

# Supporting Information

## Toward an Understanding of the Mechanisms behind the Formation of Liquid-liquid Systems formed by Two Ionic Liquids

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## EXPERIMENTAL SECTION

**Materials.** The mutual solubilities of cholinium bis(trifluoromethylsulfonyl)imide, [Chol][NTf<sub>2</sub>] (mass fraction purity  $\approx$  99 %) and phosphonium-based ionic liquids, namely [P<sub>66614</sub>][NTf<sub>2</sub>] (mass fraction purity  $>$  98 %), [P<sub>66614</sub>][Br] (mass fraction purity  $\approx$  96-98 %), [P<sub>66614</sub>][Cl] (mass fraction purity  $\approx$  93-95 %), [P<sub>66614</sub>][Deca] (mass fraction purity  $\approx$  97 %); [P<sub>66614</sub>][N(CN)<sub>2</sub>] (mass fraction purity  $\approx$  97 %), and [P<sub>66614</sub>][Phosph] (mass fraction purity  $\approx$  93 %), were investigated from (333.15 to 423.15) K. All phosphonium-based ionic liquids were kindly provided by Cytec Industries Inc, while the [Chol][NTf<sub>2</sub>] was acquired from Iolitec. All phosphonium-based ionic liquids were initially purified by repeatedly washing them with ultra-pure water (under constant stirring for a minimum of 24 h), as described elsewhere.<sup>1</sup> The water used was double distilled, passed by a reverse osmosis system and further treated with a MilliQ plus 185 water purification apparatus. It has a resistivity of 18.2 M $\Omega$ ·cm and a TOC (Total Organic Carbon content) smaller than 5  $\mu$ g·dm<sup>-3</sup>. After removing the aqueous-rich phase, ILs were additionally dried and purified under high vacuum (0.1 Pa) and moderate temperature (353 K) for at least 48 h. The final purity of each IL was evaluated by <sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra, recorded in a Bruker Avance 300 operating at 300 MHz for <sup>1</sup>H, 75 MHz for <sup>13</sup>C, 131 MHz for <sup>31</sup>P, and 282 MHz for <sup>19</sup>F. The addition of ultra-pure water for washing, followed by the high vacuum drying procedure, was repeated until no impurities in the ILs were observed. The final purity of all ILs was estimated to be  $>$  99 wt %. The water mass fraction contents, determined with a Metrohm 831 Karl Fischer coulometer, were  $33.6 \times 10^{-6}$ , (16.0, 28.6, 71.4, 15.1)  $\times 10^{-5}$  and  $10.8 \times 10^{-4}$  for [P<sub>66614</sub>][NTf<sub>2</sub>], [P<sub>66614</sub>][Br], [P<sub>66614</sub>][Cl], [P<sub>66614</sub>][Deca], [P<sub>66614</sub>][N(CN)<sub>2</sub>] and [P<sub>66614</sub>][Phosph], respectively. The analyte used for the coulometric Karl-Fischer titration was the Hydranal<sup>®</sup> - Coulomat AG from Riedel-de Haën. The dodecane used was from Aldrich, with 99 wt % of purity. To color the phases of the four-

phase system, different dyes were used, namely the textile Sudan III dye from Merck, the food additive dye Tartrazine (E102) from Globo, and methylene blue from Riedel-de Haën.

**Experimental procedure.** Mixtures of two ionic liquids ([Chol][NTf<sub>2</sub>] and different phosphonium-based ILs) were prepared, vigorously agitated and allowed to equilibrate in a Julabo ME-18V Visco bath for, at least, 48 h at each temperature (time required to guarantee a complete separation of the two phases and to reach the equilibrium of the phases, as properly optimized by us). Mutual solubilities were determined in the temperature range between (333.15 and 423.15) K. For the quantification of the ILs, a sample of each phase was taken, inserted in an NMR tube and diluted in DMSO, d<sub>6</sub>. For the cations quantification, <sup>1</sup>H NMR spectroscopy was used. To quantify the cholinium cation, the peak at 3.84 ppm, which corresponds to 2H, was used. On the other hand, the peak at 0.86 ppm was used for the quantify [P<sub>66614</sub>]<sup>+</sup>. This peak corresponds to 12H, with exception of mixtures with phosphinate (21H) and decanoate (15H) anions. The mole fraction of each cation in each phase was determined according to the following equations:

$$x_{[\text{Chol}]^+} = \frac{a/2}{\frac{a}{2} + \frac{b}{12}} \quad (1)$$

$$x_{[\text{P}_{66614}]^+} = 1 - x_{[\text{Chol}]^+} \quad (2)$$

where *a* and *b* are equal to the integrated under the peaks of reference from cholinium and phosphonium, respectively.

In order to quantify the ion exchange, internal standards were used at 1%, namely benzene from BDH with 99% purity for <sup>1</sup>H NMR, and perfluorobenzene from Fluorochem with 99.99% purity for <sup>19</sup>F NMR. The cholinium cation was quantified by <sup>1</sup>H NMR and the [NTf<sub>2</sub>]<sup>-</sup> by <sup>19</sup>F NMR.

Electrospray ionization tandem mass spectra (ESI-MS-MS) were acquired with a Micromass Q-ToF2 (Micromass, Manchester, U.K.), operating in the positive ion mode, equipped with a Z-spray source. Source and desolvation temperatures were 353 and 373 K, respectively. Ionic liquid solutions in methanol, at concentrations of  $\sim 10^{-4}$  mol·dm<sup>-3</sup>, were introduced at a 10 mm<sup>3</sup>·min<sup>-1</sup> flow rate. The capillary and the cone voltage were 2600 V and 30 V, respectively. Nitrogen was used as the nebulization gas and argon as the collision gas. ESI-MS-MS spectra were acquired by selecting the precursor ion with the quadrupole and performing collisions in the hexapole with argon at variable energies. Each spectrum represents an average of approximately 100 scans, and the values of  $E_{\text{lab},1/2}$  were determined as the collision energy at which the relative abundance of the precursor ion is 50%. Triplicate measurements were performed for each selected precursor ion, and standard deviations that varied between 0.3 and 5% were obtained. The energy required to dissociate 50% of the precursor ion was registered as  $E_{\text{lab},1/2}$ . In this inelastic collision of the projectile ion with the target neutral, the total available energy for conversion of translational (or kinetic) to internal (or vibrational) energy of the projectile ion is the center of mass energy ( $E_{\text{cm}}$ ), which can be calculated from  $E_{\text{lab}}$ , and from the masses of the neutral target ( $m_t$ ) and precursor ion ( $m_p$ ), by the following,

$$E_{\text{cm}} = E_{\text{lab}} \left( \frac{m_t}{m_p + m_t} \right) \quad (3)$$

The calculated dissociation energies from the experimental  $E_{\text{lab}}$  values represent the energy required to separate a cation (or anion) from the neutral ionic liquid molecule in the gas phase and, as such, can be considered a good approximation to the cation-anion interaction energy.

In order to prepare the four phases system, each solvent was colored separately: [P<sub>66614</sub>][NTf<sub>2</sub>] with Sudan III dye, [Cho][NTf<sub>2</sub>] with the food additive E102, and water with methylene blue. At this stage, dodecane was not colored. After this step, close

volumes of each dyed solvent were mixed and stirred in a vortex. The phases separate almost immediately, but to guarantee the complete separation, the sample was additionally centrifuged at 1000 rpm for 5 min. This experiment was carried out at 298 K.

## RESULTS

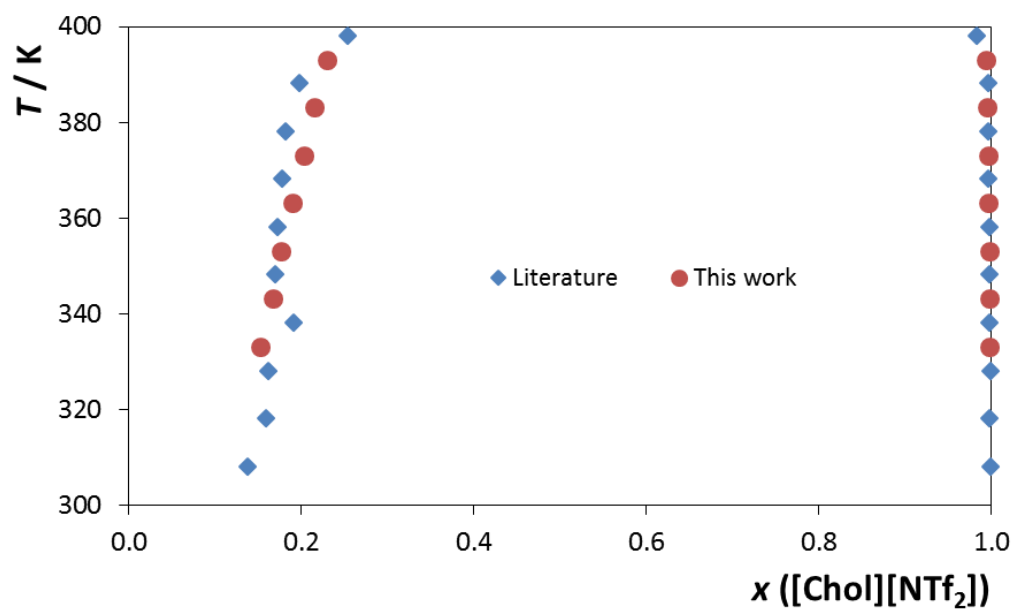
**Table S1.** Experimental mole fraction solubility of the cholinium cation,  $x_{[\text{Chol}]^+}$ , in the  $[\text{Chol}]^-$ - and  $[\text{P}_{66614}]^-$ -rich phases, as a function of temperature and at 0.1 MPa.

Phase	$T / \text{K}$	$x_{[\text{Chol}]^+} \pm \sigma$					
		$[\text{Phosph}]^-$	$[\text{N}(\text{CN})_2]^-$	$[\text{Deca}]^-$	$[\text{NTf}_2]^-$	$\text{Br}^-$	$\text{Cl}^-$
$[\text{P}_{66614}]^+$	333.15	$0.396 \pm 0.012$	$0.117 \pm 0.006$	$0.25 \pm 0.03$	$0.153 \pm 0.006$	$0.106 \pm 0.021$	$0.072 \pm 0.017$
	343.15	$0.399 \pm 0.014$	$0.142 \pm 0.007$	$0.25 \pm 0.02$	$0.167 \pm 0.005$	$0.111 \pm 0.021$	$0.088 \pm 0.017$
	353.15	$0.422 \pm 0.005$	$0.145 \pm 0.002$	$0.25 \pm 0.02$	$0.176 \pm 0.008$	$0.109 \pm 0.054$	$0.089 \pm 0.033$
	363.15	$0.438 \pm 0.015$	$0.147 \pm 0.003$	$0.27 \pm 0.03$	$0.189 \pm 0.005$	$0.116 \pm 0.039$	$0.092 \pm 0.027$
	373.15	$0.459 \pm 0.001$	$0.147 \pm 0.002$	$0.29 \pm 0.03$	$0.203 \pm 0.001$	$0.131 \pm 0.019$	$0.114 \pm 0.012$
	383.15	$0.467 \pm 0.026$	$0.148 \pm 0.011$	$0.32 \pm 0.02$	$0.214 \pm 0.004$	$0.146 \pm 0.003$	$0.126 \pm 0.012$
	393.15	$0.479 \pm 0.012$	$0.166 \pm 0.025$	$0.32 \pm 0.03$	$0.230 \pm 0.002$	$0.158 \pm 0.012$	$0.137 \pm 0.020$
	403.15	$0.480 \pm 0.012$	$0.170 \pm 0.009$	$0.35 \pm 0.03$	$0.240 \pm 0.006$	$0.169 \pm 0.021$	$0.151 \pm 0.017$
	413.15	$0.512 \pm 0.012$	$0.188 \pm 0.015$	$0.42 \pm 0.04$	$0.263 \pm 0.015$	$0.174 \pm 0.010$	$0.149 \pm 0.001$
	423.15	$0.576 \pm 0.012$	$0.199 \pm 0.014$	$0.47 \pm 0.03$	$0.284 \pm 0.006$	$0.182 \pm 0.008$	$0.171 \pm 0.013$
$[\text{Chol}]^+$	333.15	$0.890 \pm 0.021$	$0.9974 \pm 0.0002$	$0.96 \pm 0.01$	$0.9975 \pm 0.0005$	$0.9982 \pm 0.0009$	$0.9984 \pm 0.0006$
	343.15	$0.899 \pm 0.023$	$0.9973 \pm 0.0003$	$0.95 \pm 0.01$	$0.9971 \pm 0.0001$	$0.9975 \pm 0.0009$	$0.9991 \pm 0.0006$

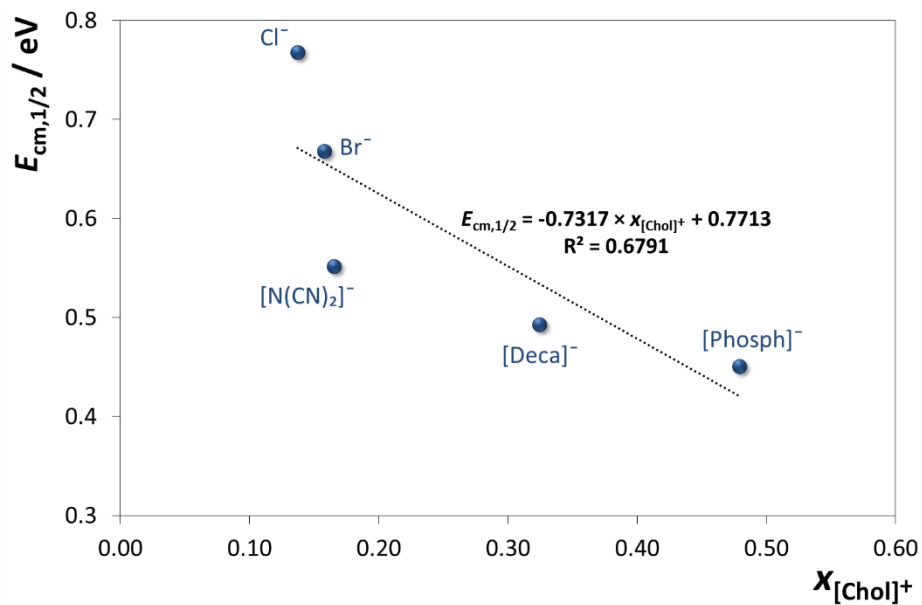
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353.15	$0.889 \pm 0.023$	$0.9966 \pm 0.0003$	$0.94 \pm 0.01$	$0.9969 \pm 0.0002$	$0.9973 \pm 0.0006$	$0.9978 \pm 0.0018$
363.15	$0.888 \pm 0.019$	$0.9948 \pm 0.0028$	$0.94 \pm 0.01$	$0.9954 \pm 0.0003$	$0.9976 \pm 0.0002$	$0.9982 \pm 0.0001$
373.15	$0.889 \pm 0.017$	$0.9939 \pm 0.0021$	$0.94 \pm 0.01$	$0.9960 \pm 0.0009$	$0.9979 \pm 0.0001$	$0.9982 \pm 0.0002$
383.15	$0.886 \pm 0.018$	$0.9932 \pm 0.0006$	$0.93 \pm 0.01$	$0.9949 \pm 0.0001$	$0.9977 \pm 0.0026$	$0.9980 \pm 0.0003$
393.15	$0.884 \pm 0.018$	$0.9895 \pm 0.0019$	$0.93 \pm 0.02$	$0.9937 \pm 0.0006$	$0.9971 \pm 0.0009$	$0.9979 \pm 0.0007$
403.15	$0.882 \pm 0.021$	$0.9850 \pm 0.0015$	$0.93 \pm 0.01$	$0.9953 \pm 0.0005$	$0.9962 \pm 0.0009$	$0.9979 \pm 0.0006$
413.15	$0.879 \pm 0.023$	$0.9812 \pm 0.0013$	$0.93 \pm 0.02$	$0.9907 \pm 0.0013$	$0.9958 \pm 0.0019$	$0.9974 \pm 0.0002$
423.15	$0.877 \pm 0.025$	$0.9746 \pm 0.0043$	$0.92 \pm 0.03$	$0.9889 \pm 0.0004$	$0.9955 \pm 0.0002$	$0.9966 \pm 0.0007$

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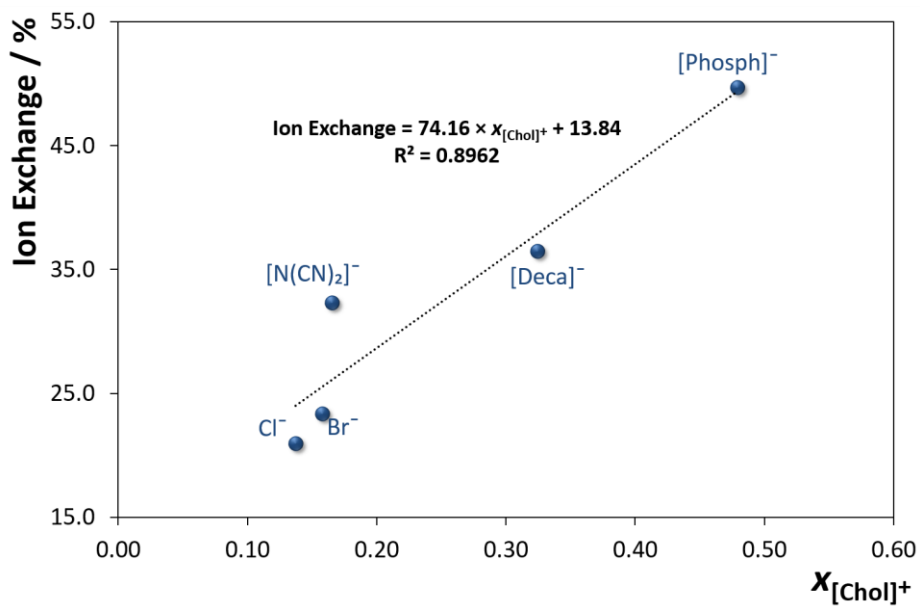


**Figure S1.** Comparison of the experimental data obtained in this work and those reported in the literature<sup>2</sup> for the binary system composed of [Chol][NTf<sub>2</sub>] + [P<sub>66614</sub>][NTf<sub>2</sub>].



**Figure S2.** Relative cation–anion interaction energies ( $E_{cm,1/2}$ ) as a function of mole fraction solubility of cholinium in the phosphonium-rich phase at 393.15 K.





**Figure S3.** Ion Exchange as a function of the mole fraction solubility of cholinium in the phosphonium-rich phase at 393.15 K.

**Table S2.**  $E_{cm,1/2}$  values for the dissociation of the ions [(cation)<sub>2</sub>anion]<sup>+</sup>.

Ionic Liquid	$E_{cm,1/2}$ / eV
[P <sub>66614</sub> ]Cl	0.77
[P <sub>66614</sub> ]Br	0.67
[P <sub>66614</sub> ][N(CN) <sub>2</sub> ]	0.55
[P <sub>66614</sub> ][Deca]	0.49
[P <sub>66614</sub> ][Phosph]	0.45
[P <sub>66614</sub> ][NTf <sub>2</sub> ]	0.39
[Chol][NTf <sub>2</sub> ]	0.81

## REFERENCES

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