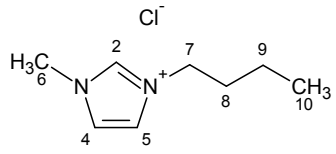
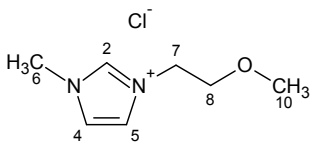
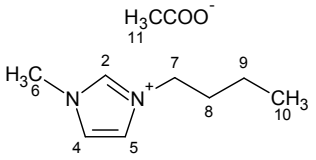
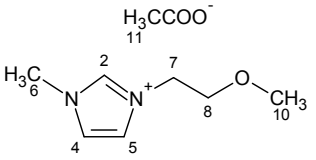
Electronic Supplementary Information for

***Experimental and theoretical studies on solvation in aqueous solutions of ionic liquids carrying different side chains: The n-butyl- versus the* methoxyethyl group**

Jéssica C. de Jesus,[1] Paulo A. R. Pires, [1] Rizwana Mustafa,[2] Naheed Riaz,[2] and Omar A. El Seoud[1,*]
1- Institute of Chemistry, the University of São Paulo
748 Professor Lineu Prestes Av., 05508-000 São Paulo, SP, Brazil; e-mail: elseoud@usp.br
2- Department of Chemistry, the University of Bahawalpur, Bahawalpur 63100, Pakistan

Table ESI-1: ^{1}H NMR chemical shifts **(δ, ppm)** for the ionic liquids 1-(1-butyl)-3-methylimidazolium chloride, C_4MeImCl, 1-(2-methoxyethyl)-3-methylimidazolium chloride, C_3OMeImCl, and their respective acetates (500 MHz; $CDCl_3$).[a]

				
C_4MeImCl		**C_3OMeImCl**	**C_4MeImAc**	**C_3OMeImAc**
Hydrogen	**(δ, ppm)**	**(δ, ppm)**	**(δ, ppm)**	**(δ, ppm)**
H11	-	-	2.00(s)	2.00(s)
H10	0.96(t)	3.37(s)	0.96(t)	3.36(s)
H9	1.39(m)	-	1.38(m)	-
H8	1.91(m)	3.78(t)	1.87(m)	3.74(t)
H7	4.34(t)	4.60(t)	4.30(t)	4.54(t)
H6	4.13(s)	4.11(s)	4.06(s)	4.02(s)
H5	7.68(t)	7.61(t)	7.27(s)	7.37(s)
H4	7.53(t)	7.60(t)	7.22(s)	7.19(s)
H2	10.53(s)	10.40(s)	11.25(s)	10.89(s)

a-Bruker DRX-500 NMR spectrometer. ^{1}H NMR peak multiplicities (m, s, t) refer to mutiplet, singlet, and triplet, respectively.

Table ESI-2- Compositions of the systems simulated by molecular dynamics.[a,b]

System	Number of IL molecules	Number of W molecules[c]	χ_w[d]	System	Number of IL molecules	Number of W molecules[c]	χ_w[d]
C_4MeImAc				C_3OMeImAc			
A1	670	330	0.33	A2	670	330	0.33
B1	330	670	0.67	B2	330	670	0.67
C_4MeImCl				C_3OMeImCl			
C1	330	670	0.67	C2	330	670	0.67

a- All simulations refer to WB in IL-Ac-W mixtures; the number of WB molecules was 20.

b- Acronyms for the ILs: C_4MeImAc, 1-(n-butyl)-3-methylimidazolium acetate; C_4MeImCl, 1-(n-butyl)-3-methylimidazolium chloride; C_3OMeImAc; 1-(methoxyethyl)-3-methylimidazolium acetate; C_3OMeImCl; 1-(methoxyethyl)-3-methylimidazolium chloride.

c- We employed SPC/E model of W molecules.(42)

d- χ_W is water mole fraction in the simulated mixture.

Molar concentration in the simulation boxes

The number of molecules listed in Table ESI-2 above correspond to the following concentrations (in mol L^{-1}) for WB, IL and W, respectively, for the following systems: (A1): 0.27, 4.45, and 9.04; (A2): 0.26, 4.22, and 8.57; (B1): 0.16, 5.26, and 2.59; (B2): 0.15, 4.91, and 2.42; (C1): 0.28, 4.70, and 9.54 and (C2): 0.27, 4.42, and 8.98. The concentrations were calculated based on box volumes (in nm^3) of 123.048 (A1), 129.798 (A2), 211.617 (B1), 226.397 (B2), 116.591 (C1) and 123.846 (system C2).

Dependence of E_T(WB) on the composition of the binary solvent mixture

Table ESI-3- Polynomial dependence of E_T(WB) on the analytical mole fraction of water (χ_W) at different temperatures. [a]

$$E_T(WB) = A + B(\chi_W) + C(\chi_W)^2 + D(\chi_W)^3 + E(\chi_W)^4 + F(\chi_W)^5 + G(\chi_W)^6$$

C_4MeImAc									
T, °C	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**$r^{2'}$**	**ΣQ^2**
15	59.8324	-9.5182	180.0520	-866.723	1843.639	-1796.54	659.3602	0.99321	0.68674
25	59.4775	-4.4441	139.2435	-738.810	1657.185	-1668.85	626.0020	0.99541	0.45627
40	59.1703	-3.3346	90.8191	-486.534	1150.271	-1221.37	480.1549	0.99185	0.78838
60	58.6134	-3.3352	120.1905	-617.993	1343.067	-1317.12	485.0922	0.99488	0.49029
C_3OMeImAc									
T, °C	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**$r^{2'}$**	**ΣQ^2**
15	59.5891	3.6597	-19.4024	72.9841	-112.1493	74.8720	-9.0624	0.99930	0.09997
25	59.5371	0.8858	-6.6316	57.1122	-124.1659	109.3973	-26.0698	0.99907	0.12710
40	59.0883	4.4955	-33.1494	136.3334	-237.7854	186.8840	-46.3893	0.99935	0.08426
60	58.8036	1.0996	-3.0562	14.1312	-4.2232	-19.6074	21.6870	0.99865	0.16773

a- **$r^{2'}$** and **ΣQ^2** refer to the nonlinear correlation coefficient and the sum of the squares of the residuals, respectively.

Calculations

Model employed for analysis of the solvatochromic data

We carried out these calculations as detailed previously.[1,2]. In the following discussion, the probe is WB, dissolved in mixtures of ionic liquid (IL) and water (W). Equation ESI-*1* refers to the formation of the IL-W mixed solvent, whereas the solvent exchange equilibria in the solvation layer of WB, whose constants are the fractionation factors, φ are given by Eqns. ESI-2 to ESI-4.

$$IL + W \rightleftharpoons IL\text{-}W \qquad \text{(ESI-1)}$$

$$Probe(IL)_m + m\,(W) \rightleftharpoons Probe(W)_m + m\,IL \qquad \text{(ESI-2)}$$

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

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

After algebraic manipulation, we obtain the following Eqns. for the calculation of φ:

$$\varphi_{\mathrm{W/IL}} = \frac{x_{\mathrm{W}}^{\mathrm{Probe}} / x_{\mathrm{IL}}^{\mathrm{Probe}}}{\left(x_{\mathrm{W}}^{\mathrm{Bk;\,Effective}} / x_{\mathrm{IL}}^{\mathrm{Bk;\,Effective}}\right)^{\mathrm{m}}} \qquad \text{(ESI-5)}$$

$$\varphi_{\mathrm{IL\text{-}W/IL}} = \frac{x_{\mathrm{IL\text{-}W}}^{\mathrm{Probe}} / x_{\mathrm{IL}}^{\mathrm{Probe}}}{\left(x_{\mathrm{IL\text{-}W}}^{\mathrm{Bk;\,Effective}} / x_{\mathrm{IL}}^{\mathrm{Bk;\,Effective}}\right)^{\mathrm{m}}} \qquad \text{(ESI-6)}$$

$$\varphi_{\mathrm{IL\text{-}W/W}} = \frac{x_{\mathrm{IL\text{-}W}}^{\mathrm{Probe}} / x_{\mathrm{W}}^{\mathrm{Probe}}}{\left(x_{\mathrm{IL\text{-}W}}^{\mathrm{Bk;\,Effective}} / x_{\mathrm{W}}^{\mathrm{Bk;\,Effective}}\right)^{\mathrm{m}}} \qquad \text{(ESI-7)}$$

Where the superscripts “probe, BK, and effective” refer to the solvation layer of WB, bulk binary solvent, and effective (or local) concentration of the solvent species, respectively. The meaning of $\varphi_{\mathbf{W/IL}}$, $\varphi_{\mathbf{IL\text{-}W/IL}}$, and $\varphi_{\mathbf{IL\text{-}W/W}}$ is explained in the main Text. We used Eqns. ESI-8 and ESI-9 to calculate the appropriate (φ) by iteration:

$$E_T^{Obs} = \chi_W^{Probe} E_T^W + \chi_{IL}^{Probe} E_T^{IL} + \chi_{IL-W}^{Probe} E_T^{IL-W} \qquad \text{(ESI-8)}$$

$$E_T^{Obs} = \frac{\left(\chi_{IL}^{Bk;Effective}\right)^m E_T^{IL} + \varphi_{W/IL}\left(\chi_W^{Bk;Effective}\right)^m E_T^W + \varphi_{IL-W/IL}\left(\chi^{Bk}\right.}{\left(\chi_{IL}^{Bk;Effective}\right)^m + \varphi_{W/IL} + \left(\chi_W^{Bk;Effective}\right)^m + \varphi_{IL-W/IL}\left(\chi^{\right.} \qquad \text{(ESI-9)}$$

The effective concentrations of IL, S, and IL-W are calculated from density data as follows:[3,4] we use the density (ρ) of the pure solvents, plus IL-W mixtures (eighteen samples in all) to calculate (by iteration) the dissociation constant $K_{\mathbf{dissoc}}$ of the IL-W mixed solvent, according to Eqn. ESI-10. Based on $K_{\mathbf{dissoc}}$ we calculate the effective concentrations of IL, W, IL-W for all binary solvent mixtures employed, and then solve Eqns. ESI-8 and ESI-9 to get the required φ.

We calculate the effective concentrations of the species in the solvent from the dependence of the density (ρ) on the volume fraction (ϕ) of the solvent species:

[5]

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

Where ρ_{mixt} refers to the measured density of the binary mixture, M and V refer to the molar mass and molar volume of the solvent. Figure ESI-2 shows examples of the application of Eqn. ESI-10 to our density data; the points are experimental and the lines are calculated by iteration.

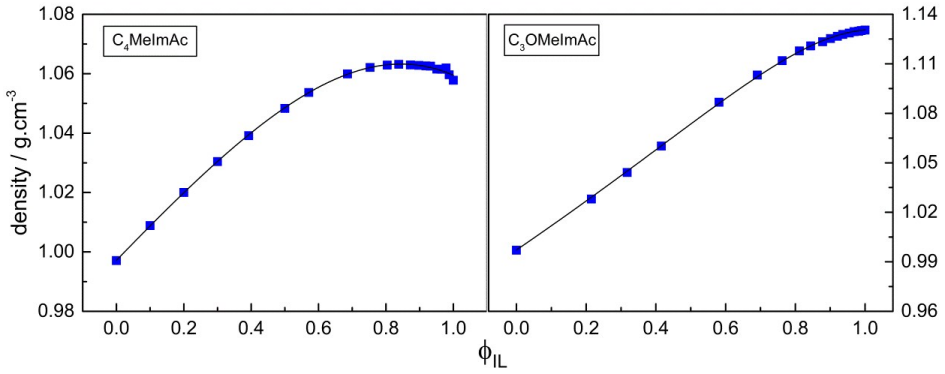


Figure ESI-1**:** Dependence of the densities on the volume fraction of IL (ϕ_{IL}) at 25°C. The points are experimental; Eqn. We used Eqn. ESI-10 to calculate the lines.

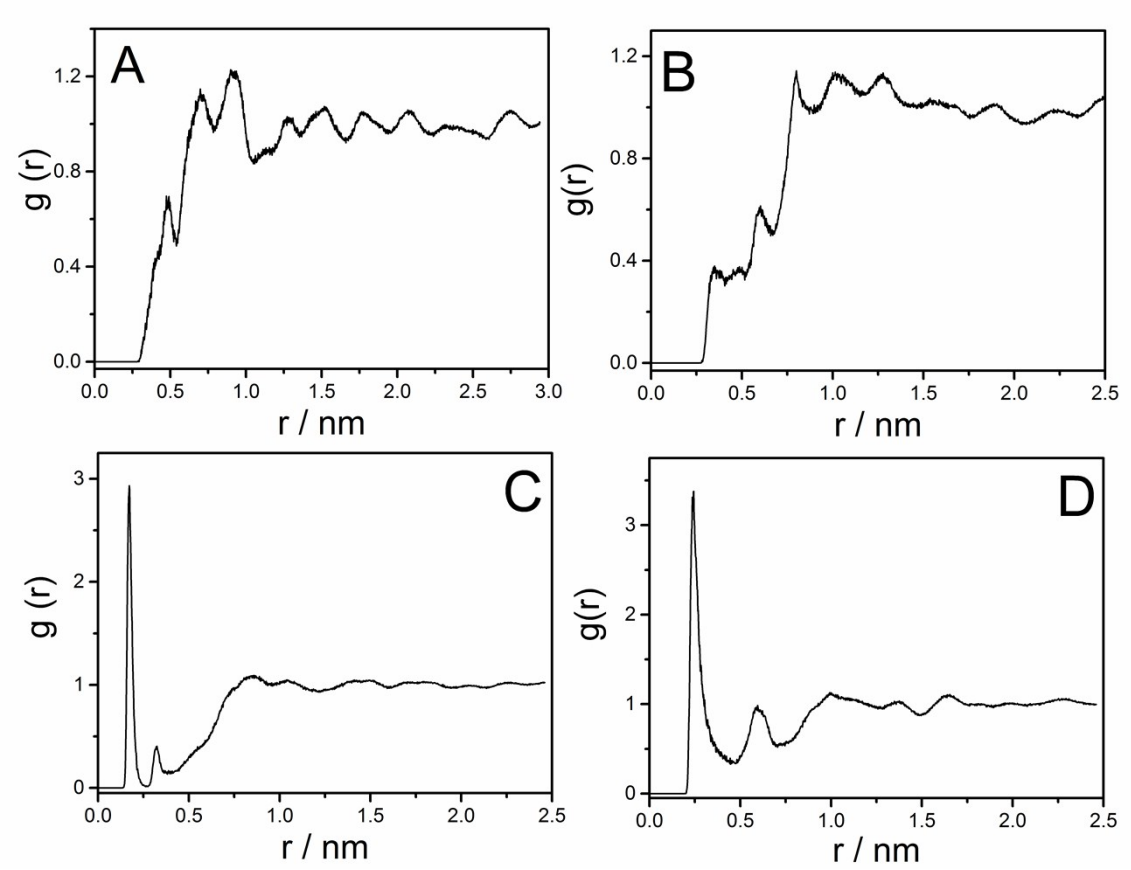


Figure ESI-2. Examples of radial distribution function of pairs of atoms (RDF) between: the pyridinium (N^+) of WB and (-O-) of C_3OMeImAc at χ_W=0.33 (part A); the pyridinium (N^+) of WB and (-O-) of water at χ_W=0.67 (part B); the phenolate oxygen of WB and H of water at χ_W=0.67 (part C); the phenolate oxygen of WB and C2-***H*** of C_4MeImAc at χ_W=0.67 (part C).

Figure ESI-3 shows the dependence of the effective mole fractions of the species present on binary solvent composition.

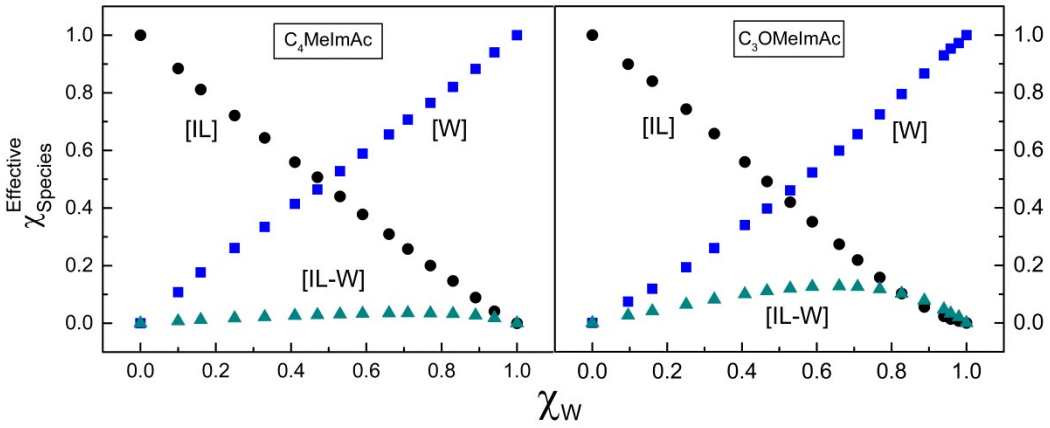


Figure ESI-3**:** Dependence of the effective concentration of the species in the IL-W binary mixtures on the mole fraction of water, χ_w at 25°C.

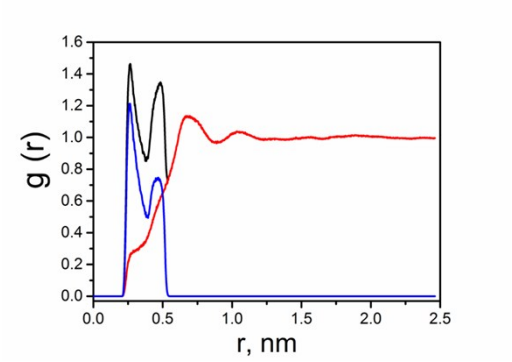


Figure ESI-4. Example of *R*adial *D*istribution *F*unction (RDF) between C2-***H***-and (-O-) of C_3OMeIm^+, at χ_W = 0.67. Black curve = intra- and intermolecular interactions; red curve = intermolecular interactions; blue curve = intramolecular interactions (difference between the black and red curves).

References for ESI

[1] El Seoud OA. Pure Appl Chem 2007;79:1135–51.

[2] El Seoud OA. Pure Appl Chem 2009;81:697–707.

[3] Katz ED, Ogan K, Scott RPW. J Chromatogr A 1986;352:67–90.

[4] Silva PL, Bastos EL, El Seoud OA. J Phys Chem B 2007;111:6173–80.