

Supplementary Information

Phase behavior of new aqueous two-phase systems: 1-Butyl-3-methylimidazolium tetrafluoroborate + anionic surfactants +water

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Synthesis of long-chain ionic liquids 1-alkyl-3-methylimidazolium bromide [C_nmim]Br) and 3-*p*-nonylphenoxy-2-hydroxypropyl trimethyl ammonium bromide (*p*-*n*-C₉H₁₉C₆H₄OCH₂CH(OH)CH₂NMe₃⁺Br⁻, NPTAB).

(1) Synthetic method of [C_nmim]Br (n=8,10,12 and14)

The IL samples were prepared according to the procedure reported by Wei et al.

Under a nitrogen atmosphere 1-methylimidazole and an excess molar amount of appropriate alkyl bromide were dissolved in dichloromethane, and the mixture was stirred at 75-80 °C for 48 h. The dichloromethane was then removed by the use of rotary evaporator under reduced pressure. The product was purified by recrystallization from ethyl acetate at least six times and then dried under vacuum for 1 day. The purity of the product was ascertained by ¹HNMR spectrum in CDCl₃.

¹H NMR and elemental analysis dates of products

[C₈mim]Br

¹HNMR: δH (400MHz, CDCl₃), 0.871 (3H, t, -N(CH₂)₁₁CH₃), 1.287(18H, m, -NCH₂CH₂(CH₂)₉CH₃), 1.917(2H, t, -NCH₂CH₂(CH₂)₉-CH₃), 4.140 (3H, s, -NCH₃), 4.327 (2H, t, NCH₂),

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7.421 (1H, t, $H(5)$), 7.583 (1H, t, $H(4)$), 10.405(1H, s, $H(2)$).

Elemental analysis: measured value (theoretical value) (%): C 52.86(52.36), H 8.58(8.36), N 10.84(10.26).

[C₁₀mim]Br

¹HNMR: δ H (400MHz, CDCl₃), 0.875 (3H, t, -N(CH₂)₁₁CH₃), 1.301(18H, m, -NCH₂CH₂(CH₂)₉CH₃), 1.920(2H, t, -NCH₂CH₂(CH₂)₉-CH₃), 4.140 (3H, s, -NCH₃), 4.326 (2H, t, NCH₂), 7.440 (1H, d, $H(5)$), 7.610 (1H, d, $H(4)$), 10.362(1H, s, $H(2)$).

Elemental analysis: measured value (theoretical value) (%): C 54.86(55.45), H 9.18(8.91), N 9.04(9.24).

[C₁₂mim]Br·H₂O

¹HNMR: δ H (400MHz, CDCl₃), 0.879 (3H, t, -N(CH₂)₁₁CH₃), 1.245(18H, t, -NCH₂CH₂(CH₂)₉CH₃), 1.910(2H, s, -NCH₂CH₂(CH₂)₉-CH₃), 4.138 (3H, s, -NCH₃), 4.321 (2H, t, NCH₂), 7.368 (1H, t, $H(5)$), 7.510 (1H, t, $H(4)$), 10.369 (1H, d, $H(2)$).

Elemental analysis: measured value (theoretical value) (%): C 54.86(55.01), H 9.98(9.52), N 8.04(8.02).

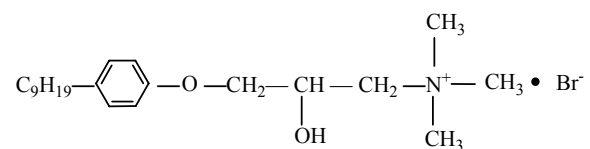
[C₁₄mim]Br·H₂O

¹HNMR: δ H (400MHz, CDCl₃), 0.878 (3H, t, -N(CH₂)₁₁CH₃), 1.248(18H, t, -NCH₂CH₂(CH₂)₉CH₃), 1.914(2H, s, -NCH₂CH₂(CH₂)₉-CH₃), 4.139 (3H, s, -NCH₃), 4.321 (2H, t, NCH₂), 7.404 (1H, t, $H(5)$), 7.572 (1H, t, $H(4)$), 10.429 (1H, d, $H(2)$).

Elemental analysis: measured value (theoretical value) (%): C 59.59(59.25), H 10.68(10.19), N 6.91(6.91).

(2) Synthetic method of NPTAB

The molecular structure of NPTAB



Synthetic method of NPTAB

p-nonyl phenol (22 g, 0.1mol), toluene (50 ml) and 10g sodium hydroxide aqueous liquid (40%) were added into the 250ml round bottom flask equipped with condenser tube. The mixture

was stirred and heated to 50°C, 14g(0.115mol) epichlorohydrin was added to mixture and was reflux for 2-4 h in the presence of tetrabutyl ammonium bromide as phase transfer catalyst at 50°C -80°C. The reaction was stopped and the product was first washed 2-3 times with hot water, and then product was dried with anhydrous sodium sulfate, the solvent was removed under reduced pressure to afford the *p*-nonylphenyl glycidyl ether, and finally the NPTAB was synthesized by the reaction of trimethyl ammonium bromide with *p*-nonylphenyl glycidyl ether and was purified by recrystallization from ethyl acetate three times, Yield: 70~85%, the purity of the final product was determined by surface tension measurements.

¹H NMR and elemental analysis data of products

¹H NMR: δH (400MHz, CDCl₃, TMS) 0.70 (3H, t, CH₃CH₂), 1.0~1.6 [14H,m, CH₃(CH₂)₇], 2.86 (2H, CH₂C₆H₄), 3.49 [9H,s, N(CH₃)], 3.75(2H,d,OCH₂CH), 6.7~7.2 (4H,b, C₆H₄).

Elemental analysis: measured value (theoretical value) (%): C 60.0 (60.58), H 10.0 (9.13), N 4.0(3.36), O, 7.8(7.69).