Supporting Information

Tailored Ionic Liquid-Based Surfactants for the Formation of Microemulsions with Water and a Hydrophobic Ionic Liquid

Jan H. Porada, Diana Zauser, Birgit Feucht, Cosima Stubenrauch*
Universität Stuttgart, Institut für Physikalische Chemie, Pfaffenwaldring 55, 70569 Stuttgart (Germany)

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Materials

Water or air sensitive reactions were carried out under nitrogen atmosphere using Schlenk techniques. The glassware was flame-dried in high vacuum (0.5-1 mbar) and allowed to cool down under nitrogen atmosphere. The syringes, needles and transfer cannulas were dried in an oven at 70°C and were flushed with nitrogen directly before use. All chemicals were purchased from Aldrich, Fluka or Acros and were used without further purification. Amberlyst A26 was obtained from Acros Organics. Anhydrous DMF was obtained by distillation from MgSO₄ at reduced pressure and stored over molecular sieve (3 Å) under nitrogen.

Methods

¹H-NMR spectra and ¹H broad band decoupled ¹³C-NMR spectra were measured on an Advance 500 spectrometer from Bruker. The measurements were performed at room temperature using CDCl₃, D₂O or CD₃OD from Euriso-top as solvent with a deuterium content of 99.8% and TMS as internal standard. Splitting patterns in ¹H-NMR are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; ¹³C-NMR spectra were recorded using an APT sequence with complete proton decoupling. Multiplicities [C (s), CH (d), CH₂ (t), CH₃ (q)] were deduced from these spectra. High and low resolution mass spectra were measured under ESI conditions with a micrOTOF-Q from Bruker Daltonics. Elemental analysis was performed with an Elemental Analyzer Model 1106 from Carlo Erba Strumentazione.

The composition of the coexisting phases in the three-phase regions was determined by ¹H-NMR. After the three phases have separated at the given temperature (70 °C for H₂O – [BMIm]PF₆ – C₁₂E₆ and 50 °C for H₂O – [BMIm]PF₆ – [In-C₈-MIm]/[In-C₁₀-MIm]PF₆ at δ=0.8) 0.1 ml of each phase was transferred into a NMR tube and diluted with 0.5 ml of dry DMSO-d₆. The measurements were performed at room temperature on a 500 MHz spectrometer with each 128 pulses. In order to account for the water content of the DMSO-d₆ used a pure sample of DMSO-d₆ was also measured. In each spectrum the integral of the DMSO peak was normalized to 1 and the peak area of the water signal of the solvent sample was subtracted from the water peak integrals of other samples. Knowing the number of hydrogens for each signal the molar ratio for all three components could be calculated. In case of a signal overlap (mainly with the water peak) the intensity of the overlapping signal was estimated according to the number of hydrogens and the molar ratio (known from other non-overlapping signals of the component) and subtracted from the combined signal. Using the molar masses \( M_{\text{H}_2\text{O}} = 18.0 \ \text{g mol}^{-1} \), \( M_{[\text{BMIm}]\text{PF}_6} = 284.2 \ \text{g mol}^{-1} \), \( M_{\text{C}_{12}\text{E}_6} = 450.7 \ \text{g mol}^{-1} \) and \( M_{[\text{In-C}_8\text{MIm}]/[\text{In-C}_10\text{MIm}]\text{PF}_6} = 540.9 \ \text{g mol}^{-1} \) (δ = 0.8) the molar ratios were converted to the mass ratios \( \gamma \), \( \omega_{\text{H}_2\text{O}} \), and \( \omega_{\text{IL}} \). The latter are defined as

\[
\gamma = \frac{m_{\text{surfactant}}}{m_{\text{H}_2\text{O}} + m_{\text{IL}} + m_{\text{surfactant}}},
\]

\[
\omega_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{m_{\text{H}_2\text{O}} + m_{\text{IL}} + m_{\text{surfactant}}},
\]
\[ w_{\text{IL}} = \frac{m_{\text{IL}}}{m_{\text{H}_2\text{O}} + m_{\text{IL}} + m_{\text{surfactant}}}. \]  

The samples for ROESY-NMR were taken from the middle phase of the three-phase samples prepared for the determination of the composition of the coexisting phases. The measurements were carried out at either 70 °C for \( \text{H}_2\text{O} - [\text{BMIm}]\text{PF}_6 - \text{C}_{12}\text{E}_6 \) or 50 °C for \( \text{H}_2\text{O} - [\text{BMIm}]\text{PF}_6 - ([\text{In}-\text{C}_8-\text{MIm}]/[\text{In}-\text{C}_{10}-\text{MIm}]\text{PF}_6 \) \( (\delta = 0.8) \) with an Advance 500 from Bruker equipped with a 5mm BBO probe head with a z-gradient. A closed capillary with \( \text{D}_2\text{O} \) was inserted into the sample tube to allow for locking of the signal. The standard Bruker roesyph pulse sequence was used with relaxation delay of 2 s and mixing time of 200 ms under low power spin lock conditions over a bandwidth of 9.6 ppm. The spin-lock field strength was 2000 Hz. Complex data (1K) were collected in 256 increments with 8 (water-rich sample) or 16 (IL-rich sample) transients each. Phase sensitive two-dimensional time domains were recorded and were processed using TPPI protocol. Prior to zero-filling and FT a pure square cosine window function was used in both dimensions. For better visibility of the cross peaks the spectrum was symmetrized.

**Synthesis**

- **Myo-inositol monoorthoformate (2)**

  The monoorthoformate 2 was synthesized from myo-inositol (1) according to published reaction conditions\(^1\) with modification.\(^2\) 160 ml (960 mmol) triethylorthoformate was added to a solution of 96 g (532 mmol) myo-inositol and 16 g (80 mmol) \( p \)-tolenesulfonic acid hydrate in 1000 ml of dry DMF. The reaction mixture was stirred for 18 h at 100 °C, during which the solution turned orange. After cooling to r.t. 60 ml of a saturated aqueous \( \text{NaHCO}_3 \) solution was added and the solution was stirred for another 30 min. The precipitate was filtered off and the filtrate was condensed under vacuum which results in a thick orange oil. A small amount of ethanol was added upon which a slightly yellow solid precipitated. The solid was filtered off, rinsed with cold ethanol and was recrystallized from hot ethanol yielding 88.5 g (465 mmol, 87%) of 2 as a white solid. The spectroscopic data was in accordance with the previously reported ones.\(^1\)

  \(^1\text{H-NMR} \) (500 MHz, \( \text{D}_2\text{O} \)): \( \delta = 5.61 \) (s, 1H), 4.59 (t, \( J = 3.8 \) Hz, 2H), 4.34 (dt, \( J = 3.8, 2.1 \) Hz, 1H), 4.28 (d, \( J = 1.8 \) Hz, 1H), 4.24 (dd, \( J = 4.1, 2.1 \) Hz, 2H); \(^{13}\text{C-NMR} \) (125.8 MHz, \( \text{D}_2\text{O} \)): \( \delta = 102.12, 73.82, 69.31, 66.72, 59.54. \)
• ω-bromoalkyl myo-inositol monoorthoformate (rac-3)

![Reaction Scheme]

To solution of 9.51 g (50 mmol) of myo-inositol monoorthoformate (2) in 150 ml of dry DMF under nitrogen atmosphere at r.t. 2.20 g (55 mmol) of NaH (60% in paraffin) was added. The reaction solution was stirred at r. t. until no further evolution of hydrogen was observed (~2 h). 27.6 ml (40.8 g, 150 mmol) of 1,8-dibromoocatane was added rapidly and the reaction solution was stirred at 100 °C for 14 h. DMF was removed under vacuum. The excess of 1,8-dibromoocatane was extracted with hexane and could be recycled distillation. The oily residue was purified chromatographically on silica with DCM/EtOAc 4:1 as eluent giving 11.96 g (31.4 mmol, 63%) of 3a as a white solid. 3b was synthesized in an analogous way from 9.51 g (50.0 mmol) 2 with 2.20 g (55 mmol) of NaH (60% in paraffin) and 33.7 ml (45.0 g, 150 mmol) 1,10-dibromodecane yielding 9.32 g (22.8 mmol, 46%).

**Compound 3a**

$^1$H-NMR (500 MHz, CDCl$_3$): δ = 5.46 (s, 1H), 4.46 (ddd, J = 10.5, 5.4, 2.9 Hz, 1H), 4.35 – 4.27 (m, 3H), 4.24 – 4.18 (m, 1H), 4.07 – 4.00 (m, 1H), 3.80 (d, J = 10.2 Hz, 1H; OH), 3.70 – 3.58 (m, 2H), 3.41 (t, J = 6.9 Hz, 2H), 3.38 (d, J = 8.8 Hz, 1H; OH), 1.85 (p, J = 6.9 Hz, 2H), 1.59 (p, J = 7.0 Hz, 2H), 1.43 (p, J = 7.0 Hz, 2H), 1.36 – 1.28 (m, 6H); $^{13}$C-NMR (125.8 MHz, CDCl$_3$): δ = 102.73 (d), 75.05 (d), 74.77 (d), 72.19 (d), 71.41 (t), 67.82 (d), 67.18 (d), 60.72 (d), 33.94 (t), 32.71 (t), 29.65 (t), 29.10 (t), 28.59 (t), 28.04 (t), 25.78 (t).

**Compound 3b**

$^1$H-NMR (500 MHz, CDCl$_3$): δ = 5.46 (s, 1H), 4.46 (dd, J = 6.6, 3.5 Hz, 1H), 4.36 – 4.27 (m, 3H), 4.21 (s, 1H), 4.04 (s, 1H), 3.82 (d, J = 10.2 Hz, 1H; OH), 3.71 – 3.57 (m, 2H), 3.41 (t, J = 6.9 Hz, 2H), 3.21 (s, 1H; OH), 1.85 (p, J = 6.9 Hz, 2H), 1.58 (p, J = 6.5 Hz, 2H), 1.42 (p, J = 7.0 Hz, 2H), 1.34 – 1.24 (m, 10H); $^{13}$C-NMR (125.8 MHz, CDCl$_3$): δ = 102.73 (d), 75.03 (d), 74.78 (d), 72.21 (d), 71.47 (t), 67.83 (d), 67.19 (d), 60.72 (d), 34.05 (t), 32.80 (t), 29.68 (t), 29.33 (t), 29.31 (t), 29.23 (t), 28.70 (t), 28.13 (t), 25.85 (t).

• ω-bromoalkyl myo-inositol (rac-4)

![Reaction Scheme]
11.68 g (30.6 mmol) of 3a were solved in 300 ml water and 40 ml of 0.5M HCl was added. The reaction solution was refluxed for 2 h and water was removed under vacuum. The remaining white solid was recrystallized from ethanol yielding 10.27 g (27.7 mmol, 91 %) of 4a as a white solid. It was paid special attention to the high purity of this building block, since the following steps yield ionic compounds which can neither be distilled nor purified chromatographically. 4b was synthesized in an analogous way from 14.77 g (36.1 mmol) 3b yielding 13.47 g (33.7 mmol, 93 %).

**Compound 4a**

\[ \text{\textsuperscript{1}H-NMR (500 MHz, D_2O): } \delta = 4.04 \text{ (t, } J = 2.9 \text{ Hz, } 1H), 3.79 \text{ (t, } J = 7.2 \text{ Hz, } 2H), 3.62 \text{ (t, } J = 9.7 \text{ Hz, } 1H), 3.58 \text{ (dd, } J = 9.9, 2.9 \text{ Hz, } 1H), 3.52 \text{ (t, } J = 6.8 \text{ Hz, } 2H), 3.49 \text{ (dd, } J = 10.0, 2.9 \text{ Hz, } 1H), 3.46 \text{ (t, } J = 9.7 \text{ Hz, } 1H), 3.32 \text{ (t, } J = 9.4 \text{ Hz, } 1H), 1.86 \text{ (p, } J = 6.9 \text{ Hz, } 2H), 1.62 \text{ (p, } J = 7.0 \text{ Hz, } 2H), 1.44 \text{ (p, } J = 6.8 \text{ Hz, } 2H), 1.40 – 1.28 \text{ (m, } 6H) ; \text{ \textsuperscript{13}C-NMR (125.8 MHz, D_2O): } \delta = 81.04 \text{ (d), 73.90 (d), 73.33 (t), 72.47 (d), 72.28 (d), 70.95 (d), 70.77 (d), 35.31 (t), 32.07 (t), 32.20 (t), 28.31 (t), 27.72 (t), 27.24 (t), 24.98 (t)) ; \text{ HR-MS (ESI, 70 eV, positive) } m/z: \text{ calc. for } C_{14}H_{27}BrO_6Na^+ [M+Na^+]: 393.0883, \text{ found: 393.0879.} \]

**Compound 4b**

\[ \text{\textsuperscript{1}H-NMR (500 MHz, CD_3OD): } \delta = 3.93 \text{ (s, } 1H), 3.77 \text{ (td, } J = 7.1, 3.0 \text{ Hz, } 2H), 3.61 \text{ (t, } J = 9.5 \text{ Hz, } 1H), 3.43 \text{ (t, } J = 6.7 \text{ Hz, } 2H), 3.42 – 3.39 (m, } 2H), 3.35 – 3.28 (m, } 1H), 3.21 \text{ (p, } J = 4.7 \text{ Hz, } 1H), 1.83 \text{ (p, } J = 7.0 \text{ Hz, } 2H), 1.62 \text{ (p, } J = 7.1 \text{ Hz, } 2H), 1.50 – 1.40 (m, } 2H), 1.40 – 1.26 (m, } 10H) ; \text{ \textsuperscript{13}C-NMR (125.8 MHz, CD_3OD): } \delta = 83.08 \text{ (d), 76.34 (d), 74.51 (d), 74.40 (d), 74.35 (t), 73.36 (d), 73.26 (d), 34.54 (t), 34.06 (t), 31.38 (t), 30.72 (t), 30.69 (t), 30.61 (t), 29.91 (t), 29.23 (t), 27.17 (t)) ; \text{ HR-MS (ESI, 70 eV, positive) } m/z: \text{ calc. for } C_{16}H_{31}BrO_6Na^+ [M+Na^+]: 421.1196, \text{ found: 421.1181.} \]

- **1-methyl-3-(ω-myo-inositol alkyl)-imidazolium bromide (**rac-5**)**

9.97 g (26.9 mmol) of 4a was solved in 20 ml (250 mmol) of freshly distilled N-methylimidazole and stirred under nitrogen atmosphere for 14 h at 80 °C. Excessive N-methylimidazole was distilled off under high vacuum at 80 °C. The crude product was solved in 20 ml of methanol and precipitated by the addition 200 ml acetone. The suspension was given in the freezer and the excessive solvent was decanted. This procedure was repeated two more times, before 100 ml of methanol and 4 g of activated charcoal were added. The suspension was stirred at r.t. for 12 h and filtered over celite. The solvent was removed and the product was heated to 40 °C for 6 h under high vacuum giving 12.06 g (26.6 mmol, 99 %) of a clear, highly viscous oil. 5b was synthesized in an analogous way from 13.47 g (33.7 mmol) 4b yielding 15.92 g (33.1 mmol, 98 %).
**Compound 5a**

$^1$H-NMR (500 MHz, D$_2$O): $\delta = 8.70$ (s, 1H), 7.46 (s, 1H), 7.42 (s, 1H), 4.18 (t, $J = 7.1$ Hz, 2H), 4.02 (t, $J = 3.0$ Hz, 1H), 3.76 (t, $J = 7.0$ Hz, 2H), 3.61 (t, $J = 9.6$ Hz, 1H), 3.56 (dd, $J = 10.0$, 2.8 Hz, 1H), 3.48 (dd, $J = 9.9$, 2.9 Hz, 1H), 3.44 (t, $J = 9.7$ Hz, 1H), 3.30 (t, $J = 9.4$ Hz, 1H), 1.86 (p, $J = 6.9$ Hz, 2H), 1.58 (p, $J = 6.9$ Hz, 2H), 1.39 – 1.23 (m, 8H); $^{13}$C-NMR (125.8 MHz, D$_2$O): $\delta = 135.75$ (d; seen in HSQC), 123.43 (d), 122.16 (d), 81.04 (d), 73.89 (d), 73.27 (t), 72.48 (d), 72.29 (d), 70.96 (d), 70.76 (d), 49.49 (t), 35.60 (q), 29.18 (t), 29.11 (t), 28.23 (t), 27.91 (t), 25.19 (t), 24.94 (t); HR-MS (ESI, 70 eV, positive) m/z: calc. for C$_{18}$H$_{33}$N$_2$O$_6^+$ [M$^+$]: 373.2333, found: 373.2331.

**Compound 5b**

$^1$H-NMR (500 MHz, D$_2$O): $\delta = 8.62$ (s, 1H), 7.39 (s, 1H), 7.35 (s, 1H), 4.10 (t, $J = 7.0$ Hz, 2H), 3.95 (t, $J = 2.8$ Hz, 1H), 3.81 (s, 3H), 3.69 (t, $J = 7.0$ Hz, 2H), 3.54 (t, $J = 9.7$ Hz, 1H), 3.49 (dd, $J = 10.0$, 2.9 Hz, 1H), 3.41 (dd, $J = 10.1$, 3.0 Hz, 1H), 3.37 (t, $J = 9.7$ Hz, 1H), 3.23 (t, $J = 9.4$ Hz, 1H), 1.78 (p, $J = 7.3$ Hz, 2H), 1.52 (p, $J = 6.9$ Hz, 2H), 1.30 – 1.15 (m, 12H); $^{13}$C-NMR (125.8 MHz, D$_2$O): $\delta = 123.40$ (d), 122.13 (d), 81.04 (d), 73.90 (d), 73.35 (t), 72.49 (d), 72.30 (d), 70.97 (d), 70.77 (d), 49.51 (t), 35.58 (q), 29.26 (t), 29.11 (t), 28.48 (t), 28.37 (t), 27.95 (t), 25.23 (t), 25.10 (t); HR-MS (ESI, 70 eV, positive) m/z: calc. for C$_{20}$H$_{37}$N$_2$O$_6^+$ [M$^+$]: 401.2646, found: 401.2645.

- 1-methyl-3-(ω-my-o-inositol alkyl)-imidazolium hexafluorophosphate (rac-6)

The ion exchange was performed according to a published procedure using the strongly basic anion exchange resin Amberlyst A26. The process is divided in three steps:

**Loading of the anion exchange column**

A column was filled with 60 g of Amberlyst A26 in the OH-form and rinsed with water until pH 7. Then a 1:1 mixture of water and methanol was given on the column. A 1 wt.-% solution of HPF$_6$ in 1:1 water/MeOH was given onto the column until full loading, seen by the color change of the resin from pink to yellow. Afterwards the column was rinsed with 1:1 water/MeOH until pH 7.

**Exchange of the anion**

8.1 g (17.9 mmol) of 5a was solved in 300 ml of a 1:1 mixture of water/MeOH and slowly given onto the column filled with the loaded anion exchange resin. After the volume passed through the column, it was rinsed with another 300 ml of a 1:1 mixture of water/MeOH. The solvent of the collected solution was
distilled off in vacuum and the procedure was repeated two more times on a column with freshly regenerated and loaded resin. Afterwards the crude product was recrystallized from ethanol, yielding 8.34 g (16.1 mmol, 90 %) of 6a as a white solid. The bromine content was determined to be below 0.3 wt.-% by elemental analysis. 6b was synthesized in an analogous way from 8.00 g (16.5 mmol) 5b yielding 7.9 g (14.5 mmol, 88 %).

Regeneration of the anion exchange column
The column was rinsed with an aqueous 10 wt.-% NaOH solution until the resin changed the color from yellow to pink again. Then the same amount of NaOH solution was given on the column before it was rinsed with water until pH 7. The column was now ready for loading.

Compound 6a
$^1$H-NMR (500 MHz, D$_2$O): $\delta = 8.61$ (s, 1H), 7.39 (t, $J = 1.9$ Hz, 1H), 7.35 (t, $J = 1.9$ Hz, 1H), 4.11 (t, $J = 7.1$ Hz, 2H), 3.97 (t, $J = 3.0$ Hz, 1H), 3.82 (s, 3H), 3.70 (t, $J = 7.2$ Hz, 2H), 3.55 (t, $J = 9.7$ Hz, 1H), 3.51 (dd, $J = 10.0$, 2.9 Hz, 1H), 3.42 (dd, $J = 10.0$, 2.9 Hz, 1H), 3.38 (t, $J = 9.7$ Hz, 1H), 3.25 (t, $J = 9.4$ Hz, 1H), 1.80 (p, $J = 7.1$ Hz, 2H), 1.53 (p, $J = 7.0$ Hz, 2H), 1.34 – 1.18 (m, 8H); $^{13}$C-NMR (125.8 MHz, D$_2$O): $\delta = 123.44$ (d), 122.15 (d), 81.05 (d), 73.90 (d), 73.25 (t), 72.51 (d), 72.31 (d), 70.98 (d), 70.77 (d), 49.51 (t), 35.55 (q), 29.19 (t), 29.10 (t), 28.23 (t), 27.91 (t), 25.19 (t), 24.95 (t); HR-MS (ESI, 70 eV, positive) m/z: calc. for C$_{18}$H$_{33}$N$_2$O$_6^+$ [M$^+$]: 373.2333, found: 373.2322; EA (%) calc. for C$_{18}$H$_{33}$F$_6$N$_2$O$_6$P: C 41.70, H 6.42, N , 5.40, P 5.97 found: C 41.92, H 6.60, N , 5.40, P 5.81.

Compound 6b
$^1$H-NMR (500 MHz, D$_2$O): $\delta = 8.62$ (s, 1H), 7.39 (t, $J = 1.8$ Hz, 1H), 7.35 (t, $J = 2.0$ Hz, 1H), 4.11 (t, $J = 7.1$ Hz, 2H), 3.97 (t, $J = 2.9$ Hz, 1H), 3.82 (s, 3H), 3.70 (t, $J = 7.1$ Hz, 2H), 3.55 (t, $J = 9.7$ Hz, 1H), 3.50 (dd, $J = 10.0$, 2.9 Hz, 1H), 3.42 (dd, $J = 10.0$, 2.9 Hz, 1H), 3.38 (t, $J = 9.7$ Hz, 1H), 3.25 (t, $J = 9.4$ Hz, 1H), 1.79 (p, $J = 7.2$ Hz, 2H), 1.53 (p, $J = 7.0$ Hz, 2H), 1.32 – 1.16 (m, 12H); $^{13}$C-NMR (125.8 MHz, D$_2$O): $\delta = 123.43$ (d), 122.16 (d), 81.05 (d), 73.90 (d), 73.35 (t), 72.50 (d), 72.30 (d), 70.98 (d), 70.78 (d), 49.53 (t), 35.55 (q), 29.26 (t), 29.10 (t), 28.26 (t), 27.93 (t), 25.21 (t), 25.09 (t); HR-MS (ESI, 70 eV, positive) m/z: calc. for C$_{20}$H$_{35}$N$_2$O$_6^+$ [M$^+$]: 401.2646, found: 401.2647; EA (%) calc. for C$_{20}$H$_{37}$F$_6$N$_2$O$_6$P: C 43.96, H 6.82, N 5.13, P 5.67 found: C 43.96, H 6.86, N 5.07, P 5.67.
**Figure S1.** Phase diagram of the system H$_2$O – [BMIm]PF$_6$ – surfactant with C$_{12}$E$_6$ as surfactant at 70 °C (left) and the IL-based surfactant mixture at δ = 0.8 and 50 °C (right), respectively. The tie lines and the phase boundary of the three-phase region were determined by NMR. The phase boundary and the tie lines of the two-phase regions are only estimates (not measured). The determined phase boundaries are in good accordance with the $T$(γ)-cuts of the corresponding systems. The scaling is based on mass fractions. One main difference is the higher efficiency of the IL-based surfactant mixture compared to C$_{12}$E$_6$. As regards the monomeric solubility of the surfactant(s) in the excess phases one finds that C$_{12}$E$_6$ (left) is preferentially dissolved in the lower IL-rich phase (~10 wt.-%), while no surfactant was detected in the upper water-rich phase. In the system with the IL-based surfactant mixture (right) ~8 wt.-% of surfactant are found in the upper aqueous phase and only ~2 wt.-% in the IL-rich excess phase. The exact compositions of all samples and phases are summarized in Table S1.
Table S1. Prepared compositions of the initial samples and determined compositions of the phases.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Temperature</th>
<th>Sample/Phase</th>
<th>( \omega_{H2O} )</th>
<th>( \omega_{\text{IL}} )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{12})E(_6)</td>
<td>70 °C</td>
<td>sample</td>
<td>0.339</td>
<td>0.463</td>
<td>0.198</td>
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<tr>
<td></td>
<td>70 °C</td>
<td>upper phase</td>
<td>0.945</td>
<td>0.051</td>
<td>0.004</td>
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<tr>
<td></td>
<td>70 °C</td>
<td>middle phase</td>
<td>0.412</td>
<td>0.213</td>
<td>0.375</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>lower phase</td>
<td>0.086</td>
<td>0.818</td>
<td>0.096</td>
</tr>
<tr>
<td>[In-C(<em>8)-MIm]/[In-C(</em>{10})-MIm]PF(_6) at ( \delta = 0.8 )</td>
<td>50 °C</td>
<td>sample</td>
<td>0.388</td>
<td>0.536</td>
<td>0.076</td>
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<tr>
<td></td>
<td>50 °C</td>
<td>upper phase</td>
<td>0.894</td>
<td>0.034</td>
<td>0.072</td>
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<tr>
<td></td>
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<td>middle phase</td>
<td>0.296</td>
<td>0.517</td>
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</tr>
<tr>
<td></td>
<td>50 °C</td>
<td>lower phase</td>
<td>0.065</td>
<td>0.910</td>
<td>0.025</td>
</tr>
</tbody>
</table>

**ROESY-NMR**

A ROESY spectrum taken from the ternary mixture \( \text{H}_2\text{O} - [\text{BMIm}]\text{PF}_6 - [\text{In-C}_8\text{-MIm}]/[\text{In-C}_{10}\text{-MIm}]\text{PF}_6 \) at \( \delta = 0.8 \) and 50 °C with the composition of the middle phase (see Table S1) is shown on the next page. The signals of [BMIm]\text{PF}_6 are assigned with green numbers and those of the surfactant with letters. Green letters indicate the IL-oophilic side of the surfactant and blue letters the hydrophilic side. The assignment is shown below.

![Figure S2](image)

**Figure S2.** Assignment for the proton signals of [BMIm]\(^+\) and [In-C\(_8\)-MIm]\(^+\) for the ROESY spectrum shown on the next page.

Due to the fact that the structure of the IL is identical with the IL-oophilic part of the surfactant structure it cannot be distinguished whether the cross peaks originate from an IL-IL interaction or an IL-surfactant interaction. However, what can be seen from the spectrum is that water has cross peaks only with the protons g, i and j found on the hydrophilic side of the surfactant indicated by the black arrows in the spectrum. A second interesting observation is the cross peak 9/10 or 9/d indicated by the red arrow. The distance between the positions 9 and 10 is too large for this coupling being intramolecular. Thus, the coupling can only be intermolecular which supports our argument that an IL bulk phase is formed.
**SAXS measurement**

For the SAXS measurement a SAXBess camera by Anton Paar equipped with a Mythen 1K 1D Diode Array Detector by Dectris and a Cu-Kα radiation source (wavelength = 1.5406 Å) was used. The sample was taken from the ternary mixture H₂O – [BMI]PF₆ – [In-C₈-MIm]/[In-C₁₀-MIm]PF₆ at δ = 0.8 and 50 °C with the composition of the middle phase (see Table S1). The measurement was done at 50 °C. 60 frames of each 15 seconds illumination were added and the background (pure [BMI]PF₆ with identical parameters) was subtracted. The resulting scattering curve was desmeared using the SAXS Quant software by Anton Paar and is shown below.

![SAXS Curve](image)

**Figure S3.** Small angle X-ray Scattering curve of H₂O – [BMI]PF₆ – [In-C₈-MIm]/[In-C₁₀-MIm]PF₆ at δ = 0.8 and 50 °C at the composition of the middle phase (see Table S1).

The scattering curve clearly evidences the presence of a nano-structure within a q-range typical for microemulsions. The shape of the curve indicates the presence of cylindrical micelles. For the exact determination of the structure size the correct form factor as well as fitting parameters like volume fractions of the nano-phases, thickness of the surfactant film, polydispersity, scattering length densities of the interior of the micelles, the film and the bulk phase would be required. Note that a detailed analysis of the scattering results is not the scope of the present study.
References