

Association of Ionic Liquids in Solution: Conductivity Studies of [BMIM][Cl] and [BMIM][PF₆] in Binary Mixtures of Acetonitrile + Methanol

Ion Association in Ionic Liquid Solutions

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Abstract The concentration dependence of molar conductance for 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium hexafluorophosphate in binary mixtures of acetonitrile + methanol was investigated to explore the ion association behavior of imidazolium based ionic liquids. The limiting molar conductance (Λ_m^0), association constants (K_a^0) and the maximal distance between the oppositely charged ions in ion pairs (R_{ij}) in the mixed solvent mixtures were evaluated following the framework of Barthel's low-concentration chemical model. The investigated ILs display opposing trends in ion association behavior with change in solvent composition of acetonitrile + methanol binary mixtures. The results are discussed in light of ionic liquid and solvent specific ion–solvent and ion–ion interactions in the mixed solvent systems.

Keywords Ionic liquids · Ion association · Barthel's low-concentration chemical model · Association constants

1 Introduction

Ionic liquids (ILs) in recent years have been attracting a considerable attention from the scientific and industrial community in general and electrochemists in particular [1–4]. On account of their unique and tunable inherent physicochemical characteristics, ILs are now increasingly being used as reaction media, novel solvents for separation and analysis and as electrolytes in electrically, photochemically or chemically driven electrochemical setups [1–3, 5]. A comprehensive understanding of ion–ion and ion–solvent interactions in ILs and IL+ co-solvent mixtures is a must to achieve the as desired characteristics of ILs in such systems. Among the large variety of ILs known until now, those based on imidazolium cations are probably the most intensively investigated and used, perhaps on account of their high air, moisture, thermal, electrochemical and chemical stability [3, 6]. The imidazolium based ILs are very complex innovative systems which are capable of

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interacting simultaneously with other molecules via dispersive, ionic, π – π , dipolar and hydrogen bonding interactions. These interactions when understood completely can be intelligently made use of in changing the course of chemical or electrochemical reactions through a proper use of ILs as solvents or electrolytes [4, 7–11].

In view of the recent developments related to theory of conductance of electrolyte solutions [12, 13], conductometry is increasingly being used as a reliable, affordable and convenient bench level technique that provides valuable information about the ion–ion and ion–solvent interactions in electrolyte solutions. In view of the fact that mixed solvents enable the variation of properties such as dielectric constant and viscosity over a wide range, conductometric investigations of ILs in mixed solvent systems seems very interesting. Such studies are expected to shed new light on the mechanism and extent of ion–ion and ion–solvent interactions and solvation of ILs in solutions, wherein non-electrostatic forces contribute significantly to the equilibrium and dynamic characteristics of constituent ions. In view of the above mentioned facts, we carried out detailed conductometric investigations of 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) in binary acetonitrile (MeCN) + methanol (MeOH) mixed solvent systems. The studies were aimed at exploring the solvent and ion specific transport and ionic association characteristics of imidazolium based IL electrolyte solutions. Such studies are of considerable interest for the optimal and desired use of IL+ mixed organic solvent systems in high energy batteries [14] and other electrochemical systems, and for understanding the ion pair effect and organic reaction mechanisms in such systems [7, 8, 15].

2 Experimental

MeCN (GR grade, 99.9 %) and MeOH (GR grade, 99.9 %) were purchased from Merck, India and purified following reported standard methods [16]. Electrochemical purity grade ILs used were synthesized following a two step procedure [17] as reported earlier [7, 8]. Briefly, in the first step 1-methylimidazole was refluxed with *n*-butyl chloride for 90 h under argon atmosphere for the synthesis of 1-butyl-3-methylimidazolium chloride as a white crystalline solid. In the next step the halide anion was exchanged with PF₆[−] by treatment with HPF₆. The ILs were vacuum dried and stored in desiccators under an inert atmosphere and were characterized through ¹H-NMR, mass spectrometry and ¹³C-NMR spectroscopy. The water content of dried ILs was less than 50 ppm, as analyzed by Karl Fischer titration. Binary solvent mixtures were prepared by mixing the required volumes of MeCN and MeOH. The value of relative dielectric constant (ϵ_r) and coefficient of viscosity (η) of the solvent mixtures were obtained by interpolation of literature [18, 19] values for MeCN + MeOH mixtures at 298.15 K. The physical properties of the used mixture composition are listed in Table 1.

Stock solutions of ILs were prepared by adding their required mass into the mixed solvent system to be investigated. Conductivity was recorded by a digital microprocessor based conductivity meter (CYBERSCAN CON 500) from Eutech instruments having a sensitivity of 0.1 $\mu\text{S}\cdot\text{cm}^{-1}$; details are reported elsewhere [20]. During data processing the conductivity of the solvent system was subtracted from the recorded values to obtain IL only conductivity in the solution. Numerical calculations and data fitting was performed through codes written in Origin 6.0 (Microcal Software Inc.)

Table 1 Dielectric constant (ϵ_r) and viscosity (η) of methanol (MeOH) + acetonitrile (MeCN) mixtures at 298.15 K; the values were calculated by interpolation of the literature reported [18, 19] values for these parameters for MeCN + MeOH mixed solvent systems

$W_{\text{MeOH}}\%$ of solvent mixture	ϵ_r	$\eta/\text{mPa}\cdot\text{s}$
0	35.96	0.3413
10	35.62	0.3421
20	35.37	0.3486
30	35.17	0.3613
40	34.99	0.3791
50	34.78	0.4012
60	34.52	0.4270
70	34.19	0.4559
80	33.78	0.4874
90	33.29	0.5210
100	32.63	0.5438

3 Results and Discussions

The concentration dependent molar conductance values (Λ_m) for [BMIM][Cl] and [BMIM][PF₆] in MeCN + MeOH mixtures with changing volume fractions of MeOH ($W_{\text{MeOH}}\%$) are presented as Fig. 1. The conductance results were analyzed by following the framework of Barthel's low-concentration chemical model (lcCM) [13]. According to this framework:

$$\Lambda_m = \alpha \left(\Lambda_m^0 - S(\alpha C)^{1/2} + E\alpha C \ln(\alpha c) + J_1 \alpha C - J_2 (\alpha C)^{3/2} \right) \quad (1)$$

where

$$K_a^0 = \frac{1 - \alpha}{\alpha^2 C (y_{\pm})^2} \quad (2)$$

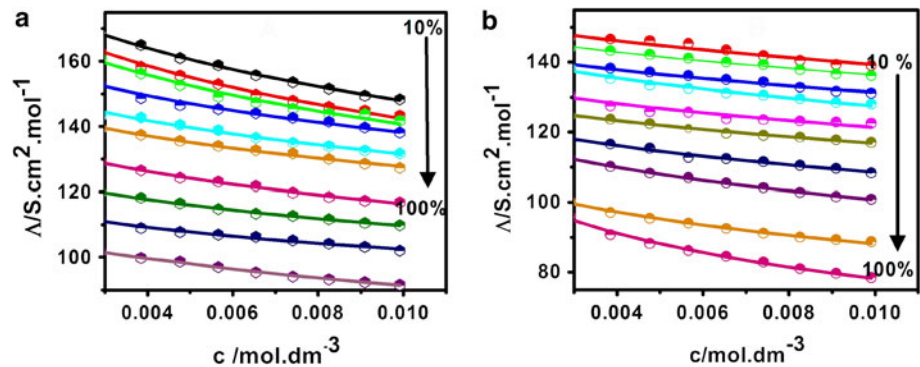


Fig. 1 Molar conductivities (Λ_m) of (a) [BMIM][Cl] and (b) [BMIM][PF₆] in methanol + acetonitrile mixtures in the composition range 10–100 % methanol (by volume) in steps of 10 %. Lines show the results of the lcCM calculations

$$y_{\pm} = \exp\left(\frac{-k_D q}{1 + k_D R}\right) \quad (3)$$

$$k_D = (16\pi N_A q \alpha C)^{1/2} \quad (4)$$

$$q = \frac{e^2}{8\pi\epsilon_0\epsilon_r k_B T} \quad (5)$$

where Λ_m^0 is the molar conductivity at infinite dilution, $(1 - \alpha)$ is the fraction of charged ions bound as ion pairs, and K_a^0 is the standard state association constant. The activity coefficient of the free cation (y_+) and free anion (y_-) are defined as

$$(y_{\pm})^2 = y_+ y_- \quad (6)$$

where k_D is the Debye parameter, e is the proton charge, ϵ_0 the dielectric constant of the vacuum and ϵ_r the dielectric constant of the solvent system. T is the Kelvin temperature and N_A and k_B are the Avogadro's and Boltzmann's constants, respectively.

According to the lcCM model two oppositely charged ions are counted as ion pairs if the inter-ionic distance, r , is within the limits of $a < r < R$, where a is the lower limit for distance of closest approach and taken as the sum of their crystallographic radii ($a = a_+ + a_-$) and R , the upper limit of distance of closest approach for ion pair formation taken as $R = a + n \cdot s$. Expressions for the coefficients S , E , J_1 and J_2 are given by Barthel et al. [13]. The limiting slope S and the parameter E are fully defined by the known values of ϵ_r and η (Table 1) of the solvent system. The coefficients J_1 and J_2 are both functions of the distance parameter R , representing the distance up to which oppositely charged ions can move as freely moving particles in solution. In the present study, the data analysis was carried out by a non-linear least square fitting procedure with the coefficients S , E and J_1 preset to their calculated values and with Λ_m^0 , K_a^0 and J_2 as adjustable parameters. For these calculations $a_+ = 0.330$ nm [21], $a_{Cl^-} = 0.181$ nm [13] and $a_{PF_6^-} = 0.256$ nm [22] were used. In calculations for R , n was taken as 1 and in view of the literature reports [23], $s = 0.47$ nm for MeOH and $s = 0.58$ nm for MeCN; s for the mixed solvent systems employed in present study was calculated through the equation;

$$s = X_{MeOH} \cdot 0.47 + (1 - X_{MeOH}) \cdot 0.58 \quad (7)$$

where X_{MeOH} is the mole fraction of MeOH in the mixed solvent system.

Figure 1 compares the experimental Λ_m values for [BMIM][Cl] (Fig. 1a) and for [BMIM][PF₆] (Fig. 1b) solutions in the mixed solvent systems of changing compositions with the results of the lcCM calculations, Eqs. 1–5. The estimated values for Λ_m^0 together with the K_a^0 and distance parameter R_{ij} calculated from the last term of Eq. 1 are presented in Table 2.

The value of R_{ij} can be used as a compatibility control of the fit as it should be similar to the input radius $R = a + n \cdot s$ chosen for calculation of J_2 and y_{\pm} . As evident from the Table 2, R and R_{ij} are in good agreement for both the ILs. The values of Λ_m^0 estimated for the investigated ILs in the present work seem a bit higher than those reported in MeOH and MeCN in earlier reports [24–26]. However the data presented in earlier reports related to conductance of ILs in molecular solvents [24–27] indicates a significant variation in the values of Λ_m^0 , reported for the same ILs in the same solvents. Such discrepancies in the reported values of Λ_m^0 are being attributed to (a) estimation of Λ_m^0 through use of different conductivity equations and (b) the use of concentration data in different ranges for the

Table 2 Association constants (K_a^0), limiting molar conductivities (Λ_m^0), input radii (R) and parameter (R_{ij}) for [BMIM][Cl] and [BMIM][PF₆] in MeCN+MeOH mixed solvent systems at 298.15 K

W_{MeOH} % of solvent mixture	$K_a^0 \text{ dm}^3 \cdot \text{mol}^{-1}$	$\Lambda_m^0 \text{ S cm}^2 \cdot \text{mol}^{-1}$	$R \text{ nm}$	$R_{ij} \text{ nm}$
[BMIM][Cl]				
0	88.5	196.52	1.089	1.093
10	58.3	189.27	1.077	1.092
20	48.9	184.46	1.064	1.061
30	45.3	179.89	1.052	1.052
40	35.4	167.41	1.040	1.037
50	29.8	158.35	1.029	1.033
60	27.8	152.41	1.019	1.022
70	33.9	142.39	1.009	1.012
80	28.4	131.16	0.999	1.005
90	25.8	120.96	0.990	0.974
100	20.7	114.65	0.981	0.966
[BMIM][PF₆]				
0	27.0	158.52	1.166	1.184
10	15.1	156.80	1.152	1.153
20	14.8	153.24	1.139	1.137
30	15.7	148.26	1.127	1.125
50	19.0	139.14	1.104	1.103
60	19.0	133.89	1.094	1.094
70	26.1	128.39	1.084	1.088
80	37.9	124.90	1.074	1.083
90	45.5	112.33	1.065	1.071
100	100.8	116.46	1.056	0.996

estimation of said values. As can be clearly seen from the entries in Table 2, the values for Λ_m^0 for [BMIM][PF₆] and [BMIM][Cl] fall with the increase in MeOH fraction in the mixed solvent system. This is in line with the decrease in the dielectric constant of the solvent and increase in its viscosity with decrease of MeCN fraction in the solvent system. Nevertheless, it was observed that the Walden product ($\Lambda_m^0 \cdot \eta$) does not remain constant as expected in cases where ion–solvent interactions do not vary with changing composition of solvent [12]. This implies that the changing mole fractions of MeCN and MeOH lead to changes in ion–solvent interactions in the present case. Similar observations have been made for RTILs in earlier studies [28].

Interestingly, for all solvent compositions (except at $w_{\text{MeCN}} = 0$) investigated, the Λ_m^0 values for [BMIM][Cl] were found to be higher than the corresponding values for [BMIM][PF₆]. As depicted in Fig. 2a the relative difference between the Λ_m^0 values for the investigated ILs decreases with increase in W_{MeOH} of the mixed solvent system. Since the the investigated ILs have a common cation, the observed variations in Λ_m^0 can be attributed to differences in solvation and mobility characteristics of Cl⁻ and PF₆⁻ in the mixed solvent systems. As has been reported in the literature [29], while MeOH interacts strongly with anions in such systems, MeCN on the contrary interacts preferentially with the imidazolium cation suggesting that the observed variations in Λ_m^0 are anion driven. In the light of

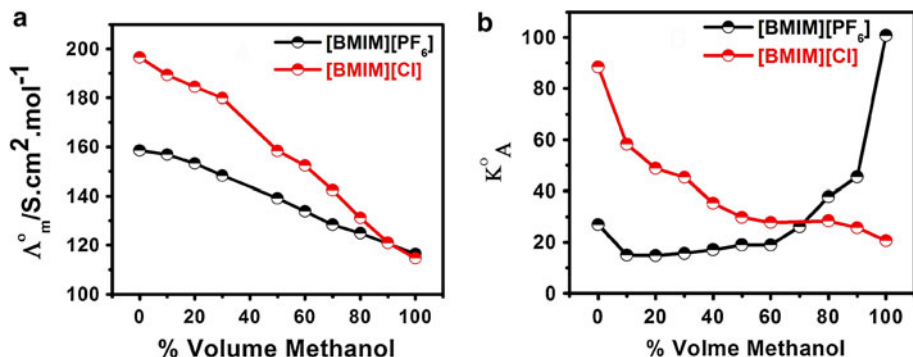


Fig. 2 (a) Limiting ion conductance (Λ_m^0) and (b) ion association constant (K_a^0) of [BMIM][Cl] and (b) [BMIM][PF₆] in methanol + acetonitrile mixtures in the composition range 0–100 % methanol (by volume) in steps of 10 %

our observations, it can be safely argued that while in MeCN the mobility of Cl[−] is more than that for PF₆[−], in MeOH solutions the reverse is true. This trend suggests that the greater is the size of anion the smaller is its mobility in MeCN, while in MeOH the reverse is true, which we attribute to differing ion solvating abilities of the two solvents. In view of its smaller size, Cl[−] has a higher charge density than that of PF₆[−]; thus the former species interacts with MeOH more than the latter which is more solvated by MeCN on account of its higher polarizability.

More interesting findings of the present investigations are the relative magnitudes of the K_a^0 and its variations in the mixed solvent systems for the two ILs with a common cation. As seen from Table 2 and Fig. 2b, at lower fractions of MeOH in the mixed solvent system the K_a^0 of [BMIM][Cl] was higher than that observed for [BMIM][PF₆], whereas in MeOH rich solvent systems the reverse was observed. In addition while for [BMIM][Cl] the K_a^0 value decreases with increase of MeOH fraction in the mixed solvent system, for [BMIM][PF₆] an increasing trend was observed. While the trend observed for variation of K_a^0 of [BMIM][Cl] with the change in content of MeOH fraction in the solvent system is quite expected in light of the resulting variations in ϵ_r , the trend observed in the case of [BMIM][PF₆] is quite unexpected. We observed a similar trend for the IL [BMIM][BF₄]. From molecular dynamic studies [29] it has been established that hydrogen bonding solutes like MeOH strongly solvate halide ions by forming hydrogen bonds, while non hydrogen bonding solvents like MeCN interact more strongly with easily polarizable solutes through ion–dipole interactions. In light of these reports, on account of its smaller size and higher charge density, Cl[−] is expected to show weaker ion–solvent and stronger ion–ion interactions with its imidazolium counterpart and hence larger K_a^0 values in solvents like MeCN. However, in solvents like MeOH where Cl[−] is expected to be strongly solvated due to its ability to engage in strong hydrogen bonding interactions with the solvent molecules, an opposite trend is expected. For the IL [BMIM][PF₆], where the anion is more polarizable, the ion–solvent interactions are expected to be stronger and hence K_a^0 values lower than for the [BMIM][Cl] homologue in solvents like MeCN. However, in solvents like MeOH the ion–ion interactions for [BMIM][PF₆] are expected to be stronger and hence expected to show K_a^0 values larger than its chloride counterpart (Fig. 2).

In light of these facts we propose that for an IL with smaller anions, like [BMIM][Cl], the stronger ion–ion plus weak ion–solvent interactions are replaced by weaker ion–ion

and stronger ion–solvent interactions with increase of the MeOH fraction in the MeCN + MeOH mixed solvent systems, which is responsible for the resulting decrease in K_a^0 . On the contrary, in ILs with larger anions like [BMIM][PF₆], the weaker ion–ion plus strong ion–solvent interactions are replaced by stronger ion–ion and weaker ion–solvent interactions with increase of MeOH fraction in the MeCN + MeOH mixed solvent systems resulting in the observed variations in K_a^0 with changing fraction of MeOH. This is in agreement with the report by Mohammed et al. [30] wherein it has been proved that, while the interaction energy for the [BMIM][PF₆] + MeCN system is negative, for [BMIM][PF₆] + MeOH the same quantity is positive. The present studies are an excellent example of tuning the physicochemical characteristics of closely related IL electrolytes through alterations in solvophobicity achieved through similar variations in the composition of the mixed solvent systems.

4 Conclusions

Conductometric investigations of imidazolium based ILs, viz 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) were performed in binary acetonitrile + methanol. The data were analyzed with Barthel's low-concentration chemical model, establishing that the conducting behavior and ion association is highly specific to the nature of IL and composition of the mixed solvent system. Thus, while in MeOH ion-association and Λ_m^0 were found to be larger for [BMIM][PF₆] than for [BMIM][Cl], in MeCN the opposite was observed. Also, with an increase in MeOH fraction in MeCN + MeOH mixed solvent systems, while Λ_m^0 was observed to decrease for both the ILs investigated, opposing trends were observed in the variation of K_a^0 . For [BMIM][PF₆] there was an increase in K_a^0 while for [BMIM][Cl] a decrease in the corresponding value was observed.

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