Electronic Supplementary Information

Biphasic liquid mixtures of ionic liquids and polyethylene glycols

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Quadratic fittings in the van't Hoff plots

For correlation of the data points in the van't Hoff plot of the main manuscript (Figure 4), the following quadratic equation was used:

$$\ln K = a + \frac{b}{T} + \frac{c}{T^2}$$

whose elements are already described in the main manuscript (eq. 2). The resulting parameters from the fitting are reported in Table S.1, along with the square of the correlation coefficient, as an indicator of the quality of the fitting.

Table S.1. Fitting parameters (a, b, c) of eq. 2, and corresponding square values of the correlation coefficients (R^2), for the correlation of the LLE data of the binary systems IL+PEG.

System	a	b / 10^3 K	c / 10^5 K^2	R^2
[C_2mim]Cl + PEG-1500	-2.39	1.28	-1.88	0.9990
[C_2mim]Cl + PEG-2000	-6.48	4.01	-6.59	0.9979
[C_2mim]Cl + PEG-3400	-14.7	9.60	-16.3	0.9990
[C_4mim]Cl + PEG-2000	-1.11	0.633	-1.01	0.9811
[C_4mim]Cl + PEG-3400	-6.87	4.54	-7.75	0.9939

Comparison of enthalpic and entropic contributions to the change of Gibbs free energy of mixing (ΔG_m)

With the coefficients reported in Table S.1, the change of enthalpy of mixing (ΔH_m) and change of entropy of mixing (ΔS_m) can be easily calculated by means of eq. 3 and 4 in the main manuscript. Table S.2 reports ΔH_m (which is the enthalpic contribution to ΔG_m), ΔS_m,

and the product $T \cdot \Delta S_m$, (which corresponds to the entropic contribution to ΔG_m), allowing direct comparison of the enthalpic and the entropic contribution to the change of Gibbs free energy of mixing, for all the studied LLE systems at the different experimental temperatures.

Table S.2. Change of enthalpy of mixing (ΔH_m) and change of entropy of mixing (ΔS_m) calculated from the LLE data of the binary systems IL+PEG. The entropic contribution ($T \cdot \Delta S_m$) to the Gibbs free energy of mixing (ΔG_m, see eq. 5) is also reported, for direct comparison with ΔH_m.

T / K	ΔH_m / kJ·mol^{-1}	ΔS_m / J·mol^{-1}·K^{-1}	$T \cdot \Delta S_m$ / kJ·mol^{-1}
	[C_2mim]Cl + PEG-1500		
333.15	-1.37	-5.96	-1.98
353.15	-1.89	-7.49	-2.64
373.15	-2.36	-8.78	-3.27
393.15	-2.78	-9.87	-3.88
413.15	-3.16	-10.8	-4.47
	[C_2mim]Cl + PEG-2000		
333.15	-0.464	-4.48	-1.49
353.15	-2.33	-9.91	-3.50
373.15	-3.99	-14.5	-5.41
393.15	-5.48	-18.4	-7.23
413.15	-6.83	-21.7	-8.98
	[C_2mim]Cl + PEG-3400		
333.15	1.32	-0.406	-0.135
353.15	-3.28	-13.8	-4.88
373.15	-7.38	-25.1	-9.37
393.15	-11.1	-34.7	-13.7
413.15	-14.4	-43.0	-17.8
	[C_4mim]Cl + PEG-2000		
333.15	-0.202	-1.60	-0.532
353.15	-0.489	-2.43	-0.859
373.15	-0.745	-3.14	-1.17
393.15	-0.974	-3.74	-1.47
413.15	-1.18	-4.25	-1.76
	[C_4mim]Cl + PEG-3400		
333.15	0.939	0.915	0.305
353.15	-1.25	-5.47	-1.93
373.15	-3.21	-10.9	-4.05
393.15	-4.96	-15.4	-6.07
413.15	-6.55	-19.4	-8.01