

Effect of Cosolvent on Bulk and Interfacial Characteristics of Imidazolium Based Room Temperature Ionic Liquids

Impact of Cosolvent on Physicochemical Characteristics of Ionic Liquids

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Abstract Here we report a systematic study on electrical conductivity and surface tension of various concentrated solutions of imidazolium based room temperature ionic liquids (RTILs), viz. 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) in the cosolvents methanol and acetonitrile at 298.15 K. The aim of the investigations was to explore the impact of cosolvents on bulk and interfacial characteristics of imidazolium based RTILs. It was observed that both methanol and acetonitrile mix non-ideally with and enhance the transport parameters of the imidazolium based RTILs. An interesting outcome of the presented work is that the investigated RTILs retain their inherent structural characteristics up to a high dilution limit with cosolvent, and this limit is higher in acetonitrile than in methanol as cosolvent. The findings establish that, in comparison to methanol, acetonitrile is a better cosolvent that can be used for enhancing the transport parameters of imidazolium based RTILs for electrochemical and other applications. The results are explained in light of structure-composition-property relations and ion-ion and ion-cosolvent interactions.

Keywords Room temperature ionic liquid (RTIL) · Cosolvent · Surface tension · Specific conductance · Interface

1 Introduction

Attractive and tunable physicochemical characteristics of room temperature ionic liquids (RTILs) have established them as novel compounds with potential to act as green solvents, catalysts, lubricants and electrolytes [1–4]. Presently researchers from diverse fields are showing an increasing interest in studies aimed at the use of RTILs for their applications in

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fields like catalysis, organic synthesis, lubrication, thermal separation processes and electrochemistry [1–5]. However, the poor transport properties, high viscosity and low conductivity of RTILs are some of the major obstacles that limit their general use in such applications. Working at high temperatures [6–8] and/or addition of a cosolvent that reduces the viscosity are the two options currently advocated by solution chemists to overcome the viscosity concerns of RTILs [9–12]. However, an increase of temperature may be unsuitable when chemical/devices are poorly heat resistant. Hence the use of cosolvents seems a better option to overcome viscosity related challenges in RTILs. Interestingly the RTIL + cosolvent mixtures in some cases have been reported to possess altered and improved physicochemical properties [13–16]. The low viscosity of such mixtures ensures easy mass transport, thereby minimizing the energy requirements for the use of RTILs in many engineering processes. However, addition of a cosolvent always leads to loss in structural organization in RTILs, which is mainly responsible for many of their desirable characteristics. The above mentioned facts imply that the general use of RTILs as an alternative to conventional solvents in industry and academia demand detailed and comprehensive investigations about the physicochemical properties of the RTIL + cosolvent binary mixtures. Based on the results from their molecular dynamics simulation studies, Chaban and Prezhdo [17] have predicted that the volatility and hence the toxic effects of molecular solvents can be reduced through addition of appropriate RTILs to these solvents. In view of such demands and presaged potential applications of RTIL-cosolvent mixtures, recently there has been a significant upsurge in the physicochemical studies of such mixtures and much useful data about their interesting properties has been published [18–25].

In view of the above we carried out a detailed and systematic study on electrical conductivity and surface tension of imidazolium based RTILs, viz. 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) plus methanol and acetonitrile mixtures to explore and understand the impact of latter as cosolvents on the bulk and interfacial characteristics of RTILs. The solvents methanol and acetonitrile were chosen not only because of their industrial /environmental relevance but also because of the different nature of the molecular interactions they can engage with the chosen RTIL constituents. Thus, while methanol is a highly associating liquid that interacts mainly through hydrogen bonding, acetonitrile is a dipolar non-associating molecule with potential to engage the RTIL constituents in ion-dipole interactions.

2 Experimental

The RTILs, [BMIM][PF₆] and [BMIM][BF₄] were synthesized, purified, dried and characterized following procedures reported elsewhere [25–27]. The synthesized RTILs were vacuum dried and stored in desiccators under inert atmosphere. The water content of the dried RTILs were less than 50 ppm, as analyzed by Karl Fischer titration. Acetonitrile (GR grade, 99.9) and methanol (GR grade, 99.9) were purchased from Merck India and purified following reported standard methods [28]. Conductivity was recorded by a digital microprocessor based conductivity meter (CYBERSCAN CON 500) from Eutech instruments having a sensitivity of 0.1 $\mu\text{S}\cdot\text{cm}^{-1}$. Surface tension measurements were made with a K9 Tensiometer (Kruss, Germany) by the ring detachment technique. The measured values were corrected according to the procedure of Harkins and Jordan built into the

instrument software. Temperature was maintained at the desired value (within ± 0.1 °C) by circulating thermostatted water from a HAAKE GH bath. The details of experimental measurements and data processing procedures were reported elsewhere [25, 29].

3 Results and Discussions

3.1 Cosolvent Effects of Acetonitrile and Methanol on the Bulk Characteristics of [BMIM][BF₄] and [BMIM][PF₆]

Conductance studies have proven to be one of the reliable means of extracting information about bulk characteristics of fluid phase conducting media. Fig. 1 depicts the relative influence of cosolvent mole fraction of acetonitrile and methanol on the conductivity of (A) [BMIM][BF₄] and (B) [BMIM][PF₆]. As is clear from these figures, addition of both methanol and acetonitrile increases the conductivity of the investigated RTILs, it reaches a maxima and then falls. Similar trends have been reported for the variation of specific conductance (κ) of RTIL + cosolvent mixtures by many groups in the recent past [25, 30, 31]. Such a trend is observed for concentrated solutions of strongly associating electrolytes in solvents wherein they have high solubility [32, 33]. As is clear from the figure, the extent of increase is more when the cosolvent is acetonitrile and the increase is more for [BMIM][BF₄] than for [BMIM][PF₆]. The increase in conductivity values with addition of cosolvent to the RTILs in the RTIL rich regime has been attributed to the decrease in ion-ion interactions prevailing in the large ionic clusters present in the RTILs [34]. With increase in the cosolvent a fraction of the anions is released from the clusters that leads to their faster motion. Anions in the present case being lighter and more compact than the imidazolium cations, their motion is more strongly accelerated upon dilution. Since BF₄⁻ is smaller than that of PF₆⁻, the increase in conductivity on dilution is expected to be greater in the case of [BMIM][BF₄] than for [BMIM][PF₆] as observed. The decrease in κ_{\max} and x_{\max} with the increase in size of the RTIL anion as observed in the present study has also been reported by Kaugin et al. [35] for a range of RTILs in acetonitrile mixtures. Interestingly, in the case of RTIL + cosolvent mixtures, the conductivity increase is correlated with the intrinsic mobility of the molecular solvent which, in the present case, are acetonitrile and methanol. Since the intrinsic mobility of acetonitrile is higher than that of methanol, the later is expected to be less effective in increasing the conductivity of investigated RTILs than the former as is observed.

The observed variations of the conductivity with composition can be attributed to net effect of two competing factors: (1) increase in the number of charge carriers on account of dissociation of added RTIL (dominates the low concentration regime) and (2) aggregation of ions that leads to an increase in size and hence decrease in mobility and charge, besides an increase in viscosity of the solution (dominates the RTIL rich regime). The electrical conductivity has a relationship with ion mobility and number of charge carriers [19, 36] which is expressed as:

$$\kappa = \sum n_i q_i \mu_i \quad (1)$$

where n_i is the number of charge carriers of charge q_i and μ_i the ionic mobility of species i . In the low RTIL concentration regime, the increase in conductivity can be attributed to an increase in the number of charge carriers due to increasing RTIL fraction that out weighs

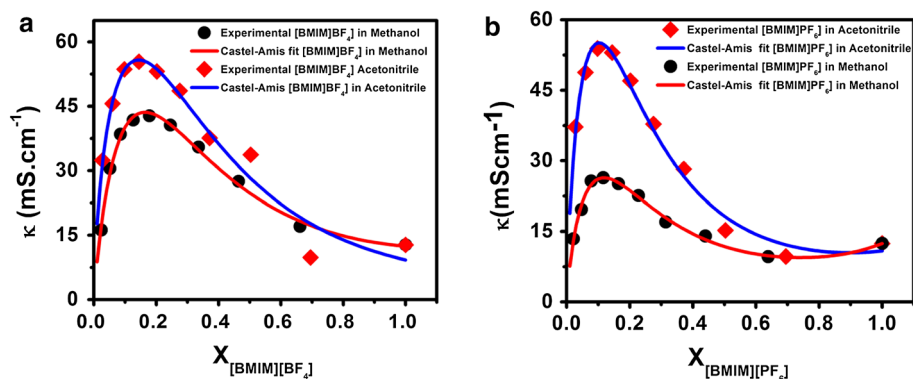


Fig. 1 Specific conductance (κ) as a function of composition in acetonitrile and methanol of **a** [BMIM][BF₄], **b** [BMIM][PF₆] and their Casteel-Amis fit as per Eq. 2 at 298 K. Experimental values are represented by *symbols* and *lines* show Casteel-Amis fit

the decrease in conductivity expected in view of their reduced mobility on account of increased ion-ion interaction. However in the RTIL-rich fraction, aggregate formation on account of strong ion-ion interactions becomes the dominant factor and hence leads to a significant decrease in the ionic mobility and hence conductivity [37–39]. The observed dependence of conductivity as a function of the RTIL mole fraction in the organic cosolvents was analyzed using the Casteel-Amis equation [40, 41]:

$$\kappa = \kappa_{\max} \left(\frac{x}{x_{\max}} \right)^a \exp \left[b(x - x_{\max})^2 - \frac{a}{x_{\max}}(x - x_{\max}) \right] \quad (2)$$

where κ_{\max} is the maximum conductivity and x_{\max} the corresponding mole fraction of the RTIL, and a and b are fitting parameters that depend upon the shape of the conductivity curve. The fits to the equation are represented as lines in the Fig. 1 and their corresponding fit parameters are presented in Table 1. Similar trends for variation of κ with mole fraction of RTILs in mixtures of [BMIM][BF₄] in acetonitrile and methanol, and [BMIM][PF₆] in acetonitrile has been reported by Stoppa et al. [41]. A comparison of the data from the said report and our present work establishes that though there is a good agreement in the value of x_{\max} for the investigated systems in the two studies, the value of κ_{\max} and the conductivity for RTIL rich concentrations observed in present study are slightly higher than those reported in reference [41]. Such mismatches in RTIL conductivity data reported by different groups are usually due to the different sources of RTILs used and different methods of conductivity measurements employed in such studies.

According to the simulation studies by Padua and co-workers [42] the imidazolium based ionic liquids possess a characteristic nanostructural organization wherein nonpolar domains permeate the polar channels formed by imidazolium cations and anions. The incremental addition of cosolvents to the RTILs can lead to initial aggregation of these solutes in the domains that give them more thermodynamic stability; this is expected to cause a disruption in the organized structural network of the RTILs. Further addition of solvent is expected to make the ions aggregate into small clusters that in turn dissociate like conventional electrolytes at low concentration of RTIL. Thus one can safely presume that x_{\max} in plots of κ versus cosolvent fraction in RTIL + cosolvent systems represents the composition where a transition from conduction due to ion aggregates to conduction due to

Table 1 Fitted values of the empirical parameters, κ_{\max} , x_{\max} , a and b of the Casteel–Amis equation fit for κ versus mole fraction of cosolvent for [BMIM][BF₄] and [BMIM][PF₆] plus cosolvent (methanol and acetonitrile mixtures at 298 K

RTIL	$\kappa_{\max}(mS \cdot cm^{-1})$	x_{\max}	a	b
Methanol				
[BMIM][BF ₄]	43.60 (± 0.54)	0.164 (± 0.0035)	0.898 (± 0.0478)	2.44 (± 0.311)
[BMIM][PF ₆]	26.37 (± 0.38)	0.118 (± 0.0027)	0.840 (± 0.0469)	4.79 (± 0.312)
Acetonitrile				
[BMIM][BF ₄]	55.79 (± 0.252)	0.144 (± 0.0113)	0.680 (± 0.1496)	1.26 (± 0.23)
[BMIM][PF ₆]	55.08 (± 0.208)	0.103 (± 0.0039)	0.779 (± 0.0768)	4.20 (± 0.625)

ions moving under the influence of decreasing ion-ion interactions takes place. Obviously this limit should depend upon the strength of cation-anion and cosolvent-cation, cosolvent-anion interactions. Thus while stronger cation-anion interactions are expected to push x_{\max} to lower RTIL concentrations, stronger ion-cosolvent interactions are expected to push the x_{\max} towards higher RTIL concentrations.

Both methanol (protic solvent) and acetonitrile (aprotic solvent) belong to the cosolvent category that have significant affinity for both the polar and non-polar domains present in imidazolium based RTILs. It is on account of these factors that these cosolvents are fairly soluble in [BMIM][BF₄] and [BMIM][PF₆] in all compositions. Simulation studies [43] have established that both acetonitrile and methanol interact strongly with the anion BF₄⁻, the interaction being less directional in the case of acetonitrile in comparison to methanol. It has been observed that while in methanol the –OH group interacts with the anion and the Me-group faces the imidazolium cation, in acetonitrile the Me-group points preferentially towards the anion. Thus, it can be argued that compared to methanol, the interaction of imidazolium cation with acetonitrile is stronger. Also, in view of the higher Lewis basicity of BF₄⁻, it is expected to interact more strongly with methanol in comparison to PF₆⁻. In light of these facts, it can be safely argued that the dilution limit up to which the imidazolium based RTIL can maintain the structural ordering of constituents will be higher when acetonitrile is used as cosolvent in comparison to dilution with methanol. On similar grounds it can be assumed that the said limit will be higher in the case of [BMIM][BF₄] than in [BMIM][PF₆]. This is also clearly evident from the data presented in Table 1. In view of the data presented in Fig. 1 and Table 1, it seems that compared to methanol, acetonitrile is a better cosolvent that better enhances the transport properties of imidazolium RTILs with less impact on the structural ordering of the constituents. These observations are in agreement with the recently reported predictions by Chaban et al. [44] for imidazolium based RTIL + cosolvent mixtures. Such behavior is of considerable importance for investigations wherein addition of cosolvents to the RTILs is done to enhance their transport characteristics while producing minimal variations in the structural organization within the RTILs.

3.2 Cosolvent Effects of Acetonitrile and Methanol on the Interfacial Characteristics of [BMIM][BF₄] and [BMIM][PF₆]

Structural aspects of RTIL/solid, RTIL/vapor are of prime importance in many areas related to applications of such interfaces [45–47]. A comprehensive molecular level understanding of such interfaces is a prerequisite for the optimal utilization of the novel

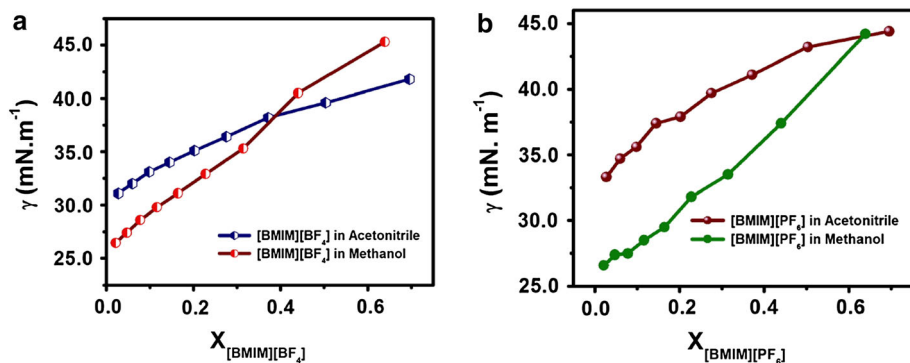


Fig. 2 Surface tension (γ) as a function of composition in acetonitrile and methanol of **a** [BMIM][BF₄] and **b** [BMIM][PF₆] at 298 K

features related to such interfaces for their desired properties in interface-based applications [48, 49]. Surface properties of RTIL + cosolvent mixtures are of particular interest for two reasons. First, they are often considered as key to obtaining valuable information about the transfer of mass and energy of dissolved molecules across the RTIL-based interfaces and these also provide information about the aggregation behavior and drop formation in RTIL-based partially miscible liquid mixtures. Such information is valuable in understanding the behavior of RTILs as components in mixed solvent systems, which is very useful for their use in processes like liquid-liquid extraction. Secondly, these properties provide valuable information about composition of mixture at the interface which usually differs from that in the bulk phase.

Figure 2 depicts the variation in surface tension (γ) of RTILs, viz. (a) [BMIM][BF₄] and (b) [BMIM][PF₆], with change in mole fraction of the RTIL in acetonitrile and methanol. As is obvious from the plots, γ of [BMIM][PF₆] and [BMIM][BF₄] increase with increasing mole fraction of RTIL in both methanol and acetonitrile, but the variation is clearly not linear. These observed deviations from linear behavior are an indication of non-ideal mixing and Domanska et al. [50] have also reported similar observations for addition of alcohols to imidazolium based RTILs. Non-ideal mixing of RTILs with molecular cosolvents has also been reported in the past and specific non-bonded interactions have been found to play a significant role in such mixing in these mixtures. To visualize the non-ideal mixing more clearly we calculated the deviations for observed γ values from those expected for ideal values, i.e. $\Delta\gamma$ through the following equation:

$$\Delta\gamma = \gamma - (X_{\text{RTIL}}\gamma_{\text{RTIL}} + X_{\text{cosolvent}}\gamma_{\text{cosolvent}}) \quad (3)$$

The variation of $\Delta\gamma$ as a function of RTIL mole fraction is depicted in Fig. 3 which clearly shows that the mixing of RTIL with acetonitrile and methanol is non-ideal. Similar trends for the variation of γ and $\Delta\gamma$ with the addition of [BMIM][BF₄] and [BMIM][PF₆] to acetonitrile were observed in our previously reported studies [25]. While the deviation from ideal behavior is more pronounced for [BMIM][PF₆] than [BMIM][BF₄] in acetonitrile, the opposite occurs in methanol. This can be attributed to the composition dependent structural organization and ion-solvent interactions for RTIL-cosolvent mixtures. In the low RTIL concentration region, cation-anion interaction is weakened due to stronger solvation of RTIL ions by cosolvents leading to low surface tensions, but when the

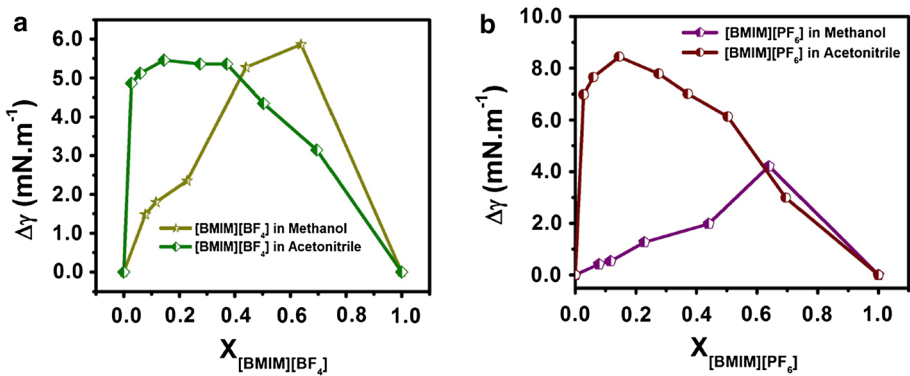


Fig. 3 Deviations in surface tension ($\Delta\gamma$) as a function of composition in acetonitrile and methanol of **a** [BMIM][BF₄] and **b** [BMIM][PF₆] at 298 K

concentration of RTIL is increased in the mixture, cation-anion interaction predominates due to which surface tension increases.

As clearly seen from the Fig. 2, the addition of both methanol and acetonitrile to the investigated RTILs decreases their surface tension. The surface excess of cosolvent in the RTIL and that of RTIL in the cosolvent was estimated from the γ versus concentration data of cosolvent-rich and RTIL-rich mixtures, respectively, by using the Gibbs adsorption equation [51]:

$$\Gamma = -\frac{1}{RT} \left(\frac{\partial\gamma}{\partial\ln(C)} \right) \tag{4}$$

where Γ , C , γ , R , and T are the surface excess, bulk solute concentration, surface tension of the mixture, ideal gas constant and the temperature, respectively. The estimated values of surface excess are given in Table 2.

As is clear from the entries in Table 2, while the surface excess of RTIL in the investigated cosolvents is negative, the surface excess of cosolvents in RTILs in the RTIL-rich regimes is positive. A comparison of the magnitudes of the surface excess indicates that while acetonitrile shows stronger interaction with [BMIM][PF₆] than

Table 2 Surface excess Γ , of cosolvent (methanol and acetonitrile) in [BMIM][BF₄] and [BMIM][PF₆] in RTIL-rich regime and of RTILs ([BMIM][BF₄] and [BMIM][PF₆]) in methanol and acetonitrile in the cosolvent rich regime of RTIL plus cosolvent mixtures at 298 K

RTIL	$\Gamma(\text{mol}\cdot\text{m}^{-2})$ Methanol in RTIL	$\Gamma(\text{mol}\cdot\text{m}^{-2})$ Acetonitrile in RTIL
[BMIM][BF ₄]	3.59×10^{-06}	1.33×10^{-06}
[BMIM][PF ₆]	3.91×10^{-06}	1.17×10^{-06}
	RTIL in Methanol	RTIL in Acetonitrile
[BMIM][BF ₄]	-7.66×10^{-07}	-7.26×10^{-07}
[BMIM][PF ₆]	-3.63×10^{-07}	-8.47×10^{-07}

[BMIM][BF₄], in the case of methanol the reverse is true. This can be attributed to the nature of specific solute-solvent interaction energies in RTIL+ cosolvent mixtures. As regards the solute for imidazolium based RTILs, while methanol is regarded as an associating solute that forms strong hydrogen bonds with the charged parts of RTILs (especially anions), acetonitrile is regarded as a dipolar solute that interacts with the charged head groups of the ions and nonpolar domains in RTILs [52]. Through molecular dynamic simulation, Lopes and co-workers [42, 43] have established that both acetonitrile and methanol interact strongly with the anions BF₄⁻ and PF₆⁻. On account of its smaller size, BF₄⁻ interacts more strongly than PF₆⁻. The difference between methanol and acetonitrile interactions with imidazolium-based RTILs lies in their interaction with C2-H of the imidazolium ion. This interaction energy is comparatively stronger for acetonitrile than for methanol and is expected to be greater for PF₆⁻ than BF₄⁻ on account of larger polarizability of the former. In light of these facts it can be safely argued that between methanol and acetonitrile as solutes, while [BMIM][BF₄] will show stronger interaction energies with methanol, in the case of [BMIM][PF₆] acetonitrile will more strongly interact with the RTIL domains than methanol. This very well justifies the relative variations observed for γ values of [BMIM][BF₄] and [BMIM][PF₆] on addition of methanol and acetonitrile.

An overall view of the observed trends in γ , $\Delta\gamma$ and κ leads us to propose that in the low RTIL regime, the fraction of free conducting species increases leading to increases in γ , $\Delta\gamma$ and κ . However in the RTIL-rich fraction, aggregate formation on account of strong ion-ion interactions becomes the dominant factor and hence leads to the overall decreases in γ , $\Delta\gamma$ and κ . Thus, we propose that the maxima in $\Delta\gamma$ and κ versus mole fraction plots actually represent the RTIL-cosolvent composition beyond which the mixture behaves like a structured solvent.

4 Conclusion

Conductance and surface tension studies on mixtures of imidazolium based RTILs, viz. 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) plus methanol and acetonitrile mixtures, were carried out to explore and understand the impact of the latter as cosolvents on the bulk and interfacial characteristics of RTILs. It was found that both methanol and acetonitrile as cosolvents enhance the transport parameters of the investigated RTILs, with the later being more effective. An interesting finding of the present work is that with cosolvent addition, the RTILs preserve their characteristic structural aspects up to a certain definite limit of dilution: in acetonitrile, $X_{IL} = 0.144$ for [BMIM][BF₄] and $X_{IL} = 0.103$ for [BMIM][PF₆]; in methanol, $X_{IL} = 0.164$ for [BMIM][BF₄] and $X_{IL} = 0.118$ for [BMIM][PF₆]. In acetonitrile both RTILs retain their chemical characteristics up to a higher dilution limit and there is also larger increase of ionic conductivity than in methanol. Therefore acetonitrile seems to be a better cosolvent for boosting the conductivity of imidazolium ionic liquids and enhancing their transport for electrochemical and other applications wherein high viscosity limits the use of RTILs.

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References

1. Wasserscheid, P., Welton, T.: *Ionic Liquids in Synthesis*. Wiley, Weinheim (2003)
2. Welton, T.: Room temperature ionic liquids-solvents for synthesis and catalysis. *Chem. Rev.* **99**, 2071–2083 (1999)
3. Hapiot, P., Lagrost, C.: Electrochemical reactivity in room temperature ionic liquids. *Chem. Rev.* **108**, 2238–2264 (2008)
4. Lu, X., Burrell, G., Separovic, F., Zhao, C.: Electrochemistry of room temperature protic ionic liquids: a critical assessment for use as electrolytes in electrochemical applications. *J. Phys. Chem. B* **116**, 9160–9170 (2012)
5. Liu, W., Ye, C., Gong, Q., Wang, H., Wang, P.: Tribological performance of room-temperature ionic liquids as lubricant. *Tribol. Lett.* **13**, 81–85 (2002)
6. Harris, K.R., Woolf, L.A.: Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Chem. Eng. Data* **50**, 1777–1782 (2005)
7. Harris, K.R., Kanakubo, M., Woolf, L.A.: Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate: viscosity and density relationships in ionic liquids. *J. Chem. Eng. Data* **52**, 2425–2430 (2007)
8. Jacquemin, J., Ge, R., Nancarrow, P., Rooney, D.W., Gomes, M.F.C., Padua, A.A.H., Hardacre, C.: Prediction of ionic liquid properties. I. Volumetric properties as a function of temperature at 0.1 MPa. *J. Chem. Eng. Data* **53**, 716–726 (2008)
9. Hayamizu, K., Aihara, Y., Nakagawa, H., Nukada, T., Price, W.S.: Ionic conduction and ion diffusion in binary room temperature ionic liquids composed of [emim][BF₄] and LiBF₄. *J. Phys. Chem. B* **108**, 19527–19532 (2004)
10. Nicotera, I., Oliviera, C., Henderson, W.A., Appetecchi, G.B., Passerini, S.J.: NMR investigation of ionic liquid-LiX mixtures: pyrrolidinium cations and TFSI- anions. *J. Phys. Chem. B* **109**, 22814–22819 (2005)
11. Li, W., Zhang, Z., Han, B., Hu, S., Xie, Y., Yang, G.: Effect of water and organic solvents on the ionic dissociation of ionic liquids. *J. Phys. Chem. B* **111**, 6452–6456 (2007)
12. Gericke, M., Liebert, T., Seoud, O.A.E., Heinze, T.: Tailored media for homogeneous cellulose chemistry: ionic liquid/co-solvent mixtures. *Macromol. Mater. Eng.* **296**, 483–493 (2011)
13. Sarkar, A., Trivedi, S., Pandey, S.: Unusual solvatochromism within 1-butyl-3-methylimidazolium hexafluorophosphate + poly(ethylene glycol) mixtures. *J. Phys. Chem. B* **112**, 9042–9049 (2008)
14. Sarkar, A., Trivedi, S., Pandey, S.: Polymer molecular weight-dependent unusual fluorescence probe behavior within 1-butyl-3-methylimidazolium hexafluorophosphate + poly(ethylene glycol). *J. Phys. Chem. B* **113**, 7606–7614 (2009)
15. Trivedi, S., Malek, N.I., Behera, K., Pandey, S.: Temperature-dependent solvatochromic probe behavior within ionic liquids and (ionic liquid + water) mixtures. *J. Phys. Chem. B* **114**, 8118–8125 (2010)
16. Chaban, V.V., Prezhdo, O.V.: Ionic and molecular liquids: working together for robust engineering. *J. Phys. Chem. Lett.* **4**, 1423–1431 (2013)
17. Chaban, V.V., Prezhdo, O.V.: How toxic are ionic liquid/acetonitrile mixtures? *J. Phys. Chem. Lett.* **2**, 2499–2503 (2011)
18. Zhang, S.J., Li, X., Chen, H.P., Wang, J.F., Zhang, J.M., Zhang, M.L.: Determination of physical properties for the binary system of 1-ethyl-3-methylimidazolium tetrafluoroborate + H₂O. *J. Chem. Eng. Data* **49**, 760–764 (2004)
19. Jan, R., Rather, G.M., Bhat, M.A.: 15. Association of ionic liquids in solution: conductivity studies of [BMIM][Cl] and [BMIM][PF₆] in binary mixtures of acetonitrile + methanol. *J. Solution Chem.* **42**, 738–745 (2013)
20. Zhou, Q., Wang, L.S., Chen, H.P.: Densities and viscosities of 1-butyl-3-methylimidazolium tetrafluoroborate + H₂O binary mixtures from (303.15 to 353.15) K. *J. Chem. Eng. Data* **51**, 905–908 (2006)
21. Herzig, T., Schreiner, C., Bruglachner, H., Jordan, S., Schmidt, M., Gores, H.J.: Temperature and concentration dependence of conductivities of some new semichelatorborates in acetonitrile and comparison with other borates. *J. Chem. Eng. Data* **53**, 434–438 (2008)
22. Domanska, U., Pobudkowska, A., Wisniewska, A.: Solubility and excess molar properties of 1,3-dimethylimidazolium methylsulfate, or 1-butyl-3-methylimidazolium methylsulfate, or 1-butyl-3-methylimidazolium octylsulfate ionic liquids with *n*-alkanes and alcohols: analysis in terms of the PFP and FBT models. *J. Solution Chem.* **35**, 311–334 (2006)
23. Ge, M.L., Ren, X.G., Song, Y.J., Wang, L.S.: Densities and viscosities of 1-propyl-2,3-dimethylimidazolium tetrafluoroborate + H₂O at *T* = (298.15 to 343.15) K. *J. Chem. Eng. Data* **54**, 1400–1402 (2009)

24. Domanska, U., Laskowska, M.: Temperature and composition dependence of the density and viscosity of binary mixtures of 1-butyl-3-methylimidazolium thiocyanate + 1-alcohols. *J. Chem. Eng. Data* **54**, 2113–2119 (2009)
25. Bhat, M.A., Dutta, C.K., Rather, G.M.: Exploring physicochemical aspects of *N*-Nalkylimidazolium. *J. Mol. Liq.* **181**, 142–151 (2013)
26. Dupont, J., Consorti, C.S., Saurez, P.A.Z., deSouza, R.F.: Preparation of 1-butyl-3-methylimidazolium-based room temperature ionic liquids. *Org. Synth.* **79**, 236–243 (2002)
27. Bhat, M.A., Chaudhari, V.R., Ingole, P.P., Haram, S.K.: Outer sphere electroreduction of CCl_4 in 1-butyl-3-methylimidazolium tetrafluoroborate; an example of solvent effects of ionic liquid. *J. Phys. Chem. B* **113**, 2848–2853 (2009)
28. Perrin, D.D., Armarego, W.L.F.: Purification of Laboratory Chemicals, 3rd edn. Pregamon Press, London (1998)
29. Bhat, M.A., Dar, A.A., Rasheed, P.I., Rather, G.M.: Temperature dependence of transport and equilibrium properties of properties of alkylpyridinium surfactants. *J. Chem. Thermodyn.* **39**, 1500–1507 (2007)
30. Hunger, J., Stoppa, A., Buchner, R., Hefter, G.: From ionic liquid to electrolyte solution: dynamics of 1-*N*-butyl-3-*N*-methylimidazolium tetrafluoroborate/dichloromethane mixtures. *J. Phys. Chem. B* **112**, 12913–12919 (2008)
31. Tokuda, H., Baek, S.J., Watanabe, M.: Room temperature ionic liquid-organic solvent mixtures: conductivity and ionic association. *Electrochemistry* **73**, 620–622 (2005)
32. Neuder, R., Barthel, J.: Electrolyte Data Collection. DECHEMA Chemistry Data Series, vol. XII. Part1a, Frankfurt (1993)
33. Gores, H.J., Barthel, J.: Conductance of salts at moderate and high concentrations in propylene carbonate-dimethoxyethane mixtures at temperatures from -45 to 25°C . *J. Solution Chem.* **9**, 939–954 (1980)
34. Chaban, V.V., Prezhdo, O.V.: A new force field model of 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid and acetonitrile mixtures. *Phys. Chem. Chem. Phys.* **13**, 19345–19354 (2011)
35. Kalugin, O.N., Voroshylova, I.V., Riabchunova, A.V., Lukinova, E.V., Chaban, V.V.: Conductometric study of binary systems based on ionic liquids and acetonitrile in a wide concentration range. *Electrochim. Acta* **105**, 188–199 (2013)
36. Every, H., Bishop, A.G., Forsyth, M., MacFarlane, D.R.: Ion diffusion in molten salt mixtures. *Electrochim. Acta* **45**, 1279–1284 (2000)
37. Wang, J.J., Wang, H.Y., Zhang, S.L., Zhang, H.C., Zhao, Y.: Conductivities, volumes, fluorescence, and aggregation behavior of ionic liquids $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_n\text{mim}]\text{Br}$ ($n = 4, 6, 8, 10, 12$) in aqueous solutions. *J. Phys. Chem. B* **111**, 6181–6188 (2007)
38. Shi, L.J., Li, N., Yan, H., Gao, Y.A., Zheng, L.Q.: Aggregation behavior of long-chain *N*-aryl imidazolium bromide in aqueous solution. *Langmuir* **27**, 1618–1625 (2011)
39. Dorbritz, S., Ruth, W., Kragl, U.: Investigation on aggregate formation of ionic liquids. *Adv. Synth. Catal.* **347**, 1273–1279 (2005)
40. Casteel, J.F., Amis, E.S.: Specific conductance of concentrated solutions of magnesium salts in water-ethanol system. *J. Chem. Eng. Data* **17**, 55–59 (1972)
41. Stoppa, A., Hunger, J., Buchner, R.: Conductivities of binary mixtures of ionic liquids with polar solvents. *J. Chem. Eng. Data* **54**, 472–479 (2009)
42. Lopes, J.N.C., Padua, A.A.H.: Nanostructural organization in ionic liquids. *J. Phys. Chem. B* **110**, 3330–3335 (2006)
43. Lopes, J.N.C., Gomes, M.F.C., Padua, A.A.H.: Nonpolar, polar, and associating solutes in ionic liquids. *J. Phys. Chem. B* **110**, 16816–16818 (2006)
44. Chaban, V.V., Voroshylova, I.V., Kalugin, O.N., Prezhdo, O.V.: Acetonitrile boosts conductivity of imidazolium ionic liquids. *J. Phys. Chem. B* **116**, 7719–7727 (2012)
45. Aliaga, C., Santos, C.S., Baldelli, S.: Surface chemistry of room-temperature ionic liquids. *Phys. Chem. Chem. Phys.* **9**, 3683–3700 (2007)
46. Mezger, M., Schrder, H., Reichert, H., Schramm, S., Okasinski, J.S., Schder, S., Honkimki, V., Deutsch, M., Ocko, B.M., Rohwerder, M., Stratmann, M., Dosch, H.: Molecular layering of fluorinated ionic liquids at a charged sapphire(0001) surface. *Science* **322**, 424–428 (2008)
47. Lovelock, K.R.J., Kolbeck, C., Cremer, T., Paape, N., Schulz, P.S., Wasserscheid, P., Maier, F., Steinruck, H.P.: Influence of different substituents on the surface composition of ionic liquids studied using ARXPS. *J. Phys. Chem. B* **113**, 2854–2864 (2009)
48. Carvalho, P.J., Freire, M.G., Marrucho, I.M., Queimada, A.J., Coutinho, J.A.P.: Surface tensions for the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids. *J. Chem. Eng. Data* **53**, 1346–1350 (2008)

49. Endres, F., ElAbedin, S.Z.: Air and water stable ionic liquids in physical chemistry. *Phys. Chem. Chem. Phys.* **8**, 2101–2116 (2006)
50. Domanska, U., Krolikowska, M.: Effect of temperature and composition on the surface tension and thermodynamic properties of binary mixtures of 1-butyl-3-methylimidazolium thiocyanate with alcohols. *J. Colloid Interface Sci.* **348**, 661–667 (2010)
51. Adamson, A.W.: *Physical Chemistry of Surfaces*, 6th edn. Wiley, New York (1997)
52. Shimizu, K., Gomes, M.F.C., Padua, A.A.H., Rebelo, L.P.N.: Three commentaries on the nano-segregated structure of ionic liquids. *J. Mol. Struct. Theor.* **946**, 70–76 (2010)