# Electronic Supplementary Information

## Temperature dependency of aqueous biphasic systems: an alternative approach for exploring the differences between Coulombic-dominated salts and ionic liquids

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## References

## Experimental methods

### *Ternary phase diagrams*

The poly(ethylene) glycol polymer with an average molecular weight of 2000 g mol$^{-1}$ (abbreviated as PEG 2000) was purchased from Sigma Aldrich®. The ammonium halides used, namely tetramethylammonium chloride, $[N_{1111}]Cl$ (purity 97 %), tetraethylammonium chloride, $[N_{2222}]Cl$ (purity ≥98 %), tetrapropylammonium chloride, $[N_{3333}]Cl$ (purity 98 %), methyltributylammonium chloride, $[N_{1444}]Cl$ (75 wt% in water), 2-hydroxyethyltrimethylammonium chloride, $[N_{1112(OH)}]Cl$ (purity ≥98 %), and tetrabutylammonium chloride, $[N_{4444}]Cl$ (purity ≥ 97 %) were acquired from Sigma Aldrich®. The ammonium halide $[N_{1444}]Cl$ was dried under vacuum, for a minimum of 48 h, in order to remove the water content since this was received as an aqueous solution. The ammonium chlorides purities were checked using $^{1}H$ and $^{13}C$ NMR spectroscopy and found to fit the purity levels stated by the suppliers.

Two distinct approaches were adopted for the ternary phase diagrams determination: one for the shorter side chains ammonium halides (*i.e.,* $[N_{1111}]Cl$, $[N_{2222}]Cl$ and $[N_{1112(OH)}]Cl$) and another for the longer side chains ones (*i.e.,* $[N_{3333}]Cl$, $[N_{1444}]Cl$ and $[N_{4444}]Cl$). The first set of binodal curves was established through the cloud point titration method at controlled temperatures (40, 50 and 60 °C), at atmospheric pressure and under constant stirring. The protocol conducted was according to literature.[1, 2] Aqueous solutions of ammonium halides at *ca.* 60 – 80 wt% and of PEG 2000 at *ca.* 60 – 80 wt% and water were used. The protocol consisted on the sequential and alternate drop-wise addition of the PEG 2000 solution to each ammonium halide solution until the visual inspection of a cloudy point (biphasic region), followed by the drop-wise addition of water until the detection of a clear solution (monophasic region). The determination of each system composition was based on the weight quantification of the mixture components added within an uncertainty of ± $10^{-4}$ g. The second group of phase diagrams, *i.e.,* for the longer side chains halides, was determined based on a protocol firstly established by Ruiz-Angel *et al.*[3] and already adopted by us in a previous work.[4] At least four distinct binary mixtures composed of PEG 2000 + ammonium chloride (80 wt% + 20 wt%; 60 wt% + 40 wt%; 40 wt% + 60 wt%) are prepared and placed at 30, 40, 50 or 60 °C under constant stirring. Water was then added until the detection of a clear solution (monophasic region). This step was followed by the addition of either pure PEG 2000 or pure ammonium halide until the visualization of a cloudy solution (biphasic region). This procedure was repeated several times. The same procedure for determining the phase diagrams was applied.

### ***$^1$H NMR***

Poly(ethylene) glycol polymer with an average molecular weight of 200 g mol$^{-1}$ (abbreviated as PEG 200) was purchased from Fluka®. Only the most representative ammonium halides, *i.e.* [$N_{1111}$]Cl and [$N_{3333}$]Cl that display different trends in what concerns their ABS dependence on temperature, were considered for the $^1$H NMR measurements. Deuterium oxide ($D_2O$) with 99.90 % D atoms and 3-(trimethylsilyl)propionic-2,2,3,3-$d_4$ acid sodium salt (TSP) with 99 % D atoms were supplied by Euriso-top®.

$^1$H NMR experiments were carried out according to a protocol previously employed by us[5], notwithstanding some modifications. Three distinct sets of experiments, as shown in Table S.1, were performed: (*i*) varying the PEG 200 molalities, (*ii*) different [$N_{1111}$]Cl or [$N_{3333}$]Cl molalities, and (*iii*) changing the water concentration. Aqueous solutions of [$N_{1111}$]Cl or [$N_{3333}$]Cl (1st approach) or PEG 200 (2nd approach) were initially prepared at *ca.* 0.5 mol kg$^{-1}$ in distilled water. Solutions of PEG 200 ranging from 0 to 0.5 mol kg$^{-1}$ (1st approach) and of [$N_{1111}$]Cl or [$N_{3333}$]Cl ranging from 0 to 0.5 mol kg$^{-1}$ in the corresponding initial solution were gravimetrically prepared (± $10^{-4}$ g). For the third approach, instead, the initial solution is composed of [$N_{1111}$]Cl or [$N_{3333}$]Cl at *ca.* 0.5 mol kg$^{-1}$ in PEG 200, being then used to gravimetrically produce aqueous solutions with increasing water content (from 0 – 5 mol kg$^{-1}$). In all cases, the mixtures belong to regions of complete miscibility (monophasic regime). The $^1$H NMR spectra were obtained using a Bruker Avance 300 spectrometer operating at 300.13 MHz and varying the temperature within 25, 40 and 60 °C in flame-sealed capillaries. $D_2O$ was employed as external lock and TSP as internal reference. The chemical shift deviations ($\Delta\delta_H$) were determined as the difference between the chemical shift of the protons ($\delta_H$) in the ternary mixture and those in the initial mixture, as provided in detail in Table S.1.

### ***Differential scanning calorimetry***

A differential scanning calorimeter (DSC) Hitachi DSC7000X which operates at atmospheric pressure was used to determine the melting temperatures of pure ammonium halides. Prior to carry out such measurements, the DSC was calibrated using primary calibration standards, namely indium and tin, with purities >99 wt%, at a heating rate of 2 $K.min^{-1}$. The samples weight was *circa* 6 to 10 mg and these were firmly sealed in aluminium crucibles in each experiment. All halides were submitted to one cooling-heating cycle at 2 $K.min^{-1}$ from an initial temperature of 100 ºC for $[N_{1111}]Cl$, $[N_{2222}]Cl$ and $[N_{3333}]Cl$, of 80 ºC for $[N_{4441}]Cl$ and of 60 ºC for $[N_{4444}]Cl$ up to a temperature higher than their melting temperatures. Aiming to avoid water condensation at lower temperatures inside the oven, the DSC cell was fed with a constant nitrogen flow of 50 $cm^3.min^{-1}$. At the end, the pure halides melting temperatures were taken as the peak temperature.

## Computational methods

### ***COSMO-RS predictions section***

The standard procedure for COSMO-RS modelling comprises two major steps. First, the continuum solvation COSMO calculations of electronic density and molecular geometry of PEG-2000, ammonium-based compounds, and water were performed with the TURBOMOLE 6.1 program package on the density functional theory, utilizing the BP functional B88-P86 with a triple-ζ valence polarized basis set (TZVP) and the resolution of identity standard (RI).[6] All the optimized structures were confirmed to be minima on potential energy surface *via* vibrational frequency analysis. The absence of imaginary or negative frequencies indicated that the structure is a global minimum.[7] In a second step, the thermodynamic properties calculations, namely partial excess molar enthalpy, were performed with the COSMOthermX_2.1 program using the parameter file BP_TZVP_C21_0111 (COSMOlogic GmbH & Co KG, Leverkusen, Germany).[8] In all calculations, the salts and ILs were treated as isolated ions. Further details on calculating the partial excess molar enthalpy can be found in the literature.[9]

## Tables

**Table S.1:** Summary of the $^1$H NMR spectroscopic studies: solutions, chemical shift deviations calculation and relevant conditions.

| | Component | Solvent | Molality (mol kg$^{-1}$) | $T$ / °C |
|---|---|---|---|---|
| | | **1st approach** | | |
| Initial mixture | $[N_{1111}]Cl$ or $[N_{3333}]Cl$ | Water | 0.5 | 25, 40, 60 |
| Mixtures for $^1$H NMR measurements | PEG 200 | Ammonium + water | 0 – 0.5 | |
| $\Delta\delta_H$ definition | $\Delta\delta_H = \delta_H$(ammonium + PEG 200 + water) - $\delta_H$(ammonium + water) | | | |
| | | **2nd approach** | | |
| Initial mixture | PEG 200 | Water | 0.5 | 25, 40, 60 |
| Mixtures for $^1$H NMR measurements | $[N_{1111}]Cl$ or $[N_{3333}]Cl$ | PEG 200 + Water | 0 – 0.5 | |
| $\Delta\delta_H$ definition | $\Delta\delta_H = \delta_H$ (ammonium + PEG 200 + water) - $\delta_H$(PEG 200 + water) | | | |
| | | **3rd approach** | | |
| Initial mixture | $[N_{1111}]Cl$ or $[N_{3333}]Cl$ | PEG 200 | 0.5 | 25, 40, 60 |
| Mixtures for $^1$H NMR measurements | Water | Ammonium + PEG 200 | 0 – 5 | |
| $\Delta\delta_H$ definition | $\Delta\delta_H = \delta_H$(ammonium + PEG 200 + water) - $\delta_H$(ammonium + PEG 200) | | | |

**Table S.2:** Weight fraction ($w_x$) experimental data for the ternary systems composed of $[N_{1111}]Cl$ + PEG 2000 + water at 40, 50 and 60 °C.

| **$[N_{1111}]Cl$ + PEG 2000 + water** | | | | | |
|---|---|---|---|---|---|
| $T$= 40 °C | | $T$= 50 °C | | $T$= 60 °C | |
| 100 $w_{[N1111]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N1111]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N1111]Cl}$ | 100 $w_{PEG\ 2000}$ |
| 32.022 | 17.137 | 27.760 | 20.594 | 23.211 | 28.867 |
| 29.500 | 21.366 | 24.797 | 25.913 | 21.155 | 31.217 |
| 27.377 | 24.779 | 23.491 | 28.286 | 19.235 | 34.628 |
| 23.619 | 30.808 | 21.633 | 31.253 | 18.253 | 36.404 |
| 21.251 | 34.949 | 20.182 | 34.290 | 15.766 | 39.434 |
| 19.997 | 37.166 | 19.214 | 36.263 | 13.940 | 43.113 |
| 18.944 | 38.737 | 18.441 | 36.664 | 13.082 | 44.057 |
| 17.621 | 40.767 | 17.586 | 38.558 | 11.462 | 46.755 |
| 16.486 | 42.927 | 15.433 | 41.412 | 10.256 | 49.285 |
| 15.365 | 44.873 | 13.632 | 45.121 | 9.590 | 50.172 |
| 14.277 | 46.782 | 12.603 | 47.314 | 9.029 | 51.115 |
| 13.289 | 48.556 | 11.702 | 49.325 | | |
| 12.066 | 50.000 | 11.220 | 50.517 | | |
| | | 10.700 | 51.473 | | |
| | | 10.410 | 52.021 | | |
| | | 9.675 | 52.494 | | |
| | | 9.220 | 53.100 | | |

**Table S.3:** Weight fraction ($w_x$) experimental data for the ternary systems composed of $[N_{2222}]Cl$ + PEG 2000 + water at 40, 50 and 60 °C.

| $[N_{2222}]Cl$ + PEG 2000 + water | | | | | |
|---|---|---|---|---|---|
| $T$= 40 °C | | $T$= 50 °C | | $T$= 60 °C | |
| 100 $w_{[N2222]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N2222]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N2222]Cl}$ | 100 $w_{PEG\ 2000}$ |
| 46.643 | 9.695 | 36.115 | 21.914 | 40.867 | 13.707 |
| 41.966 | 15.282 | 34.735 | 23.449 | 39.152 | 15.904 |
| 37.665 | 20.989 | 33.946 | 24.607 | 36.481 | 19.290 |
| 34.648 | 25.487 | 32.930 | 26.170 | 32.431 | 25.018 |
| 29.396 | 33.467 | 29.625 | 31.026 | 31.267 | 26.801 |
| 21.264 | 45.185 | 26.483 | 35.520 | 29.740 | 28.649 |
| 17.151 | 51.503 | 17.256 | 50.531 | 28.244 | 29.933 |
| | | | | 27.241 | 31.078 |
| | | | | 26.505 | 31.604 |
| | | | | 25.139 | 32.334 |
| | | | | 24.602 | 32.785 |

**Table S.4:** Weight fraction ($w_x$) experimental data for the ternary systems composed of $[N_{1112(OH)}]Cl$ + PEG 2000 + water at 40, 50 and 60 °C.

| $[N_{1112(OH)}]Cl$ + PEG 2000 + water | | | | | |
|---|---|---|---|---|---|
| $T$= 40 °C | | $T$= 50 °C | | $T$= 60 °C | |
| 100 $w_{[N1112(OH)]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N1112(OH)]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N1112(OH)]Cl}$ | 100 $w_{PEG\ 2000}$ |
| 52.439 | 8.126 | 43.531 | 11.483 | 43.597 | 8.209 |
| 51.222 | 7.561 | 40.088 | 15.972 | 38.142 | 14.624 |
| 47.098 | 10.583 | 34.780 | 22.475 | 33.610 | 21.814 |
| 43.901 | 14.005 | 32.111 | 26.584 | 31.888 | 23.154 |
| 35.666 | 24.829 | 30.073 | 29.167 | 28.110 | 27.975 |
| 32.995 | 28.768 | 29.295 | 29.826 | 24.945 | 33.513 |
| 19.980 | 47.307 | 23.703 | 37.392 | 23.986 | 34.864 |
| 16.880 | 52.116 | 21.866 | 40.752 | 23.415 | 35.632 |
| 15.195 | 54.066 | | | 19.957 | 41.195 |
| | | | | 19.732 | 41.313 |
| | | | | 17.694 | 43.805 |
| | | | | 16.238 | 46.936 |
| | | | | 15.931 | 46.574 |
| | | | | 13.608 | 50.344 |
| | | | | 12.150 | 52.534 |
| | | | | 11.438 | 56.116 |
| | | | | 9.614 | 59.418 |

**Table S.5:** Weight fraction ($w_x$) experimental data for the ternary systems composed of $[N_{3333}]Cl$ + PEG 2000 + water at 40, 50 and 60 °C.

| **$[N_{3333}]Cl$ + PEG 2000 + water** | | | | | |
|---|---|---|---|---|---|
| *T*= 40 °C | | *T*= 50 °C | | *T*= 60 °C | |
| 100 $w_{[N3333]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N3333]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N3333]Cl}$ | 100 $w_{PEG\ 2000}$ |
| 54.370 | 22.626 | 46.842 | 41.267 | 56.395 | 34.385 |
| 50.934 | 25.635 | 44.922 | 45.343 | 38.271 | 56.215 |
| 49.467 | 26.150 | 40.093 | 49.818 | 23.218 | 72.530 |
| 48.425 | 27.912 | 32.336 | 57.498 | 20.320 | 75.775 |
| 45.437 | 29.427 | 30.014 | 59.756 | 10.789 | 87.167 |
| 44.342 | 32.560 | 25.481 | 64.016 | | |
| 40.466 | 36.472 | 15.609 | 75.250 | | |
| 36.399 | 40.081 | 10.228 | 83.796 | | |
| 31.882 | 43.243 | | | | |
| 28.886 | 47.241 | | | | |
| 27.603 | 48.755 | | | | |
| 26.485 | 52.892 | | | | |
| 23.813 | 56.725 | | | | |
| 16.573 | 65.754 | | | | |

**Table S.6:** Weight fraction ($w_x$) experimental data for the ternary systems composed of $[N_{1444}]Cl$ + PEG 2000 + water at 40, 50 and 60 °C.

| **$[N_{1444}]Cl$ + PEG 2000 + water** | | | | | |
|---|---|---|---|---|---|
| $T$= 40 °C | | $T$= 50 °C | | $T$= 60 °C | |
| 100 $w_{[N1444]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N1444]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N1444]Cl}$ | 100 $w_{PEG\ 2000}$ |
| 42.755 | 39.992 | 68.131 | 19.188 | 64.424 | 27.552 |
| 39.279 | 44.221 | 63.01 | 26.991 | 54.842 | 34.973 |
| 36.272 | 45.382 | 54.709 | 36.605 | 47.669 | 44.054 |
| 29.140 | 55.218 | 34.658 | 59.709 | 46.046 | 45.259 |
| 27.333 | 57.887 | 10.714 | 85.193 | 41.725 | 51.323 |
| 18.134 | 65.980 | | | 41.177 | 51.556 |
| 15.104 | 70.264 | | | 39.207 | 59.106 |
| | | | | 33.457 | 61.112 |
| | | | | 29.468 | 69.285 |

**Table S.7:** Weight fraction ($w_x$) experimental data for the ternary systems composed of $[N_{4444}]Cl$ + PEG 2000 + water at 30, 40 and 50 ºC.

| **$[N_{4444}]Cl$ + PEG 2000 + water** | | | | | |
|---|---|---|---|---|---|
| $T$= 30 °C | | $T$= 40 °C | | $T$= 50 °C | |
| 100 $w_{[N4444]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N4444]Cl}$ | 100 $w_{PEG\ 2000}$ | 100 $w_{[N4444]Cl}$ | 100 $w_{PEG\ 2000}$ |
| 81.768 | 2.442 | 86.736 | 4.813 | 90.872 | 6.002 |
| 80.674 | 3.361 | 81.451 | 9.200 | 76.534 | 20.065 |
| 80.244 | 4.567 | 71.626 | 16.632 | 58.081 | 38.672 |
| 76.989 | 6.639 | 70.987 | 19.205 | 47.800 | 48.309 |
| 76.346 | 8.989 | 67.785 | 17.584 | | |
| 73.158 | 11.390 | 65.635 | 22.337 | | |
| 69.196 | 13.282 | 59.429 | 29.121 | | |
| 67.223 | 16.845 | 41.899 | 44.731 | | |
| 61.654 | 21.627 | | | | |

## Figures

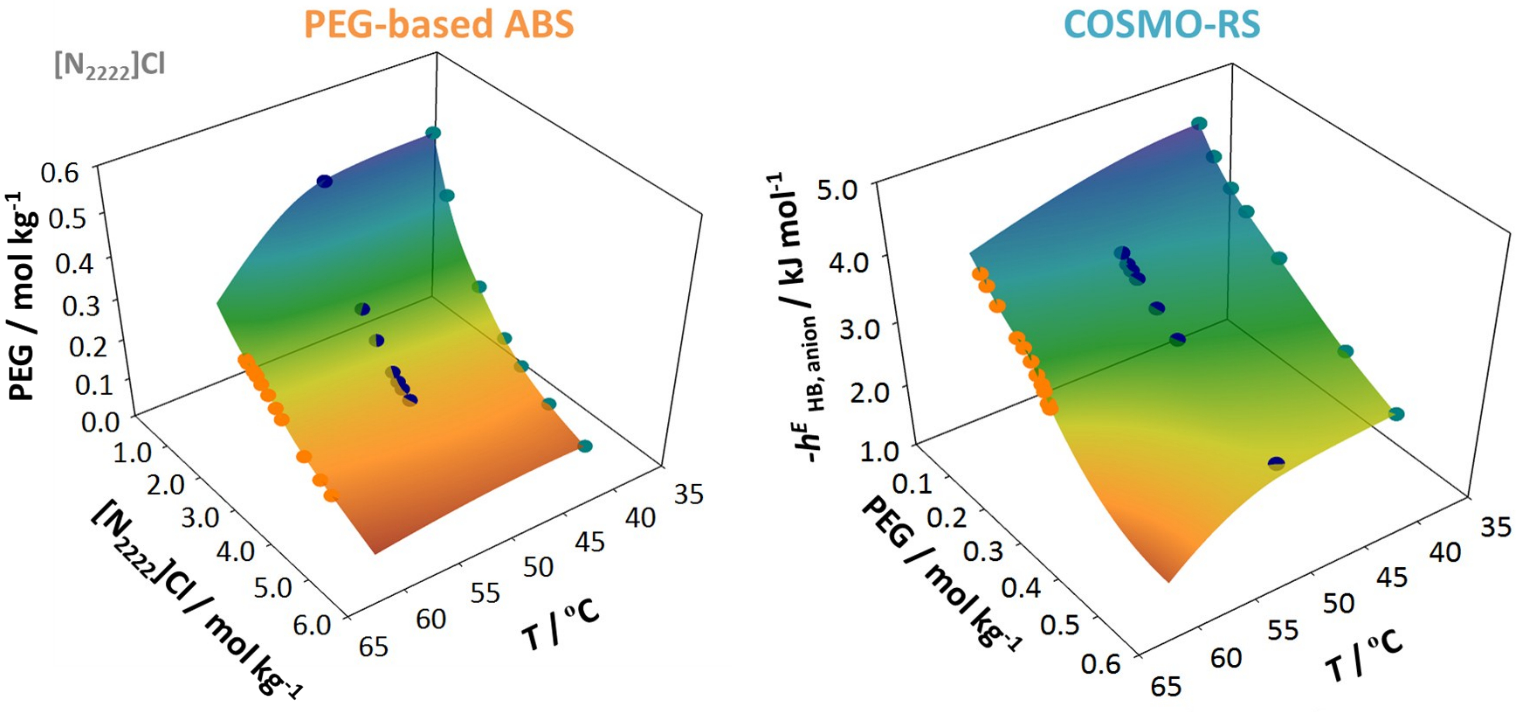

**Figure S.1:** Phase diagrams of the ternary system $[N_{2222}]Cl$ + PEG + water at 40, 50 and 60 $^{o}C$; partial molar excess enthalpies of the ammonium anion in the ternary mixture predicted by COSMO-RS as a function of PEG molality at 40, 50 and 60 $^{o}C$.

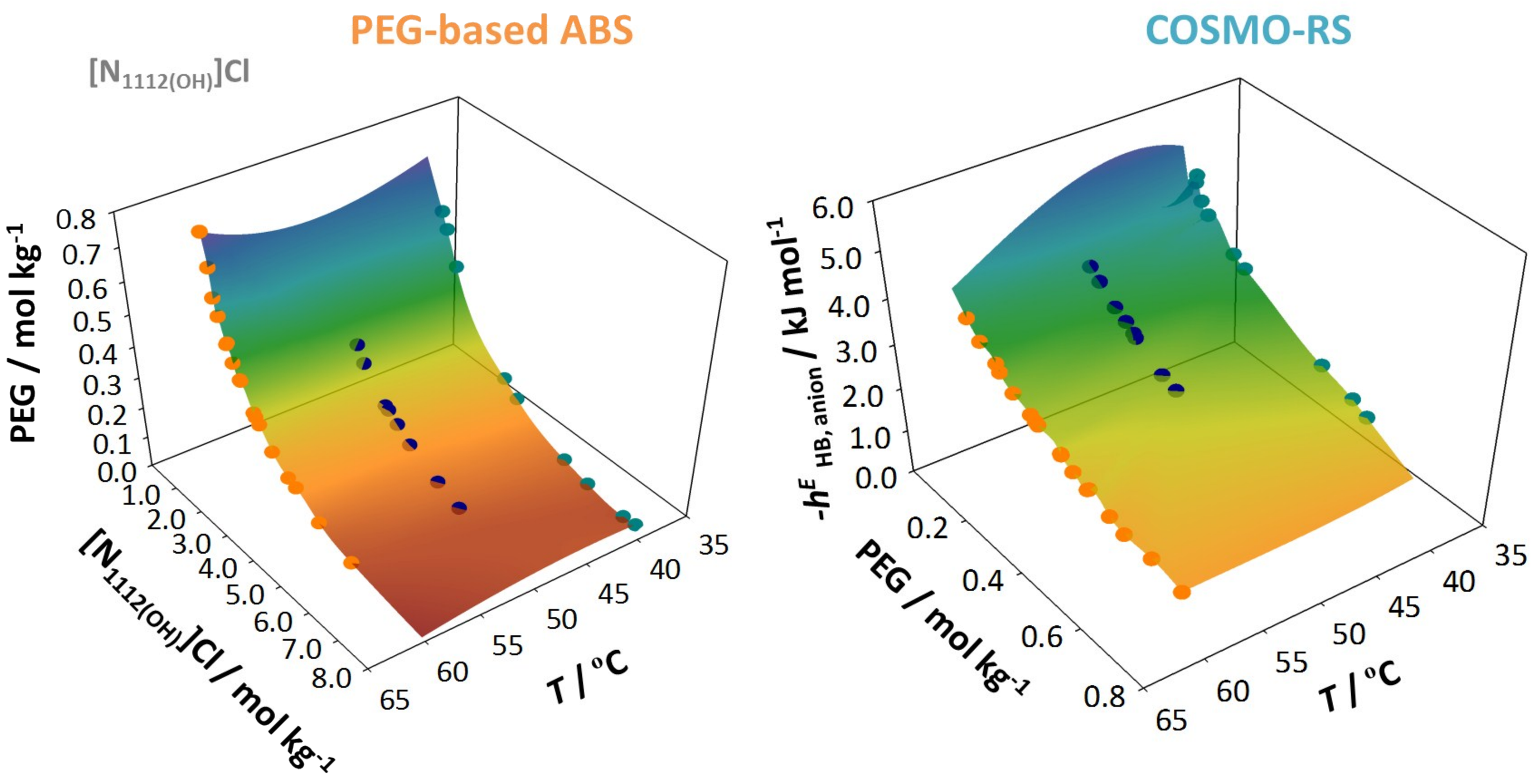

**Figure S.2:** Phase diagrams of the ternary system $[N_{1112(OH)}]Cl$ + PEG + water at 40, 50 and 60 $^{o}$C; partial molar excess enthalpies of the ammonium anion in the ternary mixture predicted by COSMO-RS as a function of PEG molality at 40, 50 and 60 $^{o}$C.

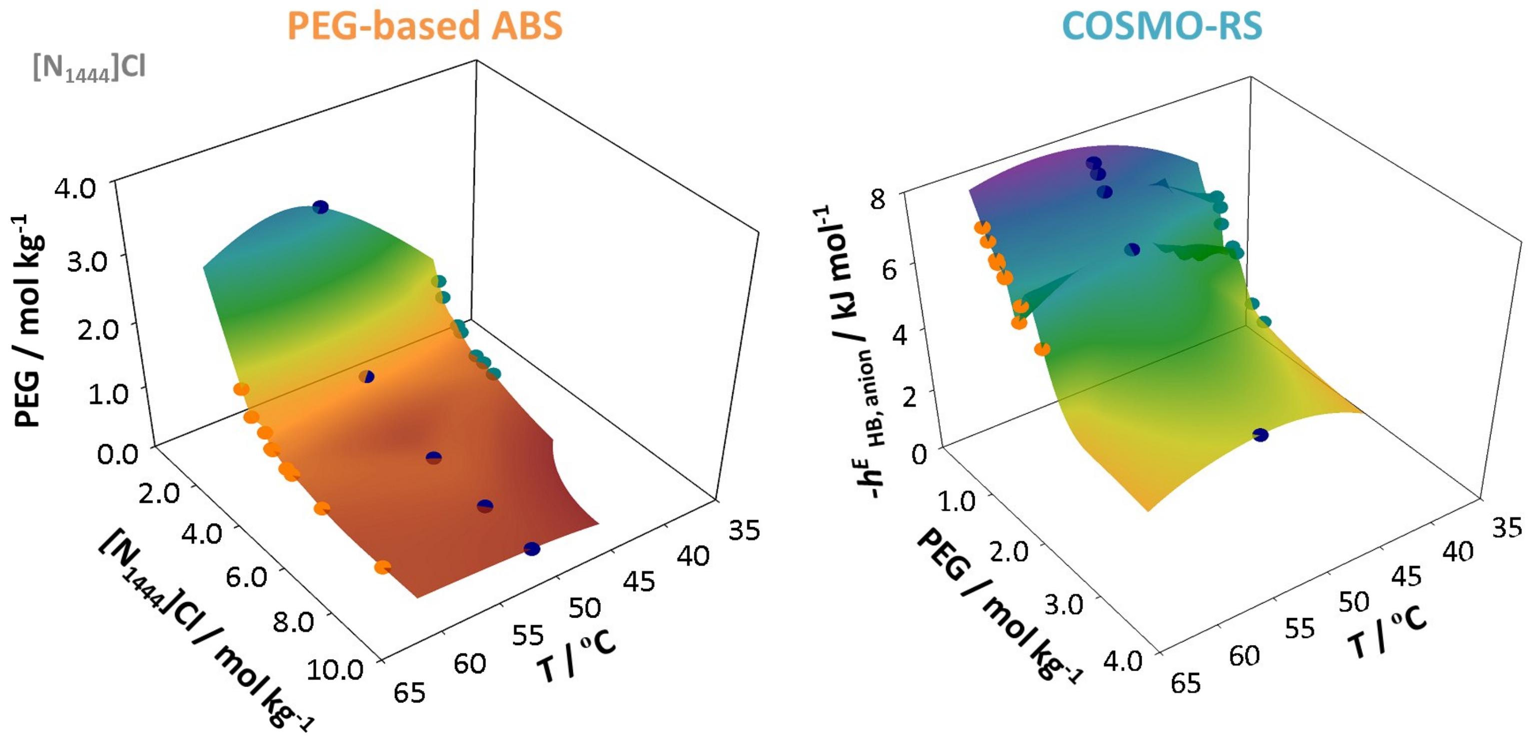

**Figure S.3:** Phase diagrams of the ternary system $[N_{1444}]Cl$ + PEG + water at 40, 50 and 60 °C; partial molar excess enthalpies of the ammonium anion in the ternary mixture predicted by COSMO-RS as a function of PEG molality at 40, 50 and 60 °C.

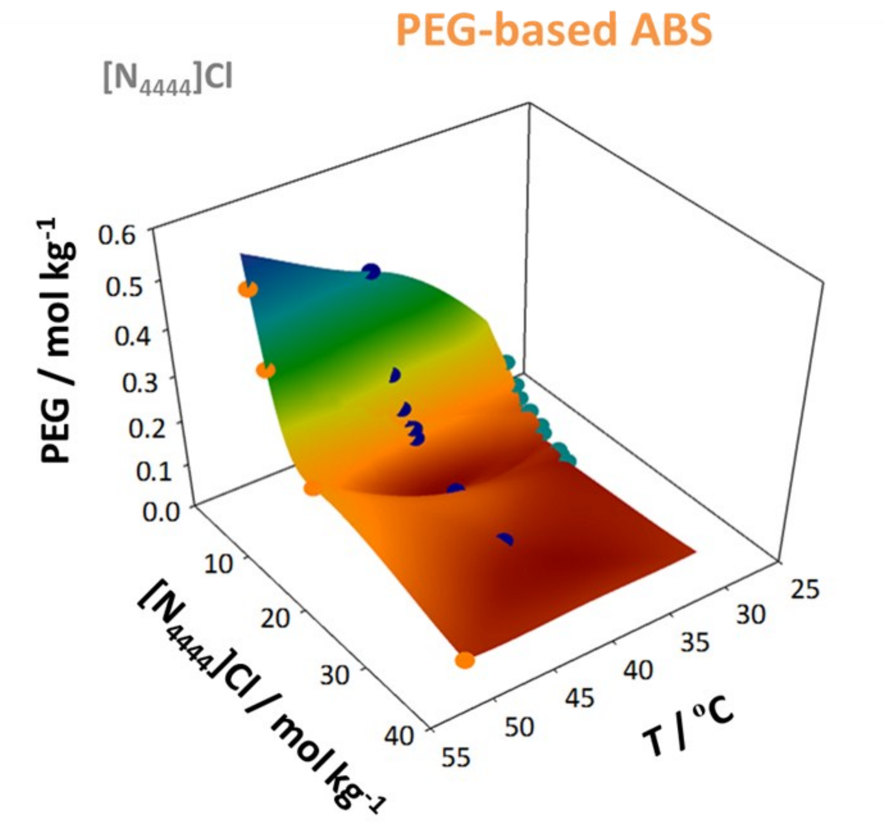

**Figure S.4:** Phase diagrams of the ternary system $[N_{4444}]Cl$ + PEG + water at 30, 40 and 50 °C.

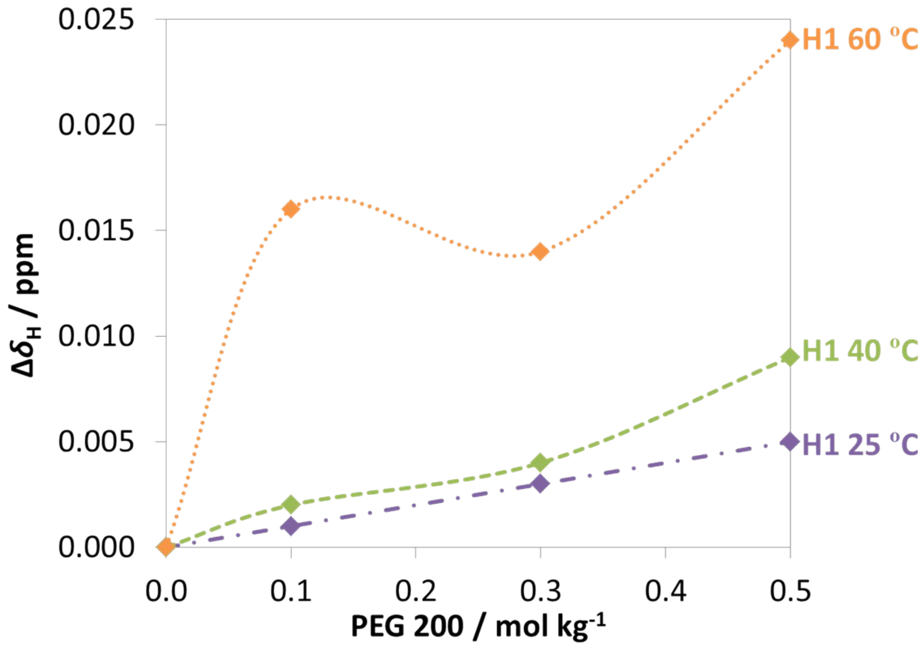

**Figure S.5:** $^1$H NMR chemical shift deviations of [$N_{1111}$]Cl protons relative to those of the initial [$N_{1111}$]Cl/water binary mixture as a function of PEG 200 molality at 25, 40 and 60 $^o$C.

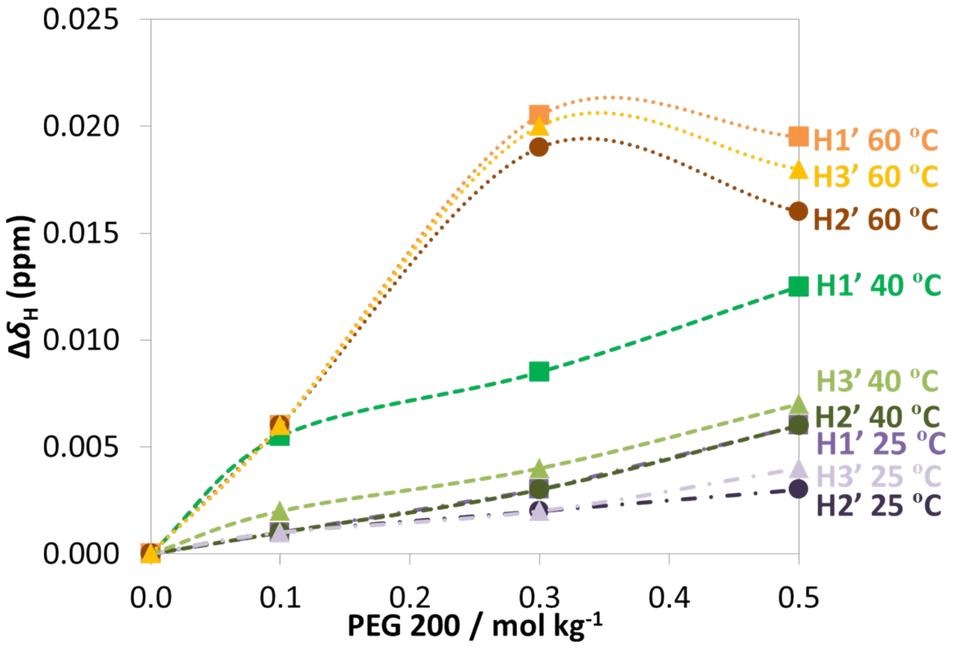

**Figure S.6:** $^1$H NMR chemical shift deviations of [$N_{3333}$]Cl protons relative to those of the initial [$N_{3333}$]Cl/water binary mixture as a function of PEG 200 molality at 25, 40 and 60 $^o$C.

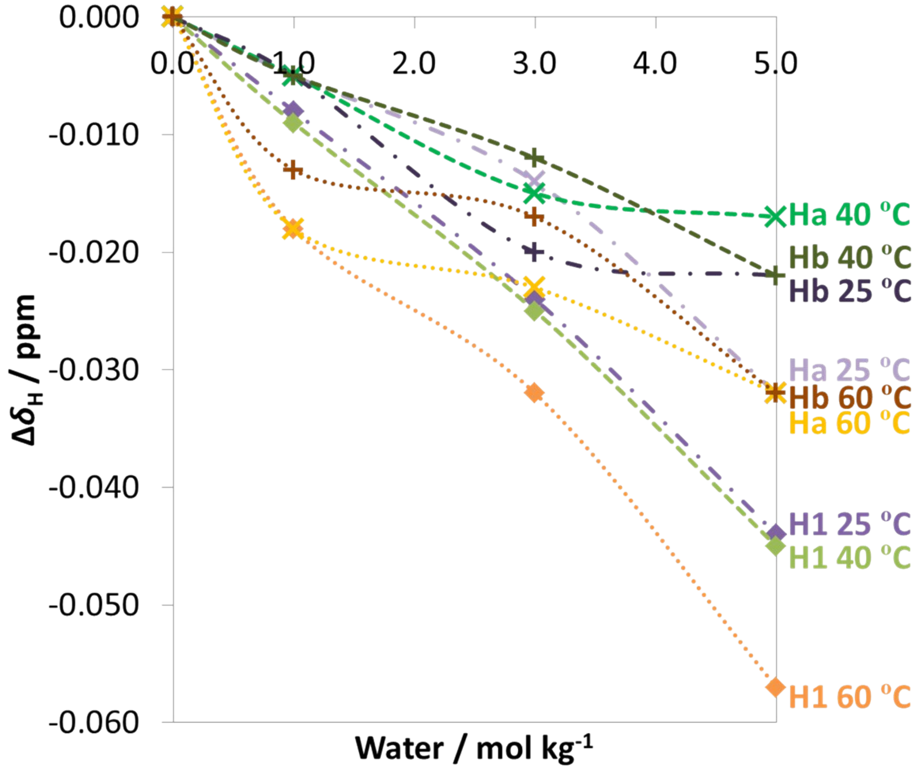

**Figure S.7:** $^1$H NMR chemical shift deviations of [$N_{1111}$]Cl and PEG 200 protons relative to those of the initial [$N_{1111}$]Cl/PEG 200 binary mixture as a function of water molality at 25, 40 and 60 °C.

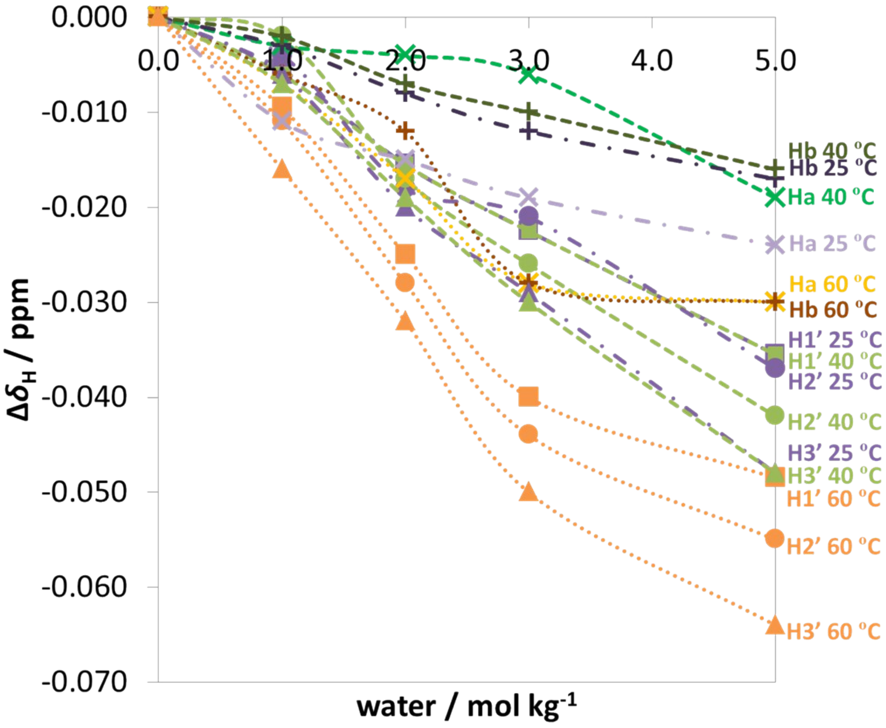

**Figure S.8:** $^{1}$H NMR chemical shift deviations of [$N_{3333}$]Cl and PEG 200 protons relative to those of the initial [$N_{3333}$]Cl/PEG 200 binary mixture as a function of water molality at 25, 40 and 60 °C.

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