

Electronic Supplementary Information

Ionic liquids showing phase separation with water prepared by mixing hydrophilic and polar amino acid ionic liquids.

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Preparation of amino acid ionic liquids

Trihexyl-*n*-octylphosphonium L-lysinate ([P₆₆₆₈][Lys]), trihexyl-*n*-octylphosphonium L-aspartate ([P₆₆₆₈][Asp]), trihexyl-*n*-octylphosphonium L-serinate ([P₆₆₆₈][Ser]), trihexyl-*n*-octylphosphonium L-alaninate ([P₆₆₆₈][Ala]), and trihexyl-*n*-octylphosphonium L-glutamate ([P₆₆₆₈][Glu]) were synthesised by neutralised trihexyl-*n*-octylphosphonium hydroxide ([P₆₆₆₈]OH) and corresponding amino acids. [P₆₆₆₈]OH was prepared by passing trihexyl-*n*-octylphosphonium bromide ([P₆₆₆₈]Br) through a column filled with anion exchange resin (Amberlite IRN 78) in methanol-water mixture. [P₆₆₆₈]Br was obtained by refluxing trihexylphosphine with octylbromide in hexane under dry nitrogen at 80 °C for 48 h. All amino acid ionic liquids (AAILs) were dried *in vacuo* for at least 24 h at 40 °C before experiments. The structures of these AAILs were confirmed by ¹H NMR.

[P₆₆₆₈][Lys] Trihexyl-*n*-octylphosphonium L-lysinate

δ_{H} (400 MHz; CDCl₃; δ /ppm relative to TMS): 0.82-0.96 (12H, m, CH₂CH₃), 1.20–1.37 (20H, m, CH₂CH₂CH₃ and (CH₂)₃CH₂CH₂(CH₂)₂CH₃), 1.37-1.60 (20H, m, P-CH₂CH₂CH₂, NH₂-CH₂CH₂CH₂), 1.60-1.71 (1H, m C-CHH-CH₂), 1.75-1.88 (1H, m C-CHH-CH₂'), 2.36–2.52 (8H, m, P-CH₂), 2.62-2.70 (2H, m, NH₂-CH₂), 3.12-3.17 (1H, m, C-H).

[P₆₆₆₈][Asp] Trihexyl-*n*-octylphosphonium L-aspartate

δ_{H} (400 MHz; CDCl₃; δ /ppm relative to TMS): 0.80-0.99 (12H, m, CH₂CH₃), 1.20-1.40 (20H, m, CH₂CH₂CH₃ and (CH₂)₃CH₂CH₂(CH₂)₂CH₃), 1.41-1.61 (16H, m, P-CH₂CH₂CH₂), 2.22–2.39 (8H, m, P-CH₂), 2.52-2.61 (1H, m COOH-CHH), 2.68-2.78 (1H, m COOH-CHH'), 3.58-3.66 (1H, m, C-H).

[P₆₆₆₈][Ser] Trihexyl-*n*-octylphosphonium L-serinate

δ_{H} (400 MHz; CDCl₃; δ /ppm relative to TMS): 0.84-0.96 (12H, m, CH₂CH₃), 1.22-1.39 (20H, m, CH₂CH₂CH₃ and (CH₂)₃CH₂CH₂(CH₂)₂CH₃), 1.42-1.61 (16H, m, P-CH₂CH₂CH₂), 2.30–2.43 (8H, m, P-CH₂), 2.22-2.29 (1H, m OH-CHH), 3.52-3.45 (1H, m OH-CHH'), 3.65-3.73 (1H, m, C-H).

[P₆₆₈][Ala] Trihexyl-*n*-octylphosphonium L-alanate

δ_{H} (400 MHz; CDCl₃; δ /ppm relative to TMS): 0.82-0.95 (12H, m, CH₂CH₃), 1.22-1.38 (23H, m, CH₂CH₂CH₃, (CH₂)₃CH₂CH₂(CH₂)₂CH₃ and C-CH₃), 1.42-1.61 (16H, m, P-CH₂CH₂CH₂), 2.36-2.49 (8H, m, P-CH₂), 3.24-3.32 (1H, m, C-H).

[P₆₆₈][Glu] Trihexyl-*n*-octylphosphonium L-glutamate

δ_{H} (400 MHz; CDCl₃; δ /ppm relative to TMS): 0.81-0.95 (12H, m, CH₂CH₃), 1.19-1.39 (20H, m, CH₂CH₂CH₃ and (CH₂)₃CH₂CH₂(CH₂)₂CH₃), 1.42-1.63 (16H, m, P-CH₂CH₂CH₂), 1.97-2.21 (2H, m, COOH-CH₂CH₂), 2.25-2.39 (8H, m, P-CH₂), 2.39-2.59 (2H, m, COOH-CH₂CH₂), 3.48-3.56 (1H, m, C-H).

Estimation of Kamlet-Taft parameters

The Kamlet-Taft parameters of a series of AAILs were measured as follows¹. Two different dye molecules such as N,N-diethyl-4-nitroaniline and 4-nitroaniline were used for this experiment. A concentrated dry methanol solution of the dye was added to the neat AAILs, then methanol was removed by vacuum drying at 40 °C. For Kamlet-Taft parameters of separated AAIL rich phase, we mixed probe dyes directly with aqueous AAILs and gently stirred the resulting mixture. To prevent dye aggregation, the dye concentration in any series of AAILs was set to be low but sufficient to get an absorbance greater than 0.1.

These dye solutions were placed in quartz cells with an optical path length of 0.1 mm. The temperature of the quartz cell was maintained at 25 °C. Once maximum absorption wavelength (λ_{max}) was determined, the Kamlet-Taft parameters (β : hydrogen bonding basicity and π^* : dipolarity) were calculated from the following equations:

$$\beta = (1.035v_{(N,N\text{-diethyl-4-nitroaniline})} + 2.64 - v_{(4\text{-nitroaniline})})/2.80$$
$$\pi^* = 0.314(27.52 - v_{(N,N\text{-diethyl-4-nitroaniline})})$$

¹³C NMR measurements of [P₆₆₈][Lys]- [P₆₆₈][Asp]-water mixture

¹³C NMR spectroscopy for [P₆₆₈][Lys]-[P₆₆₈][Asp]-water mixture was measured using a double NMR tube technique at 25 °C. [P₆₆₈][Lys] and [P₆₆₈][Asp] were individually mixed with pure water to reach the concentration of 0.92 mol·kg⁻¹ and the resulting aqueous solutions were mixed to become desired molar ratio. Since mixture of water and [P₆₆₈]₁[Lys]_{0.15}[Glu]_{0.85}, [P₆₆₈]₁[Lys]_{0.25}[Glu]_{0.75}, [P₆₆₈]₁[Lys]_{0.33}[Glu]_{0.67}, or [P₆₆₈]₁[Lys]_{0.5}[Glu]_{0.5} were phase separation at 25 °C, separated AAIL rich phase (upper phase) was put into the inner tube, and the outer tube was filled with chloroform containing tetramethylsilane (TMS) as an internal standard. ¹³C NMR spectra were obtained with JEIL JNM-ECA500.

Table S1 Phase behaviour of [P₆₆₆₈][Lys]-[P₆₆₆₈][Glu]-water mixtures at various proportion. Concentration of ionic liquids in aqueous solution is 0.92 mol·kg⁻¹.

mole fraction of [P ₆₆₆₈][Glu]	0	0.25	0.33	0.50	0.67	0.75	0.85	0.9	1.0
mole fraction of [P ₆₆₆₈][Lys]	1.0	0.75	0.67	0.50	0.33	0.25	0.15	0.10	0
phase behaviour	H ^{*1}	H ^{*1}	LCST ^{*3} (T _c = 39 °C)	S ^{*2}	S ^{*2}	S ^{*2}	LCST ^{*3} (T _c = 19 °C)	H ^{*1}	H ^{*1}

*1 Homogeneous solution at temperature in the range from 0 °C to 70 °C.

*2 Phase separation at temperature in the range from 0 °C to 70 °C.

*3 Mixture showed lower critical solution temperature(LCST)-type phase transition, and “T_c” represents phase separation temperature.

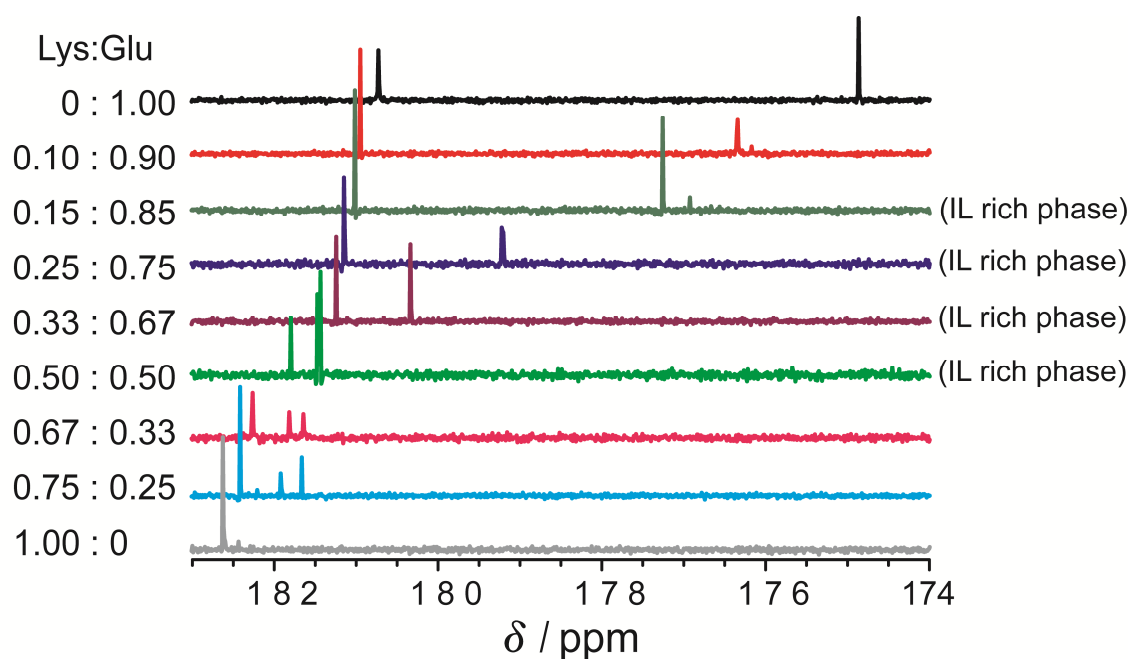


Fig. S1 ¹³C NMR spectra of [P₆₆₆₈][Lys]-[P₆₆₆₈][Glu]-water mixture at various molar ratio at 25 °C. Chemical shifts for carboxyl groups on [P₆₆₆₈][Lys] or [P₆₆₆₈][Glu] were shown in the range of 174-183 ppm.

Reference

¹ Y. Fukaya, and H. Ohno, *PCCP.*, 2013, **15**, 4066.