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Physical Chemistry of Ionic Liquids

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Physical chemistry of ionic liquids
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Thermo-solvatochromism in binary mixtures of water and ionic liquids: on the relative importance of solvophobic interactions†

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The thermo-solvatochromism of 2,6-dibromo-4-[(*E*)-2-(1-methylpyridinium-4-yl)ethenyl] phenolate, $MePMBr_2$, has been studied in mixtures of water, W, with ionic liquids, ILs, in the temperature range of 10 to 60 °C, where feasible. The objectives of the study were to test the applicability of a recently introduced solvation model, and to assess the relative importance of solute–solvent solvophobic interactions. The ILs were 1-allyl-3-alkylimidazolium chlorides, where the alkyl groups are methyl, 1-butyl, and 1-hexyl, respectively. The equilibrium constants for the interaction of W and the ILs were calculated from density data; they were found to be linearly dependent on N_C, the number of carbon atoms of the alkyl group; van't Hoff equation (log K *versus* $1/T$) applied satisfactorily. Plots of the empirical solvent polarities, E_T ($MePMBr_2$) in kcal mol^{-1}, *versus* the mole fraction of water in the binary mixture, χ_w, showed non-linear, *i.e.*, non-ideal behavior. The dependence of E_T ($MePMBr_2$) on χ_w, has been conveniently quantified in terms of solvation by W, IL, and the "complex" solvent IL-W. The non-ideal behavior is due to preferential solvation by the IL and, more efficiently, by IL-W. The deviation from linearity increases as a function of increasing N_C of the IL, and is stronger than that observed for solvation of $MePMBr_2$ by aqueous 1-propanol, a solvent whose lipophilicity is 12.8 to 52.1 times larger than those of the ILs investigated. The dependence on N_C is attributed to solute–solvent solvophobic interactions, whose relative contribution to solvation are presumably greater than that in mixtures of water and 1-propanol.

Introduction

Understanding solvation by aqueous mixtures is important because water is the greenest solvent; the properties of the binary mixture, in particular its solvating power, can be continuously "modulated" by changing the composition of the medium. One of the most important properties of ionic liquids, ILs, is their structural versatility; the combination of a myriad of ions leads to a practically unlimited number of compounds whose properties can be "fine tuned" to the application desired.[1–5] The class of ILs that has received much attention is that based on the 1,3-dialkylimidazolium cation, RR'ImX, where R and R', Im, and X refer to alkyl groups, the imidazolium ring, and the counter–ion, respectively; for simplicity, the charges on the ions are not shown. ILs have been employed as mixtures (mostly binary) with other solvents including water, alcohols, *etc*. The use of aqueous ILs as solvents is appealing because the IL can be recovered by simple schemes, *e.g.*, salting out, and recycling into the process.[6] This use calls for understanding the IL–water interactions, as well as those between dissolved solute, if present, and each component of the binary mixture.

Information about the mechanism and relative importance of interactions of a solute with both components of a binary solvent mixture can be readily extracted from the study of solvatochromic substances, hereafter denoted as "probes". These are compounds whose UV-vis spectra, absorption or emission, are sensitively dependent on the "medium", pure solvent, solvent mixture, solid interface, *etc*. For *any* probe, the energy of the intra-molecular solvent-sensitive charge-transfer, E_T(probe), is given by:

$$E_T \text{ (probe), kcal mol}^{-1} = 28591.5/\lambda_{max}\text{, nm} \qquad (1)$$

where λ_{max} is the wavelength maximum of the charge-transfer band. The values of E_T(probe) are then rationalized in terms of non-specific and specific probe-solvent interaction mechanisms, including dipole/dipole, dipole induced/dipole, dispersion interactions, hydrogen-bonding, and solvophobic interactions.[7a–c,8a,b] An extensively employed probe is 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (RB, for Reichardt's betaine); its empirical polarity scale is designated as $E_T(30)$.

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† Electronic supplementary information (ESI) available: Determination of log P of the IL by condutometric titration of the chloride ion in the aqueous phase by standardized $AgNO_3$ solution (Fig. S1); dependence of log P of the ILs on N_C, the number of carbon atoms in the R group of AlRImCl (Fig. S2); representative van't Hoff plot of the dependence of Kassoc of IL-W (AlBuImCl) on T (Fig. S3); dependence of ln Kassoc on N_C, the number of carbon atoms in the alkyl group of the IL (Fig. S4); molecular structures and ^1H NMR spectral results of AlMeImCl and AlHxImCl (Table S1); dependence of the association constant of the IL-W complex solvent on T (Table S2). See DOI: 10.1039/b921391k

Solvatochromism in binary solvent mixtures is complex because it involves interactions between the components of the mixture, and between the probe and each one of these. Additionally, the properties, *e.g.*, density, viscosity, relative permittivity, ε_r, and hydrogen bonding ability,[8c] of these mixtures are not simple functions of compositions, due to the mutual interactions of their components. By using probes, the molecular structures of which have been varied in a systematic manner, we have explained solvatochromism in binary mixtures by employing a solvation model that takes into account solvent–solvent interactions, in particular hydrogen-bonding.[8a,b]

Recently, we have studied the thermo-solvatochromism (effect of temperature, *T*, on solvatochromism) in aqueous $BuMeImBF_4$, and compared the results with those of solvation in aqueous alcohols. The limited data from this study did not offer a clear-cut conclusion about the relative importance of probe–solvent solvophobic interactions.[9] In order to address this question, we have investigated the thermo-solvatochromism of the probe 2,6-dibromo-4-[(*E*)-2-(1-methylpyridinium-4-yl)-ethenyl] phenolate, $MePMBr_2$, in a series of ILs of increasing hydrophobicity, 1-allyl-3-alkylimidazolium chlorides, where the alkyl groups are methyl (AlMeImCl), 1-butyl (AlBuImCl), and 1-hexyl (AlHxImCl), respectively. Fig. 1 shows the molecular structures of the probe and the ILs employed, along with their log *P*, a measure of hydrophobic character, *vide infra* for determination of log P. We have investigated the entire composition range, from pure water to pure IL, at a temperature of, where feasible, 10, 25, 40, and 60 °C, respectively. The solvatochromic data were successfully treated according to the model that we have previously employed for mixtures of water, W, with molecular solvents, *i.e.*, by considering that the aqueous IL is composed of the two precursor solvents plus the hydrogen-bonded species IL-W. Our data indicated that the probe is preferentially solvated by the IL and, more efficiently, by IL-W. A comparison with solvation of $MePMBr_2$ by aqueous 1-propanol, PrOH, showed that the solute–solvent solvophobic interactions in the aqueous ILs are stronger than those in the aqueous alcohol.

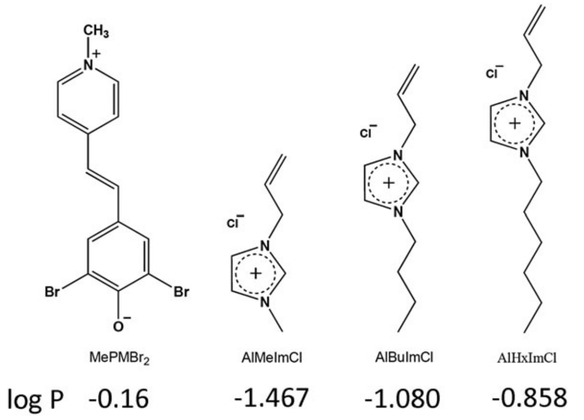


Fig. 1 Molecular structures of $MePMBr_2$ and the ionic liquids employed in the present study, along with their experimentally determined values of log *P*.

Experimental

Materials and synthesis

The chemicals were purchased from Acros, or Apagão-2 Química (DF) and were purified as recommended elsewhere;[10] $MePMBr_2$ and AlBuImCl were available from previous studies.[6,11]

Synthesis of the ILs

The synthesis of the ILs was carried out in a stainless steel reactor provided with an inner glass cup, covered with PTFE lid. AlMeImCl was obtained by stirring a mixture of 1-methylimidazole (20 mL, 0.25 mol), allyl chloride (24.4 mL, 0.3 mol), and 75 mL of acetonitrile for 6h, under pressure (10 atm, oxygen-free N_2), at 85 °C. After removing the volatiles, the product was further dried at 110 °C, 1mm Hg for 12 h; yield 85%, light amber-colored liquid that solidifies on standing, m.p. 52–53 °C. The ^1H NMR data of AlMeImCl are listed in Table S1 of the ESI.†

The precursor 1-(1-hexyl)imidazole was obtained by phase-transfer catalysis by a modification of a published procedure.[12] Namely, we used sonication, and Aliquat 336 as a phase-transfer catalyst. Imidazole (10.21 g, 0.15 mol) and pulverized NaOH (8.0 g, 0.2 mol) were suspended in 15 mL of acetonitrile. The suspension was mechanically agitated and sonicated for 1 h (Fritsch Ultrasonic-cleaner laborrette 17, Bandelin Electronic, Berlin). A solution of 1-bromohexane (30.07 g, 0.18 mol) and Aliquat 336 (6.06 g, 0.015 mol) in 15 mL acetonitrile was slowly added. The mixture was kept under these conditions (agitation and sonication) for 12 h, at *ca.* 60 °C. The mixture was diluted with an equal volume of CH_2Cl_2, filtered, passed through a short flash column chromatography, and further purified by distillation; yield 80%. AlHxImCl was synthesized as shown above for AlMeImCl, by reacting 1-(1-hexyl)imidazole (76 g, 0.5 mol) with allyl chloride (47.04 g, 0.615 mol) in 150 mL of acetonitrile. Yield 86%; ^1H NMR data are listed in Table S1.†

Determination of log *P*, the partition coefficient of the IL between water and 1-octanol

Equal volumes of deionized water and 1-octanol were agitated for 3 h (tube rotator), and the phases separated. The mutually saturated solvents, 12 mL each, were added to a flask containing 1.67×10^{-4} mol of the IL, the flask was agitated for 12 h, at 25 °C. After phase separation, 3 mL of the aqueous phase was diluted with deionized water to 10 mL; the resulting solution was titrated with a standardized $AgNO_3$ solution. Conductivity measurements were recorded at 25 °C with a PC-interfaced Fisher Accumet AR50 ion–meter, provided with a DMC-010 micro-conductivity cell (Digimed, São Paulo) and Schott Titronic T200 programmed burette. The results of this titration is shown in Fig. S1 of the ESI.† Log P for $MePMBr_2$ has been previously determined.[11]

Thermo-solvatochromic response in IL-W mixtures: preparation of the IL-W mixtures; spectroscopic determination of $E_T(MePMBr_2)$, and measurements of solution densities

Binary mixtures (16 per set) of IL and W were prepared by weight at 25 °C. The required amount of the IL was weighted then dried at 60 °C, under reduced pressure, over P_4O_{10}, until constant weight. Aliquots of the probe solution in acetone were pipetted into 2 mL volumetric tubes, followed by evaporation of acetone at room temperature, under reduced pressure, in the presence of P_4O_{10}. IL, W, or IL-W mixtures were added so that the probe final concentration was 2×10^{-5} mol L^{-1}. A Shimadzu UV 2550 UV-vis spectrophotometer was used. The temperature *inside* the thermostatted cell-holder was controlled to within ±0.05 °C with a digital thermometer (model 4000A, Yellow Springs Instruments, Yellow Springs). Each spectrum was recorded twice at a rate of 140 nm min^{-1}; the values of λ_{max} were determined from the first derivative of the absorption spectra. The uncertainty in $E_T(MePMBr_2)$ is ≤ 0.15 kcal mol^{-1}. Thermo-solvatochromism was studied in the temperature range from 10 to 60 °C. Densities of the liquids were determined at 25, 35, 40 and 45 °C with a DMA 40 resonating-tube densimeter (Anton Paar, Graz).

Results and discussion

Note: Details of all calculations performed are given in the Calculations section.

The probe and the ILs employed

We have employed $MePMBr_2$ because its empirical polarity scale, $E_T(MePMBr_2)$ is linearly correlated with $E_T(30)$ (34 solvents, correlation coefficient, r = 0.9685), the most extensively investigated polarity scale. Although the susceptibility of $MePMBr_2$ and RB to solvent "acidity" and dipolarity/polarizability are practically the same, the former probe is sensitive to solvent lipophilicity, as given by the empirical scale log P.[11] The latter is extensively employed as a measure of lipophilicity or hydrophobic character; it refers to the partition coefficient of a substance between 1-octanol and water, both mutually saturated: $\log P = \log([\text{substance}]_{1\text{-octanol}}/[\text{substance}]_{\text{water}})$.[13] The values of log P were found to be −1.467, −1.080, and −0.858, for AlMeImCl, AlBuImCl, and AlHxImCl, respectively, *i.e.*, all ILs are more soluble in water than in 1-octanol. As expected, their lipophilicity increases as a function of increasing the number of carbon atoms, N_C, of the (variable) alkyl group R in AlRImCl, according to the equation: $\text{Log } P = 1.583 + 0.122\ N_C$; $r = 0.9968$, see Fig. S2.† In summary, we have employed a probe that is sensitive to the hydrophobic character of the medium; the ILs employed differ in their solubility in 1-octanol (hence lipophilicty) by a factor of 4.1. Note that log P of the reference molecular solvent, PrOH, is 0.25, *i.e.*, its lipophilicity is 52.1, 21.4, and 12.8 times that of AlMeImCl, AlBuImCl, and AlHxImCl, respectively. As given in the Experimental section, the m.p. of AlMeImCl is 52–53 °C; once melted, this IL takes several hours to solidify at room temperature. Therefore, we were able to determine its empirical polarity in the temperature range studied, except at 10 °C.

Thermo-solvatochromism in mixtures of ILs and water

Fig. 2 shows the solvatochromic responses of $MePMBr_2$ as a function of the mole fraction of water in the binary mixture, χ_W, at 25 °C. All plots shown are non-linear, *i.e.*, solvation is non-ideal; this may be attributed to several factors and/or solute–solvent interaction mechanisms. Enrichment of the probe solvation shell in the solvent of higher ε_r leads to "dielectric enrichment", and consequently to non-ideal behavior.[14] However, ε_r (W) is > ε_r (IL),[15] *i.e.*, if dielectric enrichment were operative, all curves of Fig. 2 should lie above-, not below the straight line that connects the polarities of the two pure liquids; this is not the case.

Non-ideal behavior can originate from preferential solvation of the probe by a component of the mixture, due to solute–solvent specific interactions, *e.g.*, hydrogen-bonding and dipole–dipole interactions. As discussed elsewhere,[8a,b] most binary mixtures of solvents are micro-heterogeneous; there exists the possibility of preferential solvation of the probe by the less polar micro-domains, leading to below-the-line deviation, as shown in Fig. 2. In summary, non-ideal solvation behavior is not unexpected.

An important objective of the present work is to evaluate the application to aqueous ILs of the solvation model that we have applied to analyze solvatochromism in binary mixtures of water with protic or aprotic solvents. The basis of this model is that the binary mixture is made of the two pure solvents, plus a "complex" one; the latter is constituted of hydrogen-bonded species. Therefore, the medium employed is composed of IL, W, and a 1 : 1 IL-W hydrogen-bonded complex, as given by eqn (2). These three solvents compete for the solvation of the probe, as described by eqn (3)–(5):[8a,b,9]

$$\text{IL} + \text{W} \rightleftharpoons \text{IL-W} \tag{2}$$

$$\text{Probe(IL)}_m + m\,(\text{W}) \rightleftharpoons \text{Probe(W)}_m + m\,\text{IL} \tag{3}$$

$$\text{Probe(IL)}_m + m\,(\text{IL-W}) \rightleftharpoons \text{Probe(IL-W)}_m + m\,\text{IL} \tag{4}$$

$$\text{Probe(W)}_m + m\,(\text{IL-W}) \rightleftharpoons \text{Probe(IL-W)}_m + m\,\text{W} \tag{5}$$

where (m) represents the *average* number of solvent molecules whose exchange in the probe solvation shell affects E_T(probe); usually $m \leq 2$; (m) should not be confused with *the total number* of solvent molecules that solvate the probe. An important consequence of this model is that the mole fractions that we have employed in our calculations (except those of Table 1) are "*effective*" *not analytical* ones. In order to keep these calculations tractable, working assumptions are included, namely, a single value is attributed to (m); the stoichiometry of IL-W species is taken as 1 : 1. The former has proved to be valid for the solvation of many probes, including the one employed here.[8a,b] The formation of hydrogen-bonded complexes between ILs, *e.g.*, $BuMeImBF_4$ or AlBuImCl and water has been demonstrated by IR,[16a,b] NIR,[17] ^{1}H NMR,[9] and predicted by theoretical calculations.[18] A plausible structure for this complex is water-mediated hydrogen bonding between the anion and the cation, in particular the relatively acidic H2 of the imidazolium ring. Formation of complexes composed of the IL with one or more water molecules can be envisaged;[19] the species with stoichiometry other than 1 : 1 may be treated, to a good approximation, as mixtures of the 1 : 1 structure plus excess solvent (IL or W). The appropriateness of the 1 : 1 stoichiometry, and the model itself can be further tested by the goodness of fit of the regression analyses of $E_T(MePMBr_2)$ *versus* χ_W, *vide infra*, and agreement of the

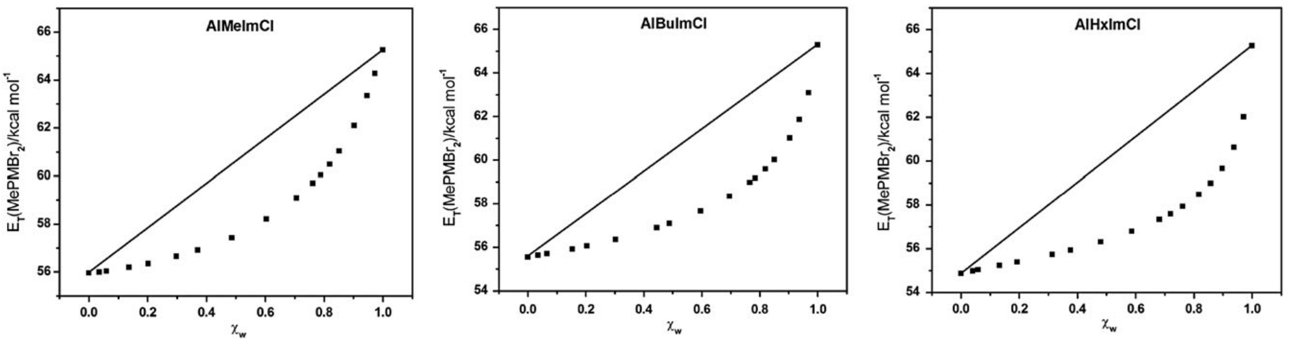


Fig. 2 Dependence of the empirical solvent polarity parameter $E_T(MePMBr_2)$ on the mole fraction of water, χ_W, at 25 °C, for mixtures of water with ILs. The straight lines connecting the polarities of the pure solvents are theoretical, plotted merely to depict the ideal solvation of the probe by the binary mixtures, see text for details.

results thus calculated with what is known, *e.g.*, about the relationship between the molecular structure of the probe and its solvation in other (molecular) solvents.

The equilibrium constants of eqn (3) to (5) are termed solvent "fractionation factors, φ", defined on the mole fraction scale, after rearrangement, as:

$$\varphi_{W/IL} = \frac{x_W^{Probe}/x_{IL}^{Probe}}{(x_W^{Bk;\ Effective}/x_{IL}^{Bk;\ Effective})^m} \quad (6)$$

$$\varphi_{IL\text{-}W/IL} = \frac{x_{IL\text{-}W}^{Probe}/x_{IL}^{Probe}}{(x_{IL\text{-}W}^{Bk;\ Effective}/x_{IL}^{Bk;\ Effective})^m} \quad (7)$$

$$\varphi_{IL\text{-}W/W} = \frac{x_{IL\text{-}W}^{Probe}/x_W^{Probe}}{(x_{IL\text{-}W}^{Bk;\ Effective}/x_W^{Bk;\ Effective})^m} \quad (8)$$

Where (Bk,Effective) refers to the effective concentration of a solvent species (IL, W, IL-W) in bulk solvent. Eqn (6) to (8) show that preferential solvation can be readily *deduced and quantified* from the values of φ. For example, eqn (6) refers to (W) substituting IL in the probe solvation shell. For $\varphi_{W/IL} > 1$, the shell is richer in (W) than the bulk mixture, *i.e.*, the probe is preferentially solvated by (W). The converse holds for $\varphi_{W/IL} < 1$, *i.e.*, the probe is preferentially solvated by IL. The same line of reasoning applies to $\varphi_{IL\text{-}W/IL}$ (complex solvent substitutes IL) and $\varphi_{IL\text{-}W/W}$ (complex solvent substitutes W), eqn (7) and (8), respectively. Finally, a solvent fractionation factor of unity indicates an ideal behavior, *i.e.*, solvation shell and bulk mixture have the same composition. As shown below, this result has not been observed.

The calculation of the effective concentrations of the solvent species present requires knowledge of the association constant, K_{assoc}, between IL and water. As shown in the Calculations section, K_{dissoc} is calculated from experimental data; $K_{dissoc} = 1/K_{assoc}$. For convenience, however, we will report and discuss K_{assoc}. Calculation of this constant has been carried out by regression analyses of the dependence of the density of the mixtures (16 samples) on the volume fraction of the IL, at different temperatures; typical results are shown in Fig. 3; the values of K_{assoc} are listed in Table S2.† The dependence of ln K_{assoc} on $1/T$ (van't Hoff equation) is linear with excellent correlation coefficients. The slopes of these lines are linearly dependent on N_C of the alkyl group, $r = 0.9968$, see Calculations section and Fig. S3 and S4. The corresponding enthalpies are −0.64, −1.20, and −1.33 kcal mol^{-1}, for AlMeImCl, AlBuImCl, and AlHxImCl, respectively. These results show that our density data are adequately described by the 1 : 1 stoichiometry; the formation of IL-W is exothermic; there is no "discontinuity" in the IL-W interactions, as a function of increasing N_C. That last conclusion is relevant, in particular for AlHxImCl, because the formation of an aggregate, akin to a micelle, should not be overlooked.

Fig. 3 indicates an interesting result: as a function of increasing N_C, the maximum mole fraction of the complex solvent, $\chi_{AlRImCl\text{-}W}$, decreases, 0.110, 0.066, 0.050, and shifts towards the water-rich region χ_w = 0.63, 0.68, 0.71, for AlMeImCl, AlBuImCl, AlHxImCl, respectively. We have observed a similar trend for *the same* IL-W mixtures at different temperatures. For example, the maximum $\chi_{AlBuImCl\text{-}W}$ decreases, 0.066, 0.048, and 0.032, for 25, 40, and 60 °C, respectively. The corresponding χ_w are 0.68, 0.70, and 0.72, respectively, see Fig. 4. These results, also observed for mixtures of water and molecular solvents,[8a,b] indicate that an increase in temperature disrupts hydrogen-bonding

Table 1 Thermo-solvatochromic data for $MePMBr_2$ in AlBuImCl-W. The polynomial dependence of $E_T(MePMBr_2)$ on the analytical mole fraction of water in the binary mixture, $x_w^{Analytical}$, has been calculated according to the equation: $E_T(MePMBr_2) = E_T(RPMBr_2)_{IL} + B(\chi_W) + C(\chi_W)^2 + D(\chi_W)^3 + E(\chi_W)^4 + F(\chi_W)^5 + G(\chi_W)^6$

Binary mixture	T/°C	$E_T(MePMBr_2)_{IL}$[a]	B	C	D	E	F	G	r^2[b]	sd[b]
AlBuImCl/W	10	55.737 [0.075]	−4.430	95.616	−249.029	1048.987	−1070.042	408.823	0.9982	0.1541
	25	55.596 [0.056]	−2.826	71.991	−355.988	803.336	−823.752	316.759	0.9989	0.1187
	40	55.445 [0.101]	−2.745	75.560	−380.640	862.692	−885.245	339.935	0.9985	0.1378
	60	55.294 [0.054]	−2.968	71.173	−359.766	819.255	−845.100	326.827	0.9987	0.1223

[a] The values inside the brackets are E_T(probe, calculated) − E_T(probe, experimental). [b] The symbols (r^2) and (sd) refer to the correlation coefficient and standard deviation, respectively.

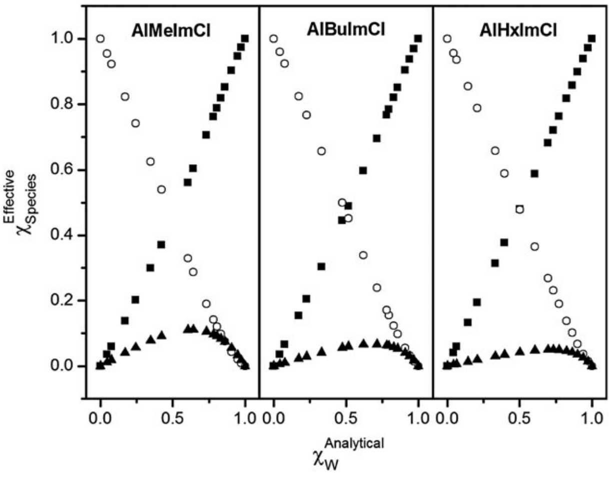


Fig. 3 Representative dependence of the concentrations of the species in the IL-W binary mixtures on the length of R of AlRImCl. The data shown are for 25 °C; the symbols employed are ○, ■, ▲ for IL, W, and the IL-W 1 : 1 complex, respectively.

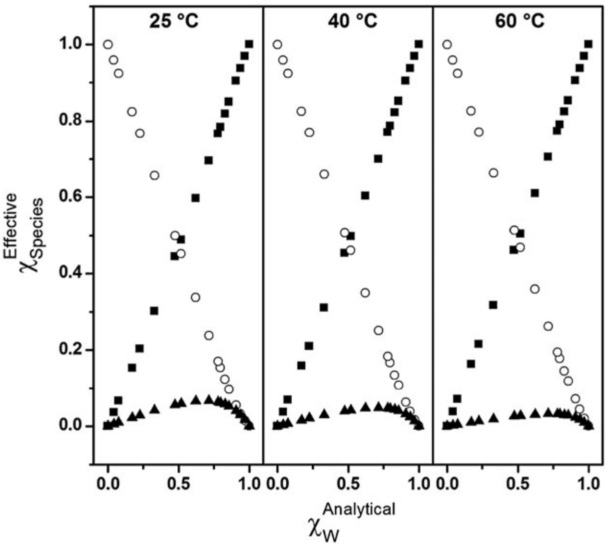


Fig. 4 Representative dependence of the concentrations of the species in the IL-W binary mixtures on temperature. The plots are for AlBuImCl, at 25, 40, and 60 °C, respectively; the symbols employed are ○, ■, ▲ for the IL, W, and the IL-W 1 : 1 complex, respectively.

between IL and W, as can be deduced below from the values of φ.

From the thermo-solvatochromic data, we have calculated the polynomial dependence of E_T(MePMBr$_2$) on the *analytical* mole fraction of water, in the temperature range from 10 to 60 °C; typical results (AlBuImCl) are listed in Table 1, along with the corresponding multiple correlation coefficients, r^2, and standard deviations (sd). The quality of the fit is evidenced by the values of these statistical parameters, and by the excellent agreement between calculated and experimental E_T(MePMBr$_2$)$_{\text{IL}}$, *at all temperatures*, see Table 1.

Fig. 5 shows the solvent polarity-temperature-solvent composition contours for the probe employed in the three IL-W mixtures in the temperature range studied; the results of the application of the above-discussed solvation model are listed in Table 2. For convenience, we have organized the data in the latter as a function of increasing the lipophilicity of the IL and included, at each temperature, our previous data on solvation of the same probe in aqueous PrOH.[11]

The following can be deduced from these data:

(i) The quality of fit of the above-discussed solvation model to our data is shown by values of (r^2) and Chi^2, and by the excellent agreement between experimental and calculated E_T(MePMBr$_2$)$_{\text{IL}}$ and E_T(MePMBr$_2$)$_{\text{W}}$, respectively, at different temperatures.

(ii) Values of (m) are close to unity, and decrease as a function of increasing temperature. Likewise, *all* values of E_T(MePMBr$_2$)$_{\text{IL}}$ and E_T(MePMBr$_2$)$_{\text{W}}$ decrease as a function of increasing temperature. This probe desolvation agrees with the known effect of temperature on the structure of molecular solvents, due to less efficient hydrogen-bonding and dipolar interactions,[20] and the fact that hydrogen-bonding is certainly more temperature dependent than Coulombic interactions;

(iii) Values of $\varphi_{\text{W/IL}}$ are much less than unity, *i.e.*, water is not efficient in displacing the IL from the probe solvation shell (*vide supra* the meaning of the magnitude of φ). It is plausible that the IL solvates the probe by a combination of several interaction mechanisms: hydrogen-bonding, especially that between the relatively acidic H2 of the imidazolium ring and the probe phenolate oxygen;[21] dipole–dipole interactions between its cation (AlRIm$^+$) and the phenolate oxygen, and its Cl$^-$ and the positively charged nitrogen; solvophobic interactions, because of the above-mentioned susceptibility of the solvation of this probe to medium lipophilicity;

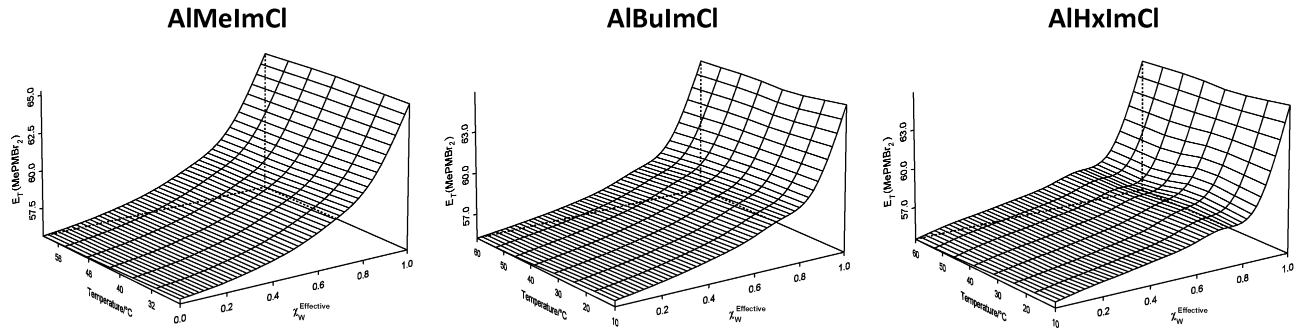


Fig. 5 Solvent polarity-temperature-solvent composition contours for MePMBr$_2$ in mixtures of water with AlMeImCl, AlBuImCl, and AlHxImCl, respectively.

Table 2 Analysis of thermo-solvatochromic responses of $MePMBr_2$ in IL-W mixtures, according to eqn (14) and (15)

Solvent	$T/°C$	m	$\varphi_{W/Solv}$	$\varphi_{Solv\text{-}W/Solv}$	$\varphi_{Solv\text{-}W/W}$	$E_T(MePMBr_2)_{Solv}$	$E_T(MePMBr_2)_W$	$E_T(MePMBr_2)_{Solv\text{-}W}$	r^2	Chi^2
AlBuImCl	10	0.998	0.066	1.486	22.398	55.66 [±0.03]	65.87 [±0.05]	60.61 [±0.08]	0.9998	0.0024
AlHxImCl		1.000	0.062	1.524	24.589	54.98 [±0.02]	65.87 [±0.03]	59.70 [±0.06]	0.9999	0.0012
1-Propanol[a]		1.580	0.211	71.138	337.147	55.45 [±0.06]	66.00 [±0.08]	59.76 [±0.11]	0.9995	0.0069
AlMeImCl	25	1.183	0.078	1.285	16.474	55.95 [±0.02]	65.26 [±0.05]	60.40 [±0.04]	0.9994	0.0015
AlBuImCl		0.973	0.075	1.428	19.040	55.54 [±0.07]	65.28 [±0.02]	61.56 [±0.03]	0.9995	0.0036
AlHxImCl		0.858	0.070	1.468	20.954	54.86 [±0.02]	65.27 [±0.03]	61.16 [±0.04]	0.9999	0.0006
1-Propanol[a]		1.359	0.215	32.546	151.377	54.95 [±0.08]	65.42 [±0.11]	59.68 [±0.25]	0.999	0.0133
AlMeImCl	40	1.091	0.087	1.182	13.586	55.77 [±0.05]	65.17 [±0.04]	60.74 [±0.05]	0.9989	0.0080
AlBuImCl		0.907	0.084	1.314	15.703	55.34 [±0.01]	65.16 [±0.02]	62.72 [±0.07]	0.9999	0.0006
AlHxImCl		0.711	0.078	1.358	17.383	54.68 [±0.01]	65.16 [±0.01]	61.42 [±0.03]	0.9999	0.0001
1-Propanol[a]		1.300	0.233	27.653	118.682	54.34 [±0.09]	65.21 [±0.12]	59.35 [±0.33]	0.999	0.0142
AlMeImCl	60	1.066	0.099	1.128	11.394	55.64 [±0.04]	64.83 [±0.05]	60.93 [±0.04]	0.9998	0.0024
AlBuImCl		0.917	0.095	1.254	13.195	55.24 [±0.02]	64.89 [±0.05]	62.10 [±0.05]	0.9997	0.0027
AlHxImCl		0.669	0.089	1.301	14.629	46.42 [±0.03]	57.50 [±0.05]	53.21 [±0.15]	0.9997	0.0022
1-Propanol[a]		1.110	0.239	13.105	54.833	53.70 [±0.10]	64.88 [±0.13]	59.60 [±0.70]	0.9989	0.0166

[a] Data taken from ref. 11.

(iv) All $\varphi_{IL\text{-}W/IL}$ and $\varphi_{IL\text{-}W/W}$ are > unity, indicating that all probes are preferentially solvated by IL-W than by the precursor solvents. Likewise, *all* $\varphi_{IL\text{-}W/W}$ are larger than the corresponding $\varphi_{IL\text{-}W/IL}$, indicating that IL-W is more efficient in displacing water than IL from the probe solvation shell. Whereas water solvates the probe by hydrogen-bonding to its phenolate oxygen;[21] hydrogen-bonding, dipole–dipole, and solvophobic interactions are operative for both IL and IL-W. The range of $\varphi_{IL\text{-}W/IL}$ calculated is not far from unity indicating, not unexpectedly, that dipolar- and solvophobic interactions represent important solvation mechanisms in ILs;

(v) The dependence of $E_T(MePMBr_2)$ on the lipophilic character of the medium is best discussed in terms of the effect of R on the deviations from linearity, in plots of $E_T(MePMBr_2)$ *versus* χ_W. For comparison, we have also included the corresponding plots for the same probe in aqueous PrOH, a solvent that is more hydrophobic that the ILs employed, *vide supra*. Fig. 6 shows these plots at three temperatures. To turn the comparison between ILs and PrOH possible, all $E_T(MePMBr_2)$ were converted into reduced scales, given by: $E_T(MePMBr_2)_{Reduced} = (E_T(MePMBr_2)_{solvent\ or\ binary\ mixture} - E_T(MePMBr_2)_{solvent})/(E_T(MePMBr_2)_W - E_T(MePMBr_2)_{solvent})$. As Fig. 6 shows, the deviation from linearity, hence preferential solvation, increases as a function of increasing the length of R. This is in agreement with the data of Table 2 where *at any temperature*, the order of both $\varphi_{IL\text{-}W/W}$ and $\varphi_{IL\text{-}W/IL}$ is: AlHxImCl > AlBuImCl > AlMeImCl. Note that increasing the length of R should have a negligible effect on the probe-IL dipolar interactions. The reason is that Hammett σ_{para} of alkyl groups are almost identical, *e.g.*, −0.17, −0.16, −0.15, for methyl, 1-butyl and 1-pentyl, respectively;[22] this leaves solvophobic interactions as the major discriminating mechanism. Equally important, the extent of deviation is clearly larger than that for solvation by aqueous PrOH, practically over the entire χ_W range. Therefore, the present data indicate that solvophobic interactions are important to solvation by aqueous ILs; its contribution is larger than in solvation by PrOH–W. More work is required, however, in order to validate the generality of this conclusion.

Conclusions

The thermo-solvatochromic data of $MePMBr_2$ in mixtures of water with three ILs has been studied and the data obtained were compared to those of the same probe in aqueous PrOH. The dependence of $E_T(MePMBr_2)$ on χ_W is nonlinear, similar to the dependence of other macroscopic properties on the composition of binary IL-W. Solvation by IL-W mixtures can be conveniently described by the same model that we have employed with aqueous organic solvents. The temperature effect on φ can be rationalized in terms of the structures of water and IL and their mutual interactions. Temperature increase results in a gradual desolvation of the probe, *i.e.*, decreased stabilization of its ground-state by W, IL, and IL-W. The dependence of the deviation from linearity of $E_T(MePMBr_2)$ *versus* χ_W plots on the length of R of the IL, and a comparison with the data of aqueous PrOH, indicate that solute–solvent solvophobic interactions may play a larger role in solvation by aqueous ILs.

Calculations

Calculation of the dissociation constant of IL-W, K_{dissoc}

Calculation of this constant from density data has been discussed in details elsewhere[8a,b] and will be addressed here only briefly. Knowledge of K_{dissoc} allows calculation of the effective mole fractions of all solvent species present. It is calculated from the dependence of binary mixture density (ρ_{mixt}, measured at 25, 35 and 45 °C, respectively) on its composition, as given by eqn (9) and (10) for IL/W mixtures:[23]

$$K_{dissoc} = \frac{[IL]_{Bk;\ Effective}[W]_{Bk;\ Effective}}{[IL\text{-}W]_{Bk;\ Effective}} \qquad (9)$$

$$\rho_{mixt} = \frac{[W]_{Bk;Effective}M_W + [IL]_{Bk;Effective}M_{IL} + [IL\text{-}W]_{Bk;Effective}M_{IL\text{-}W}}{[W]_{Bk;Effective}V_W + [IL]_{Bk;Effective}V_{IL} + [IL\text{-}W]_{Bk;Effective}V_{IL\text{-}W}} \qquad (10)$$

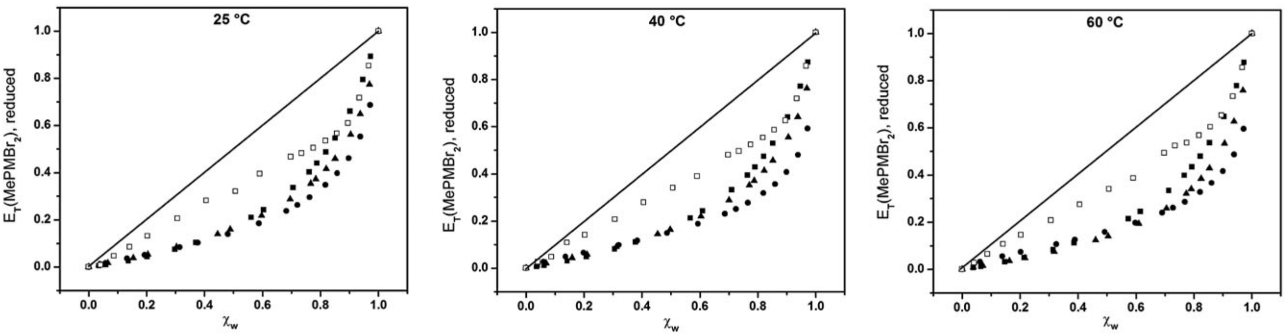


Fig. 6 Comparative thermo-solvatochromism of $\mathrm{MePMBr_2}$ in binary mixtures of W with ILs and with PrOH; the symbols employed are □, ■, ▲, ● for PrOH, AlMeImCl, AlBuImCl, AlHxImCl, respectively.

where M and V refer to molar mass and molar volume of the species, respectively. $V_{\text{IL-W}}$ can be calculated from eqn (10), by iteration. The values of K_{assoc} at different temperatures are listed in Table S2. As shown by eqn (11) to (13), van't Hoff equation applies satisfactorily to the dependence of K_{assoc} on temperature, and was employed in order to obtain K_{assoc} at temperatures other than those measured.

$$\ln K_{\text{assoc}} = -0.490 + 1269.611\ \mathrm{T}^{-1}\ (\mathrm{K}),\ r = -0.9996,\quad \mathrm{sd} = 0.0053 \qquad (11)$$

$$\ln K_{\text{assoc}} = -4.661 + 2388.870\ \mathrm{T}^{-1}\ (\mathrm{K}),\ r = -0.9985,\quad \mathrm{sd} = 0.0147 \qquad (12)$$

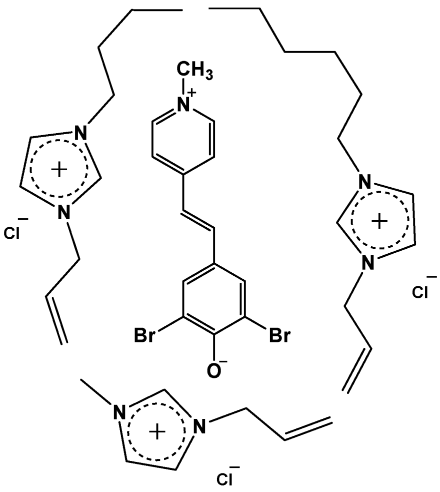
$$\ln K_{\text{assoc}} = -5.731 + 2641.625\ \mathrm{T}^{-1}\ (\mathrm{K}),\ r = -0.9999,\quad \mathrm{sd} = 0.0018 \qquad (13)$$

Calculation of the fractionation factors

The probe solvation shell is composed of W, IL, and IL-W. Observed E_{T}, $E_{\mathrm{T}}^{\mathrm{Obs}}$, is the sum of the polarity of each component, $E_{\mathrm{T}}^{\mathrm{W}}$, $E_{\mathrm{T}}^{\mathrm{IL}}$, $E_{\mathrm{T}}^{\mathrm{IL\text{-}W}}$, respectively, multiplied by the corresponding mole fraction in the probe solvation shell, $x_{\mathrm{w}}^{\mathrm{Probe}}$, $X_{\mathrm{IL}}^{\mathrm{Probe}}$, and $X_{\mathrm{IL\text{-}w}}^{\mathrm{Probe}}$, respectively:

$$E_{\mathrm{T}}^{\mathrm{Obs}} = x_{\mathrm{w}}^{\mathrm{Probe}} E_{\mathrm{T}}^{\mathrm{W}} + x_{\mathrm{IL}}^{\mathrm{Probe}} E_{\mathrm{T}}^{\mathrm{IL}} + x_{\mathrm{IL\text{-}W}}^{\mathrm{Probe}} E_{\mathrm{T}}^{\mathrm{IL\text{-}W}} \qquad (14)$$

Eqn (14) and (15) can then be solved to get $E_{\mathrm{T}}^{\mathrm{IL\text{-}W}}$, and the appropriate solvent fractionation factors, respectively.



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$$\mathrm{E_T^{Obs}} = \frac{(x_{\mathrm{IL}}^{\text{Bk; Effective}})^{\mathrm{m}}\,\mathrm{E_T^{IL}} + \varphi_{\mathrm{W/IL}}(x_{\mathrm{W}}^{\text{Bk; Effective}})^{\mathrm{m}}\,\mathrm{E_T^{W}} + \varphi_{\mathrm{IL\text{-}W/IL}}(x_{\mathrm{IL\text{-}W}}^{\text{Bk; Effective}})^{\mathrm{m}}\,\mathrm{E_T^{IL\text{-}W}}}{(x_{\mathrm{IL}}^{\text{Bk; Effective}})^{\mathrm{m}} + \varphi_{\mathrm{W/IL}}(x_{\mathrm{W}}^{\text{Bk; Effective}})^{\mathrm{m}} + \varphi_{\mathrm{IL\text{-}W/IL}}(x_{\mathrm{IL\text{-}W}}^{\text{Bk; Effective}})^{\mathrm{m}}} \qquad (15)$$

The input data to solve eqn (15) include $E_{\mathrm{T}}^{\mathrm{Obs}}$, $E_{\mathrm{T}}^{\mathrm{W}}$, $E_{\mathrm{T}}^{\mathrm{IL}}$, and $x_{\text{Species}}^{\text{Effective}}$, along with initial guesses for (m), $E_{\mathrm{T}}^{\mathrm{IL\text{-}W}}$, and the different φ. The fractionation factor $\varphi_{\mathrm{IL\text{-}W/W}}$ is obtained by dividing $\varphi_{\mathrm{IL\text{-}W/IL}}$ by $\varphi_{\mathrm{W/IL}}$. VThe values of $E_{\mathrm{T}}^{\mathrm{Obs}}$ were calculated by iteration until the sum of the squares of the residuals was not reduced; calculations were carried out by employing a commercial software (Origin version 6.0, Microcal).

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