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Ionic interplay of lithium salts in binary mixtures of acetonitrile and diethyl carbonate probed by physicochemical approach

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ABSTRACT

Electrolytic conductivities, densities and viscosities of lithium salts (LiI, LIClO$_4$ and LiAsF$_6$) have been studied in (0.25, 0.50 and 0.75) mass fraction of acetonitrile (AN) in diethyl carbonate (DEC) at 298.15 K. The limiting molar conductivities (Λ_0), association constants (K_A) and the distance of closest approach of the ions (R) have been evaluated using the Fuoss conductance equation (1978). The Walden product is obtained and discussed. However, the deviation of the conductometric curves (Λ versus $\sqrt{c}$) from linearity for the electrolytes in 0.25 mass fraction of acetonitrile (AN) in diethyl carbonate (DEC) indicated triple-ion formation, and therefore the corresponding conductance data have been analysed by the Fuoss–Kraus theory of triple-ions. The observed molar conductivities were explained by the ion-pair ($M^+ + X^- \leftrightharpoons MX$) and triple-ion ($2M^+ + X^- \leftrightharpoons M_2X^+$, $M^+ + 2X^- \leftrightharpoons MX_2^-$) formation. 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.

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1. Introduction

Behaviour of electrolytic solutions can be obtained by studying their thermodynamic and transport properties. The molecular interactions within the electrolytic solution can be studied in a better way by varying the properties of the solvents such as dielectric constant or viscosity which can be attained by using mixed solvent systems. The uses of non-aqueous electrolytes [1] in high-energy batteries [2] and for understanding organic reaction mechanisms [3] are well known. The influence of the solvent mixtures on the ionic association of the electrolytes is due to the mode of solvation of the ions [4–8]. Solvent properties such 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. Thus, extensive studies on electrical conductances in various mixed organic solvents have been performed in recent years [9–13] to examine the nature and magnitude of ion–ion and ion–solvent interactions.

Volumetric and viscometric studies also render an insight into the molecular interactions prevailing in solution and help in the better understanding of the behaviour of electrolytic solutions. Studies on the apparent and limiting apparent molar volumes of the electrolyte and the dependence of viscosity on the concentration of salt have been employed as a function of studying ion–ion and ion–solvent interactions [14].

In this paper, conductometric, volumetric and viscometric studies have been carried out for lithium iodide (LiI), lithium perchlorate (LiClO$_4$) and lithium hexafluoroarsenate (LiAsF$_6$) in 0.25, 0.50, and 0.75 mass fraction of acetonitrile (AN) in diethyl carbonate (DEC). The salts used in the study when mixed with organic solvents are very good electrolytes in lithium-ion batteries. Lithium-ion batteries are widely used in products such as portable consumer electronic devices. Hence, studying the behaviour of these lithium salts in different organic solvent systems will help in the production of more useful and cost effective batteries. The solvents, i.e. acetonitrile and diethyl carbonate used in the study are also very useful in battery industries. By mixing these two solvents we obtained a wide variation in solvent properties.

2. Experimental

2.1. Materials

Lithium iodide (LiI), lithium perchlorate (LiClO$_4$) and lithium hexafluoroarsenate (LiAsF$_6$) of puriss grade were procured from Aldrich, Germany. They were used as purchased as the purity assay of the salt was $\geq$98%. Acetonitrile (AN) procured from Thomas Baker, India and diethyl carbonate (DEC) procured from Sisco Chem.

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Table 1
Density (ρ), viscosity (η) and relative permittivity (ε) of the different mass fraction (w_1) of AN in DEC at 298.15 K.

w_1	$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)		ε
	Expt.	Lit.	Expt.	Lit.	
0.00	0.96917	0.96916 [32]	0.74	0.750 [34]	02.83
0.25	0.92112		0.65		11.11
0.50	0.87325		0.57		19.39
0.75	0.82487		0.45		27.4
1.00	0.77685	0.7768 [33]	0.34	0.3409 [33]	35.95

Industries, India were purified using standard methods [15]. The purity of the AN was 99.5% and DEC was 99%.

2.2. Apparatus and procedure

A stock solution for the electrolyte was prepared by mass (Mettler Toledo AG285 with uncertainty 0.0003 g), and the working solutions were obtained by mass dilution at 298.15 K. The uncertainty of molarity of different solutions was evaluated to ±0.0001 mol dm^{-3}. The values of relative permittivity (ε) of the solvent mixtures were assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner [16].

The density (ρ) was measured by means of vibrating-tube Anton Paar density-metre (DMA 4500 M) with a precision of 0.00005 g cm^{-3}. It was calibrated by measuring the density of double-distilled water and dry air and them comparing the density values with the standard reference value given by the certificate of density standard liquids.

The viscosity was also measured with a Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield Digital Bath TC-500.

The conductance measurements were carried out in a Systronic-308 conductivity metre (accuracy ±0.01) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) cm^{-1}. Measurements were made in a water bath maintained within T = (298.15 ± 0.01) K and the cell was calibrated by the method proposed by Lind et al. [17] The conductance data were obtained at a frequency of 1 kHz.

3. Results and discussion

The solvent properties are given in Table 1. The concentrations and molar conductances (Λ) of LiI, $LiClO_4$ and $LiAsF_6$ in different mass fraction of AN in DEC are given in Table 2. The molar conductance (Λ) has been obtained from the specific conductance (κ) value using the following equation:

$$\Lambda = \frac{1000\,\kappa}{c} \tag{1}$$

Linear conductance curves (Λ versus $\sqrt{c}$) were obtained for the electrolytes in 0.50 and 0.75 mass fraction of AN in DEC and extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductance for the electrolytes. But for the electrolytes in 0.25 mass fraction of AN in DEC, a deviation in the conductance curve was obtained and shows a decrease in conductance values upto a certain concentration and again an increase in the conductance value indicating triple-ion formation.

The conductance data for the electrolytes in 0.25 mass fraction of AN in DEC have been analysed using the classical Fuoss–Kraus equation [18a,18b] for triple-ion formation

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right) c \tag{2}$$

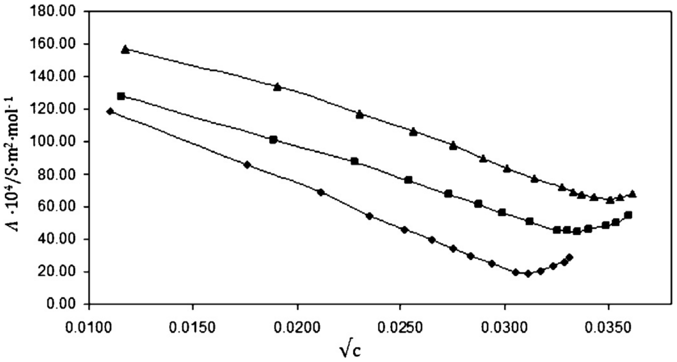

Fig. 1. Plot of molar conductance (Λ) versus $\sqrt{c}$ for LiI (♦), $LiClO_4$ (–■–) and $LiAsF_6$ (–▲–) in 0.025 mass fraction of AN in DEC at 298.15.

$$g(c) = \frac{\exp\{-2.303\ \ \beta^{/}(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1 - \Lambda/\Lambda_0)^{0.5}} \tag{3}$$

$$\beta^{/} = \frac{1.8247 \times 10^6}{(\varepsilon T)^{1.5}} \tag{4}$$

$$S = \alpha\,\Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\varepsilon T)^{1.5}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{0.5}} \tag{5}$$

In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution; $\Lambda_0{}^T$ is the sum of the conductances of the two triple-ions $Li(X_2)^-$ and $(Li)_2{}^+X$ where X = I^-, $ClO_4{}^-$ $AsF_6{}^-$; $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants. To make Eq. (2) applicable, the symmetrical approximation of the two possible constants of triple-ions equal to each other has been adopted [19] and Λ_0 values for the studied electrolytes have been calculated [20]. $\Lambda_0{}^T$ is calculated by setting the triple-ion conductance equal to $2/3\Lambda_0$ [21].

The ratio $\Lambda_0{}^T/\Lambda_0$ was thus set equal to 0.667 during linear regression analysis of Eq. (2).

Table 3 shows the calculated limiting molar conductances of simple-ion (Λ_0), limiting molar conductances of triple-ion $\Lambda_0{}^T$, slope and intercept of Eq. (2) for LiI, $LiClO_4$ and $LiAsF_6$ in 0.25 mass fraction of AN in DEC at 298.15 K.

Linear regression analysis of Eq. (2) for the electrolytes with an average regression constant, R^2 = 0.9653, RMSD = 0.0481 and standard error deviation of 0.0023, gives intercepts and slopes. These permit the calculation of other derived parameters such as K_P and K_T listed in Table 4. It is observed from Fig. 1 that Λ passes through a minimum as c increases due to the formation of triple-ions in the solution. A perusal of Table 4 shows that the major portion of the electrolytes exists as ion-pairs and a minor portion as triple-ions. The value of $\log(K_T/K_P)$ is found to be highest in LiI as given in Table 4 so it has the highest tendency to form triple-ions.

At very low permittivity of the solvent, electrostatic ionic interactions are very large. So the ion-pairs attract the free +ve and −ve ions present in the solution medium as the distance of the closest approach of the ions becomes minimum. This results in the formation of triple-ions, which acquire the charge of the respective ions in the solution [22], i.e.

$$M^+ + X^- \leftrightarrows M^+ \ldots X^- \leftrightarrows MX \tag{6}$$

$$MX + X^- \leftrightarrows MXX^-$$

$$MX + M^+ \leftrightarrows MXM^+ [M = Li \text{ and } X = I^-, ClO_4{}^-, AsF_6{}^-]$$

Furthermore, the ion-pair and triple-ion concentrations, c_P and c_T respectively of the electrolyte are also calculated at the minimum

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