

Electronic supplementary informations for :

Surfactant properties of Ionic Liquids containing short alkyl chain imidazolium cations and ibuprofenate anions

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Instrumentation

Thermogravimetric analysis (TGA) were carried out on a Netzsch STA 409 PC Luxx in alumina crucible under an air flow with a heating rate of 5°C/min up to 850°C followed by an isotherm at 850°C for 30 min.

Measurements of phase-transition temperatures were performed with a Netzsch differential scanning calorimeter model 204F1 Phoenix and the data were evaluated using Netzsch Proteus Thermal Analysis software version 4.8.1. Samples of 10-15 mg were placed in a hermetically sealed aluminum pan; an empty pan was used as reference. Pans were exposed to a N₂ flow atmosphere. The following conditions measurements were applied: 1) heating from room temperature to 130°C at a rate of 10°C/min 2) isotherm at 130°C for 5 min 3) cooling to -150°C at a rate of 10°C/min 4) isotherm at -150°C for 10 min 5) heating to 130°C at a rate of 10°C/min 6) cooling to room temperature at a rate of 10°C/min. The glass transition was determined at the midpoint of a heat-capacity change.

Mass spectrometry analyses (ES⁺ and ES⁻) were conducted using a Micromass Q-ToF spectrometer.

¹H and ¹³C liquid-state NMR were recorded on a Bruker DRX 400 and DPX 200 spectrometers at room temperature. Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks (CDCl₃: δ 7.26 ppm ¹H; δ 77.0 ppm ¹³C). Coupling constants (J) are reported in Hz. Infrared spectra were recorded on a thermo Nicolet Avatar 320-FT-IR

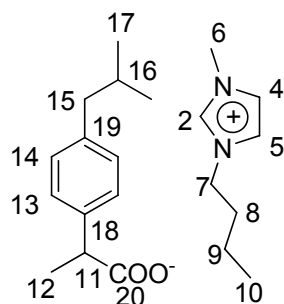
spectrometer with a resolution of 4 cm^{-1} . Elemental analyses were performed at the Center of Chemicals Analysis of the Centre National de la Recherche Scientifique (Vernaison, France).

Synthesis

General procedure for the preparation of $[\text{C}_n\text{MIm}][\text{Ibu}]$

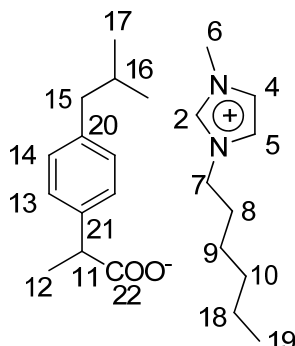
Sodium ibuprofen salt (1 Eq) was dissolved in ethanol. $[\text{C}_4\text{MIm}][\text{Cl}]$ (1 Eq) was also dissolved in a minimum of ethanol and added slowly to the previous solution. The resulting mixture was stirred at 70°C for 3 hours and overnight at room temperature. The solution was filtered on Millipore ($0.45\text{ }\mu\text{m}$) and 100 mL of acetone was added leading to the precipitation of NaCl which was further filtered and the solvent was removed under vacuum. Addition of acetone was renewed until no further precipitation of NaCl could be detected. The products were then dried under vacuum at 343 K for 48 h.

Synthesis of 1-methyl-3-butylimidazolium ibuprofenate $[\text{C}_4\text{MIm}][\text{Ibu}]$



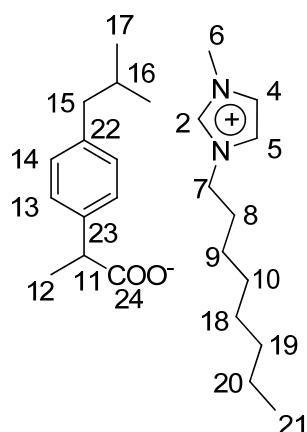
Following the general procedure, $[\text{C}_4\text{MIm}][\text{Ibu}]$ was obtained as a yellowish very viscous liquid (7.10 g, 94 %). ^1H NMR (400 MHz, CDCl_3) : δ = 10.32 (1H, s, H_2) ; 7.24 (2H, d, J = 7.9 Hz, H_{14}) ; 7.10 (1H, d, J = 1.7 Hz, H_5) ; 7.03 (1H, d, J = 1.7 Hz, H_4) ; 6.91 (2H, d, J = 7.9 Hz, H_{13}) ; 4.04 (2H, t, J = 7.3 Hz, H_7) ; 3.74 (3H, s, H_6) ; 3.50 (1H, q, J = 7.1 Hz, H_{11}) ; 2.30 (2H, d, J = 7.1 Hz, H_{15}) ; 1.69 (3H, m, H_8 , H_{16}) ; 1.36 (3H, d, J = 7.1 Hz, H_{12}) ; 1.22 (2H, s, J = 7.4 Hz, H_9) ; 0.85 (3H, t, J = 7.4 Hz, H_{10}) ; 0.51 (6H, d, J = 7.4 Hz, H_{17}). ^{13}C NMR (100.6 MHz, CDCl_3) : δ = 180.4 (C_{20}) ; 142.7 ($\text{C}_{18}/\text{C}_{19}$) ; 139.4 (C_2) ; 138.6 ($\text{C}_{18}/\text{C}_{19}$) ; 128.6 ($\text{C}_{13}/\text{C}_{14}$) ; 127.4 ($\text{C}_{13}/\text{C}_{14}$) ; 122.8 (C_4/C_5) ; 121.1 (C_4/C_5) ; 49.4 (C_7) ; 49.2 (C_{11}) ; 45.0 (C_{15}) ; 36.1 (C_6) ; 32.0 (C_8) ; 30.2 (C_{16}) ; 22.4 (C_{17}) ; 19.7 (C_{12}) ; 19.2 (C_9) ; 13.4 (C_{10}). m/z (ES^+) : 139 (M^+ , 100), m/z (ES^-) : 205 (M^- , 100) , 411 ($2\text{M}^+ + \text{H}^+$). $\nu_{\text{max}}/\text{cm}^{-1}$: 3141 and 3060 ($\nu\text{C}=\text{C}-\text{H}$ imidazolium and phenyl rings), 2949, 2925, 2864 ($\nu\text{C}-\text{H}$ alkyls), 1580 and 1372 (νCOO^-). TGA : $T_{\text{onset}5\%} = 225^\circ\text{C}$, $T_{\text{onset}10\%} = 237^\circ\text{C}$. DSC : $T_g = -26^\circ\text{C}$. % Cl : 2.6 w/w

Synthesis of 1-methyl-3-hexylimidazolium ibuprofenate [C₆MIm][Ibu]



Following the general procedure, [C₆MIm][Ibu] was obtained as a yellowish very viscous liquid (5.17 g, 93 %). ¹H NMR (400 MHz, CDCl₃) : δ = 10.75 (1H, s, H₂) ; 7.20 (2H, d, *J* = 8.0 Hz, H₁₃) ; 7.15 (1H, d, *J* = 1.6 Hz, H₄) ; 7.04 (1H, d, *J* = 1.6 Hz, H₅) ; 6.85 (2H, d, *J* = 8.0 Hz, H₁₄) ; 3.99 (2H, t, *J* = 7.6 Hz, H₇) ; 3.72 (3H, s, H₆) ; 3.48 (1H, q, *J* = 7.2 Hz, H₁₁) ; 2.25 (2H, d, *J* = 7.2 Hz, H₁₅) ; 1.66 (3H, m, H₈, H₁₆) ; 1.34 (3H, d, *J* = 7.2 Hz, H₁₂) ; 1.15 (6H, m, H₉, H₁₀, H₁₈) ; 0.74 (9H, H₁₉, H₁₇). ¹³C NMR (100.6 MHz, CDCl₃) : δ = 180.1 (C₂₂) ; 142.9 (C₂₀/C₂₁) ; 139.5 (C₂) ; 138.4 (C₂₀/C₂₁) ; 128.5 (C₁₃/C₁₄) ; 127.3 (C₁₃/C₁₄) ; 122.90 (C₄/C₅) ; 121.1 (C₄/C₅) ; 49.7 (C₇) ; 49.3 (C₁₁) ; 45.0 (C₁₅) ; 36.0 (C₆) ; 31.0 (C₈) ; 30.2 (C₁₆) ; 30.1 (C₉) ; 25.8 (C₁₀) ; 22.3 (C₁₈) ; 22.1 (C₁₇) ; 19.8 (C₁₂) ; 13.9 (C₁₉). *m/z* (ES⁺) 167 (M⁺, 100). *m/z* (ES⁻) : 161 (M⁻-COO, 27) , 205 (M⁻, 100) , 411 (2M⁻+H⁺, 5]. *v*_{max}/cm⁻¹ 3138 and 3051 (νC=C-H imidazolium and phenyl rings), 2954, 2927, 2865 (ν C-H alkyls), 1578 and 1379 (ν COO⁻). TGA : T_{onset5%} = 220 °C, T_{onset10%} = 229 °C. DSC : T_g = -35 °C. % Cl : 2.0 w/w

Synthesis of 1-methyl-3-octylimidazolium ibuprofenate [C₈MIm][Ibu]



Following the general procedure, $[C_8MIm][Ibu]$ was obtained as a yellowish very viscous liquid (4.6 g, 88 %). 1H NMR (200 MHz, $CDCl_3$) : δ = 11.36 (1H, s, H_2) ; 7.34 (2H, d, J = 8.0 Hz, H_{13}) ; 6.99 (4H, m, H_{14}, H_5, H_4) ; 4.16 (2H, t, J = 7.2 Hz, H_7) ; 3.90 (3H, s, H_6) ; 3.61 (1H, q, J = 7.2 Hz, H_{11}) ; 2.38 (2H, d, J = 7.2 Hz, H_{15}) ; 1.79 (3H, m, H_8, H_{16}) ; 1.47 (3H, d, J = 7.1 Hz, H_{12}) ; 1.25 (10H, m, $H_9, H_{10}, H_{18}, H_{19}, H_{20}$) ; 0.87 (9H, H_{21}, H_{17}). ^{13}C NMR (100.6 MHz, $CDCl_3$) : δ = 179.8 (C_{24}) ; 141.3 (C_{22}/C_{23}) ; 139.0 (C_{22}/C_{23}) ; 138.9 (C_2) ; 128.7 (C_{13}/C_{14}) ; 127.4 (C_{13}/C_{14}) ; 123.0 (C_4/C_5) ; 121.1 (C_4/C_5) ; 49.7 (C_7) ; 47.6 (C_{11}) ; 45.0 (C_{15}) ; 36.2 (C_6) ; 31.7 (C_8) ; 30.2 (C_{16}) ; 30.1 (C_9) ; 29.0 (C_{10}) ; 28.9 (C_{18}) ; 26.2 (C_{19}) ; 22.6 (C_{17}) ; 22.4 (C_{20}) ; 19.4 (C_{12}) ; 14.0 (C_{21}). m/z (ES^+) 195 (M^+ , 100). m/z (ES^-) : 205 (M^- , 100) , 411 ($2M^-+H^+$, 5]. ν_{max}/cm^{-1} 3141 and 3060 ($\nu C=C-H$ imidazolium and phenyl rings), 2953, 2924, 2856 ($\nu C-H$ alkyls), 1580 and 1376 (νCOO^-). TGA : $T_{onset5\%}$ = 222 $^{\circ}C$, $T_{onset10\%}$ = 231 $^{\circ}C$. DSC : T_g = -42 $^{\circ}C$. % Cl : 1.0 w/w