Supporting Information

On the use of ionic liquids to tune crystallization

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Table 1. Diffusion coefficients of water, cations and anions of ILs at different IL concentrations as obtained by DOSY experiments. The diffusion of H_2O in the IL-free system has been determined as $D_0 = 2.47(m^2 \cdot s^{-1}) \cdot 10^{-9}$.

IL type	Diffusing species	IL concentration, C_{IL} / M							
		1	0.8825	0.5	0.25	0.125	0.025	0.0125	0.00625
		Diffusion coefficient $D \cdot 10^9$ / $(m^2 \cdot s^{-1})$							
[EMIM][Ac]	H_2O	1.605		2.024	2.28		2.375		
	cation	0.665		0.832	0.935		0.99		
	anion	0.665		0.86	0.965		0.99		
[Ch][Ac]	H_2O	1.72			2.3		2.366		
	cation	0.675			0.916		1		
	anion	0.72			0.995		1.02		
[Ch][C_1SO_3]	H_2O	1.87		2.19	2.324		2.356		
	cation	0.733		0.877	0.95		0.985		
	anion	0.858		0.998	1.105		1.14		
[EMIM][C_2SO_3]	H_2O			2.058	2.25		2.356		
	cation			0.821	0.908		0.995		
	anion			0.821	0.908		0.995		
[EMIM][C_3SO_3]	H_2O			1.905	2.18				
	cation			0.743	0.876				
	anion			0.675	0.8				
[EMIM][C_4SO_3]	H_2O	1.48		1.99	2.15		2.37		
	cation	0.598		0.777	0.86		1.01		
	anion	0.496		0.656	0.74		0.87		
[EMIM]Cl	H_2O	1.95		2.22	2.356		2.35		
	cation	0.81		0.924	0.955		1.01		
[Ch]Cl	H_2O		2.107		2.39	2.425	2.384		
	cation		0.86		0.98	1.005	1.01		
[EMIM]Br	H_2O	2.095		2.295	2.372		2.38		
	cation	0.84		0.935	0.985		1.01		
[EMIM][SCN]	H_2O	2.04		2.29	2.386		2.365		
	cation	0.83		0.928	0.98		1.03		
[EMIM][$(CN)_4B$]	H_2O						2.357	2.44	2.385
	cation						0.99	1.03	

Solution enthalpy: Frequency of water exchange and the influence of background ions.

The measured enthalpy of solution of $BaCl_2$ (distinct for different background chloride salts)[S1] resutls from the energy gained on creating ion-water interactions - E_i (affected by the association of the background ions in solution) and the energy expended on breaking existing water-water bonds - E_0 (dependent on the water affinity of background ions). This energy difference $(\Delta E_i = E_i - E_0)$ is the quantity that describes the relative frequency of water exchange in the ion's hydration shell with respect to its exchange in the bulk[S2-S3]. Such dependence is explained by the reaction rate theory which relates activation energies of the transfer process E_i (E_0) to the mean residence time (τ)[S3]:

$$\frac{\tau_i}{\tau_0} = e^{\beta(E_i - E_0)} \qquad (1)$$

where $\beta = 1/k_BT$, k_B is the Boltzmann´s constant, T is the absolute temperature and τ_i (τ_0) is the mean residence time of water in the nearest vicinity of the ion (and in the bulk).

Heat capacity: Hydration of ([EMIM][$(CN)_4$B] and association of [EMIM][SCN].

As can be seen in Figure S1, with increasing molar fraction of the solute ([EMIM][$(CN)_4$B]), the molar heat capacity of solution increases up to a certain point and then starts to decrease. Such behavior is typically recognized as a sign of hydrophobic hydration of the solute[S4] that results in the initial increase in the heat capacity due to the reinforcement of the water structure. The further decrease is a consequence of solute association in solution. Note that [EMIM][$(CN)_4$B] is weakly soluble in water and it is expected to significantly associate at higher concentrations. The effect of hydrophobic hydration is not supposed to be induced by $[EMIM]^+$, because this behavior is not observed for any other $[EMIM]^+$ based IL. A similar pattern – namely, the relatively sharp decrease in the heat capacity

starting from a particular concentration – is exhibited also by [EMIM][SCN]. Again, this fact supports our conclusion about the [EMIM][SCN] association.

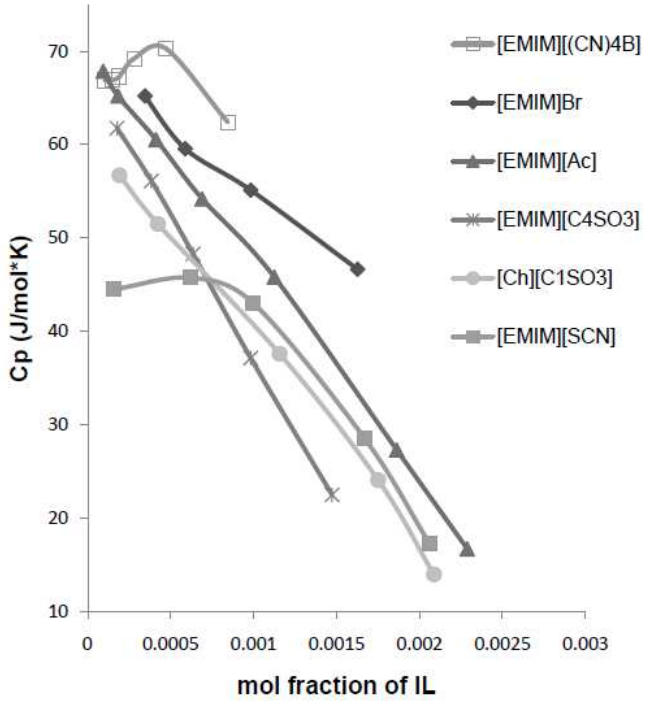

Figure S1. Molar heat capacity (C_p) isotherms (25 ˚C), of aqueous solutions of ILs as a function of their molar fraction.

References:

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[S2] Samoilov O. Y. *Structure of Aqueous Electrolyte Solutions and the Hydration of Ions.* Consultants Bureau, New York **1965**, pp. 74–106.

[S3] Chong S.-H.; Hirata F. *J. Phys. Chem.* **1997**, 101, 3209–3220.

[S4] Piekarski H.; Tkaczyk M. *Termochim. Acta* **2005**, 428, 113-118.