) which was calibrated with distilled water and air [18]. The uncertainty in the density measurement was $\pm 0.0002\,g\,cm^{-3}$.

Solvent viscosities were measured by means of a suspended Ubbelohde-type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained at ±0.01 K of the desired temperature. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ±0.01 s. The uncertainty of viscosity values is $\pm 0.003 C_P$. The details of the methods and measurement techniques had been described elsewhere [20,21].

The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy ± 0.01%) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 10%). Measurements were made in a water bath maintained within $T = (298.15 \pm 0.01)$ K and the cell were calibrated by the method proposed by Lind et al. [22]. The entire conductance data were reported at 1 kHz and were found to be ±0.3% precise. During all these measurements uncertainty of temperatures was ±0.01 K.

3. Discussion

The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. The conductance data for different electrolytes in pure DMSO and different binary mixtures having higher to moderate relative permittivity values ($\varepsilon = 46.70–17.36$), have been analyzed using the Fuoss conductance–concentration equation [23] as ion-pairs formation is results. But in pure THF having low relative permittivity value ($\varepsilon = 7.58$), conductance data shows that electrostatic ionic interactions are such that formation of symmetrical triple-ions results, hence the conductance data have been analyzed by the Fuoss–Kraus triple-ion theory [24].

3.1. Electrical conductivity of ethanoates in pure DMSO and different binary mixtures of (THF + DMSO)

The experimental values of the molar conductance, Λ against the respective concentration, c for different electrolytes in pure THF (w_1), DMSO (w_2) and their different binary mixtures at 298.15 K are recorded in Table 2.

The conductance curves (Λ versus $\sqrt{c}$) were linear and extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductances for the electrolytes. For a given set of conductivity values (c_j, Λ_j,

Table 1
Physical properties of pure THF, DMSO and different binary mixtures of (THF + DMSO) at 298.15 K.

Mass% of THF (w_1)	ρ^a ($\times 10^{-3}$ kg m^{-3})		η^b (mPa s)		ε
	Observed	Literature	Observed	Literature	
0.00	1.0958	1.0951 [15]	1.96	1.992 [15]	46.70 [16]
0.25	1.0367		1.5234		36.92 [19]
0.50	0.9847		1.1125		27.14 [19]
0.75	0.9340		0.7376		17.36 [19]
1.00	0.8811	0.8811 [16]	0.463	0.463 [16]	7.58 [16]

[a] Uncertainty ± $0.0002\,g\,cm^{-3}$.
[b] Uncertainty ± $0.003 C_P$.