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Exploring physicochemical aspects of N-alkylimidazolium based ionic liquids

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ABSTRACT

Physicochemical aspects (structural, thermodynamic and transport) of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BDMIM][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) room temperature ionic liquids (RTILs) are reported. The results based on temperature dependence of surface tension, conductivity, photoluminescence and spectroscopic measurements on RTILs and their mixtures with acetonitrile (ACN) as cosolvent are interpreted in-terms of structure–composition–property relations. The presented observations clearly indicate that a highly structured and organized arrangement of constituents prevails in the investigated RTILs, which is sensitive to temperature variations and cosolvent addition. Thermodynamic and structural parameters estimated from temperature dependency of interfacial tension demonstrate that surface characteristics are dominated by covalent interactions in imidazolium based RTILs. From composition dependence of measured parameters in RTIL–cosolvent mixtures it is shown that ACN mixes nonideally with RTIL, and interestingly the investigated RTILs retain their inherent structural order up to high dilution limits (0.3 volume fraction of RTIL), beyond which these behave as associated electrolytes. The presented findings seem useful for arriving at molecular basis of physicochemical aspects and future applications of RTILs and their binary mixtures especially with cosolvents for biphasic catalysis and heterogeneous electron transfer reactions, wherein temperature elevation and cosolvent addition are currently advocated as operationally simple means to speed up the mass transport.

1. Introduction

Room temperature ionic liquids (RTILs) are attracting significant attention as novel 'green' alternatives to conventional organic solvents for biphasic catalysis, solvent extraction, synthesis and electrochemical investigations [1–8]. Experimental and simulation studies have clearly established that a combination of dispersive and non-dispersive forces prevailing among the constituents lead to a characteristic structural organization and attractive physicochemical aspects in RTILs [9]. On account of this unique structural organization solution chemists refer to RTILs as nanofluids wherein three dimensional polar networks are permeated by non-polar domains. These uniformly distributed domains of opposite polarities make RTILs a low dimensional analog of micellar media. Supramolecular structure and nanoscale ordering in the RTILs have emerged as key to molecular level understanding of their physicochemical characteristics and their impact on various processes [10]. The structural organization of RTILs markedly affects the stability and transport of analytes and the intermediates involved in biphasic catalysis, heterogeneous electron transfer and associated chemical reactions thereby affecting the thermodynamics and kinetics of these phenomena where interface plays a significant role. Hence the use of RTILs as solvents for such applications requires a comprehensive understanding about their transport and interfacial properties vis a vis their characteristic structural organization. The use of RTILs together with organic and inorganic solvents as binary or ternary mixtures has been attempted for various technological processes. It is worth mentioning that RTIL mixtures with cosolvent possess altered and, in some cases, improved physicochemical properties [11,12].

Prediction of composition–structure–property relations in RTILs and their binary mixtures is an interesting and challenging task for present day physical chemists. Various theoretical and experimental approaches have been made use of to work out such relations for RTILs [13–16]. In the experimental approaches researchers have made use of the magnitudes and trends in variations in some measurable parameters in response to intelligently planned perturbations in selectively chosen experimental variables to arrive at a basic understanding of such relations in RTILs. Thus while surface tension measurements have proved to be very useful in prediction of microscopic ordering and estimation of thermodynamic variables [17–19], the conductance [20–22] and optical responses [23–26] have been quite effectively used for understanding the bulk characteristics and transport phenomena in fluids and fluid mixtures. In view of these facts we decided to make use of temperature variation and cosolvent addition as perturbations in experimental

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variables and surface tension, conductance and optical responses as the measurable parameters to explore the molecular basis of physicochemical aspects of imidazolium based RTILs: 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]), 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate ([BDMIM][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and their binary mixtures with acetonitrile (ANC) as cosolvent. Imidazolium based RTILs were chosen because of their air and moisture stability while we selected ACN as cosolvent on account of its electrochemical, solubility and polarity features [27]. Present study is expected to be very useful for applications wherein the temperature elevation [28–30] and cosolvent addition are employed as means to overcome the viscosity limitations in imidazolium based RTILs [31–33]. Since fluid structuring in RTILs may be very sensitive to rise in temperature and/or addition of cosolvents, a cautionary approach needs to be followed in using any one of these options to overcome viscosity related challenges in RTILs. In light of these facts the present work also serves our aim to explore and understand the impact of temperature and cosolvent on structural, transport and interfacial properties of alkylimidazolium based RTILs. Besides providing new insight into the structural features and structure–composition–property relations for imidazolium based RTILs and their binary mixtures, the study is expected to be of considerable importance for selection of optimal experimental conditions, structure and/or composition for RTIL or its binary mixture with cosolvent for a specific application.

2. Experimental section

2.1. Chemicals

RTILs used were synthesized following a two step procedure [34] as reported earlier [35]. Briefly, in the first step 1-methylimidazole or 1,2-dimethylimidazole was refluxed with n-butyl chloride for 90 h under argon atmosphere for the synthesis of 1-butyl-3-methylimidazolium chloride and 1-butyl-2, 3-dimethylimidazolium chloride respectively. In the next step the halide anion was exchanged with $[BF]_4^-$ or $[PF]_6^-$ using HBF_4 or HPF_6. The RTILs were vacuum dried and stored in desiccators under inert atmosphere and were characterized through ^1H NMR, mass spectrometry and ^{13}C NMR spectroscopy. The water content of dried RTILs was less than 50 ppm, as analyzed by Karl Fischer titration. The details of synthesis, purification, drying and characterization procedures are described in supporting information.

2.2. Measurements

Surface tension measurements (within ± 0.1 mJ m^{-2}) were made with a K9 Tensiometer (Kruss, Germany) by the ring detachment technique. Temperature was maintained at the desired value (within ± 0.1 °C) by circulating thermostated water from a HAAKE GH bath. The measured values were corrected according to the procedure of Harkins and Jordan built into the instrument software. Conductivity was recorded by a digital microprocessor based conductivity meter (CYBERSCAN CON 500) from Eutech instruments having sensitivity of 0.1 μScm^{-1}; details are reported elsewhere [36]. Steady state photoluminescence (PL) spectra were recorded at room temperature with a Shimadzu RF-5301PC spectrofluorometer. Fourier transform infrared spectroscopy (FTIR) of liquid samples was performed with a Thermo Scientific, NICOLET 6700 FT-IR spectrometer. Numerical calculations and data fitting were performed through codes written in Origin 6.0 (Microcal Software Inc.). Ab initio calculations were performed to obtain gas phase optimized geometries and electronic energies by using GAUSSIAN 03 set of codes [37], at the level of density functional theory using the exchange functional B3LYP [38] with 6-31G(d, p) basis set. Frequency analysis of the resultant geometries was performed at the same level of theory and basis set, to check whether the obtained structures are the stable minimum energy structures and no imaginary frequencies were found.

3. Results and discussion

3.1. Temperature variations

3.1.1. Surface tension measurements

Surface tension (γ) is a useful parameter for characterization of fluids and their solutions [18,19,39]. According to Langmuir [40], each part of a molecule possesses a local surface energy, hence γ of a fluid is an index of the type of molecular orientation at its surface. Thermodynamic modeling of fluid surfaces suggests that while magnitude of γ is a useful index of cohesive energy prevailing at the surface, its temperature dependence can serve as a reliable means for estimation of thermodynamic characteristics of fluids and fluid mixtures. Many groups in recent past have used inter-facial tension and its dependence on molecular structure and temperature as a means to model the molecular ordering and estimate the thermodynamic variables associated with RTIL–air interface [41–43]. In view of all these reports, we measured the γ of the chosen RTILs as a function of temperature in the range 293–323 K and the results are depicted as Fig. 1. Like most other liquids γ varies linearly with temperature, obeying Eq. (1)

$$\gamma = a - b.T \tag{1}$$

with a regression coefficient ≈0.99. In the entire temperature range investigated γ retains the order, [BDMIM][BF_4] > [BMIM][BF_4] > [BMIM][PF_6] in accordance with an earlier report by Freire et al. [43]. The measured values of γ seem slightly larger in magnitude than those reported for [BMIM][BF_4] [44] and [BMIM][PF_6] [45]. While this manuscript was being compiled, a report by Russo et al. [42] highlighting the impact of number of conceivable impurities on γ of imidazolium based RTILs appeared in the literature. In this report the authors suggest that the addition of experimentally expected impurities to RTILs tends to either decrease or have essentially no effect on the surface tension but never causes an increase in surface tension, corroborated by the findings of Freire et al. [43], that γ and thermodynamic variables estimated from its temperature dependence are not significantly affected by the presence of water.

It is expected that both cations and anions of investigated RTILs will contribute to the measured γ with the relative contribution depending upon their number density and orientation at the surface. Electroneutrality requirement warrants that the surface of RTILs cannot be preferentially enriched by any of the constituent ions; instead bulk stoichiometry should be preserved up to the surface, a fact proved through direct recoil spectrometry (DRS) experiments by Gannon et al. [46]. Since the constituent cations of RTILs are comparatively of larger size, the stoichiometric requirement of 1 cation: 1 anion at the surface warrants the dominance of cation on surface properties. As the actual

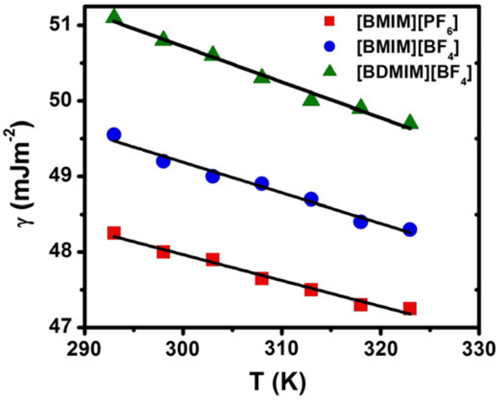

Fig. 1. Temperature dependence of γ for [BMIM][BF_4], [BDMIM][BF_4] and [BMIM][PF_6]. The straight lines show linear fits of the data (regression coefficient ≈0.99) in accordance with Eq. (1).