

Supporting Information

Ion specific effects on the mutual solubilities of water and hydrophobic ionic liquids

*Mara G. Freire^{‡§}, Pedro J. Carvalho[‡], Artur M. S. Silva[†], Luís M. N. B. F. Santos[†], Luís
P. N. Rebelo[§], Isabel M. Marrucho[‡] and João A. P. Coutinho^{‡*}*

[‡]CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro,
Portugal

[§]Instituto de Tecnologia Química e Biológica, ITQB2, Universidade Nova de Lisboa,
Av. República, Apartado 127, 2780-901 Oeiras, Portugal

[†]QOPNA, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro,
Portugal

[†]CIQ, Departamento de Química, Faculdade de Ciências da Universidade do Porto, R.
Campo Alegre 687, 4169-007 Porto, Portugal

*Corresponding author

Tel: +351-234-370200; Fax: +351-234-370084; E-mail address: jcoutinho@ua.pt

Table S1. Experimental mass fraction solubility (wt %) of [C₄mim][Tf₂N] in aqueous salt solutions at 298.15 K

Salt	Molality / (mol·kg ⁻¹)				
	0.10	0.20	0.50	1.0	1.5
Solubility of [C ₄ mim][Tf ₂ N] in aqueous salt solutions / (wt %)					
NaCl	0.844 ± 0.003	0.858 ± 0.002	0.765 ± 0.003	0.586 ± 0.004	0.467 ± 0.005
HCl	0.766 ± 0.002	---	---	0.995 ± 0.003	---
LiCl	0.781 ± 0.007	0.808 ± 0.006	0.799 ± 0.001	0.751 ± 0.002	0.650 ± 0.001
KCl	0.820 ± 0.005	0.810 ± 0.007	0.798 ± 0.001	0.762 ± 0.001	0.655 ± 0.003
NH ₄ Cl	0.812 ± 0.002	0.845 ± 0.002	0.824 ± 0.002	0.805 ± 0.006	0.733 ± 0.001
(CH ₃) ₄ NCl	0.729 ± 0.007	0.901 ± 0.003	1.82 ± 0.08	2.95 ± 0.04	3.14 ± 0.03
MgCl ₂	0.806 ± 0.005	0.767 ± 0.002	0.621 ± 0.003	0.505 ± 0.001	0.366 ± 0.003
CaCl ₂	0.827 ± 0.008	0.804 ± 0.001	0.666 ± 0.001	0.364 ± 0.002	0.305 ± 0.002
SrCl ₂	0.776 ± 0.004	0.718 ± 0.001	0.657 ± 0.003	0.431 ± 0.002	0.273 ± 0.005
NaOH	0.779 ± 0.001	---	---	1.18 ± 0.01	1.46 ± 0.01
NaNO ₃	0.747 ± 0.008	0.759 ± 0.003	0.814 ± 0.003	0.979 ± 0.005	---
NaSCN	0.756 ± 0.012	0.873 ± 0.019	1.02 ± 0.01	1.27 ± 0.01	---
NaCH ₃ COO	0.820 ± 0.005	0.753 ± 0.008	0.520 ± 0.002	0.439 ± 0.001	0.359 ± 0.005
NaHCO ₃	0.750 ± 0.005	0.745 ± 0.004	0.677 ± 0.004	0.529 ± 0.001	---
NaHSO ₄	0.739 ± 0.004	0.724 ± 0.002	0.637 ± 0.004	0.466 ± 0.009	0.362 ± 0.001
NaH ₂ PO ₄	0.683 ± 0.007	0.663 ± 0.007	0.555 ± 0.005	0.359 ± 0.009	0.322 ± 0.003
Na ₂ SO ₄	0.711 ± 0.006	0.609 ± 0.002	0.230 ± 0.007	0.171 ± 0.001	0.093 ± 0.001
Na ₂ CO ₃	0.749 ± 0.003	0.786 ± 0.007	0.610 ± 0.002	0.149 ± 0.004	0.049 ± 0.001
Na ₃ PO ₄	0.506 ± 0.005	0.471 ± 0.001	0.185 ± 0.002	---	---
Na ₃ C ₆ H ₅ O ₇	0.851 ± 0.009	0.797 ± 0.007	0.622 ± 0.009	0.296 ± 0.001	0.003 ± 0.001
Al ₂ (SO ₄) ₃	0.756 ± 0.002	0.747 ± 0.005	0.458 ± 0.001	---	---

Note: The solubility of [C₄mim][Tf₂N] in pure water is (0.709 ± 0.002) wt %.⁹

Table S2. Experimental mass fraction solubility of water in [C₄mim][Tf₂N] (wt %) at 298.15 K

Salt	Molality / (mol·kg ⁻¹)				
	0.10	0.20	0.50	1.0	1.5
	Solubility of water in [C ₄ mim][Tf ₂ N] / (wt %)				
NaCl	1.402 ± 0.003	1.392 ± 0.008	1.409 ± 0.008	1.322 ± 0.003	1.274 ± 0.003
HCl	1.420 ± 0.007	---	---	1.379 ± 0.004	1.365 ± 0.004
LiCl	1.394 ± 0.005	1.445 ± 0.005	1.410 ± 0.005	1.361 ± 0.009	1.320 ± 0.004
KCl	1.404 ± 0.002	1.418 ± 0.005	1.417 ± 0.002	1.384 ± 0.005	1.341 ± 0.001
NH ₄ Cl	1.437 ± 0.008	1.420 ± 0.004	1.419 ± 0.002	1.364 ± 0.003	1.323 ± 0.003
MgCl ₂	1.386 ± 0.011	1.371 ± 0.011	1.366 ± 0.011	1.272 ± 0.005	1.184 ± 0.004
CaCl ₂	1.419 ± 0.008	1.411 ± 0.005	1.370 ± 0.006	1.299 ± 0.002	1.203 ± 0.010
SrCl ₂	1.385 ± 0.001	1.380 ± 0.012	1.370 ± 0.007	1.291 ± 0.002	1.203 ± 0.001
NaOH	1.413 ± 0.008	---	---	1.342 ± 0.008	1.283 ± 0.005
NaNO ₃	1.406 ± 0.009	1.408 ± 0.008	1.418 ± 0.003	1.376 ± 0.002	1.335 ± 0.004
NaSCN	1.442 ± 0.009	1.444 ± 0.005	1.374 ± 0.006	1.343 ± 0.005	1.314 ± 0.004
NaCH ₃ COO	1.475 ± 0.005	1.506 ± 0.003	1.385 ± 0.006	1.318 ± 0.004	1.279 ± 0.007
NaHCO ₃	1.460 ± 0.003	1.478 ± 0.008	1.385 ± 0.001	1.354 ± 0.002	---
NaHSO ₄	1.429 ± 0.007	1.430 ± 0.003	1.375 ± 0.001	1.329 ± 0.007	1.281 ± 0.002
NaH ₂ PO ₄	1.407 ± 0.009	1.380 ± 0.007	1.374 ± 0.005	1.370 ± 0.001	1.326 ± 0.007
Na ₂ SO ₄	1.398 ± 0.005	1.424 ± 0.002	1.354 ± 0.005	1.331 ± 0.003	1.277 ± 0.008
Na ₂ CO ₃	1.436 ± 0.009	1.412 ± 0.001	1.379 ± 0.001	1.340 ± 0.008	1.287 ± 0.004
Na ₃ PO ₄	1.423 ± 0.009	1.405 ± 0.013	1.382 ± 0.011	---	---
Na ₃ C ₆ H ₅ O ₇	1.402 ± 0.003	1.380 ± 0.007	1.330 ± 0.013	1.257 ± 0.006	1.179 ± 0.007
Al ₂ (SO ₄) ₃	1.464 ± 0.008	1.392 ± 0.009	1.407 ± 0.008	---	---

Note: The solubility of pure water in [C₄mim][Tf₂N] is (1.416 ± 0.002) wt %.⁹

Table S3. ^1H NMR chemical shifts (δ/ppm relative to TSP) of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ as a function of NaSCN concentration in D_2O

Atom identification	$[\text{NaSCN}] / (\text{mol}\cdot\text{kg}^{-1})$		
	0.00	0.20	1.00
H (4) and H (5)	7.4729	7.4814	7.4951
	7.4664	7.4747	7.4886
	7.4230	7.4310	7.4442
	7.4166	7.4244	7.4377
H (6)	4.2172	4.2301	4.2526
	4.1934	4.2063	4.2288
	4.1697	4.1825	4.2049
H (7)	1.8972	1.9089	1.9286
	1.8729	1.8851	1.9048
	1.8485	1.8599	1.8810
	1.8233	1.8361	1.8544
	1.7993	1.8109	1.8319
H (8)	1.3797	1.3907	1.4076
	1.3546	1.3655	1.3838
	1.3294	1.3403	1.3600
	1.3041	1.3151	1.3333
	1.2795	1.2912	1.3081
	1.2554	1.2660	1.2843
H (9)	0.9482	0.9541	0.9610
	0.9239	0.9297	0.9367
	0.8990	0.9049	0.9118
H (10)	3.8857	3.8995	3.9259
H_2O	4.8455	4.8224	4.7097

Table S4. ^1H NMR chemical shifts (δ/ppm relative to TSP) of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ as a function of Na_2CO_3 concentration in D_2O

Atom identification	$[\text{Na}_2\text{CO}_3] / (\text{mol}\cdot\text{kg}^{-1})$				
	0.00	0.10	0.20	0.50	1.00
H (4) and H (5)	7.4733	7.4738	7.4743	7.4773	---
	7.4667	7.4674	7.4681	7.4710	7.4742
	7.4238	7.4281	7.4309	7.4398	7.4430
	7.4172	7.4220	7.4248	7.4335	---
H (6)	4.2172	4.2178	4.2179	4.2190	4.2193
	4.1935	4.1940	4.1942	4.1954	4.1957
	4.1697	4.1703	4.1705	4.1717	4.1721
H (7)	1.8981	1.8970	1.8968	1.8937	1.8899
	1.8735	1.8724	1.8718	1.8701	1.8678
	1.8492	1.8481	1.8475	1.8458	1.8429
	1.8243	1.8232	1.8225	1.8207	1.8182
	1.8001	1.7990	1.7973	1.7957	1.7935
H (8)	1.3813	1.3788	1.3771	1.3741	---
	1.3561	1.3539	1.3524	1.3486	1.3434
	1.3309	1.3288	1.3274	1.3233	1.3181
	1.3055	1.3034	1.3020	1.2980	1.2932
	1.2805	1.2787	1.2774	1.2733	1.2686
	1.2567	1.2542	1.2539	1.2495	---
H (9)	0.9488	0.9478	0.9472	0.9457	0.9433
	0.9243	0.9233	0.9227	0.9213	0.9190
	0.8996	0.8986	0.8981	0.8965	0.8943
H (10)	3.8865	3.8883	3.8893	3.8924	3.8947
H_2O	4.8210	4.8352	4.8450	4.8791	4.9191