Electronic Supplementary Material for PCCP

SUPPORTING INFORMATION

New Catanionic Surfactants based on 1-Alkyl-3-Methylimidazolium Alkylsulfonates, $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$: Mesomorphism and Aggregation

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Experimental and analytical data from ESI mass spectrometry and $^{1}H/^{13}C$ NMR spectroscopy for 1-alkyl-3-methylimidazolium alkylsulfonate salts, **1**-**7**.

(a) Alkyl alkylsulfonates ($C_nH_{2n+1}OSO_2C_mH_{2m+1}$). A solution of triethylamine (1.1 mol) and the desired alcohol ($C_nH_{2n+1}OH$; n = 4, 8, 10, 12) (1.1 mol.) in dichloromethane (430 cm^3) was cooled in an ice-bath. The respective alkylsulfonyl chloride ($C_mH_{2m+1}SO_2Cl$, m = 1, 4, 8; 1 mol eq,) dissolved in dichloromethane (100 cm^3) was added dropwise to the cooled, rapidly stirred reaction mixture while maintaining the temperature at 0 °C. The reaction mixture was then stirred for several hours at room temperature, filtered, and the solvent removed under reduced pressure. The filtrate was purified by fractional vacuum distillation to yield alkyl alkylsulfonate esters as transparent, colourless or slightly yellow liquids, exception for dodecylmethanesulfonate which was obtained as a colourless solid. All products were characterised by ^{1}H NMR spectroscopy.

(b) 1-Alkyl-3-methylimidazolium alkylsulfonates ($[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$) A solution of freshly distilled alkyl alkylsulfonate esters ($C_nH_{2n+1}SO_3C_mH_{2m+1}$) (1.1 mol eq.) and 1-methylimidazole (1 mol eq.) in ethyl ethanoate (150 cm^3) was heated under reflux with stirring overnight. The crude product formed as a dense layer and was removed, washed six times with ethyl ethanoate and any remaining solvent was removed under reduced pressure to give the corresponding 1-alkyl-3-methylimidazolium alkylsulfonates, **1**-**7**.

The 1-alkyl-3-methylimidazolium alkylsulfonate salts were characterised by ESI mass spectrometry (positive and negative ion modes) and ^{1}H- and ^{13}C-NMR spectroscopy. NMR spectra were recorded at room temperature on a Bruker Avance spectrometer DPX 300, using deuterated chloroform as solvent.

[C_8H_{17}mim][CH_3SO_3] **(1).** Following the general procedure (a) over 48 h, followed by (b) at 70 ^oC, 72 h gave **1-octyl-3-methylimidazolium methylsulfonate** as a pale yellow liquid (82 % yield) which crystallised on standing at room temperature. ^{1}H-NMR($CDCl_3$, 300MHz): δ/ppm = 0.56 (t, 3H, J=6.8 Hz, CH_2*CH_3*); 0.98 (br, 10H, *$(CH_2)_5$*CH_3); 1.59 (br, 2H, NCH_2*CH_2*); 2.46 (s, 3H, SCH_3); 3.70 (s, 3H, NCH_3); 3.98 (t, 2H, J=6.9 Hz, NCH_2); 7.27 (d, 1H, J=1.2 Hz, N*CH*CH); 7.41 (d, 1H, J=1.2 Hz, N*CH*CH); 9.48 (s, 1H, NCHN); ^{13}C-NMR($CDCl_3$, 75MHz): δ/ppm = 14.21, 22.69, 26.36, 29.08, 29.15, 30.47, 31.79, 36.42, 39.98, 49.99, 122.67, 124.18, 137.74; MS ES^+ m/z (% rel. Intensity): 195 M^+ (100). Calcd. for $C_{12}H_{23}N_2$: 195.1861; found: 195.1857; MS ES^- m/z (% rel. Intensity): 95 M^- (100). Calcd. for CH_3O_3S: 94.9803; found: 94.9798.

[$C_{10}H_{21}$mim][CH_3SO_3] **(2).** Following the general procedure (a) over 48 h, followed by (b) at 70 ^oC, 96 h gave **1-decyl-3-methylimidazolium methylsulfonate** as as a white crystalline solid (85% yield); ^{1}H-NMR($CDCl_3$, 300MHz): δ/ppm = 0.79 (t, 3H, J=6.6 Hz, CH_2*CH_3*); 1.18 (br, 14H, *$(CH_2)_7$*CH_3); 1.81 (t, 2H, J=6.6 Hz, NCH_2*CH_2*); 2.67 (s, 3H, SCH_3); 3.97 (s, 3H, NCH_3); 4.18 (t, 2H, J=7.5 Hz, NCH_2); 7.45 (s, 1H, N*CH*CH); 7.61 (s, 1H, N*CH*CH); 9.68 (s, 1H, NCHN); ^{13}C-NMR($CDCl_3$, 75MHz): δ/ppm = 14.29, 22.81, 26.43, 29.19, 29.40, 29.56, 29.63, 30.49, 31.99, 36.40, 40.00, 50.05, 122.48, 124.22, 137.80; MS ES^+ m/z (% rel. Intensity): 223 M^+ (100). Calcd. for $C_{14}H_{27}N_2$: 223.2174; found: 223.2164; MS ES^- m/z (% rel. Intensity): 95 M^- (100). Calcd. for CH_3O_3S: 94.9803; found: 94.9798.

[$C_{12}H_{25}$mim][CH_3SO_3] **(3).** Following the general procedure (a) over 48 h and (b) at 70 °C for 96 h) gave **1-dodecyl-3-methylimidazolium methylsulfonate** as a pale yellow crystalline powder (61 % yield); ^{1}H-NMR($CDCl_3$, 300MHz): δ/ppm = 0.88 (t, 3H, J=6.6 Hz, CH_2*CH_3*); 1.25 (br, 18H, *$(CH_2)_9$*CH_3); 1.87 (br, 2H, NCH_2*CH_2*); 2.76 (s, 3H, SCH_3); 4.04 (s, 3H, NCH_3); 4.25 (t, 2H, J=7.4 Hz, NCH_2); 7.34 (s, 1H, N*CH*CH); 7.49 (s, 1H, N*CH*CH); 9.73 (s, 1H, NCHN); ^{13}C-NMR($CDCl_3$, 75MHz): δ/ppm = 14.53, 22.09, 26.67, 29.38, 29.73, 29.77, 29.90, 29.99, 30.62, 32.31, 36.96, 40.01, 50.54, 121.82, 123.52, 138.97; MS ES$^+$ m/z (% rel. Intensity): 251 M^+ (100). Calcd. for $C_{12}H_{23}N_2$: 251.2487; found: 251.2481; MS ES$^-$ m/z (% rel. Intensity): 95 M^- (100). Calcd. for CH_3O_3S: 94.980; found: 94.9803.

[C_4H_9mim][$C_4H_9SO_3$] **(4).** Following the general procedure (a) for 48 h and (b) at 70 °C for 72 h gave **1-butyl-3-methylimidazolium butylsulfonate** as a white powder (81 % yield); ^{1}H-NMR($CDCl_3$, 300MHz): δ/ppm = 0.92 (br, 6H, CH_2*CH_3*); 1.38 (br, 4H, *CH_2*CH_3); 1.84 (br, 4H, NCH_2*CH_2*, SCH_2*CH_2*); 2.86 (br, 2H, SCH_2); 4.05 (s, 3H, NCH_3); 4.27 (t, 2H, J=7.3 Hz, NCH_2); 7.41 (s, 1H, N*CH*CH); 7.54 (s, 1H, N*CH*CH); 9.93 (s, 1H, NCHN); ^{13}C-NMR($CDCl_3$, 75MHz): δ/ppm = 14.15, 14.54, 20.87, 23.40, 28.61, 33.53, 36.85, 50.98, 52.94, 124.04, 125.35; MS ES$^+$ m/z (% rel. Intensity): 139 M^+ (100). Calcd. for $C_{12}H_{23}N_2$: 139.1235; found: 139.1235; MS ES$^-$ m/z (% rel. Intensity): 137 M^- (100). Calcd. for CH_3O_3S: 137.0272; found: 137.0270.

[C_4H_9mim][$C_8H_{17}SO_3$] **(5).** Following the general procedure (a) for 48 h and (b) at 70 °C for 72 h gave **1-butyl-3-methylimidazolium octylsulfonate** as white crystals (78 % yield); ^{1}H-NMR($CDCl_3$, 300MHz): δ/ppm = 0.92 (t, 3H, J=6.7 Hz, $S(CH_2)_7$*CH_3*); 1.01 (t, 3H, J=7.4 Hz, $N(CH_2)_3$*CH_3*); 1.32 (br, 10H, $S(CH_2)_2$*$(CH_2)_5$*CH_3); 1.40 (br, 2H,

$N(CH_2)_2\mathit{CH_2}CH_3$); 1.80 (br, 2H, $SCH_2\mathit{CH_2}$); 1.89 (br, 2H, $NCH_2\mathit{CH_2}$); 2.79 (br, 2H, SCH_2); 3.95 (s, 3H, NCH_3); 4.24 (t, 2H, J=7.3 Hz, NCH_2); 7.60 (s, 1H, N*CH*CH); 7.66 (s, 1H, N*CH*CH); 8.97 (s, 1H, NCHN); ^{13}C-NMR($CDCl_3$, 75MHz): δ/ppm = 14.17, 14.85, 20.88, 24.14, 26.50, 30.32, 30.68, 30.85, 36.90, 51.02, 53.24, 124.11, 125.42, 138.37; MS ES^+ m/z (% rel. Intensity): 139 M^+ (100). Calcd. for $C_{12}H_{23}N_2$: 139.1235; found: 139.1233; MS ES^- m/z (% rel. Intensity): 193 M^- (100). Calcd. for CH_3O_3S: 193.0898; found: 193.0899.

***[C_8H_{17}mim][$C_4H_9SO_3$]* (6).** Following the general procedure (a) for 48 h and (b) at 70 °C for 96 h gave **1-octyl-3-methylimidazolium butylsulfonate** as white crystals (79 % yield); ^{1}H-NMR($CDCl_3$, 300MHz): δ/ppm = 0.90 (br, 6H, $CH_2\mathit{CH_3}$); 1,29 (br, 10H, $\mathit{(CH_2)_5}CH_3$); 1.43 (m, 2H, J=7.5 Hz, $S(CH_2)_2\mathit{CH_2}$); 1.85 (br, 4H, $SCH_2\mathit{CH_2}$, $NCH_2\mathit{CH_2}$); 2.84 (br, 2H, SCH_2); 4.05 (s, 3H, NCH_3); 4.25 (t, 2H, J=7.4 Hz, NCH_2); 7.33 (s, 1H, N*CH*CH); 7.48 (s, 1H, N*CH*CH); 9.98 (s, 1H, NCHN); ^{13}C-NMR($CDCl_3$, 75MHz): δ/ppm = 13.91, 14.08, 22.21, 22.61, 26.29, 27.55, 28.99, 29.07, 30.31, 31.71, 36.47, 50.03, 51.97, 121.71, 123.53, 138.41; MS ES^+ m/z (% rel. Intensity): 195 M^+ (100). Calcd. for $C_{12}H_{23}N_2$: 195.1861; found: 195.1855; MS ES^- m/z (% rel. Intensity): 137 M^- (100). Calcd. for $C_4H_9O_3S$: 137.0272; found: 137.0271.

***[C_8H_{17}mim][$C_8H_{17}SO_3$]* (8).** Following the general procedure (a) for 48 h and (b) at 70 °C for 96 h gave **1-octyl-3-methylimidazolium octylsulfonate** as white crystals (69 % yield); ^{1}H-NMR($CDCl_3$, 300MHz): δ/ppm = 0.87 (br, 6H, $N(CH_2)_7\mathit{CH_3}$, $S(CH_2)_7\mathit{CH_3}$); 1.26 (br, 20H, $N(CH_2)_2\mathit{(CH_2)_5}CH_3$, $S(CH_2)_2\mathit{(CH_2)_5}CH_3$); 1.86 (br, 4H, $NCH_2\mathit{CH_2}$, $SCH_2\mathit{CH_2}$); 2.86 (br, 2H, SCH_2); 4.05 (s, 3H, NCH_3); 4.25 (t, 2H, J=7.4 Hz, NCH_2); 7.26 (s, 1H, N*CH*CH); 7.38 (s, 1H, N*CH*CH); 10.05 (s, 1H, NCHN); ^{13}C-

NMR($CDCl_3$, 75MHz): δ/ppm = 14.45, 14.51, 22.99, 23.07, 25.87, 26.68, 29.36, 29.44, 29.48, 29.60, 29.84, 30.64, 32.09, 32.27, 36.96, 50.53, 52.65, 121.75, 123.44, 139.32; MS ES^+ m/z (% rel. Intensity): 195 M^+ (100). Calcd. for $C_{12}H_{23}N_2$: 195.1861; found: 195.1856; MS ES^- m/z (% rel. Intensity): 193 M^- (100). Calcd. for CH_3O_3S: 193.0865; found: 193.0898.