

SUPPORTING INFORMATION

Property modification by eutectic formation in mixtures of ionic liquids

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Detailed methods for DSC analysis and interpretation of the results

Determination of the thermal transitions of the samples was performed in a Mettler Toledo DSC 1 STARe System differential scanning calorimeter. All data were collected at atmospheric pressure, with argon (10 mL/min) as a purge gas, and an empty sample pan as the reference. Samples in the range 13-18 mg were used in aluminium sample pans, sealed with lids with a pin hole. For each sample three cycles of heating and cooling ramps were performed. The temperature range was set between 193.15 K and 398.15 K, thus ensuring that the highest temperature was below the decomposition temperature of any component salts. A slow heating rate of 2.5 K/min was used. A 10-minute isotherm was used at the end of each heating or cooling ramp, to allow the samples to thermally equilibrate before the next cooling or heating ramp. The experimental protocol used was as follows:

- (1) Heating from 298.15 K to 398.15 K at a rate of 2.5 K/min
- (2) 25 min isotherm at 398.15 K
- (3) Cooling from 398.15 K to 193.15 K at a rate of 2.5 K/min
- (4) 10 min isotherm at 193.15 K
- (5) Heating from 193.15 K to 398.15 K at a rate of 2.5 K/min
- (6) 10 min isotherm at 398.15 K
- (7) Cooling from 398.15 K to 193.15 K at a rate of 2.5 K/min
- (8) 10 min isotherm at 193.15 K
- (9) Heating from 193.15 K to 398.15 K at a rate of 2.5 K/min

The results from the first heating cycle were discarded as they could represent the melting transitions of a mixture not fully homogenised. Only after initial heating of the samples above the melting temperature of both component salts, the thermal transitions observed during the second and third heating cycles were considered. Results obtained from the second and third heating ramps were compared to each other, to confirm the repeatability of the results. The melting temperatures reported in Tables S1-S3 (see below) and used in this paper correspond to the temperatures of the peak points for the thermal transitions of the analysed samples. Reporting of the peak temperatures for the thermal transitions instead of their onset is a result of the difficulty of determining the onset temperatures, either due to overlapping of the transitions with other peaks (e.g. peaks from the eutectic and from an excess component) or irregular shape of many peaks with broad onset and sharp end. In the studied systems, reporting the values for the peaks of the thermal transitions was the most reliable method, allowing suitable comparisons among the obtained results. Each thermal transition temperature reported in this work was determined using STARe Evaluation Software by Mettler Toledo.

For samples that did not show any thermal transitions in the thermograms, or for those that presented only glass transitions, or for those where thermal transitions during the second and third heating cycles were not identical, the experiment was repeated with a freshly prepared sample to confirm the results. When clear thermal transitions were obtained on the thermograms, no additional samples were analysed.

Numerical values of thermal transitions in DSC thermograms

Table S1. Thermal transition data (glass transition temperature, T_g ; eutectic melting temperature, $T_{m,eu}$; and excess component melting temperature, $T_{m,ex}$) observed in the DSC experiments for the system $[\text{C}_2\text{mim}][\text{PF}_6] + [\text{C}_2\text{mim}][\text{NO}_3]$ (with x_2 representing the mole fraction of $[\text{C}_2\text{mim}][\text{NO}_3]$).

x_2	T_g (K)	$T_{m,eu}$ (K)		$T_{m,ex}$ (K)
		1st peak	2nd peak	
0.00	--	--	--	335
0.15	--	286	--	327
0.20	--	282	--	322
0.25	199	283	291	321
0.30	201	283	291	317
0.35	200	283	291	311
0.40	199	284	292	307
0.45	199	284	292	304
0.50	198	284	292	302
0.5042	199	--	292	--
0.5352	199	--	292	--
0.5940	199	--	292	--
0.60	198	--	291	--
0.65	199	284	292	297
0.70	198	283	291	299
0.75	197	283	291	302
0.80	197	283	290	305
0.85	--	283	290	307
0.90	--	283	--	309
1.00	--	--	--	316

Table S2. Thermal transition data (glass transition temperature, T_g ; eutectic melting temperature, $T_{m,eu}$; and excess component melting temperature, $T_{m,ex}$) observed in the DSC experiments for the system $[\text{C}_2\text{mim}][\text{PF}_6] + [\text{C}_2\text{mim}]\text{Cl}$ (with x_2 representing the mole fraction of $[\text{C}_2\text{mim}]\text{Cl}$).

x_2	T_g (K)	$T_{m,eu}$ (K)	$T_{m,ex}$ (K)
0.00	--	--	335
0.10	200	--	329
0.15	200	--	328
0.20	203	--	321
0.25	205	292	318
0.30	208	--	--
0.35	207	--	--
0.3676	205	312	--
0.40	209	--	--
0.45	212	--	--
0.50	215	--	--
0.55	215	298	--
0.60	218	--	--
0.65	219	--	--
0.70	221	--	--
0.75	222	--	340
0.85	214	--	--
0.90	224	--	351
0.95	218	--	351
1.00	--	--	361

Table S3. Thermal transition data (glass transition temperature, T_g ; eutectic melting temperature, $T_{m,eu}$; and excess component melting temperature, $T_{m,ex}$) observed in the DSC experiments for the system [C₄mim]Cl + [C₂mim]Cl (with x_2 representing the mole fraction of [C₂mim]Cl).

x_2	T_g (K)	$T_{m,eu}$ (K)	$T_{m,ex}$ (K)
0.00	210	--	338
0.05	232	--	--
0.10	229	--	--
0.15	231	306	--
0.20	228	313 ^a	331 ^a
0.25	233	--	--
0.30	230	--	--
0.3298	233	317 ^a	326 ^a
0.35	230	--	--
0.40	231	315	320
0.45	229	--	--
0.50	232	318 ^a	322 ^a
0.55	228	--	--
0.60	227	--	--
0.65	227	--	332
0.70	230	--	--
0.75	228	--	--
0.80	226	--	344
0.85	229	315	350
0.90	229	--	354
0.95	226	--	356
1.00	226	--	361

^a Transitions observed only during the first heating cycle. In the subsequent cycles only the glass transitions were observed, likely due to supercooling of the samples.

DSC thermograms

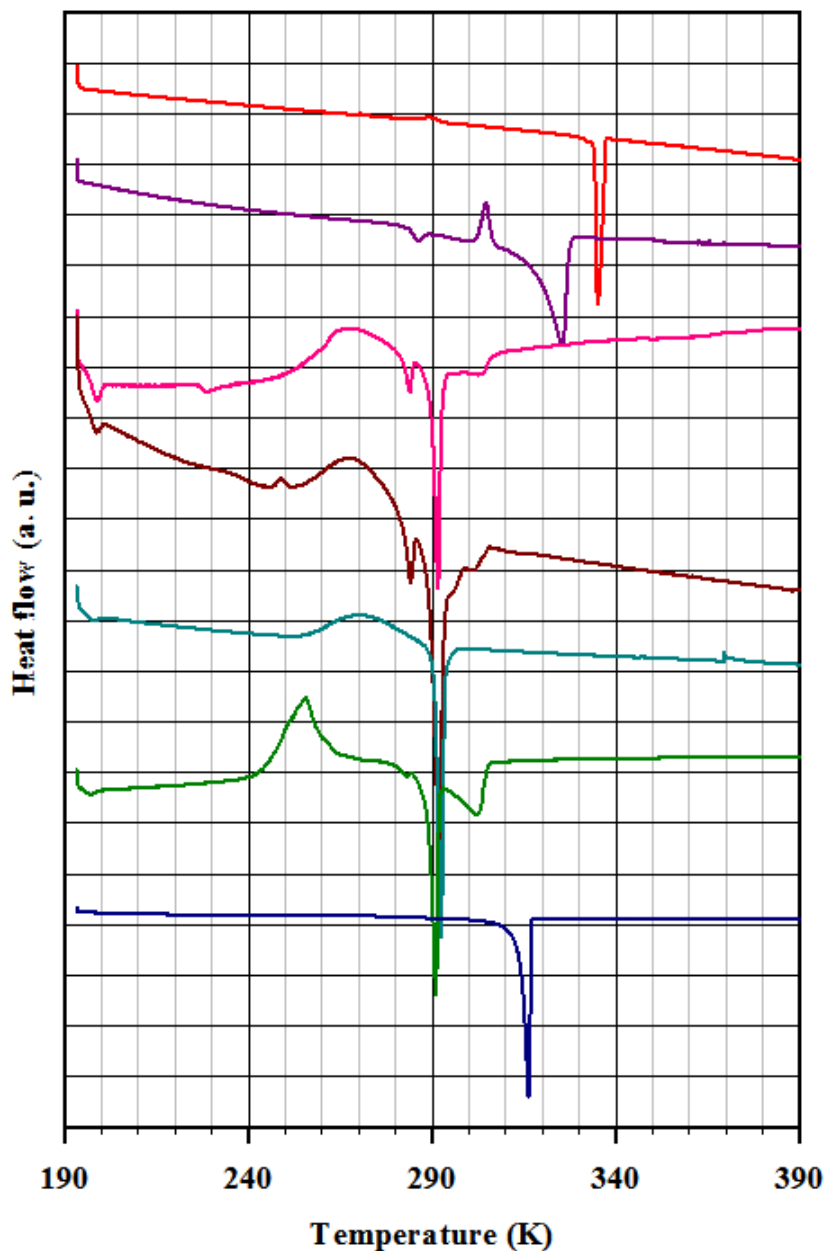


Figure S1. Selection of DSC thermograms of the system $[\text{C}_2\text{mim}][\text{PF}_6] + [\text{C}_2\text{mim}][\text{NO}_3]$, for different mole fractions x_2 of $[\text{C}_2\text{mim}][\text{NO}_3]$. From top to bottom: $x_2 = 0.00$ (pure $[\text{C}_2\text{mim}][\text{PF}_6]$, red), $x_2 = 0.15$ (violet), $x_2 = 0.45$ (fuchsia), $x_2 = 0.50$ (brown), $x_2 = 0.60$ (light blue), $x_2 = 0.75$ (green), $x_2 = 1.00$ (pure $[\text{C}_2\text{mim}][\text{NO}_3]$, dark blue). For the pure ionic liquids, the cooling and heating steps of the last cycle are shown; whereas for the mixtures only the heating step of the last cycle is shown.

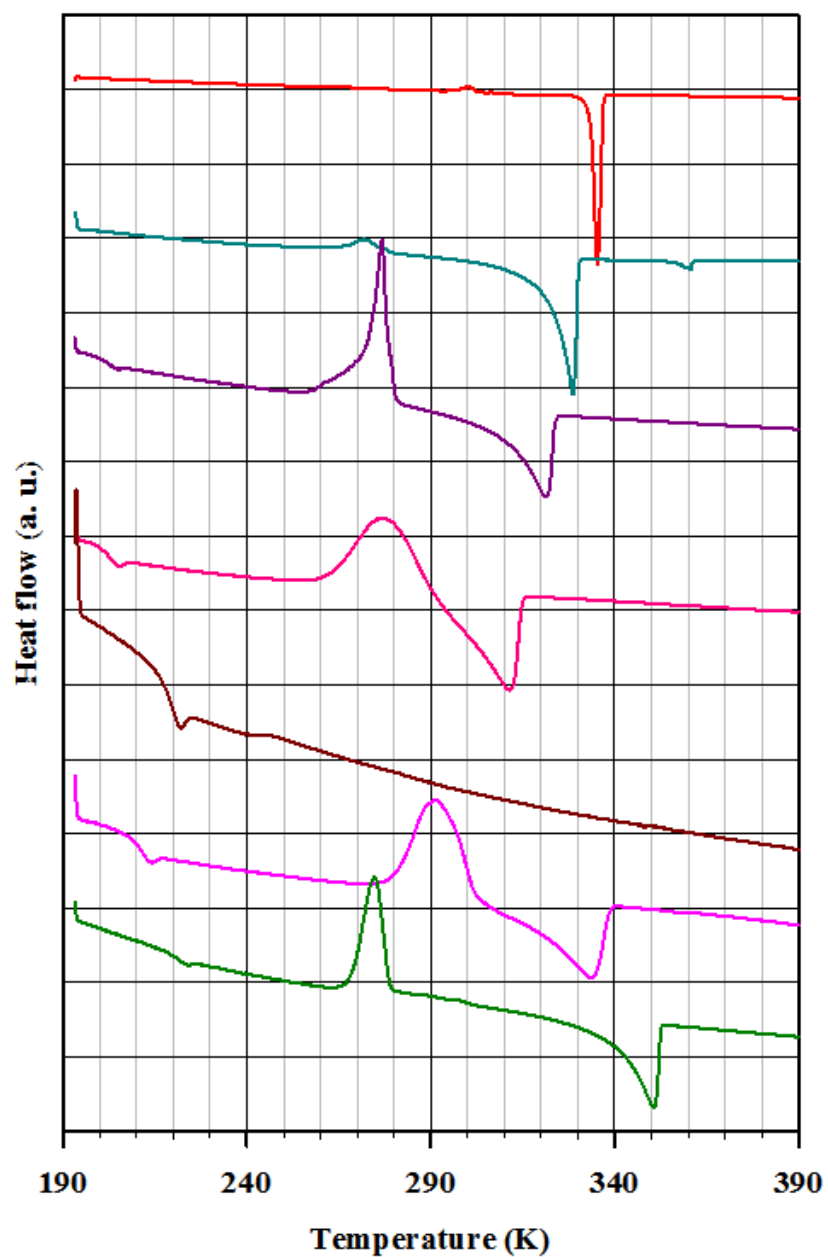


Figure S2. Selection of DSC thermograms of the system $[C_2mim][PF_6] + [C_2mim]Cl$, for different mole fractions x_2 of $[C_2mim]Cl$. From top to bottom: $x_2 = 0.00$ (pure $[C_2mim][PF_6]$, red), $x_2 = 0.15$ (light blue), $x_2 = 0.20$ (violet), $x_2 = 0.375$ (fuchsia), $x_2 = 0.70$ (brown), $x_2 = 0.85$ (purple), $x_2 = 0.90$ (green). Only the heating step of the last cycle is shown.

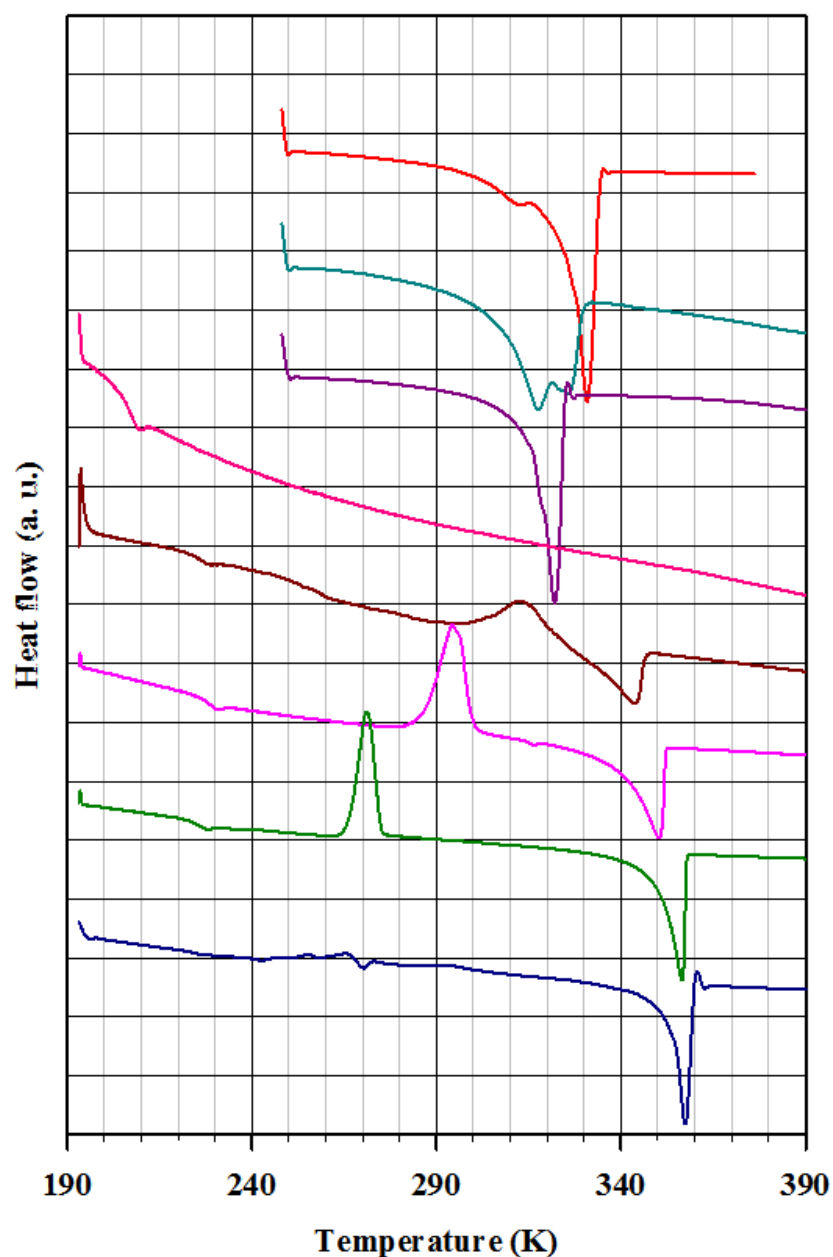


Figure S3. Selection of DSC thermograms of the system $[\text{C}_4\text{mim}]\text{Cl} + [\text{C}_2\text{mim}]\text{Cl}$, for different mole fractions x_2 of $[\text{C}_2\text{mim}]\text{Cl}$. From top to bottom: $x_2 = 0.20$ (red), $x_2 = 0.33$ (light blue), $x_2 = 0.50$ (violet), $x_2 = 0.60$ (fuchsia), $x_2 = 0.80$ (brown), $x_2 = 0.85$ (purple), $x_2 = 0.95$ (green), $x_2 = 1.00$ (pure $[\text{C}_2\text{mim}]\text{Cl}$, dark blue). For the shown thermograms with $x_2 < 0.55$, the heating step of the first cycle is plotted, since the sample remained supercooled during the subsequent cycles and the thermal transitions were not observed anymore. For the rest of the thermograms, the heating step of the last (third) cycle is plotted.

Comparison of some physical property data with literature data

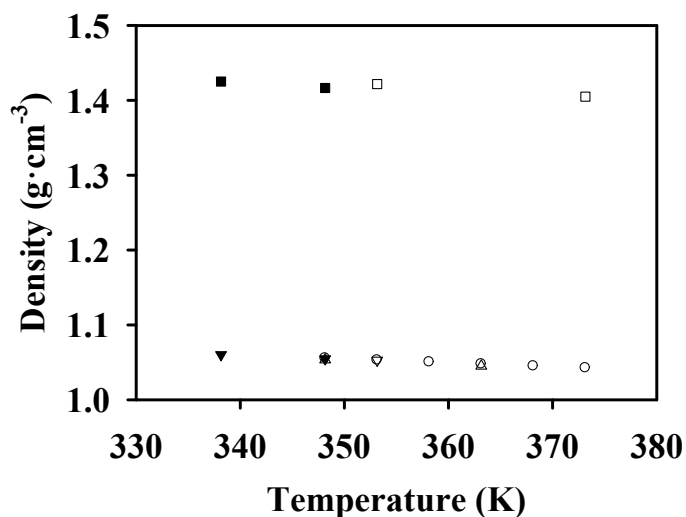


Figure S4. Comparison of literature values and the experimental values reported in this work for the density of the pure ionic liquids [C₂mim][PF₆] (■, this work; □, Taguchi et al., 2009 [S11]), and [C₄mim]Cl (▼, this work; ▽, Sun et al., 2009 [S2]; ○, Machida et al., 2011 [S3]; △, He et al., 2012 [S4]). No suitable values for comparison with [C₂mim][NO₃] were found in the literature.

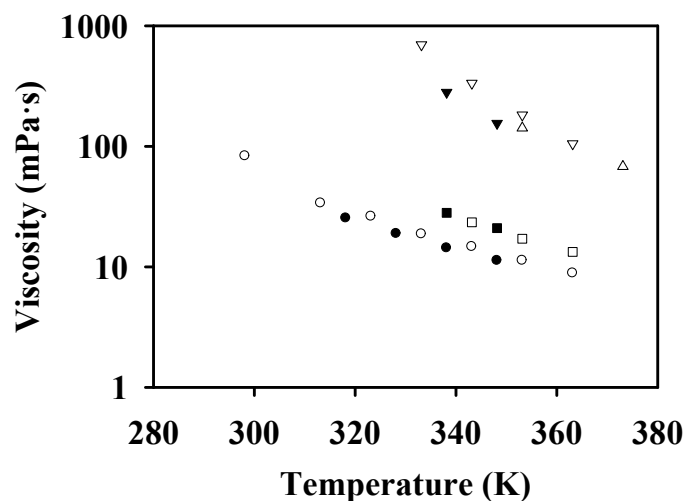


Figure S5. Comparison of literature values and the experimental values reported in this work for the viscosity of the pure ionic liquids [C₂mim][NO₃] (●, this work; ○, Seddon et al., 2002 [S5]), [C₂mim][PF₆] (■, this work; □, Seddon et al., 2002 [S5]), and [C₄mim]Cl (▼, this work; ▽, Seddon et al., 2002 [S5]; △, Fendt et al., 2011 [S6]).

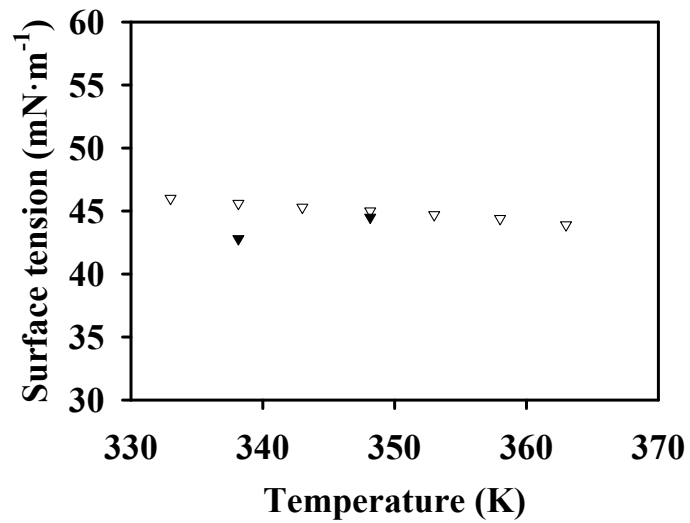


Figure S6. Comparison of literature values and the experimental values reported in this work for the surface tension of the pure ionic liquid [C₄mim]Cl (▼, this work; ▽, Ghatee and Zolghadr, 2008 ^[S7]). No suitable values for comparison with [C₂mim][PF₆] or [C₂mim][NO₃] were found in the literature.

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