



## Q3 Conductivity and association of imidazolium and pyridinium based ionic liquids in methanol

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### ABSTRACT

A detailed investigation of the dilute solutions of several imidazolium-based ([BMIM][Br], [EMIM][BF<sub>4</sub>], [BMIM][BF<sub>4</sub>], [HexMIM][BF<sub>4</sub>], [BMIM][Tf]) and pyridinium-based ([BMP][BF<sub>4</sub>]) ionic liquids, and two tetraalkylammonium salts (Bu<sub>4</sub>NBr and Bu<sub>4</sub>NBPh<sub>4</sub>) in methanol was carried out between 278.15 and 328.15 K. The limiting molar and ionic association constants were derived using the Lee–Wheaton equation. The limiting molar conductivity for room-temperature ionic liquids with common anion ([BF<sub>4</sub>)<sup>−</sup>) is found to obey the Stokes' law:  $\Lambda_0$  increases as the cation size decreases. Ionic association in all studied systems does not show definite correlation with cation structure, while it strongly depends on anion size and structure. Ion association constants are discussed and the role of non-Coulombic forces is demonstrated with the help of short-range square-mound potential. Performed data analysis indicates the formation of contact ion pair of similar structure in studied solutions of ionic liquids, with anion coordinated by imidazole or pyridine ring. The formation of H-bonding between bromide-anion and hydroxy-group of methanol was observed.

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### 1. Introduction

Room-temperature ionic liquids (RTILs) [1–4] are defined as salts with a melting point around or below room temperature. These compounds are generally formed by bulky and asymmetric cations and inorganic symmetric anions, giving rise to a variety of more than five hundred species. A set of exciting properties are reported, like negligible saturated vapor pressure [5], non-flammability, high electrical conductivity [6–9], extra large liquid temperature range, and ability to solvate most of the existing substances [10]. Since pure ionic liquid is composed exclusively of cations and anions, the interactions between the component ions are one of the most fundamental subjects in the research of these compounds [6,11].

Arguably, RTILs based on the substituted imidazolium cations are most intensively considered [12–15] so far. Nonetheless, systematic studies of the transport properties of binary mixtures of RTILs and dipolar solvents, such as their electrical conductivity, are still pretty scarce, despite the large practical interest of such systems [9,16,17]. The available data generally focus on the simple aqueous mixtures [18,19] and high contents of ionic liquids [20,21]. Certain recent studies of non-aqueous solvents aiming at the investigation of ion association processes are indeed available [6,22,23]. They reveal that the stability of an ion aggregate depends greatly on the cation lyophobic tail length, on the structure of the anion and solvent polarity. In other words, it is pointed out that the most interesting properties of RTILs, such as viscosity, ionic conductivity, and thermal properties are very closely related to the interplay of inter-ionic and ion-molecular interactions. The natural complexity of them makes it very challenging to build a general model for the RTIL/solvent binary mixtures. Both experimental (conductometry, pulsed-field-gradient spin-echo nuclear magnetic resonance, dielectric spectra, etc.) [9,24,25] and atomistic simulation studies (mostly molecular dynamics) [6,11,26] are of great importance to accumulate necessary datasets.

In the present paper, we aim towards the precise determination of the limiting molar and ion conductivities and ionic association constants

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in the solutions of 1-butyl-3-methylimidazolium bromide ([BMIM][Br]), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([HexMIM][BF<sub>4</sub>]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][Tf]) and 1-butyl-4-methylpyridinium tetrafluoroborate ([BMP][BF<sub>4</sub>]) in methanol (MeOH). In addition, we measured the conductivities of two tetraalkylammonium (TAA) salts, tetrabutylammonium tetraphenylborate (Bu<sub>4</sub>NBPh<sub>4</sub>) and tetrabutylammonium bromide (Bu<sub>4</sub>NBr), in order to obtain reliable data to divide molar electrical conductivity into the corresponding ionic components. In light of electrical conductivity, the short range potentials, ionic association constants, and thicknesses of ionic solvation spheres are discussed. Our results bring new insights to the microscopic understanding of the peculiarities of RTIL-containing non-aqueous electrolyte solutions.

## 2. Experimental part

### 2.1. Materials

All RTILs (purity > 99%) and TAA salts were purchased from The Merck Group. RTILs were dried under high vacuum at room temperature using a rotary evaporator for at least 24 h. TAA salts were purified by recrystallization from MeOH and dried at a vacuum line ( $p$  0.001 Pa) for 24 h at 328.15 K.

Methanol was received from The Merck Group and purified following the standard procedure [27]. The purified solvent had specific conductance,  $\kappa$ , in the range of  $(2.7\text{--}4.5) \cdot 10^{-7}$  S·cm<sup>-1</sup> at 298.15 K, which is in good agreement with available data [28].

### 2.2. Conductivity measurements

Conductivity measurements were performed at temperatures 278.15, 288.15, 298.15, 308.15, 318.15 and 328.15 K. Electrical resistance was measured with a high precision LCR meter Instek LCR-821 at a fixed frequency of 1000 Hz in four cells made out of molybdenum glass with platinized platinum electrodes. Cell constants were determined by calibration against aqueous solutions of KCl by the standard procedure [29]. In order to control the temperature, the cells were kept in water bath at a constant temperature (accuracy was  $\pm 0.005$  K) for 20 min. For all solutions the specific conductance of the pure solvent was taken into account at each temperature. The error in electric resistance values obtained using the LCR meter Instek LCR-821 did not exceed 0.1%.

The set of 15 solutions of each RTIL or TAA salt in MeOH in concentration range from  $1.0 \cdot 10^{-4}$  to  $5 \cdot 10^{-3}$  mol·dm<sup>-3</sup> was prepared from concentrated solution gravimetrically by dilution. All solutions were prepared in a glove box filled with nitrogen. Before taking the flasks with working solutions out of the glove-box, they were sealed with Parafilm M films, to minimize the ingress of moisture.

The molarity of solutions,  $c$ , was calculated to be  $c(T) = \tilde{m} \cdot d(\tilde{m}, T)$ , where  $\tilde{m}$  is the concentration given is mole of electrolyte per kilogram of solution (molality) and  $d(\tilde{m}, T)$  is the density of electrolyte solution as the function of concentration and temperature.

The values of  $d(\tilde{m}, T)$  for solutions of TAA salts were calculated using volume additivity of solution components [30]:

$$d(\tilde{m}, T) = d_0(T) / (1 - \tilde{m} \cdot M_{TAA}(1 - d_0(T)/d_{TAA})), \quad (1)$$

where  $d_0(T)$  is a solvent density,  $d_{TAA}$  and  $M_{TAA}$  are density and molecular weight of pure TAA salt, respectively. Eq. (1) satisfactorily describes experimental densities of 1–1 electrolyte solutions up to concentration  $1 \cdot 10^{-2}$  mol·kg<sup>-1</sup> [30]. The TAA salt densities were assumed to be independent of temperature and were taken for Bu<sub>4</sub>NBr ( $d =$

$1130 \text{ kg} \cdot \text{m}^{-3}$ ) from [31] and for Bu<sub>4</sub>NBPh<sub>4</sub> ( $d = 1023 \text{ kg} \cdot \text{m}^{-3}$ ) from [32].

The values of  $d(\tilde{m}, T)$  for RTIL solutions were determined using the following equation:

$$d(\tilde{m}, T) = d_0(T) + B\tilde{m} \quad (2)$$

where  $B$  is a density gradient. The  $B$  values were established in density studies. The experimental values of solution density at  $(298.15 \pm 0.01)$  K were determined by using a vibrating-tube densimeter (VIP-2) [33] equipped with a thermostat. The density gradients  $B$ , which are considered to be independent of temperature, for RTILs [BMIM][Br], [EMIM][BF<sub>4</sub>], [BMIM][BF<sub>4</sub>], [HexMIM][BF<sub>4</sub>], [BMIM][Tf] and [BMP][BF<sub>4</sub>] were equal, respectively, to 1831, 539, 733, 816, 1107 and  $803 \text{ kg}^2 \cdot \text{mol} \cdot \text{m}^{-3}$ .

The physical properties of pure MeOH (density,  $d$  (g·cm<sup>-1</sup>), viscosity,  $\eta$  (mPa·s), and dielectric constant,  $\epsilon$ ) were obtained with Eqs. (3)–(5) [28]:

$$d^{-1} = 1.234520 + 1.4283 \cdot 10^3(T - 273.15) + 1.52 \cdot 10^6(T - 273.15)^2 \quad (3)$$

$$\ln \eta = -5.0858 + 1.421 \cdot 10^3 T^{-1} - 2.62 \cdot 10^6 T^{-2} \quad (4)$$

$$\epsilon = -23.18 + 16.02 \cdot 10^3 T^{-1} + 0.182 \cdot 10^6 T^{-2} \quad (5)$$

where  $T$  is the temperature in K.

Experimental molar conductivities for the investigated RTILs and TAA salt solutions are listed in Table A.1 of Appendix A.

## 3. Data analysis

The set conductometric data  $c_j^{\text{st}} - \Lambda_j$ ,  $j = 1, k$  was analyzed using a least-square method by minimization of the function  $Q$ :

$$Q = \sum_{j=1}^k [\Lambda_j^{\text{exp}} - \Lambda_j^{\text{theor}}(c_j^{\text{st}}, \mathbf{A})]^2, \quad (6)$$

where  $\Lambda^{\text{exp}}$  is the experimental and  $\Lambda^{\text{theor}}$  is calculated theoretically molar conductivities for every  $j$ -th experimental stoichiometric concentration  $c_j^{\text{st}}$ ;  $\mathbf{A}$  is the set of adjustable parameters. In the framework of a chemical model [34], the set  $\mathbf{A}$  consists of limiting molar conductivity,  $\Lambda_0$ , association constant,  $K_a$ , and distance of the closest approach of ions  $R$  [35]. The values of  $\Lambda^{\text{theor}}$  can be calculated from the conductance equation (Eq. (7)), the mass action law (Eq. (8)), the material balance (Eq. (9)) and the mean ionic activity coefficients (Eq. (10)):

$$\Lambda^{\text{theor}} = c_i \Lambda(c_i, \Lambda_0, R) / c_{\text{st}}, \quad (7)$$

$$K_a = c_0 y_0 / (c_i y_{\pm})^2, \quad y_0 = 1 \quad (8)$$

$$c_{\text{st}} = c_0 + c_i, \quad (9)$$

$$y_{\pm} = \varphi(c_i, R), \quad (10)$$

where  $c_i$ ,  $c_0$  and  $c_{\text{st}}$  are the concentration of ions, ion pairs and stoichiometric concentration of electrolyte, respectively;  $\Lambda(c_i, \Lambda_0, R)$  is a theoretical conductivity equation for a electrolyte solution;  $\Lambda_0$  is a limiting molar conductivity of electrolyte;  $y_{\pm}$  and  $y_0$  are the mean ionic activity coefficient and electrolyte activity coefficient, respectively; and  $\varphi(c_i, R)$  is a theoretical equation for mean ionic activity coefficient.

As a theoretical model for the concentration dependence of  $\Lambda^{\text{theor}}$  the Lee–Wheaton equation [36,37] was used. This equation, besides the Coulombic and hard-sphere interaction, also takes into account short-range interaction via the Gurney co-sphere parameter  $R$ . We

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