Mechanisms of Phase Separation in Temperature–Responsive Acidic Aqueous Biphasic Systems

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Supporting Information Contents:

Number of pages: 11

Number of figures: 9

Number of Tables: 1
**Figures**

**Figure S1.** Polarized light microscopy images of (A) vacuum dried [P44414]Cl and (B) hydrated [P44414]Cl in the process of dissolution at room temperature (× 100 magnification). The white arrow indicates the direction of the hydration front.
Figure S2. Representative snapshot of the [P44414]Cl/H2O system (1) after production run. The polar head of [P44414]+ is represented in purple, the apolar C14 carbon tail in green and Cl− in blue. Water molecules were removed for clarity.
**Figure S3.** (A) Radial distribution functions (RDFs) between the phosphorus atom (P) of [P$_{44414}$]$^+$ and H$_2$O or Cl$^-$ in the dilute [P$_{44414}$]Cl/H$_2$O system 1 (CN – coordination number) modelled within the AA-MD formalism. (B) Spatial distribution function (SDF) of Cl$^-$ (blue surface) and H$_2$O (meshed grey surface) around [P$_{44414}$]$^+$ in the binary [P$_{44414}$]Cl/H$_2$O system. All atoms of H$_2$O were considered when calculating the RDF and SDF.
Figure S4. Cloud points of the HCl/[P_{44414}]Cl/H₂O AcABS as a function of IL concentration for a given acid concentration. Data points represent the average of two replicates.
Figure S5. Cloud points of the HCl/[P_4414]Cl/H_2O AcABS as a function of HCl concentration for a given IL concentration. Data points represent the average of two replicates.
Figure S6. CG-MD simulation snapshots for the 500 component [P_{44414}]Cl system under different NaCl concentration (systems (5) to (9) described in Table 1) at 298 K. Above 5% wt of NaCl concentration, the [P_{44414}]Cl system is clearly biphasic in accordance with experimental results. The colour code is as follows; the apolar [P_{44414}]^{+} alkyl chain tail in green, the [P_{44414}]^{+} butyl groups in purple, chloride anions in black, sodium cations in orange and water in blue.
Figure S7. RDFs between the $[P_{44414}]^+$ head and surrounding water molecules as a function of NaCl concentration in the NaCl/$[P_{44414}]Cl/H_2O$ systems (5) to (9). RDFs were scaled by 3 to consider the 3:1 mapping of polarizable water beads.
Figure S8. Density profile for (A) HCl/[P$_{44414}$]Cl/H$_2$O and (B) and NaCl/[P$_{44414}$]Cl/H$_2$O micelles for systems (3) and (2) described in Table 1, respectively. The colour code is as follows; the apolar [P$_{44414}$]$^+$ alkyl chain tail in green, the [P$_{44414}$]$^+$ butyl groups in purple, phosphorus centre of [P$_{44414}$]$^+$ in red, chloride anions in black, Na$^+$ or [H$_3$O]$^+$ cations in orange and water in blue.
Figure S9. (A) Coordination numbers (CN) of Na$^+$ and [H$_3$O]$^+$ (system (2) and (3) respectively) around [P$_{44414}$]$^+$ as a function of distance from its central phosphorus atom (P). Overlaid on these results are the RDFs for P-H$_2$O and P-Cl in the dilute HCl/[P$_{44414}$]Cl/H$_2$O system (3) to better illustrate the structuring around the micelle surface as a function of its 1$^{st}$ and 2$^{nd}$ hydration shells at 0.5 nm and 0.8 nm respectively. (B) Spatial distribution function of Cl$^-$ (blue surface), H$_2$O (meshed grey surface) and [H$_3$O]$^+$ (red surface) around [P$_{44414}$]$^+$ in the HCl/[P$_{44414}$]Cl/H$_2$O system (3). All atoms of H$_2$O and [H$_3$O]$^+$ were considered when calculating CNs, RDFs and SDF.
Tables

Table S1. Water coordination number (CN) around the [P₄₄₁₄]⁺ head as a function of the NaCl concentration at two different distances (r) corresponding to the maximum of the 1ˢᵗ (r= 0.495 nm) and 2ⁿᵈ peak (r= 0.970 nm) in Figure S7.

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References