ELECTRONIC SUPPLEMENTARY INFORMATION

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

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Figures

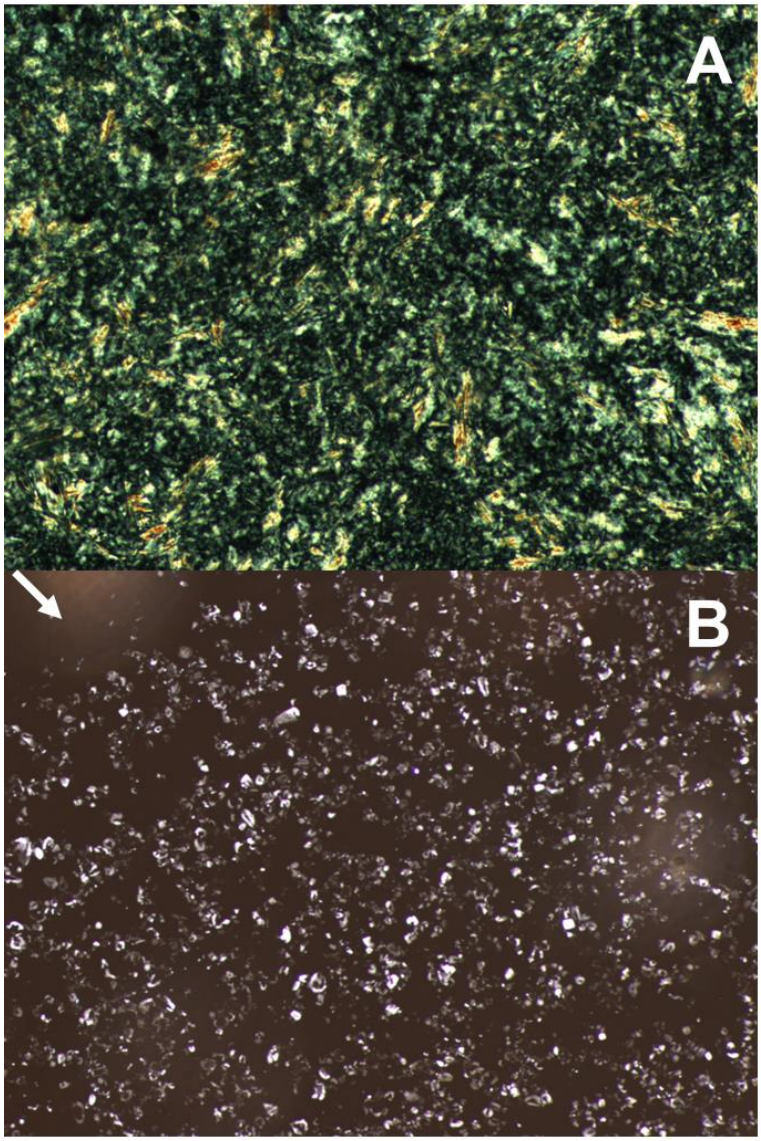

Figure S1. Polarized light microscopy images of (A) vacuum dried [P_{44414}]Cl and (B) hydrated [P_{44414}]Cl in the process of dissolution at room temperature (× 100 magnification). The white arrow indicates the direction of the hydration front.

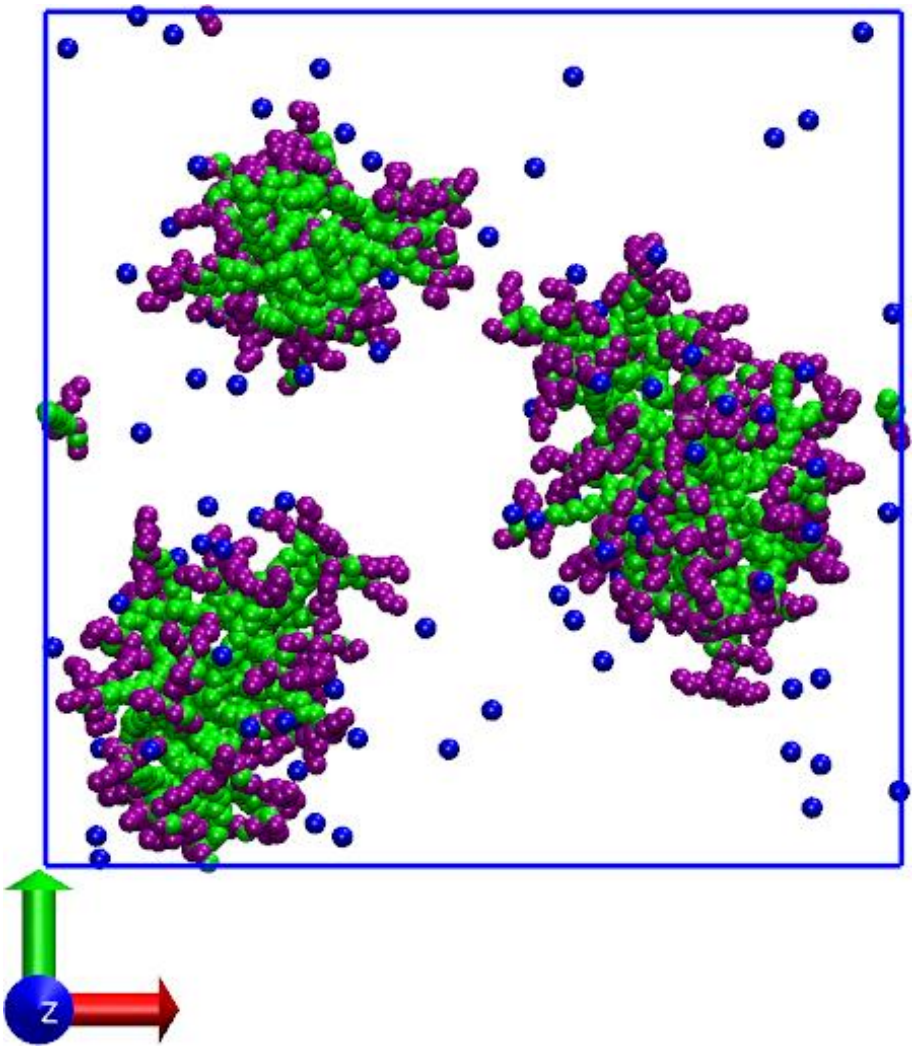

Figure S2. Representative snapshot of the $[P_{44414}]Cl/H_2O$ system (1) after production run. The polar head of $[P_{44414}]^+$ is represented in purple, the apolar C_{14} carbon tail in green and Cl^- in blue. Water molecules were removed for clarity.

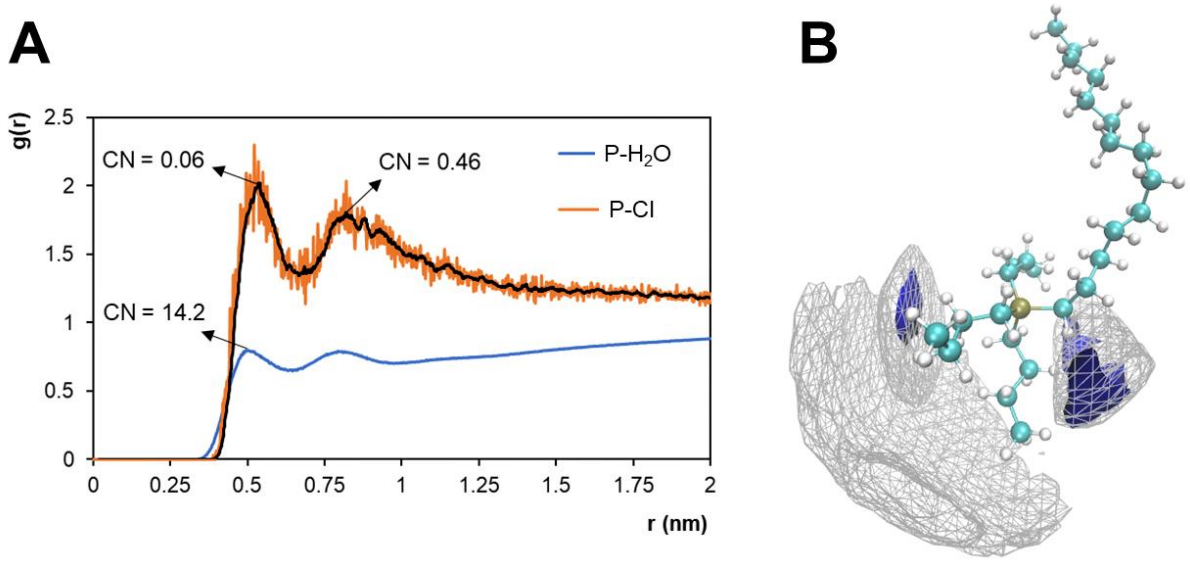

Figure S3. (A) Radial distribution functions (RDFs) between the phosphorus atom (P) of $[P_{44414}]^+$ and H_2O or Cl^- in the dilute $[P_{44414}]Cl/H_2O$ system 1 (CN – coordination number) modelled within the AA-MD formalism. (B) Spatial distribution function (SDF) of Cl^- (blue surface) and H_2O (meshed grey surface) around $[P_{44414}]^+$ in the binary $[P_{44414}]Cl/H_2O$ system. All atoms of H_2O were considered when calculating the RDF and SDF.

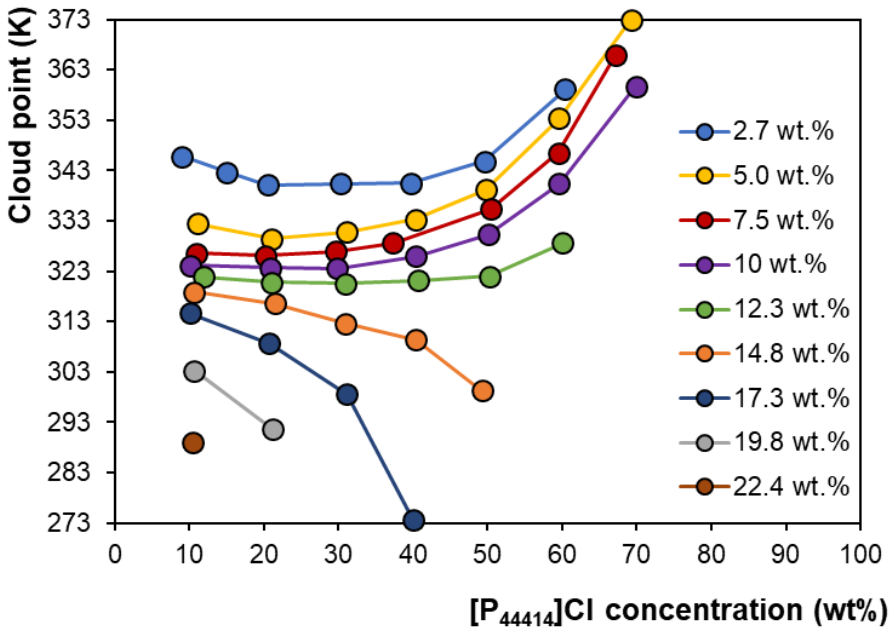

Figure S4. Cloud points of the HCl/[P_{44414}]Cl/H_2O AcABS as a function of IL concentration for a given acid concentration. Data points represent the average of two replicates.

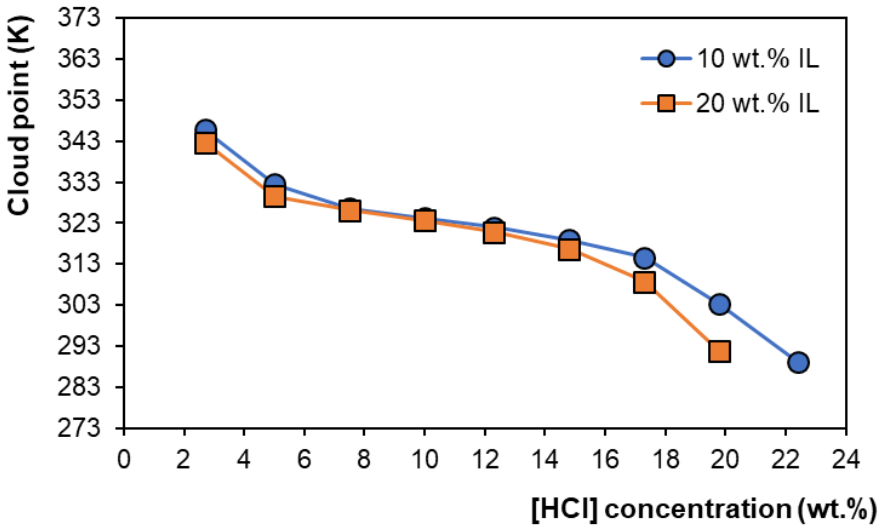

Figure S5. Cloud points of the HCl/[P_{44414}]Cl/H_2O AcABS as a function of HCl concentration for a given IL concentration. Data points represent the average of two replicates.

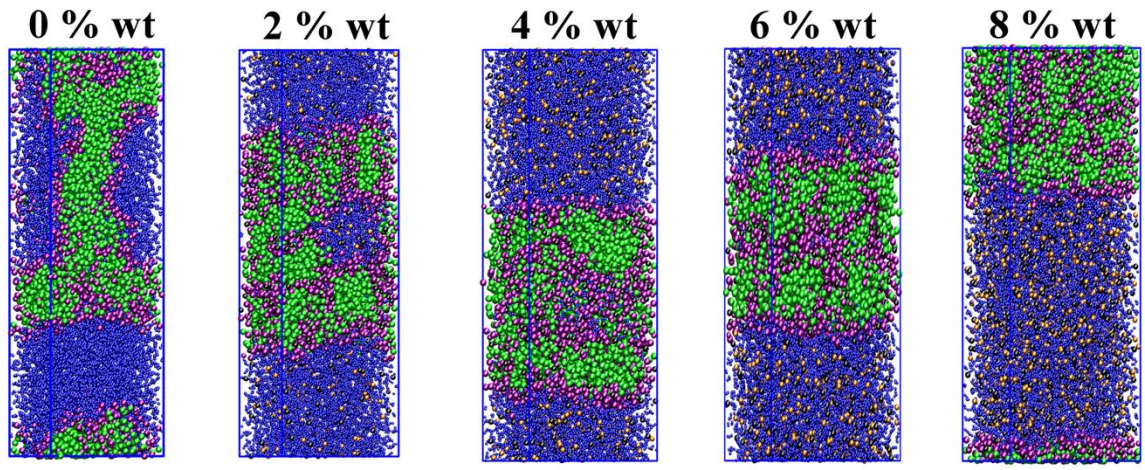

Figure S6. CG-MD simulation snapshots for the 500 component $[P_{44414}]Cl$ system under different NaCl concentration (systems (5) to (9) described in **Table 1**) at 298 K. Above 5% wt of NaCl concentration, the $[P_{44414}]Cl$ system is clearly biphasic in accordance with experimental results.[1] The 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.

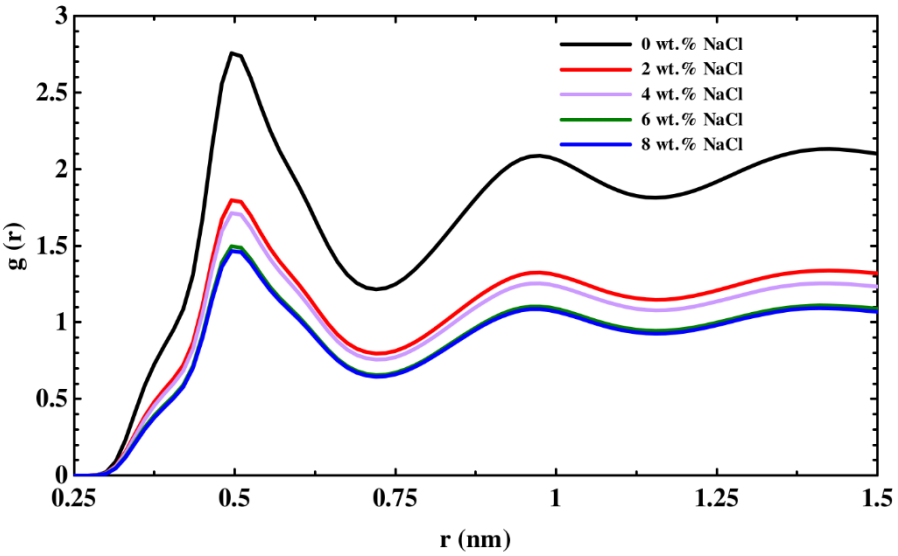

Figure S7. RDFs between the $[P_{44414}]^+$ head and surrounding water molecules as a function of NaCl concentration in the NaCl/$[P_{44414}]$Cl/H_2O systems (5) to (9). RDFs were scaled by 3 to consider the 3:1 mapping of polarizable water beads.

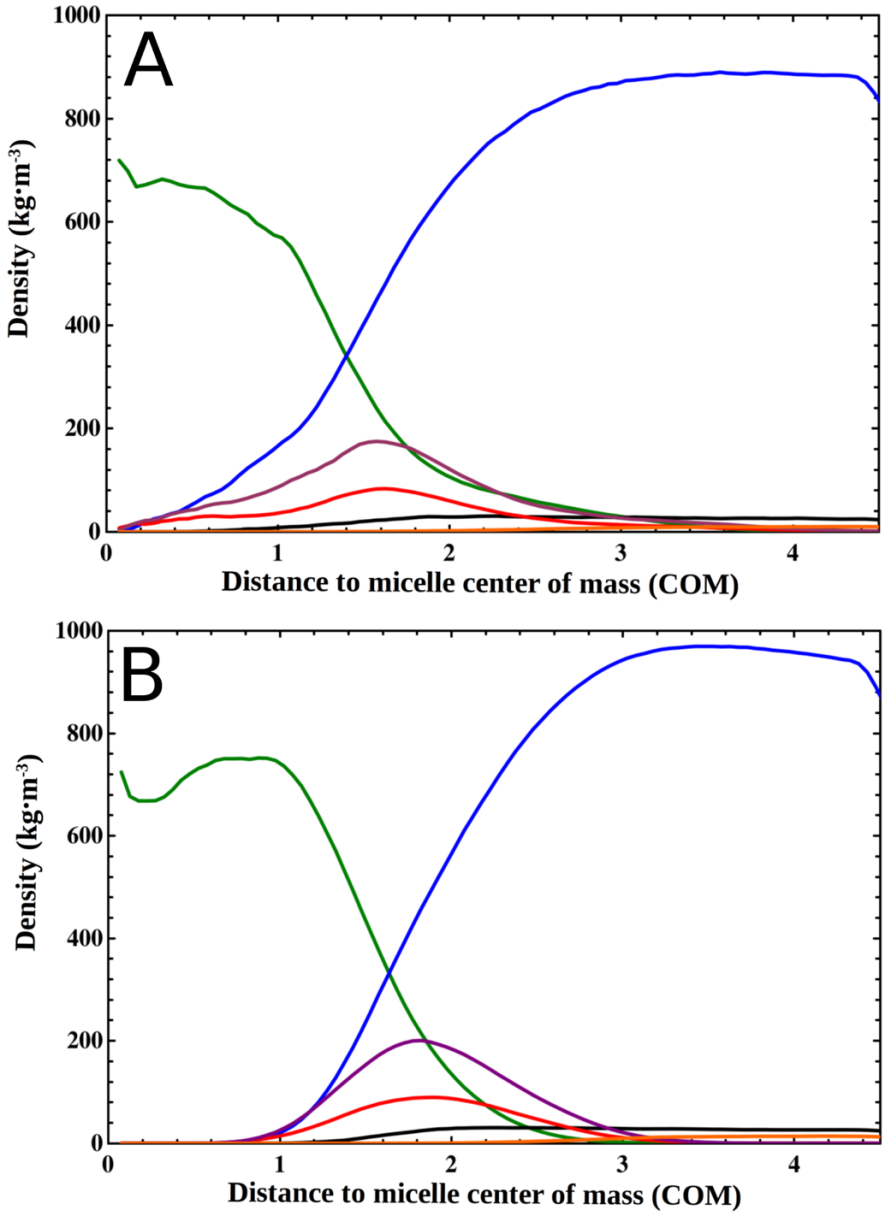

Figure S8. Density profile for (A) HCl/[P_{44414}]Cl/H_2O and (B) and NaCl/[P_{44414}]Cl/H_2O micelles for systems (3) and (2) described in **Table 1**, respectively. The colour code is as follows; the apolar $[P_{44414}]^+$ alkyl chain tail in green, the $[P_{44414}]^+$ butyl groups in purple, phosphorus centre of $[P_{44414}]^+$ in red, chloride anions in black, Na^+ or $[H_3O]^+$ cations in orange and water in blue.

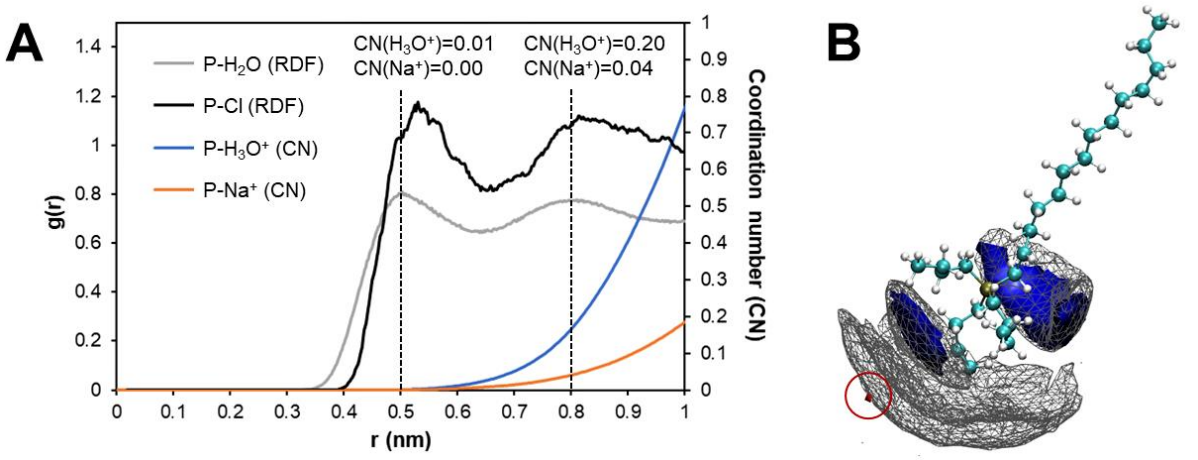

Figure S9. (A) Coordination numbers (CN) of Na^+ and $[H_3O]^+$ (system (2) and (3) respectively) around $[P_{44414}]^+$ as a function of distance from its central phosphorus atom (P). Overlaid on these results are the RDFs for P-H_2O and P-Cl in the dilute HCl/$[P_{44414}]$Cl/H_2O system (3) to better illustrate the structuring around the micelle surface as a function of its 1st and 2nd hydration shells at 0.5 nm and 0.8 nm respectively. (B) Spatial distribution function of Cl^- (blue surface), H_2O (meshed grey surface) and $[H_3O]^+$ (red surface) around $[P_{44414}]^+$ in the HCl/$[P_{44414}]$Cl/H_2O system (3). All atoms of H_2O and $[H_3O]^+$ were considered when calculating CNs, RDFs and SDF.

Tables

Table S1. Water coordination number (CN) around the $[P_{44414}]^+$ 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**.

[NaCl] (wt.%)	CN (at r = 0.495 nm)	CN (at r = 0.970 nm)
0.0	2.38	28.70
2.0	1.43	18.34
4.0	1.24	16.40
6.0	1.08	14.24
8.0	1.09	13.08

References

1) Schaeffer, N. Passos, H., Gras, M., Mogilireddy, V., Leal, J.P., Pérez-Sánchez, G., Gomes, J.R.B., Billard, I., Papaiconomou, N., Coutinho, J.A.P., Mechanism of ionic-liquid-based acidic aqueous biphasic system formation. Phys. Chem. Chem. Phys., 2018, 20, 9838-9846.