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Exploring physicochemical aspects of N-alkylimidazolium based ionic liquids

Mohsin Ahmad Bhat ^{a,*}, Chanmeet K. Dutta ^b, Ghulam Mohammad Rather ^b

^a Department of Chemistry, University of Pune, Ganeshkhind, Pune 411007, India

^b Department of Chemistry, University of Kashmir, Srinagar 190006, India

ARTICLE INFO

Article history: Received 10 February 2012 Received in revised form 16 January 2013 Accepted 21 February 2013 Available online 14 March 2013

Keywords: Room temperature ionic liquid (RTIL) Surface tension Excess surface energy Specific conductance Cosolvent Photoluminescence

ABSTRACT

Physicochemical aspects (structural, thermodynamic and transport) of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF4]), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BDMIM][BF4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) 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. © 2013 Elsevier B.V. All rights reserved.

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

^{*} Corresponding author. Tel.: +91 194 242 4900; fax: +91 194 242 0333. *E-mail address:* mohsinch@kashmiruniversity.ac.in (M.A. Bhat).

^{0167-7322/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molliq.2013.02.021

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][BF₄]), 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate ([BDMIM][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) 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] $\frac{1}{4}$ or [PF] $\frac{1}{6}$ using HBF₄ or HPF₆. The RTILs were vacuum dried and stored in desiccators under inert atmosphere and were characterized through ¹H NMR, mass spectrometry and ¹³C 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 $\pm 0.1 \text{ mJ m}^{-2}$) were made with a K9 Tensiometer (Kruss, Germany) by the ring detachment technique. Temperature was maintained at the desired value (within \pm 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 μ Scm⁻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 \approx 0.99. In the entire temperature range investigated γ retains the order, [BDMIM][BF₄] > [BMIM][BF₄] > [BMIM][PF₆] 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][BF₄] [44] and [BMIM][PF₆] [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][BF₄], [BDMIM][BF₄] and [BMIM][PF₆]. The straight lines show linear fits of the data (regression coefficient \approx 0.99) in accordance with Eq. (1).

orientation of cations at interface will be determined by their interactions with the counter anions and other cations, the extent of cationic dominance on surface characteristics will be affected by the overall composition of RTIL and the prevailing experimental conditions. The observed values of γ are close to 40.3 mJ m⁻² as reported for imidazole [47], an evidence for cationic dominance on surface properties in the investigated RTILs. While cation-anion interactions in the presently investigated RTILs seem to be purely Coulombic, the cation-cation interactions are expected to have considerable contribution from van der Waals interactions also. Taking into consideration the conformers with the lowest energy for constituent ions and the cation-anion combinations, ab initio calculations revealed the ion-interaction energy to be -160.01, -88.47 and -94.99 kcal·mol⁻¹ for [BMIM][BF₄], [BMIM][PF₆] and [BDMIM][BF₄] respectively, indicating that the interaction energy is stronger in presence of $[BF_4]^-$ than $[PF_6]^-$. This is well expected as per the Lewis basicity of anions and is evident from Fig. 2 that shows IR spectra recorded for pure [BMIM][BF₄] and [BMIM][PF₆]. Lower frequencies for C – H vibrations of imidazolium cation in [BMIM][BF₄] in comparison to [BMIM][PF₆] are a direct evidence for weaker cation-anion interactions in the latter [48]. Since stronger cation-anion interactions imply lesser residual charge at the surface, a higher interaction energy among RTIL constituents leads to higher γ values. Thus we may propose that the stronger interaction energy among constituents in [BMIM][BF₄] in comparison to that in [BMIM][PF₆] is responsible for higher γ of the former. This is in accord with the hypothesis by Deetlefs et al. [49], that an increase in ion size and hence diffuseness of charge on the RTIL ions lead to a decrease in the overall interaction among the constituents and, therefore, a decrease in surface tension. This feature of RTILs makes them behave differently than conventional organic solvents wherein increase in size of constituents leads to an increase in surface tension.

Since introduction of methyl group at the C-2 position of imidazolium cation has been proved to decrease the cation-anion interaction which we also observed in our quantum mechanical calculations, higher value of γ for [BDMIM][BF₄] in comparison to that of [BMIM][BF₄] seems quite unexpected. Similar trend has earlier been reported by Hunt et al. [50] for the melting point and viscosity of imidazolium based RTILs and by Freire et al. [43] for γ value of [BDMIM][PF₆] in comparison to [BMIM][PF₆]. Surface tension of fluids is actually a measure of the cohesive forces among their constituents at the surface. In RTILs both dispersive (van der Waals) and non-dispersive (Coulombic) interactions contribute to the overall interaction energy among constituent ions at the interface. We attribute the higher surface tension of [BDMIM][BF₄] with respect to that of [BMIM][BF₄] to increase in structural ordering of constituents. Besides inhibiting butyl chain rotation due to steric repulsion, introduction of methyl group at C₂ of imidazolium ring restricts the number of otherwise thermodynamically allowed ion pair conformers for an imidazolium (cation) plus anion combination. Both these factors are expected to enhance molecular order that ensures



Fig. 2. FTIR absorption spectra in the range 2500–3500 cm⁻¹ for pure [BMIM][BF₄] and [BMIM][PF₆] ionic liquids. Frequency assignments were done as per reference [48].

greater van der Waals interactions and hence higher surface tension. In other words, on substitution of C₂-H of imidazole with C₂-CH₃, the loss in Coulombic interactions due to steric (size) reasons is lesser than the gain in dispersive (van der Waals) interactions that arises on account of loss in entropy. Such ordering, as reported recently [41], increases the number of overall units contributing to Coulombic attractions at the surface and hence lead to an increase in the surface tension. Thus, an increase in structural order leads to a net increase in dispersive as well as non-dispersive interactions among the constituents of [BDMIM] [BF₄] [50] resulting in a higher surface tension in comparison to [BMIM][BF₄], an argument well supported by its higher viscosity [51]. Simulation studies, and neutron and X-ray reflectivity measurements [52–55] have shown that at imidazolium RTIL/air interface, two types of molecular arrangements prevail - one with side chain (butyl in present study) normal to surface and other with side chain parallel to the surface. The former with imidazolium rings parallel to the surface will have lower surface tension than the later wherein their orientation is perpendicular to the surface. Introduction of the methyl group at C-2 position in imidazolium ring is expected to favor its orientation perpendicular to surface and hence higher surface tension. Within this orientation, CH₃ substituent, besides increasing the orientational order, will also enhance van der Waals interactions among the cation rings at the surface [56], that in turn will more than compensate the decreased Coulombic interactions of imidazolium rings with their counter anions [57].

Linear fit parameters of γ vs. T plots were used to calculate thermodynamic variables for the RTIL/air interface. Thus, while the intercept gives the enthalpy of surface formation per unit surface (H^s), the slope is a measure of surface entropy (S^s) [58]. Assuming that surface tension vanishes at critical temperature (T_c), the ratio of H^s to S^s gives T_c. The resulting thermodynamic surface characteristics are listed in Table 1. The estimated values are in good agreement with those reported earlier [59-63]. According to Bloom, Davies and James [64], the magnitude of H^s can be correlated to the bonding characteristics of the fluid. The values observed for the investigated RTILs are much lower than those reported for fused electrolytes but close to those reported for organic liquids. This indicates that the surface thermodynamic characteristics are dominated by covalent interactions [58,65]. Surface energy shows an increase with increase in cation size in agreement with the report by Freire et al. [43], that increase in cation size leads to charge dispersion and hence reduction of the hydrogen bond strength. The surface entropies of the RTILs seem low in comparison to those reported for conventional organic solvents, thereby indicating a high surface organization of constituents at the RTIL surface. This is in accord with predictions based on molecular dynamics simulation calculations [66] which suggest that in imidazolium based RTILs, the imidazolium cations are strongly aligned at the liquid/vapor interface and thereby leading to negative or at least anomalously low surface excess entropy. As evident from the slopes of the fit lines in Fig. 1, which are a measure of sensitivity of surface interaction to temperature, the former decrease with increase of latter in the order [BDMIM]

Table 1

Values of surface tension (γ) (standard error = 0.20), surface entropy (S^s), surface enthalpy (H^s), critical temperature (T_c), average interstice volume (ν), interstice volume fraction (ϕ) and thermal expansion coefficient (α) for [BMIM][BF₄], [BMIM][PF₆] and [BDMIM][BF₄].

Properties	[BMIM][BF ₄]	[BMIM][PF ₆]	[BDMIM][BF ₄]
γ /mJ m ⁻² at 298 K S ^s /mJ m ^{-2 K - 1} H ^s /mJ m ⁻² T _c /K $\nu \times 10^{24}$ cm ³ at	49.2 (46.6, Ref. [44]) 0.0404 61.29 1577.17 16.42	48.0 (47.92, Ref. [45]) 0.0343 58.25 1698.34 17.04	50.8 0.0471 64.86 1377.13 15.65
$\phi imes 10^2$ at 298 K $lpha imes 10^4$ at 298 K	12.0 6.02	8.68 4.37	8.59 4.74

 $[BF_4] > [BMIM][BF_4] > [BMIM][PF_6]$, an evidence for the higher γ value of $[BDMIM][BF_4]$ in comparison to $[BMIM][BF_4]$ on account of stronger dispersive interactions in the former. These results prove the predictions of Law et al. [59] well, that the structure of cation and its orientation at surface are mainly responsible for surface properties of RTILs. The calculated values of critical temperature show that thermodynamically [PF] $\overline{_6}$ combination with imidazolium cation is more stable than its [BF] $\overline{_4}$ analog and introduction of an additional alkyl chain leads to instability.

Making use of a classical statistical mechanics based theoretical model originally proposed by Furth [67] and subsequently developed by Bokris and Reddy [68], many groups [62,69–71] have reported the use of experimentally measured values of γ for the estimation of bulk characteristics in many RTILs. According to this model, now known as interstice model, due to large size and asymmetric shape, the constituent ions are not closely packed, instead they leave a lot of interstices in between them. The model predicts that the average volume of an interstice (ν) in RTIL is related to its γ through Eq. (2)

$$\nu = 0.6791 (kT/\gamma)^{3/2} \tag{2}$$

where k is the Boltzmann constant and T the temperature. The total volume of interstices per mole formula unit (V_m^i) of RTIL (1:1 electrolyte) is given by Eq. (3)

$$V_m^i = 2N\nu \tag{3}$$

N being the Avogadro's number, leading to an interstices volume fraction (ϕ) in an RTIL of molar volume V_m equal to

$$\phi = \frac{V_m^i}{V_m}.\tag{4}$$

The model envisages the interstices moving like ions, their expansion with temperature being the cause for thermal expansion which can be characterized in terms of the thermal expansion coefficient (α) given by Eq. (5)

$$\alpha = \frac{3N\nu}{V_m T}.$$
(5)

Using Eqs. (2) to (5), the characteristic values for v, ϕ and α were estimated for the investigated RTILs and the same are presented in Table 1. While the value of α estimated for [BMIM][BF₄] in present study is in good agreement with that reported by Harris et al. [29], the value estimated for [BMIM][PF₆] is a bit lesser in magnitude than that reported in literature [72]. These values indicate that the packing of constituents is more compact in [BDMIM][BF₄] than in [BMIM][BF₄], supporting our contention that the entropic factors dominate the energetic factors which lead to higher γ value of [BDMIM][BF₄] in comparison to [BMIM][BF₄]. In a recent study Larriba et al. [73] have proposed that the interstice volume can be used to predict γ in imidazolium based RTILs. Use of interstice volume as presented in Table 1, for estimation of γ of presently investigated RTILs through this approach was found to yield values in good agreement with the experimentally observed values.

3.2. Conductivity measurements

Fig. 3A depicts the variation of specific conductance (κ) with temperature for the investigated RTILs. Conductivity increases linearly with temperature and is in the order [BDMIM][BF₄] < [BMIM][PF₆] < [BMIM][BF₄], in conformity with the trend expected on the basis of ion mobility and viscosity. We used the reported values of density and coefficient of viscosity [28–30] for calculation of molar conductance (Λ_m) and Walden product (Λ_n . η) for [BMIM][BF₄] and [BMIM][PF₆]. The resulting values are plotted as a function of temperature in Fig. 3B. It is pertinent to mention that the κ and Λ_m that we found are significantly greater in magnitude than the values reported in the literature [28–30]. This perhaps is on account of open to atmosphere condition of our setup which may allow RTILs to absorb moisture because of their hygroscopic nature. Interestingly, we found that instead of remaining constant as in conventional electrolyte solutions, the Walden product decreased with increase of temperature. This temperature dependence of Walden product seems unexpected in light of earlier reports [33,74], which suggest that viscosity is the only force impeding the motion of RTIL ions, while the dissociation of neat RTILs is independent of temperature. Our observations, besides the ion diffusion experiments [31], however indicate that the ionicity of RTILs should be temperature dependent. From electrical conductance point of view, RTILs can be modeled as an equilibrium mixture of dissociated ions (ions free to conduct-solute) dissolved in the associated part (associated ion clusters not able to conduct-solvent) [75,76], as per the equilibrium

$$A^+B^- \rightleftharpoons A^+ + B^-. \tag{6}$$

Sangoro et al. [77] on the basis of their pulsed field gradient nuclear magnetic resonance and broad band dielectric spectroscopy measurements have suggested that there is an Arrhenius type dependence for the number density of charge carriers in imidazolium based RTILs. Thus it may be argued that the equilibrium concentrations depend on



Fig. 3. (A) Specific conductance (κ) of [BMIM][BF₄], [BDMIM][BF₄] and [BMIM][PF₆] RTILs as a function of temperature; (B) Walden product (Λ_m , η) as a function of temperature. Density and η values were taken from references, [28–30].

the dissociation constant of the above equilibrium (K_{dis}) which is related to the free energy of dissociation (ΔG_{dis}^o) of RTIL as

$$K_{dis} = exp\left(\frac{-\Delta G_{dis}^{0}}{RT}\right).$$
(7)

The greater the value of ΔG_{dis}^{o} , the -smaller is the extent of dissociation. According to Bonhote et al. [78] the conductivity of an RTIL is given by Eq. (8)

$$\kappa = \left(\frac{yF^2\rho}{6\pi N_A M_w \eta}\right) \left[(\varsigma_{\text{anion}} r_{\text{anion}})^{-1} + (\varsigma_{\text{cation}} r_{\text{cation}})^{-1} \right]$$
(8)

where *y* is the degree of dissociation, *F* the Faraday's constant, ρ the density, M_w the molecular weight and η the viscosity. r_{anion} and r_{cation} are the anion and cation radii respectively and ς_{anion} and ς_{cation} , the correction factors that take into account the specific interactions among charge carriers in the RTIL. Increasing temperature is expected to increase the extent of dissociation and hence ionicity of RTIL and at the same time decrease the viscosity of the solvent. Thus the increase in molar conductance with temperature can be attributed to both these factors and hence the variation in Λ_m with temperature should be more than that expected on the basis of variation in η alone, however, our observations are quite the opposite. On the basis of Eyring's absolute rate theory [79] temperature dependence of Λ_m and η can be expressed as [80]

$$\Lambda_m = \frac{V_c^{2/3} F^2}{RT} exp\left(\frac{-\Delta G_c^{\ddagger}}{RT}\right) \tag{9}$$

and

$$\eta = \frac{hN}{V_{\nu}} exp\left(\frac{\Delta G_{\nu}^{\ddagger}}{RT}\right). \tag{10}$$

 V_c and V_v are the volumes and ΔG_c^{\ddagger} and ΔG_v^{\ddagger} are the free energies of activation of moving units for conductance and viscous flow respectively. In case the two processes occur by the same mechanism, the product, $\Lambda_m \eta$, can be presented as

$$\Lambda_m \eta = \frac{F^2 h N V_c^{2/3}}{R T V_v} exp\left(\frac{\Delta G_v^{\ddagger} - \Delta G_c^{\ddagger}}{R T}\right). \tag{11}$$

Thus constancy of Walden product demands $V_c = V_v$ and $\Delta G_c^{\ddagger} =$ $\Delta G_{\nu}^{\ddagger}$. However in the present case the slopes of the plots of ln (Λ_m) and $ln(\eta)$ vs. 1/T (Fig. S1 and Fig. S2 supporting information) clearly indicate that activation barrier for conductance is less than that for viscous flow, well in accordance with the behavior for molten salts [68]. The difference in these values can be attributed to mechanisms responsible for the two processes. The mechanistic differences for the two processes together with Eq. (11) suggest that the Walden product will show a temperature dependence as depicted in Fig. 3. These observations imply that increase of temperature does not increase the Λ_m of RTILs to the extent expected from the extent of decrease in their η . Similar behavior has been observed for polymer electrolytes [81], where ion pairing has been suggested as the possible reason for the observed trend. Such variations as have been reported earlier suggest that in RTILs, other than viscosity, there are some additional forces that impede the motion of their constituent ions in the conduction process.

In a recent report Kashyap et al. [82] suggested that increase in temperature decreases the dielectric constant of the RTIL and hence increases the magnitude of Coulombic interactions among the oppositely charged conducting ions. Thus while the lowering of η and the increase in *y* should increase the molar conductance, the enhanced

interactions among the ions that lead to higher values for ς_{anion} and ς_{cation} will result in conductance values less than expected from variations in η alone (Eq. (8)). It is in this context that deviations from Walden rule observed in RTILs have recently led to the use of fractional Walden rule [84], according to which

$$\Lambda_m \times \eta^\beta = \text{constant.} \tag{12}$$

Thus a logarithmic plot of Λ_m vs. η should give a straight line with slope β . The experimental data when plotted in the form of Eq. (12), gave value of β equal to 0.76 for both [BMIM][BF₄] and [BMIM][PF₆]. Interestingly we found that, for both these RTILs, this value matches the ratio of activation energy for Λ_m to activation energy for viscous flow as obtained from the Arrhenius plots. Such a correlation has also been reported recently by Schreiner et al. [83].

4. Cosolvent addition

4.1. Surface tension measurements

Fig. 4 depicts the variations in γ with change in volume fraction of RTIL in ACN. Surface tension increases with increase in mole fraction of RTIL, but the variation is clearly not linear. The increase in γ is particularly strong at higher concentrations, implying that the cosolvent is more effective in breaking the cohesive interactions of RTILs in the low concentration limit. Similar observations have been reported by Domanska et al. [85] for addition of alcohols to imidazolium based RTILs. To make the effect more clearly visible we calculated the γ -deviations for the mixtures using the equation

$$\Delta \gamma = \gamma - (X_{\rm IL} \gamma_{\rm IL} + X_{\rm ACN} \gamma_{\rm ACN}). \tag{13}$$

The results plotted in Fig. 4B demonstrate that mixing of RTIL with ACN is nonideal and deviations from ideal behavior are more pronounced for [BMIM][PF₆] than for [BMIM][BF₄]. This may be ascribed to the more structured nature of the former than of the latter. To trace the origin of interactions responsible for such nonideal mixing we recorded the IR spectra at different dilutions (with ACN) of the two RTILs, as are shown in Fig. 5. As evident the position of C_2 – H vibrations (which is sensitive to hydrogen bonding) of the imidazolium ring remains unchanged. A slight blue shift noticed in CH₃⁻ group vibrations of the side chain on dilution is perhaps a result of increased freedom of the said groups on account of dilution in RTIL. Since γ is a measure of cohesive interactions among constituents at the interface, the nonlinearity in γ vs. RTIL-mole fraction (a smaller slope in low concentration range followed by a larger slope in the higher RTIL concentration range) clearly implies some sort of transition in the nature of forces responsible for nonideal variation of γ and $\Delta \gamma$. While this manuscript was being prepared a report published by Ren et al. [86] demonstrated that the excess volume vs. RTIL fraction for 1,2-dimethyl-3-hexylimidazolium bis(trifluoromethylsulfonyl)imide passes through a minimum, while the curve as a whole is not symmetric. While the authors do not propose any justification for their observations, it seems that such a variation carries interesting and valuable information regarding RTIL/cosolvent mixtures. A comparison of the trends in γ , a measure of surface interactions, and excess volume, a measure of bulk interactions, suggests that change in mole fraction of RTIL changes the surface and bulk interactions in a similar fashion. In the light of our observations and the data of the above cited paper, we propose that introduction of RTIL into the organic solvent leads to formation of some strong associates in the lower mole fraction range, which are ultimately replaced by supramolecular aggregates of RTILs entrapping the small fraction of organic solvent. To have a more clear picture before proposing a justification for these observations we probed these mixtures for their conductance and optical responses.



Fig. 4. (A) γ and (B) $\Delta\gamma$ (calculated through Eq. (13)) as a function of composition in acetonitrile for [BMIM][BF₄] and [BMIM][PF₆].



Fig. 5. FTIR absorption spectra in the range 2500–3500 cm^{-1} at changing dilutions with acetonitrile for (A) [BMIM][PF₆] and (B) [BMIM][BF₄].

4.1.1. Conductivity measurements

Fig. 6A depicts the conductivity (κ) as a function of volume fraction of RTIL in ACN and Fig. 6B depicts molar conductance (Λ_m) vs. mole fraction of RTILs. For both [BMIM][BF₄] and [BMIM][PF₆], the traces pass through maxima, indicating nonideality as observed in surface tension plots. Such a conductance behavior of RTILs with addition of cosolvent [86–89] has generated immense interest among researchers and many explanations and advantages associated with it have been proposed [89,90]. A correlation of the observed variations in γ , $\Delta\gamma$, k and Λ_m with mole fraction of RTIL, in the light of earlier reports for similar RTILs [89,90] indicates that a variety of factors, viz. formation of cosolvent–RTIL and/or RTIL-supramolecular associates and entrapping of the cosolvent within the RTIL-supramolecular aggregates, whose fraction varies with mole fraction of the RTIL can be responsible for the observed trends.

According to Dupont [91], pure imidazolium based RTILs form an extended hydrogen bonded network due to self aggregation of monomeric cations under the influence of anions. Signatures of structural organization in the investigated RTILs were clearly observed in their UV–visible absorption and emission spectra as depicted by Figs. 7 and 8. The long tail of the absorption band in RTILs (Fig. 7) has been attributed to the presence of a large number of variedly-sized supramolecular aggregates that are energetically different and characterized by specific absorption maxima [24–26]. Direct evidence for presence of such supramolecular aggregates has been reported earlier [92,93].

More interesting features were observed in the emission spectra (Fig. 8) which show two maxima, one in lower and other in higher wavelength range. The position and relative intensity of both the



Fig. 6. (A) Specific conductance (κ) and (B) molar conductance (Λ_m) as a function of composition in acetonitrile for [BMIM][BF₄] and [BMIM][PF₆].

maxima were found to be excitation wavelength dependent. At lower excitation wavelengths, the maxima in the low wavelength region of emission spectrum are dominating. As the excitation wavelength increases, the maximum at higher wavelength becomes more intense while that in lower wavelength range decreases in intensity and finally disappears. Another interesting observation is that above a particular range, the upper wavelength maximum shows a significant red shift with increase of excitation wavelength.

Paul et al. [25,94] have proved that the short wavelength emission in imidazolium based RTILs is due to the monomeric form of the imidazolium cation while excitation and relaxation of varied-sized and energetically different associated forms of the constituent ions are responsible for the tail in the absorption and long wavelength components in their emission spectra. The aggregates are expected to have their specific absorption and emission maxima. With changing excitation wavelengths, different species get excited and hence different emission behavior is observed. However, the theory of emission from photo-excited assembly of variedly energetic species [95] demands that emission will always be from the least energetic species, and hence excitation wavelength dependence of maxima in emission spectrum of RTILs is unexpected. Short fluorescence lifetimes of excited species and minimal interactions among energetically different aggregates that reduce the chances of energy transfer among these species in RTILs are perhaps the reason for the excitation wavelength dependence of their emission spectra [24]. The shape and intensity of two component excitation wave length dependent photoluminescence (PL) spectra, as



Fig. 7. UV-visible absorption spectra for pure (A) $[BMIM][PF_6]$ and (B) $[BMIM][BF_4]$ ionic liquids.



Fig. 8. PL emission spectra at changing excitation wave lengths recorded for pure (A) [BMIM][PF₆] (B) [BMIM][BF₄].

shown in Fig. 8, thus also attest the presence of supramolecular aggregates in the investigated RTILs.

Marked variations were observed in the absorption and emission spectra of RTILs on dilution with ACN. Decrease in tail length of the absorption spectra upon dilution with ACN (Fig. 9), indicates the breakage of supramolecular aggregates in RTILs. However, persistence of absorption tail up to high dilution limits implies the presence of these structures, although probably of smaller size, in these solutions. Emission spectra recorded for varied RTIL/co-solvent compositions, as depicted in Fig. 10 also lead to similar conclusions. While the high wavelength emissions have been attributed to supramolecular aggregates, the low wavelength emissions arise from monomeric forms of RTILs [24,26]. As evident from the figure, the relative emission on account of monomeric forms (low wavelength hump) increases on successive dilutions with ACN in comparison to that from aggregated forms, clearly indicating the transition of aggregates into monomers. Normalizing the emission spectrum with respect to concentration, (Fig. 10B) also indicates that addition of ACN breaks the network of supramolecular aggregates in RTILs. The relative emission of monomeric forms to aggregate forms changes from dominating aggregated forms in pure RTIL to dominating monomeric forms in dilute states. However, an interesting feature worth to be underscored is that the emission from the aggregates does not vanish even at high dilutions, thereby indicating their existence even at these dilution limits. The positions of maxima in the traces in Fig. 6 and the emission spectra of Fig. 10 hence imply that the structural order of RTILs is retained up to high dilutions (RTIL volume fraction = 0.3), beyond which the RTIL exists as a conventional electrolyte that is strongly associated.



Fig. 9. UV-visible absorption spectra at changing dilutions with acetonitrile for (A) [BMIM][PF₆] and (B) [BMIM][BF₄].

A holistic view of the observed trends in γ , $\Delta \gamma$, κ and Λ_m , emission and absorption spectra makes us to propose that addition of RTIL to the cosolvent (acetonitrile in present case) in low dilution limits leads to formation of free conducting ions and their aggregates besides ion + cosolvent complexes resulting in increase of γ , $\Delta \gamma$, κ and Λ_m . Further addition of RTIL favors the formation of ion-pairs and aggregates that, besides decreasing the fraction of conducting species, increase the viscosity and γ as well. However, in low concentration region the characteristics are dominated by the ion-solvent complexes, responsible for increase in γ , $\Delta \gamma$, κ and Λ_m . At the stage when RTIL aggregates begin to dominate the free ion-solvent complexes, the solution starts behaving more like pure RTIL wherein the cosolvent molecules are entrapped in RTIL aggregates. Higher cohesive energy among RTIL constituents in the aggregates than that of RTIL-cosolvent complexes, in turn, leads to increase in viscosity, γ , and $\Delta \gamma$, and hence decrease in κ and Λ_m with further addition of RTIL. Thus the maxima in $\Delta \gamma$, κ and Λ_m vs. mole fraction plots actually represent the RTIL-cosolvent composition beyond which (more RTIL fraction) the mixture behaves more RTIL like. In other words up to the dilution limit by cosolvent, where the maxima are observed, RTIL retains its chemical characteristics and in the present case this limit is 0.3 volume fraction of the RTIL. Below this dilution limit the investigated RTILs behave like strongly associated electrolytes. This is in agreement with earlier reports based on absorption spectra and kinetic measurements [96] and dielectric relaxation spectroscopy [89] on N-alkylimidazolium based RTILs. Thus it may be inferred that the addition of ACN leads to structural distortions of RTILs and its use



Fig. 10. PL emission spectra of [BMIM][BF₄] at excitation wave length of 330 nm at changing dilutions with acetonitrile (A) as recorded spectra; (B) spectra normalized with respect to concentration.

as cosolvent for RTIL should only be made after the expected extent of structural distortions is known.

5. Conclusion

Imidazolium based RTILs and their mixtures of varying concentrations in acetonitrile (ACN) were probed at different temperatures for their surface tension, conductance and optical characteristics. The recorded results of conductivity, surface tension and spectroscopic (UV–visible, FTIR and photoluminescence) measurements indicate that these RTILs are structured fluids wherein the structural ordering is sensitive to cosolvent addition or temperature elevation. The results warrant that use of these two options to decrease the viscosity of RTILs for electrochemical investigations and biphasic catalysis, will always be at the cost of loss in structural order at the interface and in the bulk of RTIL. An interesting finding of the present work is that, with cosolvent addition, RTILs preserve their characteristic structural aspects up to a certain limit of dilution ($\phi_{RTIL} = 0.3$, for acetonitrile).

Acknowledgments

M. A. Bhat would like to thank, University authorities-especially Vice Chancellor, University of Kashmir, and Head, Department of Chemistry, University of Kashmir, for sanction of study leave in his favor. C. K. Dutta would like to thank Director School Education (J & K), for sanction of study leave in her favor and Head, Department of Chemistry, University of Kashmir, for allowing her to carry out some part of the presented work in the Department. Authors would also like to thank Dr. S. K. Haram (University of Pune) for his useful suggestions for the present work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2013.02.021.

References

- [1] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003.
- [2] Y.L. Gu, G.X. Li, Advanced Synthesis and Catalysis 351 (2009) 817–847.
- [3] X. Han, D.W. Armstrong, Accounts of Chemical Research 40 (2007) 1079-1086.
- [4] W. Keim, Green Chemistry 5 (2003) 105–111.
- [5] T. Welton, Chemical Reviews 99 (1999) 2071-2083.
- [6] J. Zhang, A.M. Bond, Analyst 130 (2005) 1132–1147.
- [7] P. Hapiot, C. Lagrost, Chemical Reviews 108 (2008) 2238-2264.
- [8] In: H. Ohno (Ed.), Electrochemical Aspects of Ionic Liquids, John Wiley and Sons, Hoboken, NJ, 2005.
- [9] J. Dupont, P.A.Z. Suarez, Physical Chemistry Chemical Physics 8 (2006) 2441–2452.
- [10] E.W. Castner Jr., C.J. Margulis, M. Maroncelli, J.F. Wishart, Annual Review of Physical Chemistry 62 (2011) 85–105.
- [11] (a) A. Sarkar, S. Trivedi, S. Pandey, The Journal of Physical Chemistry. B 112 (2008) 9042–9049;
- (b) A. Sarkar, S. Trivedi, S. Pandey, The Journal of Physical Chemistry. B 113 (2009) 7606–7614.
- [12] S. Trivedi, N.I. Malek, K. Behera, S. Pandey, The Journal of Physical Chemistry. B 114 (2010) 8118–8125.
- [13] H. Weingartner, Angewandte Chemie (International Ed. in English) 47 (2008) 654–670.
- [14] E.W. Castner Jr., J.F. Wishart, Journal of Chemical Physics 132 (2010) 120901–120909.
- [15] J.F. Wishart, E.W. Castner Jr., The Journal of Physical Chemistry. B 111 (2007) 4639–4640.
- [16] F. Endres, Physical Chemistry Chemical Physics 12 (2010) 1648.
- [17] J.P. Pandey, B.R. Chaturvedi, R.P. Pandey, Journal of Physical Chemistry 85 (1981) 1750–1752.
- [18] M. Abraham, M.-C. Abraham, I. Ziogas, Journal of the American Chemical Society 113 (1991) 8583–8590.
- [19] A. Kumar, Journal of the American Chemical Society 115 (1993) 9243–9248.
- [20] G.S. Bien, C.A. Kraus, R.M. Ruoss, Journal of the American Chemical Society 56 (1934) 1860–1865.
- [21] R.P. Seward, Journal of Physical Chemistry 73 (1951) 515-517.
- [22] R.P. Seward, Journal of Physical Chemistry 62 (1958) 758-759.
- [23] C. Reichardt, in: Solvents and Solvent Effects in Organic Chemistry, 3rd edn, WILEY-VCH Verlag GmbH and Co. KGaA, Weinheim, 2003.
- [24] A. Samanta, The Journal of Physical Chemistry. B 110 (2006) 13704–13716.
- [25] A. Paul, P.K. Mandal, A. Samanta, Chemical Physics Letters 402 (2005) 375-377.
- [26] A. Paul, A. Samanta, Journal of Chemical Sciences 118 (2006) 335–340.
- [27] In: C.G. Zoski (Ed.), Handbook of Electrochemistry, Elsevier, Oxford OX5 1GB,UK, 2007.
- [28] K.R. Harris, L.A. Woolf, Journal of Chemical & Engineering Data 50 (2005) 1777-1782.
- [29] K.R. Harris, M. Kanakubo, L.A. Woolf, Journal of Chemical & Engineering Data 52 (2007) 2425–2430.
- [30] J. Jacquemin, R. Ge, P. Nancarrow, D.W. Rooney, M.F.C. Gomes, A.A.H. Padua, C. Hardacare, Journal of Chemical & Engineering Data 53 (2008) 716–726.
- [31] K. Hayamizu, Y. Aihara, H. Nakagawa, T. Nukada, W.S. Price, The Journal of Physical Chemistry. B 108 (2004) 19527–19532.
- [32] I. Nicotera, C. Oliviera, W.A. Henderson, G.B. Appetecchi, S.J. Passerini, The Journal of Physical Chemistry, B 109 (2005) 22814–22819.
- [33] W. Li, Z. Zhang, B. Han, S. Hu, Y. Xie, G. Yang, The Journal of Physical Chemistry. B 111 (2007) 6452–6456.
- [34] (a) J. Dupont, C.S. Consorti, P.A.Z. Saurez, R.F. deSouza, Organic Synthesis 79 (2002) 236-240;
 - (b) J. Dupont, C.S. Consorti, P.A.Z. Saurez, R.F. deSouza, Organic Synthesis 10 (2004) 184–188.
- [35] M.A. Bhat, P.P. Ingole, V.R. Chaudhari, S.K. Haram, The Journal of Physical Chemistry. B 113 (2009) 2848–2853.
- [36] M.A. Bhat, A.A. Dar, A. Amin, P.I. Rasheed, G.M. Rather, Journal of Chemical Thermodynamics 39 (2007) 1500–1507.
- [37] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montogomery Jr., T. Vreven, k.n. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Homperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochtreski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, Foresma, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Cliord, J. Cioslowski, B.B. Stefanov, G. Liu, J.B.A. Liashenko,

P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A.M. Nanayakkara, P.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, Pople, Gaussian 03, Revision B.01, Gaussian, Pittsburgh PA, 2003.

- [38] (a) A.D. Becke, Journal of Chemical Physics 98 (1993) 5648–5652;
 (b) C. Lee, W. Yang, R.G. Parr, Physical Review B 37 (1988) 785–789.
- [39] S.W. Mayer, Journal of Physical Chemistry 67 (1963) 2160-2164.
- [40] I. Langmuir, Phenomena, Atoms and Molecules, Philosophical Library, New York,
- 1950.
 [41] C. Kolbeck, J. Lehmann, K.R.J. Lovelock, T. Cremer, N. Paape, P. Wasserscheid, A.P. Froba, F. Maier, H.-P. Steinruck, The Journal of Physical Chemistry. B 114 (2010) 17025–17036
- [42] J.W. Russo, M.M. Hoffmann, Journal of Chemical & Engineering Data 55 (2010) 5900–5905.
- [43] M.G. Freire, P.J. Carvalho, A.M. Fernandes, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, Journal of Colloid and Interface Science 314 (2007) 621–630.
- [44] J.G. Huddleston, A.E. Visser, M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chemistry 3 (2001) 156.
- [45] P. Kilaru, G.A. Baker, P. Scovazzo, Journal of Chemical & Engineering Data 52 (2007) 2306.
- [46] T.J. Gannon, G. Law, P.R. Watson, Langmuir 15 (1999) 8429-8434.
- [47] K. Hofmann, Imidazole and its Derivatives, vol. 1, Interscience, New York, 1953.[48] S.A. Katsyuba, E.E. Zvereva, A. Vidis, P.J. Dyson, Journal of Physical Chemistry A
- 111 (2007) 352–370. [49] M. Deetlefs, C. Hardacre, M. Nieuwenhuyzen, A. Padua, O. Sheppard, A. Soper, The
- Journal of Physical Chemistry. B 110 (2006) 12055–12061.
- [50] P.A. Hunt, The Journal of Physical Chemistry. B 111 (2007) 4844–4853.
- [51] In: S. Zhang, X. Lu, Q. Zhou, X. Li, X. Zhang, S. Li (Eds.), Ionic Liquids: Physicochemical Properties, Elsevier Sciences, Oxford, UK, 2009.
- [52] B.L. Bhargava, S. Balasubramanian, Journal of the American Chemical Society 128 (2006) 10073–10078.
- [53] C. Aliaga, C.S. Santos, S. Baldelli, Physical Chemistry Chemical Physics 9 (2007) 3700.
- [54] E. Sloutskin, B.M. Ocko, L. Tamam, I. Kuzmenko, T. Gog, M. Deutsch, Journal of the American Chemical Society 127 (2005) 7796–7804.
- [55] J. Bowers, M.C. Vergara-Gutierrez, Langmuir 20 (2004) 309-312.
- [56] C. Kolbeck, T. Cremer, K.R.J. Lovelock, N. Paape, P.S. Schulz, P. Wasserscheid, F. Maier, H.P. Steinruck, The Journal of Physical Chemistry. B 113 (2009) 8682–8688.
- [57] H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan, M. Watanabe, The Journal of Physical Chemistry. B 109 (2005) 6103–6110.
- [58] A.W. Adamson, Physical Chemistry of Surfaces, Interscience Publishers, New York, 1967. 54.
- [59] G. Law, P.R. Watson, Langmuir 17 (2001) 6138-6141.
- [60] V. Halka, R. Tsekov, W. Freyland, Physical Chemistry Chemical Physics 7 (2004) 2038–2043.
- [61] M.H. Ghatee, A.R. Zolghadr, Fluid Phase Equilibria 263 (2008) 168-175.
- [62] K.G. Bogolitsyn, T.A. Makhova, T.E. Skerbets, Russian Journal of General Chemistry 80 (2010) 1355–1357.
- [63] J. Restolho, J.L. Mata, B. Saramago, Journal of Colloid and Interface Science 340 (2009) 82–86.
- [64] H. Bloom, F.G. Davies, D.W. James, Transactions of the Faraday Society 56 (1960) 1179–1186.
- [65] G.J. Janz, R.D. Reeves, A.T. Ward, Nature 204 (1964) 1188-1189.
- [66] R.M. Lynden-Bell, Molecular Physics 101 (2003) 2625–2633.
- [67] R. Fruth, Proceedings of The Cambridge Philosophical Society 37 (1941) 252-275.
- [68] J. O'M. Bockris, A.K.N. Reddy, Modern Electrochemistry, vol. 1, Kluwer Academic Publishers, New York, 2002.
- [69] J.Z. Yang, X.M. Lu, J.S. Gui, W.G. Xu, Green Chemistry 6 (2004) 541–543.
- [70] Q.S. Liu, J. Tong, Z.C. Tan, U. Welz-Biermann, J.Z. Yang, Journal of Chemical & Engineering Data 55 (2010) 2586–2589.
- [71] J.Z. Yang, J. Tong, J.B. Li, J.G. Li, J. Tong, Journal of Colloid and Interface Science 313 (2007) 374–377.
- [72] Z. Gu, J.F. Brennecke, Journal of Chemical & Engineering Data 47 (2002) 339–345.
 [73] C. Larriba, Y. Yoshida, J.F. de la Mora, The Journal of Physical Chemistry. B 112
- (2008) 12401–12407. [74] A. Noda, K. Hayamizu, M. Watanabe, The Journal of Physical Chemistry. B 105
- (2001) 4603–4610.
 (2001) 4603–4610.
- [75] D.R. MacFarlane, M. Forsyth, E.I. Izgorodina, A.P. Abbott, G. Annat, K. Fraser, Physical Chemistry Chemical Physics 11 (2009) 4962–4967.
- [76] K. Ueno, H. Tokuda, M. Watanabe, Physical Chemistry Chemical Physics 12 (2009) 1649–1658.
- [77] J.R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Karger, C. Wespe, F. Bordusa, F. Kremer, Physical Review 77 (2008), (051202-1-4).
- [78] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gra1tzel, Inorganic Chemistry 35 (1996) 1168–1178.
- [79] S. Glasstone, K.J. Laidler, H. Eyring, The Theory of Rate Processes, 1st edition, McGraw-Hill Book Co., New York, N. Y., 1941
- [80] M.L. Miller, Journal of Physical Chemistry 60 (1956) 189–192.
- [81] M.G. McLin, C.A. Angell, Journal of Physical Chemistry 95 (1991) 9464-9469.
- [82] H.K. Kashyap, R. Biswas, The Journal of Physical Chemistry. B 114 (2010) 16811–16823.
- [83] C. Schreiner, S. Zugman, R. Hartl, H.J. Gores, Journal of Chemical & Engineering Data 55 (2010) 1784–1788.
- [84] C. Schreiner, S. Zugman, R. Hartl, H.J. Gores, Journal of Chemical & Engineering Data 55 (2010) 4372–4377.
- [85] U. Domanska, M. Krolikowska, Journal of Colloid and Interface Science 348 (2010) 661–667.

- [86] R. Ren, Y. Zuo, Q. Zhou, H. Zhang, S. Zhang, Journal of Chemical & Engineering Data 56 (2011) 27-30.
- [87] W. Liu, T. Zhao, Y. Zhang, H. Wang, M. Yu, Journal of Solution Chemistry 35 (2006) 1337-1346.
- [88] A. Stoppa, J. Hunger, R. Buchner, Journal of Chemical & Engineering Data 54 (2009) 472-479.
- (89) J. Hunger, A. Stoppa, R. Buchner, G. Hefter, The Journal of Physical Chemistry. B 112 (2008) 12913–12919.
 (90) H. Tokuda, S.J. Baek, M. Watanabe, Electrochemistry 73 (2005) 620–622.
 (91) J. Dupont, Journal of the Brazilian Chemical Society 15 (2004) 341–350.

- [92] A.G. Avent, P.A. Chaloner, M.P. Day, K.R. Seddon, T. Welton, Journal of the Chemical Society Dalton Transactions (1994) 3405–3413.
- [93] A. Elaiwi, P.B. Hitchcock, K.R. Seddon, N. Srinivasan, Y.M. Tan, T. Welton, J.A. Zora, Journal of the Chemical Society Dalton Transactions (1995) 3467–3472.
- [94] A. Paul, P.K. Mandal, A. Samanta, The Journal of Physical Chemistry. B 109 (2005) 9148-9153.
- [95] J.B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970.
 [96] G. Zhu, G. Wu, M. Sha, D. Long, S. Yao, Journal of Physical Chemistry A 112 (2008)
- 3079–3085.