



# Probing molecular interactions of ionic liquid in industrially important solvents by means of conductometric and spectroscopic approach

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## ABSTRACT

Qualitative and quantitative analysis of molecular interaction prevailing in ionic liquid-organic solvent media, probed by electrical conductances and FT-IR measurements have been reported. Conductometric studies of 1-ethyl-3-methylimidazolium bromide [EMIm]Br in acetonitrile (AN), methanol (MeOH), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMA) and dimethyl sulphoxide (DMSO) at 298.15 K reveals high molecular interaction contributed mainly by ion-dipole interaction as evident from the FT-IR measurements. 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. The interaction obtained is highest in case of DMSO in comparison to the other solvents. The greater share of the conductance of [EMIm]Br in different solvents comes from the  $\text{Br}^-$  ion than the [EMIm]<sup>+</sup> ion as evident from their ionic conductance values which is estimated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate [ $\text{Bu}_4\text{NBPPh}_4$ ] as the “reference electrolyte” method.

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## 1. Introduction

The exploration of molecular interaction existing in solution is always an interest to the chemists. Molecular interaction can be studied in solution phase by studying its thermodynamic and transport properties. These properties provide important information about the nature and strength of intermolecular forces operating among mixed components. FT-IR measurements have also been one of the most convenient methods for investigating the molecular interactions in electrolytic solutions [1–3].

Ionic liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering, their molecular interaction with the industrially important organic solvents would be of utmost importance for the chemical formulations in these industries. The inter-ionic interaction between the ions in the ionic liquid is very weak hence it easily dissolves in polar solvents providing us an excellent environment for the investigation of the molecular interaction in these solutions.

Hence we have investigated the molecular interactions of 1-ethyl-3-methylimidazolium bromide [EMIm]Br in acetonitrile (AN), methanol (MeOH), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMA) and dimethyl sulphoxide (DMSO).

## 2. Experimental

### 2.1. Materials

1-Ethyl-3-methylimidazolium bromide [EMIm]Br of puriss grade was procured from Aldrich, Germany. It was used as purchased as the purity assay of the salt was  $\geq 98.5\%$ . All the solvents of spectroscopic grade were procured from Thomas Baker, India. The purities of the solvents were  $>99.5\%$ . The solvents were dried using standard methods [4].

### 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  $\pm 0.0001 \text{ mol dm}^{-3}$ . The density ( $\rho$ ) was measured by means of vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of  $0.0005 \text{ g cm}^{-3}$ . It was calibrated by double-distilled water and dry air.

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 [5–7]. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to  $\pm 0.01 \text{ K}$ . After attainment of thermal

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**Table 1**  
Density ( $\rho$ ), viscosity ( $\eta$ ) and relative permittivity ( $\epsilon$ ) of the solvents at 298.15 K.

Solvents	$\rho \cdot 10^{-3}$ (kg m <sup>-3</sup> )		$\eta$ (mPa s)		$\epsilon$
	Lit.	Expt.	Lit.	Expt.	
AN	0.7768 [18]	0.7762	0.3409 [18]	0.346	35.95 [18]
MeOH	0.7866 [18]	0.7861	0.5445 [18]	0.546	32.70 [18]
DMF	0.9443 [18]	0.9437	0.796 [18]	0.796	36.71 [18]
DMA	0.9366 [18]	0.9359	0.919 [18]	0.923	37.78 [18]
DMSO	1.0958 [18]	1.0953	1.96 [18]	1.963	46.70 [18]

equilibrium, efflux times of flow were recorded with a stopwatch correct to  $\pm 0.1$  s. At least three repetitions of each data reproducible to  $\pm 0.1$  s were taken to average the flow times. The uncertainty of viscosity values is  $\pm 0.003$  mPa s. The details of the methods and measurement techniques have been described elsewhere [8,9].

The conductance measurements were carried out in a Systronic-308 conductivity meter (accuracy  $\pm 0.01\%$ ) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately  $(0.1 \pm 0.001)$  cm<sup>-1</sup>. Measurements were made in a water bath maintained within  $T = (298.15 \pm 0.01)$  K and the cell was calibrated by the method proposed by Lind et al. [10] The conductance data were reported at a frequency of 1 kHz and the accuracy was  $\pm 0.3\%$ .

Infrared spectra were recorded in 8300 FT-IR spectrometer (Shimadzu, Japan). The details of the instrument have already been previously described [3].

### 3. Discussion

The solvent properties are given in Table 1. The concentrations and molar conductances  $\Lambda$  of [EMIm]Br in different solvents are given in Table 2. The molar conductance ( $\Lambda$ ) have been obtained from the specific conductance ( $\kappa$ ) value using the following equation.

$$\Lambda = \frac{1000\kappa}{c} \quad (1)$$

Linear conductance curves ( $\Lambda$  versus  $\sqrt{c}$ ) were obtained and extrapolation of  $\sqrt{c} = 0$  evaluated the starting limiting molar conductances for the electrolyte. The conductance data for ion-pair formation have been analyzed using the Fuoss conductance equation [11].

So with a given set of conductivity values ( $c_j$ ,  $\Lambda_j$ ;  $j = 1, \dots, n$ ), three adjustable parameters, i.e.,  $\Lambda_0$ ,  $K_A$  and  $R$  have been derived from the Fuoss equation. Here,  $\Lambda_0$  is the limiting molar conductance,  $K_A$  is the observed association constant and  $R$  is the association distance, i.e., the maximum center to center distance between the ions in the solvent separated ion-pairs. There is no precise method [12] for determining the  $R$  value but in order to treat the data in our system,  $R$  value is assumed to be,  $R = a + d$ , where  $a$  is the sum of the crystallographic radii of the ions and  $d$  is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance,  $d$  is given by:

$$d = 1.183 \left( \frac{M}{\rho} \right)^{1/3} \quad (2)$$

where  $M$  is the molar mass and  $\rho$  is the density of the solvent. For mixed solvents,  $M$  is replaced by the mole fraction average molar mass ( $M_{av}$ ) which is given by,

$$M_{av} = \frac{W_1 M_2 + W_2 M_1}{W_1 + W_2} \quad (3)$$

where  $W_1$  is the weight fraction of the first component of molar mass  $M_1$ . Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = P\Lambda_0[(1 + R_X) + E_L] \quad (4)$$

$$P = 1 - \alpha(1 - \gamma) \quad (5)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (6)$$

$$-\ln f = \frac{\beta \kappa}{2(1 + \kappa R)} \quad (7)$$

$$\beta = \frac{e^2}{\epsilon_r k_B T} \quad (8)$$

$$K_A = \frac{K_R}{(1 - \alpha)} = \frac{K_R}{(1 + K_S)} \quad (9)$$

where,  $\Lambda_0$  is the limiting molar conductance,  $K_A$  is the observed association constant,  $R$  is the association distance,  $R_X$  is the relaxation field effect,  $E_L$  is the electrophoretic counter current,  $k$  is the radius of the ion atmosphere,  $\epsilon$  is the relative permittivity of the solvent mixture,  $e$  is the electron charge,  $c$  is the molarity of the solution,  $k_B$  is the Boltzmann constant,  $K_S$  is the association constant of the contact-pairs,  $K_R$  is the association constant of the solvent-separated pairs,  $\gamma$  is the fraction of solute present as unpaired ion,  $\alpha$  is the fraction of contact pairs,  $f$  is the activity coefficient,  $T$  is the absolute temperature and  $\beta$  is twice the Bjerrum distance.

The computations were performed using the program suggested by Fuoss. The initial  $\Lambda_0$  values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [13]. Input for the program is the no. of data,  $n$ , followed by  $\epsilon$ ,  $\eta$  (viscosity of the solvent mixture), initial  $\Lambda_0$  value,  $T$ ,  $\rho$  (density of the solvent mixture), mole fraction of the first component, molar masses,  $M_1$  and  $M_2$  along with  $c_j$ ,  $\Lambda_j$  values where  $j = 1, 2, \dots, n$  and an instruction to cover preselected range of  $R$  values.

In practice, calculations are performed by finding the values of  $\Lambda_0$  and  $\alpha$  which minimize the standard deviation,  $\delta$ , whereby

$$\delta^2 = \sum \frac{[\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2}{(n - m)} \quad (10)$$

for a sequence of  $R$  values and then plotting  $\delta$  against  $R$ , the best-fit  $R$  corresponds to the minimum of the  $\delta - R$  versus  $R$  curve. So, an approximate sum is made over a fairly wide range of  $R$  values using 0.1 increment to locate the minimum but no significant minima is found in the  $\delta - R$  curves, thus  $R$  values is assumed to be  $R = a + d$ , with terms having usual significance. Finally, the corresponding  $\Lambda_0$  and  $K_A$  values are obtained which are reported in Table 3 along with  $R$  and  $\delta$  for the all the solutions.

A perusal of Table 3 and Fig. 1 shows that the limiting molar conductance ( $\Lambda_0$ ) of [EMIm]Br is highest in AN and lowest in case of DMSO among the studied solvents. The trend in the  $\Lambda_0$  of [EMIm]Br in different solvents is as follows:

$$\text{AN} > \text{MeOH} > \text{DMF} > \text{DMA} > \text{DMSO}$$

This shows that [EMIm]Br is solvated more by DMSO, which has the highest viscosity value among the studied solvents and is evident from the  $K_A$  values given in Table 3 and Fig. 1. The weakest

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