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PAPER

Solvation in aqueous binary mixtures: consequences of the hydrophobic character of the ionic liquids and the solvatochromic probes†

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Information on the solvation in mixtures of water, W, and the ionic liquids, ILs, 1-allyl-3-R-imidazolium chlorides; R = methyl, 1-butyl, and 1-hexyl, has been obtained from the responses of the following solvatochromic probes: 2,6-dibromo-4-[(E)-2-(1-R-pyridinium-4-yl)ethenyl] phenolate, R = methyl, MePMBr₂; 1-octyl, OcPMBr₂, and the corresponding quinolinium derivative, MeQMBr₂. A model developed for solvation in binary mixtures of W and molecular solvents has been extended to the present mixtures. Our objective is to assess the relevance to solvation of hydrogen-bonding and the hydrophobic character of the IL and the solvatochromic probe. Plots of the medium empirical polarity, $E_T(\text{probe})$ versus its composition revealed non-ideal behavior, attributed to preferential solvation by the IL and, more efficiently, by the IL–W hydrogen-bonded complex. The deviation from linearity increases as a function of increasing number of carbon atoms in the alkyl group of the IL, and is larger than that observed for solvation by W plus molecular solvents (1-propanol and 2-(1-butoxy)ethanol) that are more hydrophobic than the ILs investigated. This enhanced deviation is attributed to the more organized structure of the ILs proper, which persists in their aqueous solutions. MeQMBr₂ is more susceptible to solvent lipophilicity than OcPMBr₂, although the former probe is less lipophilic. This enhanced susceptibility agrees with the important effect of annelation on the contributions of the quinonoid and zwitterionic limiting structures to the ground and excited states of the probe, hence on its response to both medium composition and lipophilicity of the IL.

Introduction

Interest in investigating the properties and applications of ionic liquids, ILs, in many fields of science and technology is intense because these solvents conform to several principles of green chemistry.^{1–3} Briefly, these call for an increase in, and/or upgrading of atom economy; process efficiency and safety, and environmental compatibility.⁴ This approach calls for a thorough understanding of the roles of all components of the chemical process, including *the solvent or solvent mixture* employed. Mixtures of ILs with other solvents such as water are of great interest for several reasons. Water is the “greenest” solvent; its adventitious presence influences the properties/performance of ILs, sometimes dramatically, with consequences for reactions that are carried out therein.^{5–7} Therefore it is important to understand the properties of these mixtures, in particular the solvation, at the molecular level.^{8–12}

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, micellar solution, *etc.* The energy of the intra-molecular, solvent-sensitive charge-transfer, $E_T(\text{probe})$, is given as:

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

where λ_{max} is the wavelength maximum of the intra-molecular charge-transfer band. Values of $E_T(\text{probe})$ are then rationalized in terms of non-specific and specific probe–solvent interactions, including hydrogen-bonding, solvophobic, dipolar, and dispersion.^{13a–c}

Solvatochromism in binary solvent mixtures is complex because it involves interactions between the component solvents, and between the probe and each one of these. Additionally, the physico-chemical properties, *e.g.*, density, viscosity, relative permittivity, ϵ_r , *etc.*, of these mixtures are not simple, *i.e.*, not linear functions of composition, due to the interactions of their components. By using probes whose molecular structure has been varied in a systematic manner, we have explained solvatochromism in binary mixtures of water (W) and molecular

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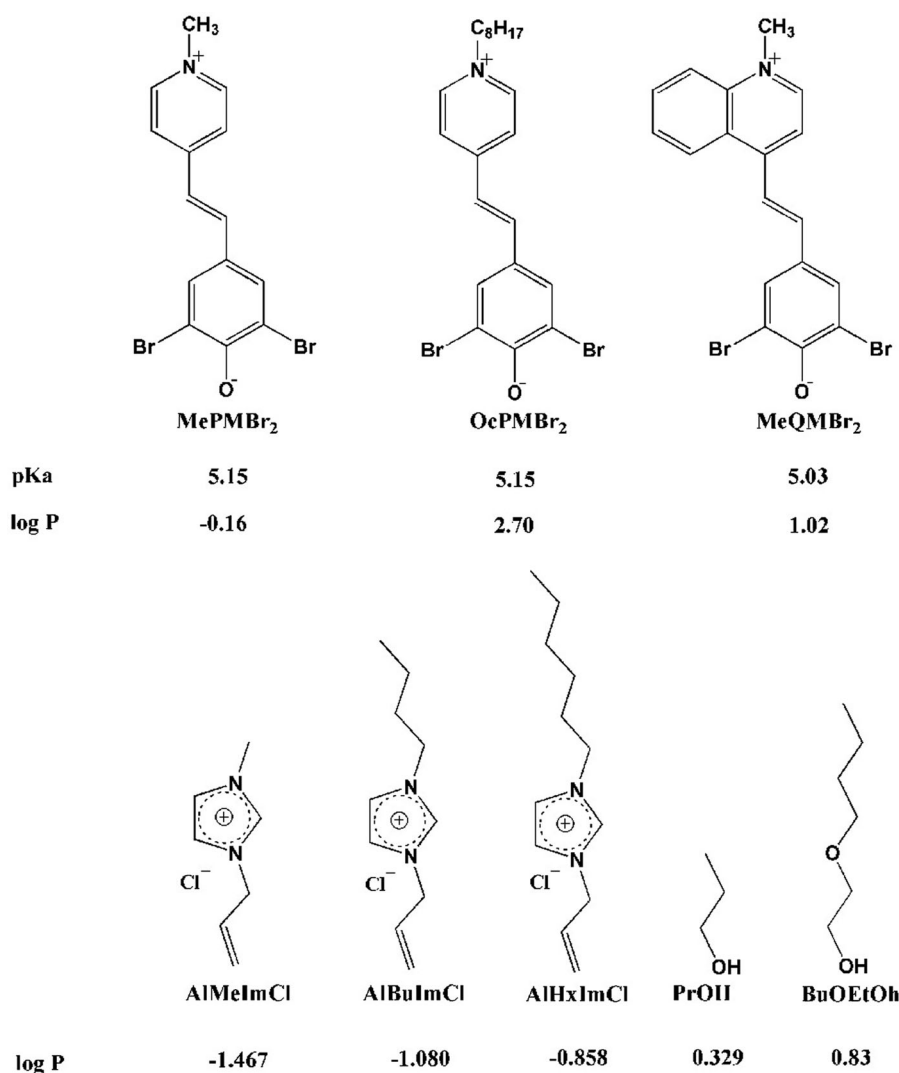


Fig. 1 Molecular structures and, where applicable, pK_a in water, and $\log P$ of the solvatochromic probes, the ionic liquids, and the molecular solvents employed in the present study.

solvents, by employing a solvation model that takes into account solvent–solvent interactions, in particular hydrogen-bonding.¹⁴

Recently, we have studied the thermo-solvatochromism (effect of temperature, T , on solvatochromism) of the probe 2,6-dibromo-4-[(*E*)-2-(1-methylpyridinium-4-yl)ethenyl] phenolate, MePMBr₂, in binary mixtures of W and ILs of increasing hydrophobic character, namely, 1-alkyl-3-alkylimidazolium chlorides, where the saturated alkyl groups are methyl (AlMeImCl), 1-butyl (AlBuImCl), and 1-hexyl (AlHxImCl), respectively.⁹ A convenient empirical scale for hydrophobicity is $\log P$, defined as the partition coefficient of a substrate between water and 1-octanol, both mutually saturated ($\log P = [\text{substrate}]_{1\text{-octanol}}/[\text{substrate}]_{\text{water}}$); positive values of $\log P$ indicate hydrophobic substances.¹⁵ In order to probe further the problem of solvophobic interactions, we have extended our study to the solvation of two additional probes, 2,6-dibromo-4-[(*E*)-2-(1-*n*-octylpyridinium-4-yl)ethenyl] phenolate, OcPMBr₂, and 2,6-dibromo-4-[(*E*)-2-(1-methylquinolinium-4-yl)ethenyl] phenolate MeQMBr₂ in mixtures of water with the above-mentioned ILs. Fig. 1 shows the molecular structures and properties of the probes and solvents employed.

The use of these probes permits determination of the effects of increasing both probe- and solvent hydrophobicity on solvation in binary mixtures. As shown in Fig. 1, this increase in $\log P$ can be achieved either by increasing the chain-length of the IL alkyl group (MePMBr₂ → OcPMBr₂), or by annelation of the probe (MePMBr₂ → MeQMBr₂).

The solvatochromic data obtained, at 25 °C, have been successfully treated according to the model that we have previously employed for mixtures of W with molecular solvents, *i.e.*, by considering that the binary mixture is composed of the two precursor solvents (W and IL) plus the hydrogen-bonded species IL–W. Our data have indicated that the probes are preferentially solvated by the ILs and, more efficiently by the “complex” solvents IL–W. A comparison with solvation of the same probes by W plus two molecular solvents that are more hydrophobic than the ILs, 1-propanol, PrOH, and 2-(1-butoxy)ethanol, BuOEtOH, has shown that the solvophobic interactions in the aqueous ILs are stronger. This is attributed to the network structures of the ILs; these probably persist in the binary mixtures.

Results and discussion

Note: details of all calculations performed are given in ESI.†

Comments on the molecular structures of the probes, the ILs, and the molecular solvents employed

An extensively investigated 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 $E_T(30)$.^{13c} Our previous data have shown that the scales $E_T(\text{MePMBR}_2)$ or $E_T(\text{OcPMBR}_2)$ correlate linearly with $E_T(30)$; 34 protic and aprotic solvents, correlation coefficients, $r = 0.9685$ and 0.9691 for MePMBR_2 , and OcPMBR_2 , respectively.¹⁸ On the other hand, $E_T(\text{MeQMBR}_2)$ correlates with $E_T(30)$ by a second-degree polynomial; 38 solvents, multiple correlation coefficient $r^2 = 0.9626$. This non-linear correlation has been attributed to variable, *i.e.*, solvent-dependent contributions of the two limiting structures (zwitterionic and quinonoid, see Fig. 2) to the ground and excited states of the probe. This is due to the effect of annelation, *i.e.*, the fusion of benzene and pyridine rings.

The study of these three probes in the binary solvent mixtures serves, therefore, to investigate: (1) effects of increasing the hydrophobic character of the probe, for the same W–IL mixtures. Note that $\log P$ of the probes are changed by two distinct structural modifications, namely: an increase in the length of the alkyl chain from methyl to 1-octyl, while keeping the energy of the intra-molecular charge-transfer essentially constant; annelation of the probe; (2) effects of increasing $\log P$ of the IL, for the same probe; (3) evaluation of solvophobic interactions in IL–W mixtures, as compared with those of molecular solvent–W mixtures. Note that PrOH is the longest straight-chain aliphatic alcohol that is miscible with water over the whole composition range. BuOEtOH has several peculiar properties: its bi-functional molecular structure leads to the formation of several inter- as well as intra-molecular H-bonded species;¹⁹ it behaves as a short-chain non-ionic surfactant; several physical properties of its aqueous solution show a sudden variation at $\chi_{\text{BuOEtOH}} \approx 0.05$ (χ refers to mole fraction);

the homogeneous aqueous solution phase separates at *ca.* 49°C .^{20,21} Thus, binary mixtures of this solvent with water are expected to affect the solvatochromic behavior of the probes *noticeably* due to a combination of: efficient probe–solvent hydrogen-bonding (probe phenolate oxygen and BuOEtOH) and dipolar interactions (probe quaternary nitrogen and BuOEtOH); hydrophobic interactions (this solvent has the largest $\log P$, see Fig. 1), and the extensive micro-heterogeneity of its mixtures with water.

A brief description of the model for treating solvation data in binary solvent mixtures

As will be shown below, solvation in S–W binary mixtures (S is a general solvent, *IL*, or *molecular solvent*) is not ideal, due to the so-called “preferential solvation”. This term describes the fact that the compositions of the probe solvation shell and bulk solvent differ due to several factors and/or solute–solvent interaction mechanisms. For mixtures of molecular solvents and water we have applied a solvation model that rests on treating the binary solvent mixture as composed of S, W plus the hydrogen-bonded complex solvent S–W. The 1 : 1 stoichiometry is a working assumption that is based on IR and NMR data,^{22a–c} and theoretical calculations.^{23a–c} It describes satisfactorily the solvatochromic responses of the probes employed in a large number of binary mixtures of W with alcohols and 2-alkoxyethanols, in the temperature range, where feasible, from 15 to 55°C .¹⁴ We would like to extend the applicability of this model to solvation by ILs–W. Details of this model are explained in ESI†, so that we outline here only the essential details. Based on this model, three species compete for the solvation of the probe, namely W, S, and S–W. Therefore, solvent-exchange equilibria in the solvation shell of the probe are described by three equations. The resulting equilibrium constants are termed solvent “fractionation factors”, ϕ . There are three such factors, $\phi_{\text{W/S}}$ (water displacing solvent in the solvation shell of the probe); $\phi_{\text{S–W/S}}$ and $\phi_{\text{S–W/W}}$ for complex solvent displacing the solvent, or water, respectively. These fractionation factors are based on the *effective, not analytical*

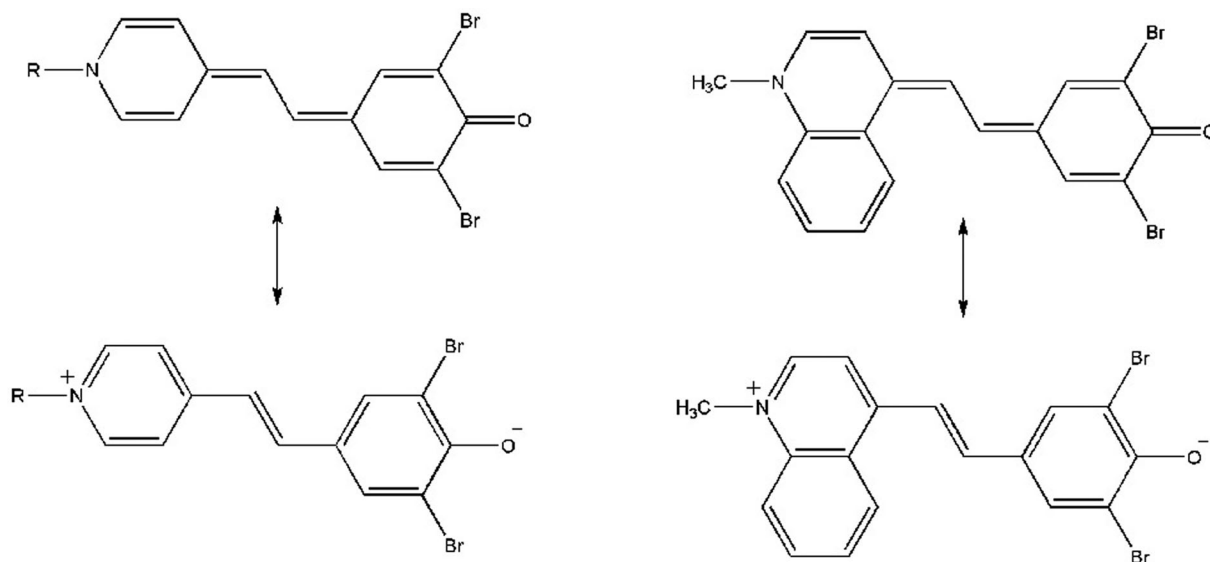


Fig. 2 The two limiting structures (zwitterionic and quinonoid) for the pyridine- and quinoline-based probes respectively.

concentrations of the solvent species present. Concentrations of the latter are calculated from the association constants of S–W. Values of these are obtained from accurate measurements of the densities of the pure solvents and their mixtures (16 binary mixtures are employed). Fig. S1 (ESI†) shows the distribution of the three solvent species.⁹ The efficiency of probe solvation by S, W, and S–W is then deduced from the value of the discrete φ , relative to unity. By definition, $\varphi = 1$ means an ideal solvation, *i.e.*, the probe solvation shell has the same composition as that of bulk binary solvent. As shown below, this result is not obtained in the present- or, in fact, in any of our previous studies on solvatochromism.^{8,14} Alternatively, $\varphi_{W/S} > 1$ means that the shell is richer in W than the bulk mixture, *i.e.*, the probe is preferentially solvated by water. The converse holds for $\varphi_{W/S} < 1$, *i.e.*, the probe is preferentially solvated by S. The same line of reasoning applies to $\varphi_{S-W/S}$ (complex solvent substitutes S) and $\varphi_{S-W/W}$ (complex solvent substitutes W).

Solvatochromism in binary mixtures of water with the solvents studied

Fig. 3 shows the solvatochromic responses of MePMBBr₂, OcPMBBr₂, MeQMBr₂ in mixtures of water with (S) as a function of the analytical mole fraction of water, χ_W , at 25 °C. The non-linear response is attributed to non-ideal solvation, due to several factors and/or solute–solvent interaction mechanisms. For example, enrichment of the probe solvation shell in the solvent of higher relative permittivity, ϵ_r , leads to “dielectric enrichment”, consequently to non-ideal behavior.²⁴ This is not the case because ϵ_r of water is larger than the corresponding values for the ILs,²⁵ and the molecular solvents studied.²⁶ If dielectric enrichment was operative, all curves of Fig. 3 should have been located above, not below the straight line that connects the polarities of (W) and (S). A more fundamental reason for non-ideal behavior

is preferential solvation of the probe by components of the mixture, due to solute–solvent specific and non-specific interactions, *e.g.*, hydrogen-bonding, dipole–dipole, and solvophobic interactions. As discussed elsewhere,¹⁴ most binary S–W mixtures are micro-heterogeneous; there exists the possibility of preferential solvation of the probe by the less polar micro-domains, *e.g.*, S–W, leading to below-the-line deviation, as shown in Fig. 3. In summary, non-ideal solvation behavior is not unexpected.

The discussion below is organized in the following order: we list the (polynomial) dependence of $E_T(\text{probe})$ on χ_W ; we show the dependence of the discrete fractionation factors on the molecular structures of the probe and S; we discuss this dependence as a function of deviation of the results from the linear behavior, *i.e.*, ideal solvation by the binary mixture.

Rather than giving extensive lists of $E_T(\text{probe})$ versus the analytical χ_W , we have calculated the corresponding polynomial correlations; the results are listed in Table 1, along with the resulting r^2 and the standard deviation (sd). The plots shown in Fig. 3 are complex, requiring the use of polynomial of the 6th power or even higher (see footnotes c and d of Table 1). *The reason for employing high order polynomials is that the best data fit was sought; this permits the reader to calculate $E_T(\text{probe})$ accurately at any medium composition.* The quality of the fit is evidenced by the values of r^2 and sd, and by the excellent agreement between calculated and experimental $E_T(\text{probe})_{\text{IL}}$, see Table 1.

Based on these results, and the *effective* mole fraction of the solvent species present, we have calculated the discrete solvent fractionation factors; these are listed in Table 2. Comparison of the solvatochromic responses as functions of the molecular structures of the probes and the solvent is simplified by: employing a reduced polarity scale $E_T(\text{probe})^r$, defined by eqn (2); calculation of the reduced deviations from the ideal

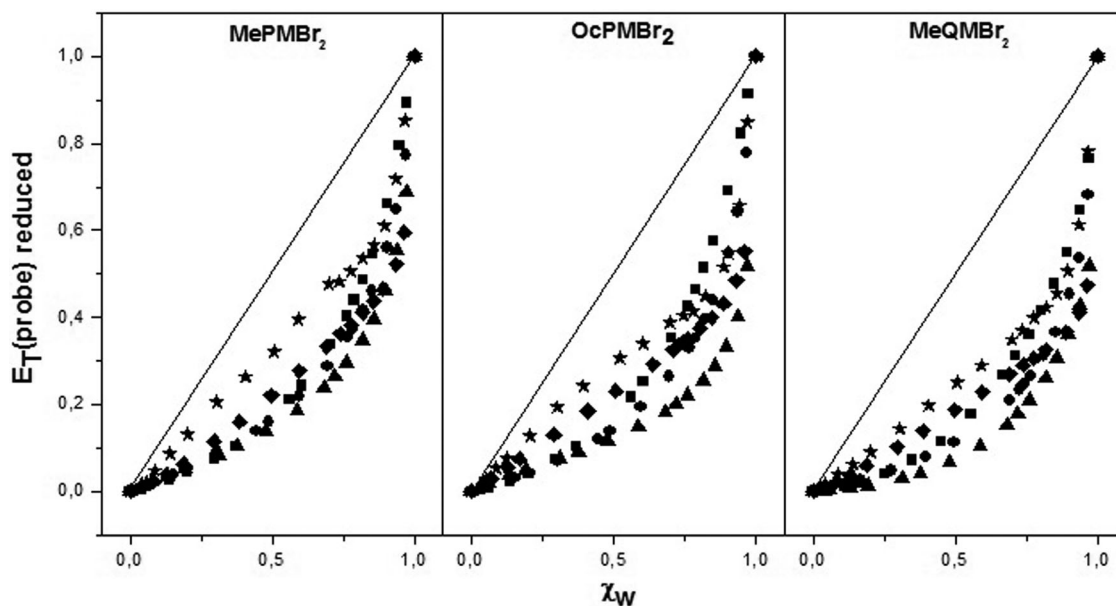


Fig. 3 Comparative solvatochromic response of MePMBBr₂, OcPMBBr₂ and MeQMBr₂ in binary mixtures of W with ILs, and the molecular solvents PrOH and BuOEtOH. The symbols employed are: ★, ◆, ■, ●, ▲ for PrOH, BuOEtOH, AlMeImCl, AlBuImCl, AlHxImCl, respectively. The straight lines that connect the polarities of the pure solvents were plotted to guide the eye, they represent ideal solvation of the probe by the binary mixture, see text for details.

Table 1 Solvatochromic data of probes in binary solvent mixtures. The polynomial dependence of $E_T(\text{probe})$ on the analytical mole fraction of water in the binary mixture, $\chi_w^{\text{Analytical}}$, has been calculated using the equation: $E_T(\text{probe}) = E_T(\text{probe})_{\text{IL}} + B(\chi_w) + C(\chi_w)^2 + D(\chi_w)^3 + E(\chi_w)^4 + F(\chi_w)^5 + G(\chi_w)^6$

IL	Probe	$E_T(\text{probe})_{\text{IL}}^b$	B	C	D	E	F	G	r^{2c}	sd ^c
AlMeImCl	MePMBR ₂	55.95 [-0.02]	0.86	9.60	-34.34	87.84	-101.69	47.06	0.9999	0.0035
	OcPMBR ₂	55.34 [-0.03]	1.48	-1.87	26.06	-46.52	35.06	-4.86	0.9982	0.1550
	MeQMBR ₂	47.72 [0.16]	-6.94	110.07	-524.67	1160.13	-1164.36	436.43	0.9972	0.3401
AlBuImCl	MePMBR ₂	55.60 [0.11]	-2.83	71.99	-355.99	803.34	-823.75	316.76	0.9999	0.0095
	OcPMBR ₂	55.01 [0.20]	-6.30	121.53	-604.41	1353.57	-1378.88	524.81	0.9945	0.5191
	MeQMBR ₂	47.19 [0.21]	-7.98	136.00	-673.53	1506.36	-1535.62	585.87	0.9941	0.6441
AlHxImCl ^d	MePMBR ₂	54.64 [0.03]	-2.99	212.11	-2131.40	9799.97	-23682.65	31154.42	0.9957	0.3078
	OcPMBR ₂	54.27 [0.05]	-10.50	385.87	-3785.88	17224.32	-41380.34	54199.45	0.9826	0.9890
	MeQMBR ₂	46.62 [0.05]	-11.79	390.38	-3759.81	17007.55	-40758.08	53328.94	0.9890	0.8999
BuOEtOH ^e	MePMBR ₂	55.08 [0.01]	-9.92	319.25	-2863.56	12629.16	-29945.77	39012.37	0.9957	0.3062
	OcPMBR ₂	53.36 [0.02]	-8.95	342.59	-3099.13	13603.16	-32141.20	41800.56	0.9949	0.3535
	MeQMBR ₂	46.17 [0.05]	-17.30	516.68	-4690.49	20698.31	-49033.58	63787.20	0.9872	0.9527

^a The data for PrOH are reported in ref. 18. ^b The values inside the brackets refer to $E_T(\text{probe})_{\text{IL}} - E_T(\text{probe})_{\text{IL}}^{\text{exp}}$. ^c The symbols r^2 and sd refer to the correlation coefficient and standard deviation, respectively. ^d A superior data fit for AlHxImCl is achieved by using the following 8th power polynomial equation $E_T(\text{probe}) = E_T(\text{probe})_{\text{IL}} + B(\chi_w) + C(\chi_w)^2 + D(\chi_w)^3 + E(\chi_w)^4 + F(\chi_w)^5 + G(\chi_w)^6 + H(\chi_w)^7 + I(\chi_w)^8$. For MePMBR₂ the H and I coefficients are, respectively, -21109.30 and 5770.29. For OcPMBR₂, the H and I coefficients are, respectively, -36588.20 and 9965.37; for MeQMBR₂ the H and I coefficients are, respectively, -35989.82 and 9804.32. ^e A superior data fit for BuOEtOH is achieved by using 8th polynomial equation $E_T(\text{probe}) = E_T(\text{probe})_{\text{IL}} + B(\chi_w) + C(\chi_w)^2 + D(\chi_w)^3 + E(\chi_w)^4 + F(\chi_w)^5 + G(\chi_w)^6 + H(\chi_w)^7 + I(\chi_w)^8$. For MePMBR₂ the H and I coefficients are, respectively, -26304.49 and 7173.75. For OcPMBR₂ the H and I coefficients are, respectively, -28172.18 and 7686.34; for MeQMBR₂ the H and I coefficients are -42931.11 and 11682.53, respectively.

Table 2 Analysis of the solvatochromic responses of MePMBR₂, OcPMBR₂, and MeQMBR₂, respectively, in mixtures of water with ILs, 1-PrOH; BuOEtOH^a

Probe	m	$\phi_{(w/s)}$	$\phi_{(s-w/s)}$	$\phi_{(s-w/w)}$	AlMeImCl			r^2	χ^2
					$E_T(\text{probe})_S$	$E_T(\text{probe})_W$	$E_T(\text{probe})_{S-W}$		
MePMBR ₂	1.183	0.078	1.285	16.474	55.95 [±0.03]	65.26 [±0.04]	60.40 [±2.12]	0.9990	0.0117
OcPMBR ₂	1.249	0.072	1.360	18.889	55.35 [±0.11]	64.64 [±0.03]	60.26 [±1.62]	0.9997	0.0008
MeQMBR ₂	1.205	0.040	1.120	28.000	47.47 [±0.10]	58.52 [±0.15]	54.68 [±3.21]	0.9998	0.0023
AlBuImCl									
MePMBR ₂	0.973	0.075	1.428	19.040	55.54 [±0.10]	65.28 [±0.15]	61.56 [±0.12]	0.9997	0.0048
OcPMBR ₂	0.943	0.071	1.529	21.535	54.91 [±0.10]	65.63 [±0.15]	60.02 [±0.42]	0.9996	0.0038
MeQMBR ₂	1.032	0.036	1.330	36.940	47.09 [±0.03]	58.62 [±0.04]	53.54 [±1.41]	0.9998	0.0019
AlHxImCl									
MePMBR ₂	0.801	0.072	1.511	20.986	54.61 [±0.14]	65.23 [±0.17]	61.74 [±1.08]	0.9997	0.0092
OcPMBR ₂	0.759	0.069	1.621	23.493	54.22 [±0.03]	64.65 [±0.03]	57.37 [±0.42]	0.9999	0.0011
MeQMBR ₂	0.902	0.032	1.574	49.187	46.57 [±0.01]	58.56 [±0.20]	52.78 [±0.52]	0.9999	0.0007
PrOH ^a									
MePMBR ₂	1.359	0.215	32.546	151.377	54.95 [±0.08]	65.42 [±0.11]	59.68 [±0.25]	0.9990	0.0133
OcPMBR ₂	1.618	0.200	98.820	494.100	54.54 [±0.07]	64.71 [±0.09]	58.00 [±0.13]	0.9992	0.0093
MeQMBR ₂	1.594	0.144	53.580	372.083	47.44 [±0.07]	57.80 [±0.10]	51.08 [±0.19]	0.9992	0.0103
BuOEtOH									
MePMBR ₂	1.100	0.121	34.505	285.165	54.87 [±0.02]	65.27 [±0.03]	59.62 [±0.13]	0.9999	0.0009
OcPMBR ₂	1.073	0.085	36.292	426.965	53.34 [±0.06]	64.64 [±0.07]	58.04 [±0.29]	0.9996	0.0045
MeQMBR ₂	1.181	0.076	42.433	558.329	46.85 [±0.02]	58.63 [±0.03]	50.24 [±0.09]	0.9999	0.0010

^a Data taken from ref. 18.

behavior over the entire χ_w range, by using eqn (3). Regarding the latter, it is worthwhile to note: the scales of $E_T(\text{probe})^f$ and χ_w are both between 0 and 1. If solvation was ideal, the correlation between both quantities should have been a straight line, going through the points 0 and 1 with a slope of unity. Under these conditions, the values of any $E_T(\text{probe})^f =$ the corresponding χ_w . Therefore eqn (3) describes the deviation of probe solvation from ideal solvation.

The results calculated are shown in Fig. 4, and Table 3, the latter shows the reduced deviations at an arbitrarily fixed $\chi_w = 0.80$.

$$E_T(\text{probe})^f = (E_T(S-W) - E_T(S))/(E_T(W) - E_T(S)) \quad (2)$$

$$(\text{Deviation})^f = \chi_w - E_T(\text{probe})^f \quad (3)$$

With regard to these results, the following are relevant (in Table 2, for brevity, we have referred to the non-aqueous component of the binary mixture by S. In the ensuing discussion we use, *where convenient for the sake of clarity*, IL and ROH, for the ionic liquid and the protic component, respectively):

(i) The quality of fit of the above-discussed solvation model to our data is shown by the values of r^2 and χ^2 , and by the excellent agreement between experimental and calculated $E_T(\text{probe})_S$ and $E_T(\text{probe})_W$, respectively, see Table 2. Thus the S-W 1 : 1 assumption seems to be a general one, covering solvation by mixtures of water with ILs or molecular solvents.

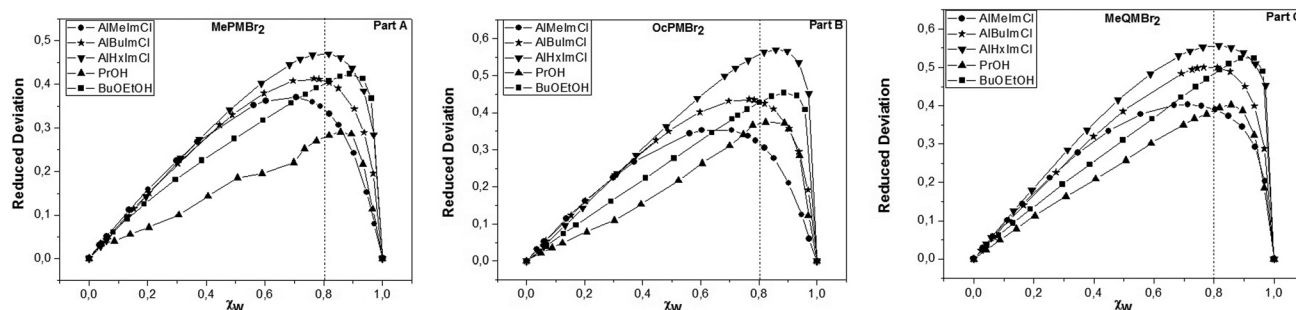


Fig. 4 Reduced deviations from linearity of the solvatochromic response curve of the probes employed as a function of the mole fraction of water, χ_w , at 25 °C. Part (A), (B), and (C), respectively, show the deviation of MePMBr₂, OcPMBr₂, and MeQMBr₂.

Table 3 Reduced deviations from linearity of the solvatochromic response of MePMBr₂, OcPMBr₂, and MeQMBr₂ as a function of the analytical mole fraction of water χ_w in its binary mixtures with the solvents employed, at $\chi_w = 0.80$

Probe/solvent	AlMeImCl	AlBuImCl	AlHxImCl	PrOH	BuOEtOH
Deviation of $E_T(\text{probe})^f$ from linearity					
MePMBr ₂	0.34	0.41	0.47	0.28	0.40
OcPMBr ₂	0.32	0.43	0.56	0.37	0.43
MeQMBr ₂	0.39	0.50	0.56	0.39	0.48

(ii) In agreement with our previous results of solvation by aqueous molecular solvents, the calculated values of (m) are between 1 and 2.¹⁴ This parameter refers to the number of solvent molecules that perturb the intra-molecular charge transfer within the probe; it should not be confused with the total number of solvent molecules that solvate the probe. Recent results, including X-ray diffraction of complexes of aliphatic alcohols (methanol to 1-butanol) with RB and several structurally related probes,^{27a} and molecular dynamics simulations on the solvation of the probe 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl) phenolate in ethanol,^{27b} have shown the formation of a 1:1 probe–alcohol complex, in agreement with the values of (m) shown in Table 2.

(iii) Values of $\phi_{W/IL}$ are much less than unity, *i.e.*, water is not efficient in displacing the IL from the probe solvation sphere (*vide supra* the meaning of the magnitude of ϕ). It is plausible that the IL solvates the probe by a combination of hydrogen-bonding, especially that between the relatively acidic C2-*H* of the imidazolium ring and the probe phenolate oxygen;^{28,29} the Cl[−] and the probe positively charged nitrogen, as well as solvophobic interactions, *vide infra*.

(iv) All $\phi_{IL-W/IL}$ and $\phi_{IL-W/W}$ are greater than unity, indicating that all probes are more efficiently solvated by IL–W than by the precursor solvents. Additionally, all $\phi_{IL-W/W}$ are larger than the corresponding $\phi_{IL-W/IL}$ indicating, in agreement with the small values of $\phi_{W/IL}$, that IL–W is more efficient in displacing water than IL from the probe solvation shell. Whereas water solvates the probe by a single mechanism (hydrogen-bonding to the phenolate oxygen);²⁸ hydrogen-bonding, dipole–dipole, and solvophobic interactions are operative for both IL and IL–W.

(v) In contrast to solvation by aqueous molecular solvents, see Table 2 and other published data,^{9,14} the range of $\phi_{IL-W/IL}$ calculated is not far from unity. This indicates that solvation by IL–W is dominated by the IL component, in part because

of the above-mentioned efficient hydrogen bonding and dipolar interactions with the imidazolium moiety.

(vi) The dependence of the solvatochromic data on the molecular structure of the probe and (S) can be best addressed by discussing: (a) the same probe in different solvents; (b) the discrete probes in the same solvent. This discussion is based on the nature of probe–IL interactions, including: weak hydrogen bonding between the CH₂ groups of the IL side chain and the π -electron system of the probe;³⁰ electrostatic interactions between the IL cation and the probe π -electron system, as indicated from the data of solubilization of aromatic compounds in ILs,³¹ and neutron scattering studies on benzene–IL binary mixtures;³² the interactions of the ions of the IL with each other and with water, as revealed by calorimetric studies of IL–water mixtures.³³

An example of point (a) above is the dependence of both $\phi_{(IL-W/IL)}$ and $\phi_{(IL-W/W)}$ for OcPMBr₂ on the hydrophobicity of the IL. Upon increasing the length of the attached alkyl group (methyl → 1-butyl → 1-hexyl) these values increase in the order of (1.360 → 1.529 → 1.621; $\phi_{(IL-W/IL)}$) and (18.889 → 21.535 → 23.493; $\phi_{(IL-W/W)}$). A similar trend is shown in Fig. 4 and Table 3, where the deviation from linearity increases in the order: 0.32 → 0.34 → 0.56 in the same direction. Because Hammett σ_{para} of alkyl groups are similar, *e.g.*, −0.17, −0.16, −0.15, for methyl, 1-butyl and 1-hexyl, respectively,³⁴ these groups are not expected to change the acidity of the imidazolium ring hydrogens differently, in particular its C2-*H*. That is, the dependence of the solvatochromic response of the same probe in different aqueous ILs reflects the increasing importance of probe–IL solvophobic interactions. In this regard, it is noteworthy that most of the reported deviations from linearity in Fig. 4 are larger for the IL–W mixtures than for the molecular solvents, although the latter are more lipophilic, as shown by the corresponding log *P*, see Fig. 1. The reason is linked to the fact that the pure ILs are more structured, with the chloride ion linked to several imidazolium rings, *via* their relatively acidic hydrogens, in particular C2-*H*.^{35–38} Several pieces of evidence, *e.g.*, NMR,^{39–41} and molecular dynamics simulations,⁴² have indicated that ILs in water, even the ones with short alkyl-chains, form organized structures over the entire χ_w range. This structuring leads to relatively efficient solvophobic interactions between the probe and the alkyl groups of the IL. Our data indicate that this structuring is more relevant to solvophobic interactions than log *P* of molecular solvents. As discussed above, BuOEtOH

tends to form aggregates in water, leading to stronger probe solvophobic interactions than those in aqueous PrOH. This expectation agrees with the results shown in Table 3 and Fig. 4. Thus, for each probe, the deviations from linearity and the values of $\varphi_{(S-W/W)}$ follow the order: BuOEtOH > PrOH. Except for a single case, MePMBR₂, the values of $\varphi_{(ROH-W/ROH)}$ show the inverse order (PrOH > BuOEtOH), indicating that it is easier to displace PrOH from the probe solvation shell than (more hydrophobic) BuOEtOH.

(vii) With regard to point (vi-b) above, the order of every φ , and the deviations from linearity (except for a single case, see Table 3) is OcPMBR₂ > MePMBR₂, i.e., the more hydrophobic probe interacts more strongly with the binary mixture, again due to solvophobic interactions.

The results of the quinoline-based probe *do not fit* this straightforward dependence on probe hydrophobicity. For example, except for a single case, all values of $\varphi_{(IL-W/W)}$ and all deviations from linearity are larger for MeQMBR₂ than for (48 times more hydrophobic) OcPMBR₂. This may be traced to the above-mentioned effect of annelation on the energy of its limiting structures. More specifically, the transition energy involved (ground state → excited state) reflects essentially the solvation of the ground state, for which two limiting structures may be written, zwitterionic and quinonoid. The contribution of the latter Lewis structure to the ground state is larger for MeQMBR₂, making this probe more susceptible to solvophobic interactions than expected from its log *P* alone. On the other hand, solvation of MeQMBR₂ in the different solvents shows the same dependence on solvent lipophilicity. That is, in all ILs and molecular solvents the order of φ , and that of the deviation from ideal behavior are the same as those observed for the other two probes, i.e., AlHxImCl > AlBuImCl > AlMeImCl; BuEtOH > PrOH.

(viii) The fact that the values of all $\varphi_{(S-W/S)}$ and $\varphi_{(S-W/W)}$ are much larger for W-ROH than those of W-ILs merits a comment because the values of $E_T(\text{probe})$ for MePMBR₂ and OcPMBR₂ in the five binary mixtures are similar (55 ± 1 kcal mol⁻¹). This difference may be attributed to the fact that the relatively strong interaction of IL with W attenuates the solvation efficiency of the complex solvent. Evidence showing that IL–W interactions are stronger than W–W interactions includes theoretical calculations and determination of the excess enthalpies of mixing of ILs with water.³³ This explanation is general, i.e., it applies to mixtures of water with molecular solvents that strongly interact with water, in particular DMSO.^{17,18}

Finally, a brief comment on the composition scale employed is in order, because it bears on the fractionation factors calculated. We dwell here on χ and volume fraction of water, $VF_W = (V_W/V_W + V_{IL})$; considering the latter scale is relevant because of the large difference in the molar volumes of IL and W. We have plotted $E_T(\text{probe})$, at 25 °C, as a function of χ_W or VF_W for the aqueous ILs employed (Fig. S2, ESI†). Whereas the former scale shows preferential solvation by the IL, the latter shows the converse! This is an intriguing result in view of the large body of data that indicate that the probes employed are preferentially solvated by the organic component of the aqueous mixture,^{43–45} and the fact that OcPMBR₂ is insoluble in water. In fact, the value of

$E_T(\text{OcPMBR}_2)$ in water has been calculated by extrapolation of the data of aqueous solvents to $[S] = 0$.¹⁸

Conclusions

Solvation by ILs and their mixtures with molecular solvents is required for a rational use of these green solvents. We have studied the solvation of three probes whose molecular structures are varied systematically in mixtures of W with ILs. The data obtained were compared with those of solvation in mixtures of W with molecular solvents. From the solvatochromic responses of the probes, information was deduced on solute–solvent interactions. Provided that the energy of the intra-molecular charge transfer within the probe is practically the same, e.g., MePMBR₂ and OcPMBR₂, all parameters of solvation (deviation from ideality; φ) can be explained by hydrogen-bonding and solvophobic interactions; the latter increase as a function of increasing lipophilic character of both the probe and IL. Although the solvatochromic response of MeQMBR₂ differs from that of its pyridine-based counterparts, it still shows the same dependence on IL lipophilicity. The deviations in the solvatochromic responses from linearity are larger for the aqueous ILs than for the molecular solvent counterparts, although the latter are more lipophilic. This is attributed to the more ordered structures of the IL; these permit efficient solvophobic solute–solvent interactions.

Experimental section

Materials and synthesis

The solvents were purchased from Acros or Δ-Mensalão2 and were purified as recommended elsewhere.¹⁶ The probes MePMBR₂, OcPMBR₂, MeQMBR₂, and ILs AlMeImCl, AlBuImCl and AlHxImCl were available from previous studies.^{8,9,17} AlBuImCl and AlHxImCl are liquids at room temperature, AlMeImCl is a solid (mp 52–53 °C), once melted it crystallizes only over a period of several days.³

Binary mixtures (16 per set) of IL and W were prepared by weight at 25 °C. Before adding water, the required amount of the IL was weighed then dried at 60 °C, under reduced pressure, over P₄O₁₀, until a 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 P₄O₁₀. IL, W, or IL–W mixtures were then added to the (solid) probe, and the latter was dissolved; the final probe 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 25 ± 0.05 °C (model 4000A digital thermometer, Yellow Springs Instruments). Each spectrum was recorded twice at a rate of 140 nm min⁻¹; slit width = 1.0 nm; sampling interval = 0.5 nm. Values of λ_{max} were determined from the first derivative of the absorption spectra. The uncertainty in $E_T(\text{probe})$ is ≤ 0.15 kcal mol⁻¹.

Calculation of the fractionation factors

As an example, we show the calculation for IL–W mixtures. The probe solvation shell is composed of W, IL, and IL–W.

The observed E_T , E_T^{obs} , is the sum of the polarity of each component, E_T^W , E_T^{IL} , $E_T^{\text{IL-W}}$, respectively, multiplied by the corresponding mole fraction in the probe solvation shell, χ_W^{Probe} , $\chi_{\text{IL}}^{\text{Probe}}$, and $\chi_{\text{IL-W}}^{\text{Probe}}$, respectively:

$$E_T^{\text{obs}} = \chi_W^{\text{Probe}} E_T^W + \chi_{\text{IL}}^{\text{Probe}} E_T^{\text{IL}} + \chi_{\text{IL-W}}^{\text{Probe}} E_T^{\text{IL-W}} \quad (4)$$

Eqn (4) and (5) can then be solved to get $E_T^{\text{IL-W}}$, and the appropriate solvent fractionation factors, respectively.

$$E_T^{\text{obs}} = \left((\chi_{\text{IL}}^{\text{BK:Effective}})^m E_T^{\text{IL}} + \phi_{W/\text{IL}} (\chi_W^{\text{BK:Effective}})^m E_T^W \right. \\ \left. + \phi_{\text{IL-W}/\text{IL}} (\chi_{\text{IL-W}}^{\text{BK:Effective}})^m E_T^{\text{IL-W}} \right) / \left((\chi_{\text{IL}}^{\text{BK:Effective}})^m \right. \\ \left. + \phi_{W/\text{IL}} (\chi_W^{\text{BK:Effective}})^m + \phi_{\text{IL-W}/\text{IL}} (\chi_{\text{IL-W}}^{\text{BK:Effective}})^m \right) \quad (5)$$

The input data to solve eqn (5) include E_T^{obs} , E_T^W , E_T^{IL} , and $\chi_{\text{Species}}^{\text{Effective}}$, along with initial guesses for (m) , $E_T^{\text{IL-W}}$, and the different ϕ . The fractionation factor $\phi_{\text{IL-W}/\text{W}}$ is obtained by dividing $\phi_{\text{IL-W}/\text{IL}}$ by $\phi_{W/\text{IL}}$. Values of E_T^{obs} were calculated by iteration until the sum of the squares of the residuals was not reduced; calculations were carried out by employing commercial software (Origin version 6.0, Microcal).

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