

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/51074046>

Polarity, Viscosity, and Ionic Conductivity of Liquid Mixtures Containing [C(4)C(1)im][Ntf(2)] and a Molecular Component

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · MAY 2011

Impact Factor: 3.3 · DOI: 10.1021/jp2012254 · Source: PubMed

CITATIONS

51

READS

366

7 AUTHORS, INCLUDING:



Jose Nuno A Canongia Lopes

Technical University of Lisbon

179 PUBLICATIONS 8,341 CITATIONS

[SEE PROFILE](#)



Margarida F Costa Gomes

French National Centre for Scientific Research

192 PUBLICATIONS 3,296 CITATIONS

[SEE PROFILE](#)



Sabine Sarraute

Université Blaise Pascal - Clermont-Ferrand II

24 PUBLICATIONS 210 CITATIONS

[SEE PROFILE](#)



Tariq Mohammad

Qatar University

51 PUBLICATIONS 567 CITATIONS

[SEE PROFILE](#)

Polarity, Viscosity, and Ionic Conductivity of Liquid Mixtures Containing $[C_4C_1im][Ntf_2]$ and a Molecular Component

J. N. Canongia Lopes,^{*,†,‡} Margarida F. Costa Gomes,^{§,⊥} Pascale Husson,^{*,§} Agílio A. H. Pádua,[§] Luis Paulo N. Rebelo,[‡] Sabine Sarraute,[§] and Mohammad Tariq[‡]

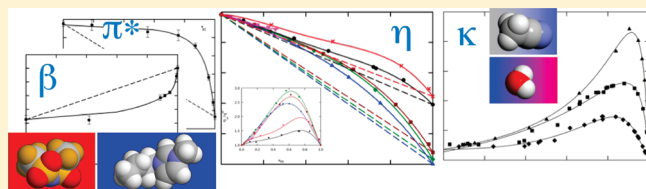
[†]Centro Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

[‡]Instituto de Tecnologia Química e Biológica, www.itqb.unl.pt, UNL, Av. República Ap. 127, 2780-901 Oeiras, Portugal

[§]Clermont Université, Université Blaise Pascal, Laboratoire Thermodynamique et Interactions Moléculaires, UMR6272, F-63177 Aubiere, France

[⊥]CNRS, Laboratoire Thermodynamique et Interactions Moléculaires, UMR6272, F-63177 Aubiere, France

ABSTRACT: In this study, we have focused on binary mixtures composed of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_4C_1im][Ntf_2]$, and a selection of six molecular components (acetonitrile, dichloromethane, methanol, 1-butanol, *t*-butanol, and water) varying in polarity, size, and isomerism. Two Kamlet–Taft parameters, the polarizability π^* and the hydrogen bond acceptor β coefficient were determined by spectroscopic measurements. In most cases, the solvent power (dipolarity/polarizability) of the ionic liquid is only slightly modified by the presence of the molecular component unless large quantities of this component are present. The viscosity and electrical conductivity of these mixtures were measured as a function of composition and the relationship between these two properties were studied through Walden plot curves. The viscosity of the ionic liquid dramatically decreases with the addition of the molecular component. This decrease is not directly related to the volumetric properties of each mixture or its interactions. The conductivity presents a maximum as a function of the composition and, except for the case of water, the conductivity maxima decrease for more viscous systems. The Walden plots indicate enhanced ionic association as the ionic liquid gets more diluted, a situation that is the inverse of that usually found for conventional electrolyte solutions.



INTRODUCTION

This study is motivated by the possibility of using mixtures of an ionic liquid and a molecular component in many synthesis or separation processes. To develop such applications, the knowledge of the solvent power (polarity) and transport properties of these systems is fundamental. From a theoretical point of view, it also provides information to understand at a molecular level the effect of the presence of the molecular component on the properties of the ionic liquid.

Ionic liquids are salts composed of voluminous organic ions with asymmetric, flexible, and charge-delocalized molecular structures. As their name implies, they are liquid over a wide temperature range — from quite low melting-point temperatures to rather high decomposition temperatures — that generally includes room temperature. Most of them have negligible vapor pressure. Because of their unique properties and variety, ionic liquids are high-performance fluids used in a wide range of engineering and material science applications both in processes like synthesis, catalysis, or separation, or in devices such as optical components, lubricants, or batteries.¹ They are also considered as promising alternative media for a more sustainable chemical industry and are often referred to as green solvents. Despite this, their effective use in industrial applications is still limited. One of the reasons behind this fact is the lack of accurate knowledge of their

physicochemical properties, including their rationalization at a molecular level. These data are crucial for process development, in particular for the characterization of transport phenomena and other solvent properties.

A few years ago, research on ionic liquids was mainly focused on the so-called conventional ionic liquids (mostly imidazolium-based cations combined with anions such as tetrafluoroborate, $[BF_4]^-$, hexafluorophosphate, $[PF_6]^-$, or bis(trifluoromethanesulfonyl)imide, $[Ntf_2]^-$).² Some of these conventional ionic liquids have either inadequate use due to their limited (water) stability or are toxic and environmentally persistent and, thus, are not biocompatible.³ A good example of recent, alternative organic salts, presenting total biocompatibility is that of the cholinium carboxylates.⁴ Cholinium, itself, is a functionalized (hydroxyl), small tetraalkylammonium. In this same vein, more recent studies are also directed toward the synthesis of task specific ionic liquids,⁵ which include ions with functional groups attached to the cation or anion, and the use of ionic liquids mixed either with another ionic liquid⁶ or with a molecular component able to modify the thermophysical properties of the pure ionic liquid.^{7,8}

Received: February 7, 2011

Revised: March 29, 2011

Published: April 25, 2011

An alternative to the latter is the exploitation of the so-called protic ionic liquids,⁹ which by acid–base proton transfer are in fact a tunable mixture of at least three components: salt and its two precursors (the parent acid and base). Physicochemical data on these two latter cases of mixtures are needed for the design and engineering of new industrial-scale processes. This particular work is focused on (ionic liquid + molecular solvent) mixtures.

It is also very important to characterize these new (ionic liquid + molecular compound) mixtures at a molecular level, both in terms of structure and of interactions. For instance, the known nanostructural organization that exists in some pure ionic liquids^{10–13} can be disrupted to different extents when the ionic liquid is progressively diluted in a molecular medium. This structural modification must be reflected by changes in some of the properties of the mixture as its composition is altered. In other words, the experimental monitoring of selected physical properties can be a tool to understand how the presence of a molecular component will affect the structure and interactions of a given ionic liquid mixture. This type of information is crucial for the choice of the best system for a given application.

The present work focuses on the study of binary systems composed of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonfyl)imide, [C₄C₁im][NTf₂] (a conventional ionic liquid), and a molecular component. Six molecular compounds with different characteristics were selected for this study: water (a strong protic solvent), methanol, 1-butanol, and *t*-butanol (a series of weaker protic solvents including two structural isomers), and acetonitrile and dichloromethane (polar aprotic solvents).

First, the solvent power of the mixture was studied through the estimation of its polarity and polarizability by the measurement of two Kamlet–Taft parameters, π^* , the dipolarity/polarizability ratio and β , the hydrogen-bond accepting basicity (HBA) obtained from the spectroscopic shift of selected solvatochromic probes.

In a second phase, two transport properties, viscosity and ionic conductivity, were considered. Viscosity characterizes the flow resistance of a fluid and it is linked to mass transport phenomena. Electrical conductivity is a measure of ion mobility in a fluid and, when coupled to viscosity data, allows for the identification of association and flow regimes of the ions. This last property generally presents nonmonotonous variations when the composition (and structure) of the system changes.

It must be stressed that, in binary mixtures of (ionic liquid + molecular compound), the structure of the system can vary from a continuous charged network of ions (in ionic liquid-rich mixtures) to solvated charged aggregates, ion pairs, or free ions (in progressively more diluted ionic liquid solutions). Conductivity studies can provide information concerning such ionic association. The combination of conductivity and viscosity results (obtained as a function of the mixture composition) allows one to calculate further dynamical and structural data.

The whole composition range (or the range where the two liquids are fully miscible) will be covered in the present study. At low concentrations of molecular compound, the properties of the mixtures should be dominated by the properties of the ionic liquid. Conversely, when the quantity of molecular compound is increased, the ionic liquid becomes a solute in a molecular medium, that is, an electrolyte solution. Between these two extremes, we expect marked changes in the structure of the solution, corresponding to the swelling of the ionic liquid network, the formation of bicontinuous microphases, and the disruption of the ionic liquid into smaller aggregates, ionic pairs, and solvated isolated ions. The description of these intermediate regimes,

between a pure molten salt and a dilute electrolyte solution, is still unclear.

EXPERIMENTAL SECTION

Materials. The [C₄C₁im][NTf₂] ionic liquid was prepared at the QUILL Research Center (Belfast) by a previously reported metathesis reaction.¹⁴ ¹H NMR analysis revealed purity levels greater than 99%. Suppressed ion chromatography detected less than 5 ppm (w/w) of bromide ion. Before their use, the ionic liquid samples were dried and degassed under vacuum (1 Pa) during 12 h. After this treatment, the mass fraction of water determined by coulometric Karl Fisher titration (Mettler Toledo DL 31) was $(50 \pm 10) \times 10^{-6}$.

Acetonitrile (Acros Organics), methanol (Sigma Aldrich), and dichloromethane (Sigma) were purchased with stated purities greater than 99.9%. 1-Butanol and *t*-butanol (Merck) were acquired with purity levels greater than 99.5%. All of these components were distilled before use. The water used in this work was triply distilled in an all-quartz installation.

Two solvatochromic probes – *N,N*-diethyl-4-nitroaniline (Fluorochem, probe1) and 4-nitroaniline (Merck, probe2) – were used for the determination of the Kamlet–Taft parameters.

Preparation of Mixtures. The binary mixtures used in the conductivity and viscosity determinations were prepared by weighing the components using an AE240 Mettler Toledo balance with an accuracy of ± 0.1 mg. The vials were always nearly totally filled to minimize the vapor phase and thus an uncontrolled change in the liquid phase composition. The estimated uncertainty on the mole fraction composition is ± 0.0001 .

For the experiments involving the determination of the Kamlet–Taft parameters, solutions of each probe in dichloromethane (typical concentration 10^{-5} mol.L⁻¹) were prepared. These solutions were added to pure ionic liquid samples and the dichloromethane removed under vacuum conditions (24 h). The obtained solution was then kept under nitrogen atmosphere. Finally, the ionic liquid (plus probe) – molecular component solutions were prepared following the procedure described in the previous paragraph.

Viscosity and Density Measurements. The dynamic viscosity of the mixture, η , has been measured using an Anton Paar Microviscosimeter (AMVn) based on a falling-ball principle. A laser sensor detects the time, t_1 , taken by the ball to fall a given distance in a capillary tube of calibrated diameter filled with the mixture. The viscosity of the mixture, η , is calculated from the values of t_1 , the capillary calibration constant, K , and the densities of the ball and of the mixture, ρ_b and ρ_m , respectively:

$$\eta = K \times (\rho_m - \rho_b) \times t_1 \quad (1)$$

Except for systems containing water and methanol, the mixture density was calculated from the densities of its pure components by assuming an ideal volumetric behavior. The error induced by this assumption is estimated to be lower than 0.05%, considering typical maximum values for the excess molar volume of the studied mixtures. Two capillaries of 1.6 and 1.8 mm nominal diameter were used to perform viscosity determinations in the 0.1 to 50 mPa.s range. They were calibrated using appropriate viscosity standards (Cannon). For each mixture, 12 measurements were made using 3 different capillary tilt angles. The temperature of the apparatus was controlled within ± 0.01 K using a built-in Peltier device. The statistical analysis of the results yielded an estimated uncertainty of 1.5%.

Conductivity Measurements. An ac impedance bridge technique was used to measure the electrical conductivity, κ , as a function of the mixture composition. The measurements were carried out in a small-volume commercial conductivity cell (Materials Mates) made of borosilicate glass and equipped with two platinum electrodes. The cell was sealed in order to avoid contact with air. Its constant, K_{cell} , was precisely determined with conductivity standards (aqueous KCl solutions, Hanna) and approximately equals 100 m^{-1} . The cell was immersed in a Julabo thermostatted bath filled with ethylene glycol whose temperature was measured by a 100 Ohm platinum resistance thermometer (calibrated at the Laboratoire National d'Essais, France) with an uncertainty of $\pm 0.1 \text{ K}$. Before each measurement, the conductivity cell was carefully cleaned using deionized water and ethanol and dried with a flow of dry nitrogen. The pure ionic liquid was first inserted in the cell, then subsequent additions of molecular compound were made using a gastight syringe. The cell was immediately sealed to avoid evaporation. The mole fraction composition of the mixture was calculated from the amount of molecular component added in each injection, determined gravimetrically. When there was no more space available in the cell, it was cleaned and filled with a new mixture of composition close to the previous one to validate the previous measurements.

A drive voltage of 1.0 V was applied to the cell and a C–R series mode was used. The resistance of the solution, R , was measured as a function of the frequency, ν , (from 800 to 5000 Hz). The value of R at infinite frequency, R_{∞} , was determined by plotting $R(\nu)$ and extrapolating the obtained line to infinite frequency. The conductivity was then calculated according to:

$$k = K_{\text{cell}}/R_{\infty} \quad (2)$$

The uncertainty of the conductivity results is estimated to be 0.6%. The uncertainty of the calculated molar conductivity values has been estimated (through error propagation analysis) to be 2%.

UV-Spectroscopy Measurements. An UV–vis spectrophotometer (Shimadzu 2550) was used for the determination of the Kamlet–Taft parameters. The π^* parameters were estimated using data obtained with *N,N*-diethyl-4-nitroaniline (solvatochromic probe 1), whereas the β parameters were estimated by using the enhanced solvatochromic shift of 4-nitroaniline (probe 2) relative to *N,N*-diethyl-4-nitroaniline (probe 1). Each spectrum was recorded from 300 to 450 nm with a step of 0.1 nm and a window of 1 nm. The values of the maximum wavelength, λ_{max} , were determined from the first derivative of the absorption spectra of the corresponding probes. The π^* and β Kamlet–Taft parameters were calculated using eqs 3 and 4.^{15,16}

$$\pi^* = (27.52 - \nu_1)/3.18 \quad (3)$$

$$\beta = (1.035\nu_1 - \nu_2 + 2.64)/(2.8) \quad (4)$$

The symbols ν_1 and ν_2 represent the frequencies corresponding to λ_{max} for probes 1 and 2, respectively. The uncertainty associated to the two parameters is 2% (estimated via error-propagation analysis).

RESULTS AND DISCUSSION

Kamlet–Taft Parameters and Polarity. The electric dipole moment, μ , the relative permittivity, ϵ_r , and the Kamlet–Taft parameters are properties related to the polarity and polarizability of a molecule. They are presented in Table 1 for the pure compounds and in Table 2 and Figure 1 for the mixtures.

Table 1. Electric Dipole Moment, μ , Relative Permittivity, ϵ_r , and Kamlet–Taft Dipolarity/Polarizability and Hydrogen-Bond Acceptor Parameters, π^* and β Respectively of Acetonitrile, Dichloromethane, Methanol, 1-Butanol, *t*-Butanol, and $[\text{C}_4\text{C}_1\text{im}][\text{Ntf}_2]$ at 298 K

	μ/D	ϵ_r	π^*	$\pi^{*\text{ litt}}$	β	$\beta^{\text{ litt}}$
acetonitrile	3.39 ¹⁷	35.95 ¹⁸	0.773	0.799 ¹⁹ 0.713 ¹⁵ 0.788 ²⁰	0.37	0.38 ²³ 0.37 ¹⁹
dichloromethane	1.90 ¹⁷	8.93	0.792	0.791 ¹⁹	−0.014	−0.014 ¹⁹
methanol	2.87 ¹⁷	32.62 ¹⁸	0.733	0.73 ¹⁹ 0.6 ²³ 0.586 ¹⁵	0.60	0.62 ¹⁶
1-butanol	2.98 ¹⁷	17.84		0.525 ¹⁵		0.85 ¹⁶
<i>t</i> -butanol		12.47		0.504 ¹⁵		0.95 ¹⁶
water	3.12 ¹⁷	78.35 ¹⁸		1.09 ¹⁵ 1.24 ²⁰		0.14 ¹⁶
$[\text{C}_4\text{C}_1\text{im}][\text{Ntf}_2]$			0.988	0.984 ¹⁹	0.23	0.243 ¹⁹

Table 2. Kamlet–Taft Dipolarity/Polarizability and Hydrogen-Bond Acceptor Parameters, π^* and β Respectively for the Mixtures of $[\text{C}_4\text{C}_1\text{im}][\text{Ntf}_2]$ + Acetonitrile, Methanol, or Dichloromethane at 298 K^a

acetonitrile		methanol		dichloromethane	
x_m	π^*	x_m	π^*	x_m	π^*
0.0000	0.988	0.0000	0.988	0.0000	0.988
0.2198	0.965	0.1889	0.984	0.0281	0.975
0.5434	0.947	0.5563	0.970	0.3948	0.960
0.7781	0.910	0.7589	0.950	0.7868	0.930
0.8648	0.890	0.8707	0.928	0.9513	0.890
0.8984	0.870	0.9593	0.840	0.9873	0.870
0.9610	0.830	0.9880	0.773	0.9942	0.841
0.9847	0.790	1.0000	0.733	1.000	0.792
1.0000	0.773				
x_m	β	x_m	β	x_m	β
0.0000	0.23	0.0000	0.23	0.0000	0.23
0.2601	0.23	0.4156	0.22	0.4018	0.07
0.4084	0.23	0.8858	0.39	0.5810	0.28
0.5510	0.23	0.9146	0.40	0.7545	0.24
0.6998	0.24	0.9482	0.42	0.8730	0.14
0.7730	0.26	0.9926	0.54	0.9442	−0.01
0.9430	0.34	1.0000	0.60	0.9710	−0.02
1.0000	0.37			0.9886	−0.01
				1.0000	−0.01

^aConcentration is given in mole fraction, x_m , of the molecular component.

The π^* parameter is sensitive to nonspecific van der Waals interactions between solute and solvent and reflects the dipolarity/polarizability of the components of the mixture.¹⁵ According to the original article from Kamlet et al.,¹⁵ probes without any hydrogen-bond capabilities (either donor or acceptor) must be used in the case of amphiprotic solvents. However, when those probes (4-nitroanisole and *N*-methyl-2-nitroaniline) are used to estimate π^* in ionic liquids, the corresponding absorbance maxima

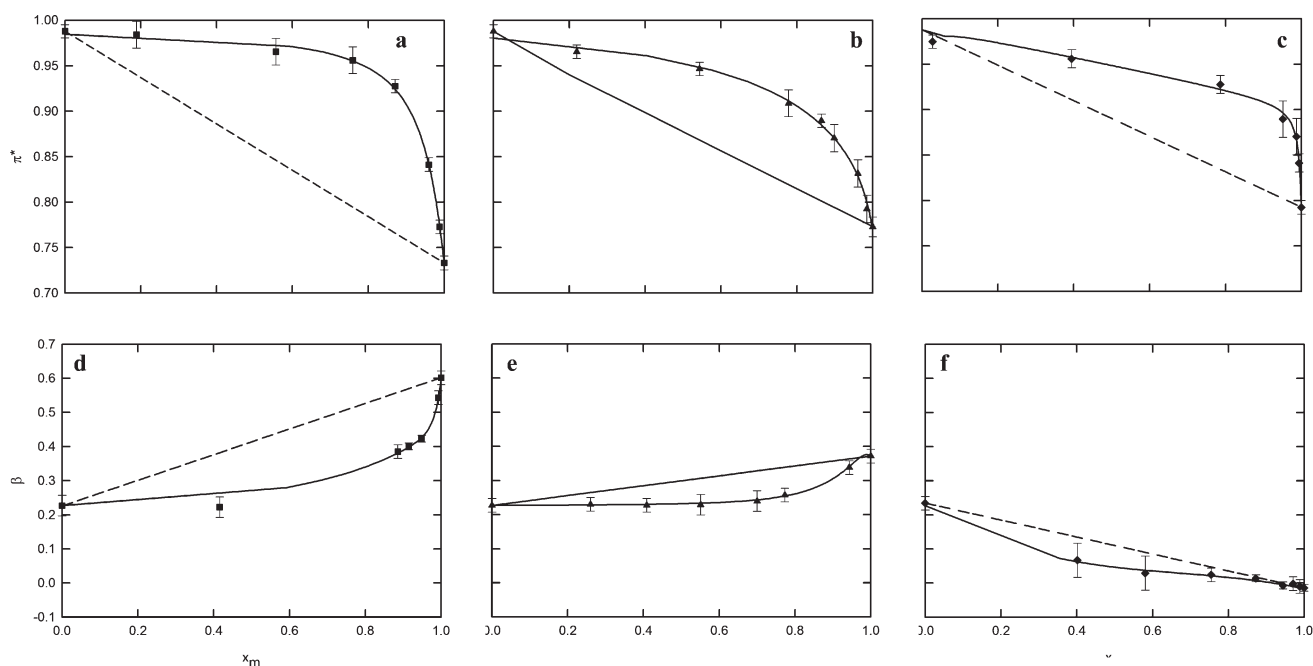


Figure 1. Dipolarity/polarizability ratio, π^* (top) and HBA basicity, β (bottom) of the mixtures $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2] + \text{molecular component}$ as a function of the composition expressed in molecular component mole fraction, x_m , at 298 K: (■, a, d), methanol, (▲, b, e), acetonitrile, (◆, c, f), dichloromethane. Lines correspond to a linear variation of π^* or β as a function of x_m .

are not sufficiently shifted toward the visible light or the results are not sufficiently sensitive to the solvent polarity.¹⁵ This is probably one of the reasons why *N,N*-diethyl-4-nitroaniline is the probe generally chosen for the estimation of π^* in systems involving ionic liquids.^{19,23,25,26}

For pure $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$, our estimated π^* parameter (0.988) agrees within experimental error with the value reported in the literature¹⁹ (0.984). These values suggest a high-polarity solvent, at the high-end of the 0-to-1 π^* parameter scale observed for most common solvents.¹⁵ For instance, small *n*-alcohols (methanol to propanol) show π^* parameters (around 0.5) lower than that of $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$, whereas aromatic or fluorinated alcohols (for example benzyl alcohol (0.984) and trifluoroethanol (1.018), respectively) and water (1.090) have similar π^* -parameter values.¹⁵ The π^* -parameter values of other ionic liquids ($0.92 < \pi^* < 1.08$) suggest that most members of this class of compounds are highly polarizable solvents.^{19–26}

For acetonitrile and dichloromethane (the two aprotic solvents studied in this work), the estimated π^* -parameter values are very close to those reported in the literature^{15,19} as can be observed in Table 1. In the case of methanol, the comparison between our estimated values and those of the literature is more difficult due to the large scatter in the latter set of data, cf. Table 1. It must be stressed that the discrepancies found cannot be explained solely by the choice of different probes: the value reported by Mellein et al.²³ is lower than ours by almost 20% and they have used the same probe. The different molecular compounds added to the ionic liquid were chosen to cover a large polarity range: water presents the highest π^* parameter (above 1), followed by dichloromethane, acetonitrile, methanol, 1-butanol, and *t*-butanol (around 0.5).

The β -parameter values are a measure of the hydrogen-bond acceptor ability of the solvents (HBA basicity).¹⁶

For $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$, our estimated value (0.23) compares favorably with that published¹⁹ (0.243). For other ionic liquids,

the β -parameter values typically range from 0.15 to 0.50,^{23,19} which corresponds to a much larger variation than that found for the π^* parameter values. Those values are lower than the HBA basicity of small alcohols (ranging from 0.6 for methanol to 0.95 for butanol) but are comparable to that of acetonitrile (0.37).

The response of the solvatochromic probes in the mixtures is a convenient way to study preferential solvation phenomena: departures from a linear behavior of β or π^* as a function of composition (usually expressed in mole fraction) signal differences in composition between the bulk of the mixture and around the probe.²⁷ It must be stressed that these deviations can be due to genuine preferential solvation phenomena but also due to the presence of the (generally quite bulky) probe itself.

Figure 1 shows the plots of the β - or π^* -parameter values as a function of composition for the mixtures of $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ ionic liquid with acetonitrile, dichloromethane, or methanol. In all cases, clear deviations from the linear behavior are observed. In the case of π^* , the addition of the molecular component to the ionic liquid has nearly no effect on the values of π^* (they remain near the values of the pure ionic liquid) up to a mole fraction of 0.8 in the molecular component, after which a decrease of π^* (toward the values of the molecular components) is observed. This indicates that the solvent power (dipolarity/polarizability) of the ionic liquid is poorly modified when mixed with acetonitrile, dichloromethane, or methanol unless large quantities of each of these molecular components are present. However, the trends are quite different for the β parameters: no change up to 0.8 mol fraction of acetonitrile, no change only up to 0.5 mol fraction of methanol, and a gradual change over all of the composition range with dichloromethane. Similar results were found in literature with $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ with various organic components.²³

One possible way to interpret these findings is to recognize ionic liquids as nanosegregated media, that is structured fluids

composed of a polar network permeated by nonpolar domains.^{11,12} These structural heterogeneities cause the solvation of the molecular components in different regions of the ionic liquid. In the case of dipolar molecules (like methanol, dichloromethane, or acetonitrile), it has been shown¹⁰ that the solvation occurs mainly at the interface between the nonpolar and polar regions. If one assumes that the polarizability of ionic liquids stems from either the nonpolar domains (van der Waals interactions between alkyl side chains) or parts of the polar regions (aromaticity of the cationic cores), one can conclude that the inclusion of some solute molecules at the interface between the two regions will not affect much the ionic liquid polarizability. This can explain qualitatively the π^* -parameter trends with composition: when the (large) solvatochromic probe is inserted in the pure ionic liquid it will direct part of its groups (those more sensitive to polarizability changes) toward the nonpolar or polar regions. When a dipolar molecular solute is added to the system, it will stay mainly at the interface between the nonpolar and polar regions and will not interact with those parts of the solvatochromic probe that are placed more deeply into either the nonpolar or polar regions. The probe will continue to yield a π^* -parameter close to that of a pure ionic liquid. This situation breaks down when the molecular solute starts to be present in large quantities (in the present case around 0.8 mol fraction of molecular component), with the concomitant change of the ionic liquid solution morphology. It must be stressed that for these molecular solutes (with molar volumes in the 40–65 cm³·mol^{−1} range) a mole fraction of 0.8 in the molecular component corresponds to a volumetric fraction of that component of only 0.4 – [C₄C₁im][Ntf₂] presents a molar volume of around 300 cm³·mol^{−1}. In other words, when approximately half of the volume starts to be occupied by the molecular solvent, the structure of the ionic liquid starts to break down.

However, the β -parameter trends are influenced by the way the added molecular solute competes with the ionic liquid in terms of hydrogen-bond acceptance relative to the probe. Previous studies¹⁰ have shown that methanol (a dipolar protic solvent) interacts strongly with the anion of the ionic liquid, whereas acetonitrile (a dipolar aprotic solvent) does not show such a preference. This means that, when small quantities of methanol are added to the ionic liquid, the anion of the latter (which is largely responsible for the hydrogen-bonding acceptance character of the ionic liquid) will become less available to interact with the hydrogen-bond donor groups of the probe and the corresponding β -parameter values will tend to decrease in spite of the fact that methanol itself has a large β -parameter value. This trend can be observed at the left-hand side of part d of Figure 1. Only when the levels of methanol start to be significant, the values of the β -parameter start to increase toward the values of pure methanol (right-hand side of part d of Figure 1). In the case of the aprotic dipolar solvents dichloromethane and acetonitrile, the lack of specific interactions between the molecular component and the anion (they interact with both the cation and anion) imply more gradual β -parameter trends. It must be stressed that the apparent constancy of the β -parameter values found for the acetonitrile mixtures is also a consequence of the fact that the β -parameter values of acetonitrile and [C₄C₁im][Ntf₂] are similar.

Viscosity. Viscosities for all of the systems have been measured at atmospheric pressure and at 298.15 K. The experimental data are presented in Table 3 and Figure 2. Except for water, all of the molecular components studied are miscible with the ionic liquid over the whole composition range at 298.15 K. At this temperature, the solubility of water in [C₄C₁im][Ntf₂] is 0.25 in

Table 3. Viscosity, η_m , of the Mixtures [C₄C₁im][Ntf₂] + Molecular Component at 298 K as a Function of the Composition Expressed in Molecular Component Mole Fraction, x_m

acetonitrile		methanol		dichloromethane	
x_m	η_m /mPa.s	x_m	η_m /mPa.s	x_m	η_m /mPa.s
0.0000	50.4	0.0000	50.4	0.0000	50.4
0.1028	39.6	0.0302	46.2	0.1758	33.7
0.1534	34.4	0.1577	35.8	0.3232	21.79
0.2508	25.4	0.1600	34.2	0.4391	15.41
0.3638	17.8	0.2298	28.8	0.5646	10.01
0.5238	9.4	0.4819	13.83	0.7283	4.253
0.6020	6.4	0.6242	8.27	1.0000	0.433
0.7518	2.73	0.8248	2.61		
1.0000	0.37	0.8953	1.47		
		0.9803	0.71		
		1.0000	0.544		

Water		1-Butanol		<i>t</i> -Butanol	
x_m	η_m /mPa.s	x_m	η_m /mPa.s	x_m	η_m /mPa.s
0.0000	50.4	0.0000	50.4	0.0000	50.4
0.0442	46.9	0.1048	41.5	0.2367	35.8
0.0832	42.8	0.1851	32.1	0.5277	20.8
0.1253	37.2	0.3437	22.9	0.8516	9.27
0.1429	35.4	0.5066	15.2	0.9818	4.38
0.1721	36.0	0.7193	8.92	1.0000	3.41
0.2222	33.1	0.7316	8.55		
0.2556	31.0	0.8618	5.83		
		1.0000	2.6		

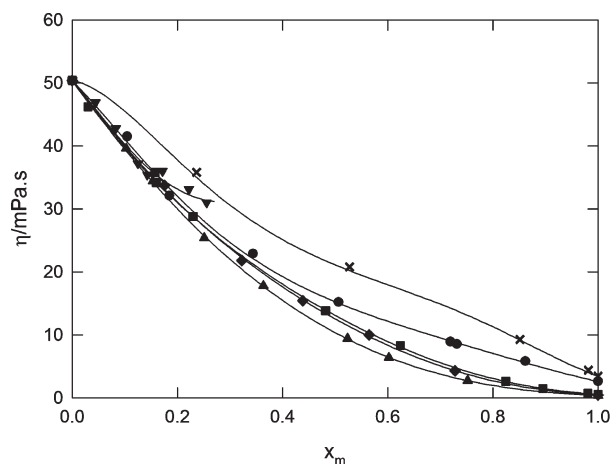


Figure 2. Viscosity, η , of the {[C₄C₁im][Ntf₂] + molecular compound} mixtures as a function of the composition expressed in molecular component mole fraction, x_m , at 298 K: ▲, acetonitrile; ■, methanol; ◆, dichloromethane; ▼, water; ●, 1-butanol; ×, *t*-butanol. Lines correspond to the fits using eq 6.

water mole fraction (0.2431 at 290.13 K and 0.2618 at 299.32 K), which corresponds to just 1.4% in water mass fraction.²⁸

The viscosity of [C₄C₁im][Ntf₂] obtained in the present study, 50.4 mPa.s at 298 K, is in fair agreement (deviation less

than 3%) with some previously reported literature data (51.9 mPa.s measured by François et al.,²⁹ 49.4 mPa.s measured by Jacquemin et al.³⁰), and in excellent agreement with very recent results (50.62 mPa.s measured by Tariq et al.³¹).

Figure 2 illustrates the known fact that the addition of a low-viscosity organic component to an ionic liquid results in a significant decrease of its viscosity. For example, the addition of only 1%

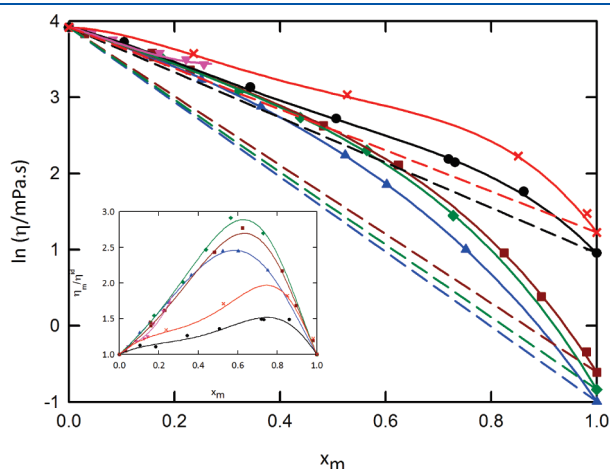


Figure 3. Logarithm of the viscosity, η_m and ratio, η_m/η_{id} (insert) of the $\{[C_4C_{1im}][Ntf_2] + \text{molecular compound}\}$ mixtures as a function of the composition expressed in molecular component mole fraction, x_m , at 298 K: blue triangles, acetoneitrile; red squares, methanol; green triangles, dichloromethane; purple triangles, water; black circles, 1-butanol; red x's, *t*-butanol. Lines correspond to the fits using eq 6.

(mass fraction) of methanol leads to a decrease of more than 30% in the viscosity of $[C_4C_{1im}][Ntf_2]$. Such a decrease can be beneficial from a technological point of view when high viscosities are a drawback in terms of mass-transfer processes. Figure 2 also shows that the decrease of the viscosity of the ionic liquid caused by the addition of a molecular component also depends on the nature of the latter, especially when the amount of added component starts to have important contributions in terms of intermolecular interactions and structural rearrangements. It is also interesting to notice that there are no intersections between the curves represented in Figure 2. This means that, for a given molar composition, the viscosities of the different mixtures follow the same order as that of the viscosities of the pure molecular components: for a given molar composition, the less viscous solutions are those containing acetoneitrile (the less viscous pure molecular component), followed by the dichloromethane and methanol mixtures (with quite similar viscosities), and finally the systems containing the

Table 4. Parameters *A*, *B*, and *C* of the Redlich–Kister-Type Fittings, eq 6, Used to Fit the Experimental Viscosity Deviations Calculated from the Data of Table 3 along with the Standard Error of the Estimation

	<i>A</i>	<i>B</i>	<i>C</i>	Std. dev.
acetoneitrile	0.3080	−1.1779	3.4960	0.01
methanol	0.6177	−2.1058	3.6676	0.03
dichloromethane	0.7290	−2.1318	3.9479	0.02
water	7.5321	−12.724	7.3482	0.03
1-butanol	1.5289	−1.3871	1.1481	0.03
<i>t</i> -butanol	2.5801	−2.1169	1.9067	0.05

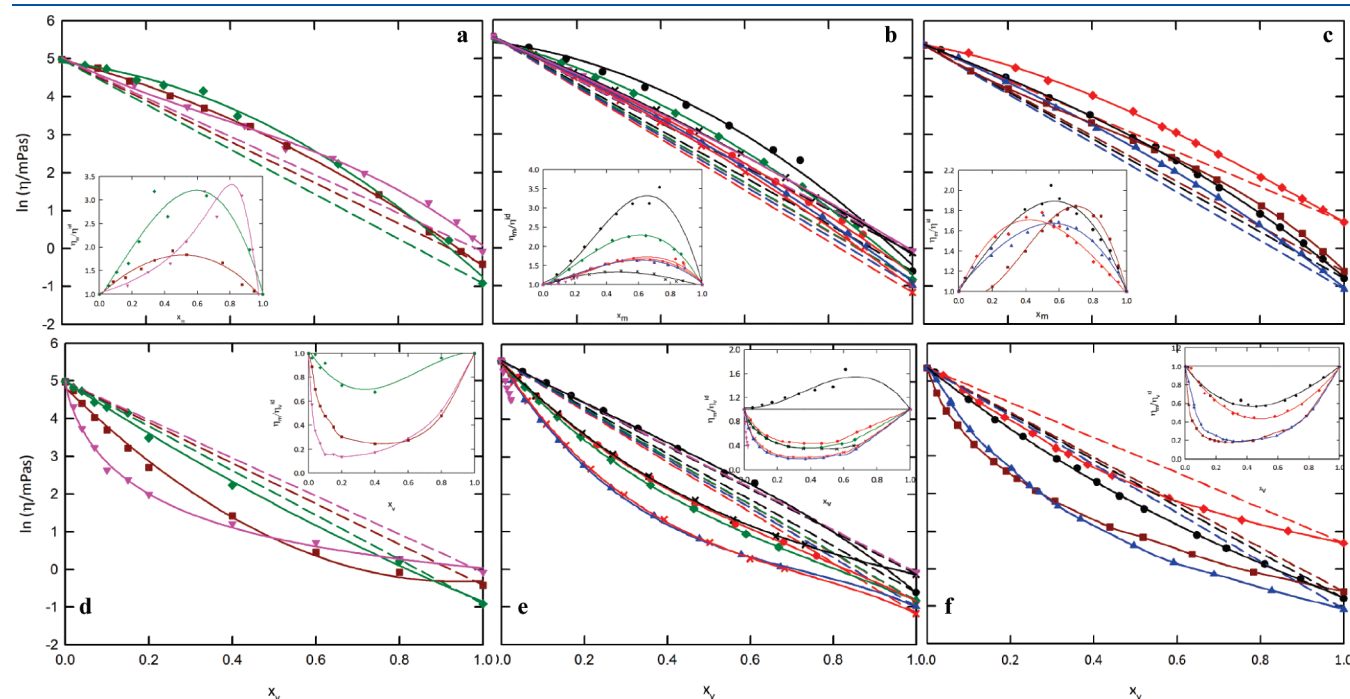


Figure 4. Logarithm of the viscosity, $\ln(\eta_m)$, and real to ideal ratio, η_m/η_{id} or η_m/η_{v}^{id} (inserts) of $\{\text{ionic liquid} + \text{molecular compound}\}$ mixtures as a function of the composition expressed in molecular component mole fraction, x_m , (a, b, c) and in molecular component volume fraction, x_v , (d, e, f) at 298 K. a and d: 1-Butylpyridinium tetrafluoroborate³⁵ + red squares, methanol; green diamonds, dichloromethane; purple triangles, water. b and e: 1-butyl-3-methylimidazolium hexafluorophosphate³⁶ plus black circles, chloroform; red circles, ethyl acetate; green diamonds, dichloromethane; black x's, pyridine; red x's, acetone; blue triangles, acetoneitrile; purple triangles, water. c and f: 1-Butyl-3-methylimidazolium hexafluorophosphate³⁷ plus black circles, tetrahydrofuran; red diamonds, dimethylsulfoxide; red squares, methanol; blue triangles, acetoneitrile. Lines are guides to the eye.

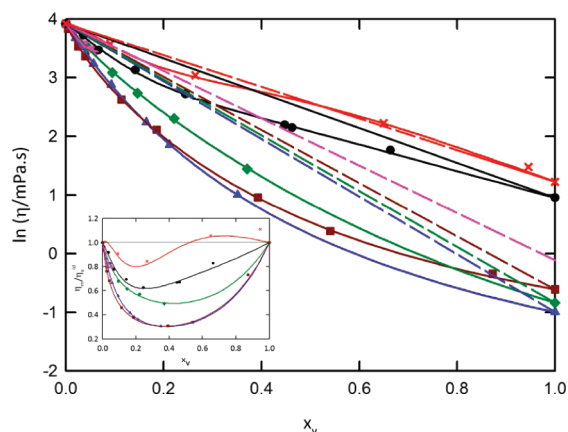


Figure 5. Logarithm of the viscosity, η_m , and real to ideal ratio, $\eta_m/\eta_v^{\text{id}}$, (insert) of the $\{[\text{C}_4\text{C}_1\text{im}][\text{Ntf}_2] + \text{molecular compound}\}$ mixtures as a function of the composition expressed in molecular component volume fraction, x_v , at 298 K: blue triangles, acetonitrile; red squares, methanol; green diamonds, dichloromethane; purple triangles, water; black circles, 1-butanol; red x's, *t*-butanol. Lines correspond to the fits using eq 6.

most viscous pure molecular components, 1-butanol and *t*-butanol. This is true for the studied systems but not necessarily so for other ionic liquid/molecular solvent systems or if compositions are given in mass or volume fractions (discussion below).

Around room temperature, the viscosity of most ionic liquids is much greater (1 to 3 orders of magnitude) than that of traditional molecular solvents (in the present case the viscosity of the molecular components range from 0.4 to 3.4 mPa.s). Given such large differences, Seddon et al.³² have proposed that, as a first approximation, the viscosity dependence on composition of a binary mixture containing one ionic liquid and a molecular component, can be fitted using an exponential equation with parameters that depend only on the ionic liquid. In other words, only the amount of molecular compound added to the ionic liquid (and not its nature) is primarily relevant to define the viscosity of the mixture. However, the same authors also stressed that more precise analyses of the results need to include the nature of the molecular component and that a simple exponential representation is not satisfactory for many purposes. On the other hand, the equations classically used to describe the evolution of the viscosity of electrolyte solutions (Jones–Dole, extended Jones–Dole, Angell³³) cannot be applied to the entire range of compositions (from diluted electrolytes to pure salts) of the mixtures under discussion. Therefore, we have chosen the use of the empirical Grunberg–Nissan equation³⁴ to describe the viscosity of the studied mixtures, η_m :

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + \ln \left(\eta_m / \eta^{\text{id}} \right) \quad (5)$$

where x_i and η_i are the mole fraction and viscosity of component i respectively, and $(\eta_m/\eta^{\text{id}})$ is the ratio between the real and ideal viscosities of the mixture. Eq 5 empirically assumes that in an ideal case the viscosity of the mixture is given by the composition-weighted geometrical mean of the viscosities of the pure components, $\eta^{\text{id}} = \eta_1^{x_1} \cdot \eta_2^{x_2}$. The term $\ln(\eta_m/\eta^{\text{id}})$ is then directly proportional to the relative deviation of the mixture viscosity from its ideal value, $(\eta_m - \eta^{\text{id}})/\eta^{\text{id}}$. A Redlich–Kister-type equation was used to correlate the viscosity coefficients, $\ln(\eta_m/\eta^{\text{id}})$

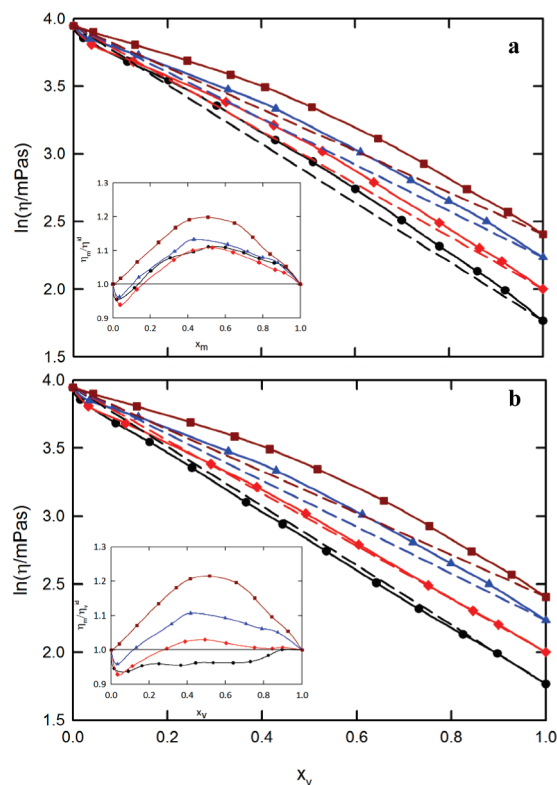


Figure 6. Logarithm of the viscosity, $\ln(\eta_m)$, and ratio, $\eta_m/\eta_v^{\text{id}}$, (insert) of $\{1\text{-butyl-3-methylimidazolium thiocyanate} + \text{molecular compound}\}$ mixtures as a function of the composition expressed in molecular component mole fraction, x_m , (a) and in molecular component volume fraction, x_v , (b) at 298 K;³⁸ black circles, heptanol; red diamonds, octanol; blue triangles, nonanol; red squares, decanol. Lines are guides to the eye.

as a function of composition:

$$\ln \left(\eta_m / \eta^{\text{id}} \right) = x_1 x_2 \left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 \right] \quad (6)$$

The $\ln(\eta_m)$ values and the corresponding viscosity ratios $(\eta_m/\eta^{\text{id}})$ are plotted in Figure 3 as a function of molar composition; the corresponding A , B , and C parameters of eq 6 are presented in Table 4.

According to eq 5, the viscosity coefficient, η_m/η^{id} , is 1 for the pure components and mixtures with an ideal viscosity. For real mixtures with a molecular component mole fraction between 0.5 and 0.8, the real to ideal ratio can reach values up to 3, the larger deviations being observed for dichloromethane, followed by methanol, acetonitrile, *t*-butanol, and *n*-butanol.

The viscosity of a liquid mixture is related to the strength of the molecular interactions between the components and also to the amount of free volume in the system. The latter can be quantified by the volumetric properties of the mixture, whereas the dielectric constant of a fluid is a good parameter to quantify the former.

Indeed, some studies^{35–37} suggest that there is a relationship between the dielectric constant of the added molecular component and the viscosity of the corresponding ionic liquid mixtures: molecular solvents of high dielectric constant are more effective in reducing the electrostatic attraction between the ions of the ionic liquids and thus should reduce their viscosity more effectively.

Table 5. Ionic Conductivity, κ , and Molar Conductivity, Λ , of the Mixtures $[\text{C}_1\text{C}_4\text{im}][\text{Ntf}_2]$ + Molecular Component at 298 K As a Function of the Composition Expressed in Molecular Component Mole Fraction, x_m ($x_m/100$ in the case of water)

x_m	$\kappa / \text{S} \cdot \text{m}^{-1}$	$10^4 \Lambda / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	x_m	$\kappa / \text{S} \cdot \text{m}^{-1}$	$10^4 \Lambda / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
1-Butanol			Methanol		
0.0121	0.408	1.20	0.0302	0.524	1.54
0.1229	0.477	1.46	0.0942	0.509	1.64
0.2936	0.561	1.86	0.1177	0.549	1.51
0.3170	0.613	2.06	0.1279	0.509	1.52
0.3394	0.578	1.96	0.1706	0.514	1.55
0.4228	0.633	2.28	0.3686	0.596	1.89
0.4428	0.667	2.44	0.3938	0.651	2.08
0.5053	0.668	2.58	0.4320	0.990	3.20
0.5180	0.677	2.65	0.5555	1.18	4.05
0.5450	0.677	2.73	0.6132	1.74	6.21
0.5556	0.676	2.76	0.6620	1.89	7.04
0.5882	0.675	2.86	0.6647	1.96	7.32
0.6080	0.674	2.93	0.7009	2.12	8.23
0.6656	0.660	3.14	0.7427	2.28	9.35
0.6796	0.670	3.27	0.7546	2.28	9.53
0.6833	0.653	3.21	0.7799	2.29	10.0
0.7316	0.590	3.21	0.7921	2.43	10.9
0.7458	0.570	3.21	0.7983	2.45	11.1
0.7645	0.560	3.31	0.8188	2.49	11.9
0.7951	0.507	3.29	0.8272	2.51	12.2
0.8349	0.418	3.17	0.8805	2.58	15.3
0.8487	0.401	3.24	0.9305	2.42	20.3
0.8623	0.368	3.20	0.9462	2.23	22.5
0.8780	0.349	3.33	0.9721	1.73	29.6
			0.9896	0.94	39.3
Dichloromethane			Water		
0.0175	0.453	1.35	0.12	0.416	1.21
0.2430	0.454	1.42	0.14	0.412	1.20
0.3949	0.464	1.55	0.53	0.412	1.20
0.4152	0.539	1.82	1.35	0.431	1.26
0.4625	0.586	2.04	2.27	0.427	1.25
0.4718	0.634	2.22	2.72	0.442	1.29
0.5413	0.657	2.42	2.73	0.444	1.30
0.6165	1.08	4.28	5.33	0.444	1.30
0.6861	1.18	5.12	7.37	0.466	1.37
0.7345	1.33	6.26	7.85	0.466	1.37
0.7725	1.47	7.52	9.15	0.472	1.39
0.7751	1.37	7.05	10.24	0.498	1.47
0.7760	1.47	7.58	11.71	0.494	1.46
0.8389	1.46	9.17	14.39	0.520	1.53
0.8744	1.36	10.1	17.33	0.549	1.62
0.9008	1.21	10.6	21.19	0.583	1.73
0.9287	0.98	11.1	24.36	0.610	1.82
0.9319	0.95	11.2	25.23	0.599	1.79
0.9459	0.797	11.3	25.59	0.614	1.83
0.9506	0.739	11.3			
0.9696	0.46	10.8			
0.9813	0.287	10.6			
0.9837	0.242	10.1			

Table 5. Continued

x_m	$\kappa / \text{S} \cdot \text{m}^{-1}$	$10^4 \Lambda / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	x_m	$\kappa / \text{S} \cdot \text{m}^{-1}$	$10^4 \Lambda / \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
<i>t</i> -Butanol			Acetonitrile		
0.3616	0.485	1.68	0.1027	0.514	1.54
0.4010	0.488	1.74	0.1514	0.567	1.71
0.4577	0.497	1.85	0.2513	0.720	2.23
0.4791	0.500	1.90	0.4169	1.08	3.57
0.5125	0.503	1.97	0.5016	1.37	4.74
0.5380	0.507	2.04	0.6610	2.25	8.90
0.5851	0.505	2.15	0.8396	3.67	20.9
0.6042	0.520	2.27	0.9050	4.42	35.2
0.6530	0.504	2.37	0.9485	4.03	51.0
0.7215	0.476	2.56	0.9667	3.41	62.3
0.7850	0.377	2.41	0.9794	2.69	75.3
			0.9937	1.14	97.6

Viscosity data from the three references cited above^{35–37} are compared in the different panels of parts a, b, and c of Figure 4, both in terms of deviation from the ideal Grundberg–Nissan behavior and also (in the inserts) in terms of the relative deviation form that same behavior. All graphs are represented as a function of the molecular component mole fraction. One can see that, in general, molecular solvents with a low dielectrical constant (like chloroform, dichloromethane, or ethylacetate) show more positive deviations from the ideal behavior (which corresponds to smaller relative decreases in viscosity) than those with higher dielectric constants like methanol, acetonitrile, or water (with larger relative drops in the viscosity). However, water — which presents one of the highest electrical permittivity values among common molecular solvents — does not always produce the most pronounced viscosity drops. This apparent lack of correlation can be resolved by taking into account that ionic liquids and the molecular solvents have in some cases huge differences in terms of molar volumes. This affects the way the two components of the mixture can interact and suggests that the Grundberg–Nissan relation for such disproportionate components should be written in terms of the volume fraction, x_v , occupied by each component of the mixture and not in terms of the mole fraction. The ideal viscosity would be given by $\eta_v^{\text{id}} = \eta_1^{x_{v1}} \cdot \eta_2^{x_{v2}}$. The different panels of parts d–f of Figures 4 depict the viscosity data of parts b–c of Figure 4 as a function of the volume fraction of the molecular component of the mixture. The correlation between the dielectric constants and the drops in viscosity is now much better. The only apparent contradictory value is now in the system $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ plus dimethylsulfoxide, DMSO,³⁷ where the relatively viscous and polar molecular component yields rather modest viscosity drops relative to the other tested molecular components. This issue will be further discussed in the next paragraph.

Figure 5 shows a representation similar to that of parts d–f of Figure 4 for the systems tested in this work. The results show a good correlation between the dielectric constants of methanol, acetonitrile, and dichloromethane and the corresponding viscosity drops. Even for water, the limited amount of data seems to confirm the expected trend. However, the two tested butanols exhibit rather modest viscosity drops relative to their (relatively high) dielectrical constant values. Like the DMSO case mentioned above, both pure 1-butanol and *t*-butanol show relatively high values of viscosity.

The interpretation of all these facts can be done using as starting point the basic idea that a fluid with a large dielectric constant is

able to interact more effectively with both ions of the ionic liquid, disrupt its polar network, and cause a decrease in the viscosity of the mixture. As we have seen, the first extension of this idea is to account for the different size of the different components of the mixture and how this affects the effectiveness of the interactions (for instance the effect of water and methanol should be compared at comparable volume fractions of the molecular component). The final development is to take into account the nanosegregated nature of the ionic liquid and the distribution of the molecular solvent in this media. Most small dipolar solvents will dissolve near the polar network and will be able to interact directly with the ions that compose it. However, molecules with a large nonpolar moiety (like 1-butanol or *t*-butanol or even DMSO with a weakly polar group ($\text{S}=\text{O}$) anchored by two methyl groups) will be partially dissolved into the nonpolar regions of the ionic liquid. This means that the dipolar part of those molecules will not be able to interact effectively with the ions of the polar network and explains the modest viscosity drops relative to the dielectric constants exhibited by the pure molecular components.

This interpretation explains very well the viscosity trends found for the three studied alcohols (*t*-butanol is the least efficient to decrease the viscosity of the ionic liquid, followed by 1-butanol and methanol, that has the strongest effect on the decrease of this property). These trends are not only coherent with the variation of their dipole moment, dielectric constant and π^* — an increase in the alcohol chain length leads to an overall less polar component and to more pronounced viscosity drops — but also with the fact that for larger alcohols a larger portion of the molecule is hidden from the polar network. In *t*-butanol, this last issue is particularly relevant: the dipolar/protic part of the molecule (the hydroxyl group) is surrounded by methyl groups that are able to anchor it further into the nonpolar regions of the ionic liquid. The concomitant effect of decreasing polarity and increasing nonpolar moiety can be further confirmed by other viscosity measurements involving ionic liquids and alcohols.^{38–41} Some of these results are presented in Figure 6.

We have also tried to check the existence of free-volume effects in the studied mixtures and possible relations to the observed viscosity drops. Mixtures of an ionic liquid and a molecular component present small excess molar volumes, typically less than $1 \text{ cm}^3 \cdot \text{mol}^{-1}$. The available data for the studied systems shows that binary systems with negative excess molar volumes (corresponding to smaller free volumes) have large viscosity drops. This is the case of acetonitrile ($V_m^E = -0.6 \text{ cm}^3 \cdot \text{mol}^{-1}$ at

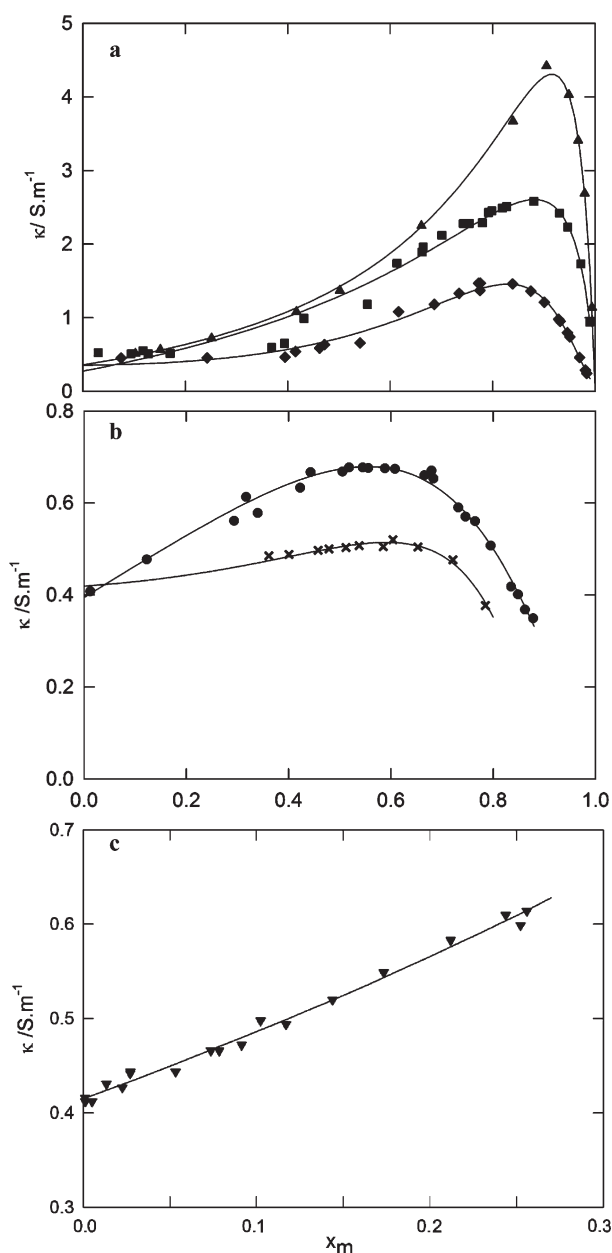


Figure 7. Ionic conductivity, κ , of the mixtures $[\text{C}_4\text{C}_1\text{im}][\text{Ntf}_2]$ + molecular component as a function of the composition expressed in molecular component mole fraction, x_m , at 298 K: (a) ▲, acetonitrile; ■, methanol; ◆, dichloromethane; (b) ●, 1-butanol; ×, *t*-butanol; (c) ▼, water. Lines correspond to the fits using eq 8.

$x_{\text{IL}} = 0.51$ and 303 K^{28}) and methanol ($V_m^E = -0.29 \text{ cm}^3 \cdot \text{mol}^{-1}$ at $x_{\text{IL}} = 0.12$ and 298 K^{42}). However, the system 1-butanol + $[\text{C}_4\text{C}_1\text{im}][\text{Ntf}_2]$ with an S shape but mostly positive excess molar volume ($V_m^E = 0.6 \text{ cm}^3 \cdot \text{mol}^{-1}$ at $x_{\text{IL}} = 0.7$ and 298 K^{43}) exhibits small viscosity drops. These are unexpected results because a reduction of the free volume should logically lead to lower viscosity drops. This means that the excess molar volumes of these mixtures, being so small (in all stated cases V_m^E/V_m is always smaller than 0.5%), are not relevant for the characterization of the corresponding viscosity trends.

Conductivity. The ionic conductivity has been measured for all the systems at atmospheric pressure and at 298.15 K. The

Table 6. Parameters A , B , C , D , and E of eq 8, Used to Fit the Experimental Molar Conductivity from the Data of Table 5 along with the Standard Error of the Estimation^a

	$10^3 A$	$10^4 B$	$10^6 C$	$10^5 D$	$10^9 E$	std. dev.
acetonitrile	12.58	2.176	1.231	−0.9945		5×10^{-5}
methanol	7.104	3.221	−1.547	1.604		5×10^{-5}
dichloromethane	3.918	5.923	−7.827	6.889	1.116	3×10^{-5}
water	−26780	−1.839	7889	−8781		2×10^{-6}
1-butanol	0.9743	0.9106	−0.7474	0.7388		7×10^{-6}
<i>t</i> -butanol	−6.655	−5.572	2.726	−2.973		3×10^{-6}

^a For the calculations, the molar conductivity is in $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ and the concentration in $\text{mol} \cdot \text{m}^{-3}$.

experimental data are presented in Table 5 and Figure 7. The whole composition range could not be covered for the systems with 1-butanol and *t*-butanol due to the low ionic conductivities in the alcohol-rich region.

The molar conductivity, Λ , is calculated from the ionic conductivity, κ , and the ionic liquid concentration, c_{IL} , according to:

$$\Lambda = \kappa / c_{\text{IL}} \quad (7)$$

This property was then fitted to the equation:

$$\Lambda = A - B c_{\text{IL}}^{1/2} + C c_{\text{IL}} \ln c_{\text{IL}} + D c_{\text{IL}} \quad (8)$$

which corresponds to the truncated series expression derived for dilute electrolyte solutions from the theory of Onsager as proposed by Stoppa et al.²¹ In the case of dichloromethane, it was necessary to extend this equation with an extra term ($+ E c_{\text{IL}}^2$). The parameters of eq 8 are presented in Table 6 along with the standard error of estimation.

A conductivity of $0.416 \text{ S} \cdot \text{m}^{-1}$, was measured for the pure ionic liquid at 298 K, 2% higher than the value of $0.406 \text{ S} \cdot \text{m}^{-1}$ measured by François et al.²⁹

For all of the considered systems except that with water, the conductivity presents a maximum as a function of composition. This property depends on the charge density (which is high in ionic liquids) and on the mobility of the ions, which is linked to their viscosity. The two factors affect the conductivity in opposite ways and vary when the composition of the mixture is changed. Depending on which one is dominant, this property will increase or decrease with the concentration of the ionic liquid. The increase initially observed when adding the cosolvent can be explained by the decrease of the viscosity of the mixture, whereas the final decrease is probably due to a decreasing number of charge carriers explained by a decrease in ionic liquid concentration and the possible occurrence of ion pairing.

The value of the maximum conductivity depends on the solvent: the mixtures with acetonitrile, methanol, and dichloromethane present the highest conductivities (maxima of 4.42, 2.58, and $1.47 \text{ S} \cdot \text{m}^{-1}$, respectively) followed by the systems composed of 1-butanol and *t*-butanol (maxima of 0.7 and $0.5 \text{ S} \cdot \text{m}^{-1}$, respectively). Because of the poor miscibility of water and ionic liquid, only an increase of ionic conductivity with the addition of molecular compound could be observed for this system. Except for water, the decreasing order of maximum conductivity is coherent with an increasing order of viscosity (less influence of the molecular compound to the viscosity drop of the mixture). However, the mixtures with methanol and

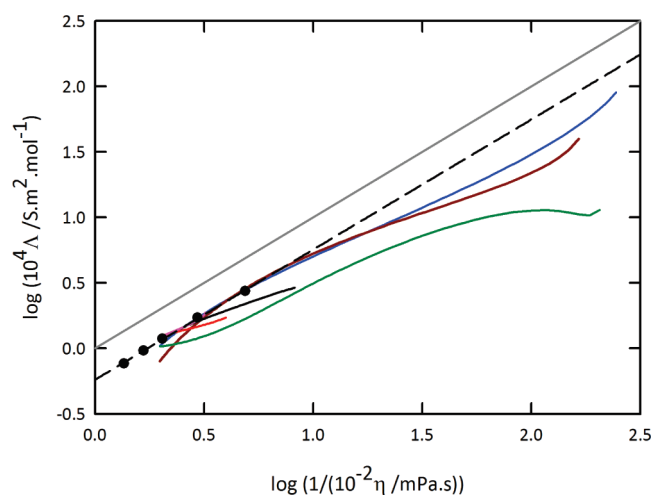


Figure 8. Walden plot of the mixtures $[C_4C_1im][Ntf_2]$ + molecular component at 298 K: (blue), acetonitrile; (brown), methanol; (green), dichloromethane; (red), *t*-butanol; (black), 1-butanol; (pink), water; (dashed), pure ionic liquid;^{21,44} (gray), KCl, 0.01 M.

acetonitrile present comparable viscosities, whereas the presence of acetonitrile in the mixture leads to higher conductivities.

The maximum conductivity is measured for a mole fraction of solvent around 0.9 for the mixtures with acetonitrile, dichloromethane, and methanol (corresponding to mass fractions between 0.3 and 0.5), the shift of the maximum being caused by the important difference in molecular weights/volumes between the two components of the mixture. These values become 0.5–0.65 (mole fraction) and 0.15–0.25 (mass fraction) in the cases of 1-butanol and *t*-butanol.

The relationship between ionic conductivity and viscosity is illustrated by the qualitative approach first developed by Walden for aqueous electrolytes. Walden plots ($\log \Lambda$ as a function of $\log \eta^{-1}$) for the pure ionic liquid at different temperatures and for the considered mixtures at 298 K are presented in Figure 8. Such graphs provide a qualitative measure of the ionicity of the medium, defined as the effective fraction of ions available to participate in conduction: if a system follows the Walden plot, its conductivity is governed mainly by ion migration according to the Stokes–Einstein equation and its viscosity is the only property determining the conductivity. Ionic liquids approximately follow the Walden rule, which means they are represented by a line in a Walden plot. Angell et al.²² have proposed to classify the ionic liquids as either good or poor, depending on their position in the Walden graph. For that purpose, an ideal line corresponding to a 0.01 M aqueous KCl solution — that exists as completely dissociated ions — was defined as a reference line. Components that lie close to this line are said to be ionic, whereas subionic (poor) ionic liquids are below this line. It must be stressed that such comparisons and classifications are mainly qualitative due to the fundamental differences between a diluted electrolyte solution (0.01 M aqueous KCl solution) and an ionic liquid.

As can be observed in Figure 6, $[C_4C_1im][Ntf_2]$ is according to this classification a good ionic liquid. In a recent article, Scheiner et al.²⁴ have discussed the theoretical foundation justifying the comparison of ionic liquid's conductivity and viscosity to that of KCl. However, in the present work, we focus our attention on the comparison between the experimental data for the mixtures and the line of the pure ionic liquid. The relation between viscosity

and conductivity of our systems is clearly modified with the addition of a molecular component: the curves deviate from the pure ionic liquid line. The relative position of the curves indicates that this phenomenon is most important for dichloromethane, 1-butanol, and *t*-butanol, the three less polar components studied. Another measure of the ionicity of these mixtures is the molar conductivity ratio⁴⁵ (conductivity measured by the electrochemical method divided by the conductivity estimated by pulse-field-gradient spin–echo NMR). Ueno et al.⁴⁵ have also observed, by studying this parameter, an enhanced ionic association of the systems ionic liquid + molecular component with the dilution of the ionic liquid. In the case of water, the mixtures present an ionicity similar to that of the pure ionic liquid: the experimental data are exactly on the line of the pure ionic liquid indicating water has no influence on the dissociation of the ionic component. In the case of conventional electrolyte solutions, the dissociation is generally promoted by the dilution with a molecular compound (decrease of the concentration of salts).

CONCLUSIONS

The solvent quality and two transport properties were studied in mixtures composed of $[C_4C_1im][Ntf_2]$ and a selection of molecular components varying in polarities, size and isomerism. The objective was to explore the modification on these properties due to the addition of a molecular compound to the ionic liquid.

The polarity was estimated through the determination of π^* and β Kamlet–Taft parameters. In most cases, the solvent quality of the ionic liquid is only slightly modified by the presence of the molecular component unless large quantities of this molecular component are added. The viscosity of the ionic liquid dramatically decreases with the addition of the molecular component. This decrease can be qualitatively explained by the interactions present in the solution, the relative sizes of the components of the mixture, and the recognition that ionic liquids are nanosegregated media. The conductivity presents a maximum as a function of composition, and, except for water, the decreasing order of maximum conductivity is coherent with an increasing order of viscosity. Finally, the relationship between the two transport properties was studied with the help of Walden plots. Enhanced ionic association was observed with the dilution of the ionic liquid, a fact quite diverse from the situation in conventional electrolyte solutions, where dilution promotes ionic dissociation.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jnlopes@ist.utl.pt (J.N.C.L.); pascale.husson@univ-bpclermont.fr (P. H.).

ACKNOWLEDGMENT

This work was supported by the Portuguese-French joint action (PESSOA-17753NF). The French laboratory thanks the Auvergne region, France, for its financial support (Project CPER Environnement). The authors would like to thank the Laboratoire de Photochimie Moléculaire et Macromoléculaire, CNRS/Blaise Pascal University for the use of the UV–vis spectrophotometer. J.N.C.L. and L.P.N.R. acknowledge the FCT (Portugal) grants PTDC/QUI-QUI/101794/2008, PTDC/QUI/71331/2006, and PTDC/QUI/66826/2006 and also the

use of NMR spectrometers that are part of the National NMR Network and were purchased in the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005, with funds from POCI 2010 (FEDER) and Fundação para a Ciência e a Tecnologia (FCT); M.T. acknowledges his postdoctoral grant SFRH/BPD/34146/2006.

REFERENCES

- (1) *Ionic Liquids in Synthesis* Vol. 2, Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2009.
- (2) *Ionic Liquids in Synthesis*, Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2003.
- (3) Petkovic, M.; Seddon, K. R.; Rebelo, L. P. N.; Pereira, C. S. *Chem. Soc. Rev.* **2011** in press.
- (4) Petkovic, M.; Ferguson, J.; Nimal Gunaratne, H. Q.; Ferreira, R.; Seddon, K. R.; Rebelo, L. P. N. *Pereira Green Chem* **2010**, 12, 643.
- (5) Davis, J. H. *Chem. Lett.* **2004**, 33, 1072.
- (6) Guedes, H. J. R.; Cordeiro, T. C.; Lopes, J. N. C.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Huq, S.; Seddon, K. R. *J. Phys. Chem. B* **2005**, 109, 3519.
- (7) Fu, D. B.; Sun, X. W.; Pu, J. J.; Zhao, S. Q. *J. Chem. Eng. Data* **2006**, 51, 371.
- (8) Hong, G.; Jacquemin, J.; Husson, P.; Gomes, M. F. C.; Deetlefs, M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C. *Ind. Eng. Chem. Res.* **2006**, 45, 8180.
- (9) Canongia Lopes, J. N.; Rebelo, L. P. N. *Phys. Chem. Chem. Phys.* **2010**, 12, 1948.
- (10) Canongia Lopes, J. N.; Costa Gomes, M. F.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, 110 (34), 16816.
- (11) Canongia Lopes, J. N. A.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, 110 (7), 3330.
- (12) Wang, Y. T.; Voth, G. A. *J. Am. Chem. Soc.* **2005**, 127 (35), 12192.
- (13) Urahata, S. M.; Ribeiro, M. C. C. *J. Chem. Phys.* **2004**, 120, 1855.
- (14) Bonhôte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundram, K.; Grätzel, M. *Inorg. Chem.* **1996**, 35, 1168.
- (15) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, 99, 6027.
- (16) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, 98, 377.
- (17) *Tables of Experimental Dipole Moments*; McClellan, A. L., W.H. Freeman and Company: San Francisco, USA, 1963.
- (18) Cunningham, G. P.; Vidulich, G. A.; Kay, R. L. *J. Chem. Eng. Data* **1967**, 12, 336.
- (19) Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, J. M.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2003**, 5, 2790.
- (20) Li, W.; Zhang, Z.; Zhang, J.; Han, B.; Wang, B.; Hou, M.; Xie, Y. *Fluid Phase Equilib.* **2006**, 248, 211.
- (21) Stoppa, A.; Hunger, J.; Buchner, R. *J. Chem. Eng. Data* **2009**, 54, 472.
- (22) Angell, C. A.; Byrne, N.; Belieres, J. P. *Acc. Chem. Res.* **2007**, 40, 1228.
- (23) Mellein, B. R.; Aki, S. N. V. K.; Ladewski, R. L.; Brennecke, J. F. *J. Phys. Chem. B* **2007**, 111, 131.
- (24) Shreiner, C.; Zugmann, S.; Hartl, R.; Gores, H. J. *J. Chem. Eng. Data* **2010**, 55, 1784.
- (25) Silva, P. L.; Trassi, M. A. S.; Martins, C. T.; El Seoud, O. A. *J. Phys. Chem. B* **2009**, 113, 9512.
- (26) Baker, S. N.; Baker, G. N.; Bright, F. V. *Green Chem.* **2002**, 4, 165.
- (27) Marcus, Y. *J. Chem. Soc., Perkin Trans.* **1994**, 2, 1015.
- (28) Wang, S.; Jacquemin, J.; Husson, P.; Hardacre, C.; Costa Gomes, M. F. *J. Chem. Thermodyn.* **2009**, 1206.
- (29) François, F.; Zhang, K.; Varenne, A.; Gareil, P. *Anal. Chim. Acta* **2006**, 562, 164.
- (30) Jacquemin, J.; Husson, P.; Padua, A. A. H.; Majer, V. *Green Chem.* **2006**, 8, 172.
- (31) Tariq, M.; Carvalho, P. J.; Coutinho, J. A. P.; Marrucho, I. M.; Canongia Lopes, J. N.; Rebelo, L. P. N. *Fluid Phase Equilib.* **2011**, 301, 22.
- (32) Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem.* **2000**, 72, 2275.
- (33) *Viscosity of Electrolytes and Related Properties*; Stokes, R.H.; Mills, R., Pergamon Press: Oxford, 1965.
- (34) Mahuddin, S.; Ismail, K. *J. Phys. Chem.* **1983**, 87, 5241.
- (35) Khupse, N. D.; Kumar, A. *J. Sol. Chem.* **2009**, 38, 589.
- (36) Li, W.; Zhang, Z.; Han, B.; Hu, S.; Xie, Y.; Li, G. Y. *J. Phys. Chem. B* **2007**, 111, 6452.
- (37) Zafarani-Moattar, M. T.; Majdan-Cegincara, R. *J. Chem. Eng. Data* **2007**, 52, 2359.
- (38) Domanska, U.; Laskowska, M. *J. Sol. Chem.* **2009**, 38, 779.
- (39) Gan, Q.; Xue, M. L.; Rooney, D. *Sep. Purif. Technol.* **2006**, 51, 185.
- (40) Gonzalez, E. J.; Alonso, L.; Dominguez, A. *J. Chem. Eng. Data* **2006**, 51, 1446.
- (41) Gonzalez, B.; Calvar, N.; Gomez, E.; Dominguez, I.; Dominguez, A. *J. Chem. Eng. Data* **2009**, 54 (4), 1353.
- (42) Unpublished data.
- (43) Wandschneider, A.; Lehmann, J. K.; Heintz, A. *J. Chem. Eng. Data* **2008**, 53, 596.
- (44) Widegren, J. A.; Magee, J. W. *J. Chem. Eng. Data* **2007**, 52, 2331.
- (45) Ueno, K.; Tokuda, H.; Watanabe, M. *Phys. Chem. Chem. Phys.* **2010**, 12, 1649.