Supporting Information

Vesicles and Reverse Vesicles of an Ionic Liquid in Ionic Liquids

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Experimental Details

Materials and Methods. Ionic Liquid (IL), 1-Butyl-3-methyl imidazolium bis-(trifluoromethylsulfonylimide) ([Bmim][Tf2N]) with stated purities higher than 98% mass fraction was purchased from Sigma Aldrich. ILs, ethanolammonium formate (EOAF) and L-proline isopropylester lauryl sulfate (ProC3LS) were synthesized in our laboratory. All the chemicals used for synthesis of ILs were of AR Grade. Brief procedure of synthesis is as follows:

Ethanolammonium formate (EOAF): The protic IL ethanolammonium formate has been synthesized by employing simple acid-base reaction following the reported procedure.1[1] Ethanolamine was taken in a round bottom flask and kept in ice bath, equimolar amount of was slowly added to it, and after complete addition the reaction was carried for several hours at room temperature. The viscous liquid obtained was heated at 70°C under high vacuum using rotary evaporator to remove excess ethanolamine and moisture present. The resulted IL was characterized by NMR and LC-MS.

1H-NMR: 200MHz (C6D6 as external solvent): δH (ppm) 3.169 (t, 2H; -CH2-N-), 3.872 (t, 2H; -CH2-O-), 7.513 (s, 3H+1H; -NH3+ OH), 8.642 (s, 1H; -H-COO-)

13C-NMR (200 MHz, C6D6 as external solvent): δC (ppm) 170.225, 59.008, 42.159.

ESIMS: (ESI+) m/z 62.06 [C2H8NO]+, (ESI-) 45.01[CHO2]−

Synthesis of L-Proline isopropylester lauryl sulphate (ProC3LS): IL surfactant ProC3LS has been synthesized by following the procedure reported earlier.[2] Typical procedure involves two steps (a) synthesis of proline ester hydrochloride (b) synthesis of Proline isopropylester laurylsulphate

(a) Synthesis of proline ester hydrochloride [ProC3Cl]
Thionyl chloride (16.02 g, 0.13 mol) was added slowly to iso-propanol (50 mL) at 0°C followed by slow addition of Proline (10g, 0.11 mol). Solution was refluxed for 4 hours. The progress of reaction was monitored by TLC. After completion of reaction, solution was concentrated in a rota-evaporator. Crude proline isopropyl ester hydrochloride was triturated with hexane at 0°C. During washing coloured impurities were removed. The resulting white solid product was collected and dried under vacuum to obtain proline isopropyl ester hydrochloride (16.90 g, 89.90% yield). Product was recrystallized using methanol: hexane and dried under vacuum. Obtained hydrochloride salt was highly hygroscopic and was stored under vacuum in dessicator.
(b) Synthesis of L-Proline isopropyl ester laurylsulphate (ProC₃LS)
For the synthesis of proline isopropyl ester lauryl sulfate, freshly synthesized and dried [ProC₃Cl] and sodium lauryl sulphate, CH₁₃(CH₂)₁₁OSO₃Na (purchased from Aldrich) were dissolved in equimolar amounts in 100 ml of hot water (60°C). Reaction was monitored through TLC. After the completion of reaction, water was slowly removed under vacuum at 70–80°C and a white solid precipitate was collected. Crude solid was dissolved in 100 ml of CH₂Cl₂ (purchased from SD fine chemicals) to extract the pure product from the mixture. Solid NaCl filtered and filtrate was washed with distilled water. Washing was repeated until it became chloride free. Two to three drops of 0.1 M AgNO₃ were added to the washings to confirm the presence/absence of chloride ions. The clear but slightly yellow viscous extract was then washed several times with water and the white solid (accounted for NaCl as by-product) was separated out. The extract was distilled to get rid of the CH₂Cl₂ solvent and finally dried under N₂ and vacuum for 5–7 h to afford the viscous product.

Yield : 85%

¹H-NMR: 200MHz (DMSO-d₆): δH (ppm) 0.839 (t, 3H; CH₃), 1.229 (m, 24H; (CH₂)₉&(CH₃)₂), 1.455 (quintet, 2H; CH₂), 1.95 (m, 4H; CH(IBA) &CH₃ (proline), 2.24 (m, 1H; CH₂), 3.216 (m, 2H; CH₂), 4.352 (t, 1H; CH), 5.007 (m, 1H; CH), 9.039 (s, 2H; CH₂), ¹³C-NMR (200 MHz, d₆-DMSO): δc 168.90, 70.54, 66.13, 59.35, 46.13, 31.82, 29.57, 28.25, 26.04, 23.42, 22.60, 21.80, 14.38 ppm. FTIR (neat) νmax = 1043, 1206, 1245, 1377, 1467, 1590, 1744, 2856, 2927, 3469 cm⁻¹.
ESIMS: (ESI⁺) m/z 158.11 [C₈H₁₆NO₂]⁺, (ESI⁻) 265.17 [C₁₂H₂₅OSO₃]⁻

Molecular structure of investigated ILs

1. \[
\begin{array}{c}
\text{HO} \\
\text{NH₃}
\end{array}
\begin{array}{c}
\text{O} \\
\equiv
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\]

Ethanol Ammonium Formate (EOAF)

2. \[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\begin{array}{c}
\text{F₃C}
\end{array}
\begin{array}{c}
\text{SO}
\end{array}
\begin{array}{c}
\equiv
\end{array}
\begin{array}{c}
\text{SO}
\end{array}
\begin{array}{c}
\text{CF₃}
\end{array}
\]

1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonilimide) ([Bmim][Tf₂N])

3. \[
\begin{array}{c}
\text{O₃SO}
\end{array}
\begin{array}{c}
\text{C}
\end{array}
\begin{array}{c}
\text{NH₂}
\end{array}
\begin{array}{c}
\equiv
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
\begin{array}{c}
\equiv
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\]

L-Proline isopropylester lauryl sulfate (ProC₃LS)
Methods.

**Surface Tension:** The surface tension measurements were performed on Data Physics SCATII Tensiometer using whelmy plate method. Aliquots of ProC₃LS stock solution were added to EOAF or [Bmim][Tf₂N] and kept under stirring at least for 15 minitues followed by 5 minitues stabilization, after ensuring homogeneous mixing the reading has been taken. All the readings were taken in triplicate, average of three readings is taken as final value.

**¹H NMR:** The ¹H NMR spectra for both the pure ILs and their mixtures were recorded using a Brüker 500MHz spectrophotometer. The proton chemical shifts were referenced with respect to an external standard TMS (δ = 0.000 ppm) in C₆D₆ (deuterated benzene).

**Isothermal Titration Calorimetry (ITC):** Calorimetric titration was performed with MicroCal ITC200 microcalorimeter. The sample and reference cells were filled with medium IL and stabilized at 25°C. 40 μl ProC₃LS stock solutions prepared in ILs were taken in instrument controlled Hamiltonian syringe and 2 μl aliquots were added to sample cell containing 200 μl medium IL with a continuous stirring (300 rpm). Vesicles were formed in the sample cell containing pure EOAF, with the addition of aliquots of stock solution. The concentrations of stock solutions taken were 17mM of ProC3LS in EOAF, 112 mM of ProC3LS in [Bmim][Tf₂N] and are selected in such a way that concentration covers a range starting from very below CVC to well above CVC in both the cases in one experiment. 2μL aliquots of stock solutions are added to sample cell containing 200μL EOAF. The concentration range covered is 0.17mM to 2.83 mM, whereas the transition concentration is 1.68mM in case of EOAF, the concentration range covered in case of [Bmim][Tf₂N] is 0.22 to 21.8mM, whereas the transition was observed at 13.01mM. The parameters like time of addition, duration between each addition were controlled by software provided with instrument. Enthalpy change at each injection was measured and plotted against concentration by using origin software provided with instrument.

**Dynamic Light Scattering (DLS):** DLS were performed at varying temperatures from 20 to 70°C on a Zetasizer Nano ZS light scattering apparatus (Malvern Instruments, U.K.) with a He-Ne laser (633 nm, 4Mw). Prior to the measurements all the ILs were filtered with 0.2μm filter, accurate viscosity and refractive index of ILs mixtures at every composition was provided to software. The temperature of the measurements was controlled to an accuracy of ± 3°C.

**TEM:** A drop of the colloidal solution for imaging was kept on parafilm, carbon coated copper grid was touched on surface of the liquid, turned around and kept for drying in vacuum desiccator for overnight. In case of EOAF, samples were imaged within the 30minitues to avoid the oxidation of copper grid. Samples were imaged under a JEOL JEM-2100 electron microscope at a working voltage of 200 kV.

**Cryo-TEM:** The images were recoreded in Prof. Timothy P. Lodge Laboratory at University of Minnesota, USA, using a FEI Tecnai G2 Spirit BioTWIN operating at 120 kV under liquid N₂ cryo condition. the images were taken with an Eagle 4 mega pixel CCD camera.

**FTIR measurements:** FTIR spectra of the pure EOAF, [Bmim][Tf₂N] and mixtures of EOAF or [Bmim][Tf₂N] with ProC3LS at concentrations ~ 10 times higher than vesicle concentrations were recorded at room temperature using NICOLET 6700 FTIR spectrometer.
Results:

Surface Tension

Figure S1. Change in surface tension of EOAF (○) and [Bmim][Tf$_2$N] (□) with the addition of ProC$_3$LS.

The tensiometric parameters, such as surface tension at cac ($\gamma_{\text{cvc}}$), adsorption efficiency ($pC_{20}$), surface pressure at cac ($\Pi_{\text{cvc}}$), and minimum surface area per molecule at the air-IL interface ($a_0$), are derived from surface tension vs. concentration plots.

The adsorption efficiency is defined as

$$pC_{20} = -\log C_{20}$$

(1)

where $C$ is the molar concentration of surfactant and $C_{20}$ stands for the concentration required to reduce the surface tension of pure solvent by 20 mN·m$^{-1}$. $C_{20}$ is regarded as the minimum concentration needed to saturate the surface adsorption. Thus, $C_{20}$ can be a measure of the adsorption efficiency of surfactant molecules at the air-solution interface. Usually, the negative logarithm of $C_{20}$ is used instead of $C_{20}$ itself as is shown in eq 1. The greater the $pC_{20}$ value, the higher the adsorption efficiency of the surfactant is. The $pC20$ value obtained for ProC3LS in OHEAF medium is higher than all hydrocarbon surfactants studied in both protic and aprotic ILs, also comparable with fluorocarbon surfactants and is little lower than the value obtained for the same surfactant in water medium.

The $\Pi_{\text{cvc}}$, which is known as surface pressure at $\text{cvc}$, is defined as

$$\Pi_{\text{cvc}} = \gamma_{\text{IL}} - \gamma_{\text{cvc}}$$

(2)

Where, $\gamma_{\text{IL}}$ is the surface tension of pure IL (EOAF) and $\gamma_{\text{cvc}}$ is the surface tension at $\text{cvc}$.

The maximum surface excess concentration, $\Gamma_{\max}$, and the area occupied by a single surfactant molecule at the air–water interface, $\text{A}_{\min}$, of BAILs which are mainly dependent upon the size of the hydrophilic head group were estimated by applying the Gibbs adsorption isotherm to the surface tension data using the equations (3) & (4)
\[ \Gamma_{\text{max}} = -\frac{1}{nRT} \frac{\partial \gamma}{\partial \ln C} \]  \hspace{1cm} (3)

\[ a_0 = \frac{1}{N_A \Gamma_{\text{max}}} \]  \hspace{1cm} (4)

Table S1. Parameters obtained from surface tension experiments for ProC$_3$LS in IL (EOAF) and aqueous medium at 298.15K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EOAF</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_{cvc} ) (mN.m$^{-1}$)</td>
<td>24.47</td>
<td>27.8</td>
</tr>
<tr>
<td>( pC_{20} )</td>
<td>3.13</td>
<td>4.55</td>
</tr>
<tr>
<td>( \Gamma_{\text{max}} ) ((\mu\text{mol.m}^{-2}))</td>
<td>6.2</td>
<td>1.74</td>
</tr>
<tr>
<td>( a_0 ) (Å$^2$)</td>
<td>26.81</td>
<td>95.5</td>
</tr>
<tr>
<td>( \Pi_{cvc} ) (mN.m$^{-1}$)</td>
<td>33.42</td>
<td>44.2</td>
</tr>
</tbody>
</table>
Nuclear Magnetic Resonance (NMR)

NMR have been recorded for a series of concentrations in a range starting from very below to well above critical aggregation concentration of ProC₃LS in both the IL medium. The transitions in chemical shift for protons of counterion, alkyl chain of surfactant and IL medium with increasing concentration suggested the aggregation of ProC₃LS in both the IL medium.

Figure S2. Changes in chemical shift for various protons in system (ProC₃LS + EAOF) as a function of ProC₃LS concentration: (A) formate proton, (B) –CH proton of ethanolammonium, (C) anionic alkyl chain multiplet of LS in EAOF (D) –CH(NH₃) proton of ProC₃ (E) NH proton of ProC₃.
Figure S3. Changes in chemical shift for various protons in system (ProC₃LS + [Bmim][Tf₂N]) as a function of ProC₃LS concentration: (A) C(2)H proton of imidazolium (B) NH proton of ProC₃ (C) -CH proton of ProC₃

Isothermal Titration Calorimetry

Figure S4. Enthalpogram of ProC₃LS in water
Enthalpy of aggregation ($\Delta H^o_{agg}$) is measured by calculating the difference between enthalpy changes before and after aggregation from enthalpograms.

Free energy of aggregation ($\Delta G^o_{agg}$) has been calculated using the relation

$$\Delta G^o_{agg} = (2 - \beta)RT \log x_{agg}$$  \hspace{1cm} (5)

Where, $\beta$ is the ionization degree of aggregation, $x_{agg}$ is the aggregate concentration in mole-fraction units. The ionization degree $\beta$ has been taken as one in IL medium, since surfactant ion was surround by complete ionic environment.[3] For water $\beta$ is measured from conductivity plots by taking the ratio of slopes of straight lines fitted for conductivity before and after aggregation.

Entropy of aggregation has been calculated by using the relation

$$\Delta G^o_{agg} = \Delta H^o_{agg} - T\Delta S^o_{agg}$$  \hspace{1cm} (6)

Where $\Delta G^o_{agg}$, $\Delta H^o_{agg}$ are calculated from enthalpograms, the obtained thermodynamic parameters were given in main text, which suggested that the process of aggregation is entropy driven in polar medium and both enthalpy and entropy driven in apolar medium.

**Dynamic Light Scattering (DLS)**

![Dynamic Light Scattering (DLS) graphs](image)

**Figure S5.** Size distributions of (left) ProC$_3$LS in water, and (right) SLS in EOAF.
Table S2. Critical Vesicular Concentration (CVC) determined using surface tension (ST), isothermal titration calorimetry (ITC) and NMR chemical shifts and thermodynamic parameters, Gibbs free energy of aggregation (ΔG), enthalpy changes (ΔH) entropy changes (ΔS) of ProC₃LS in IL medium and average hydrodynamic diameter (Dₕ) of self-assembled structures.

<table>
<thead>
<tr>
<th>Medium</th>
<th>CVC (mmol·kg⁻¹)</th>
<th>ΔG (kJ·mol⁻¹)</th>
<th>ΔH (kJ·mol⁻¹)</th>
<th>ΔS (kJ·mol⁻¹)</th>
<th>Dₕ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOAF</td>
<td>1.01 1.57 1.78</td>
<td>-25.96</td>
<td>127.7</td>
<td>153.7</td>
<td>248</td>
</tr>
<tr>
<td>[Bmim][Tf₂N]</td>
<td>- 13.01 15.3</td>
<td>-20.72</td>
<td>-3.39</td>
<td>17.33</td>
<td>230</td>
</tr>
<tr>
<td>Water</td>
<td>0.48 0.84</td>
<td>-27.50</td>
<td>1.1</td>
<td>28.60</td>
<td>100</td>
</tr>
</tbody>
</table>

Room temperature Transmission electron microscopy (TEM)

Figure S6. TEM images of ProC₃LS vesicles in EOAF (A-C), reverse vesicles in [Bmim][Tf₂N] (D,E), and aggregated micelles of ProC₃LS in water (F).
Figure S7. Cryo-TEM images of ProC₃LS vesicles in EOAF (above), reverse vesicles in [Bmim][Tf₂N] (below).
FTIR Spectra

**Figure S8.** FTIR spectra of (above) EOAF + ProC$_3$LS, and (below) [Bmim][Tf$_2$N] + ProC$_3$LS. Frequency shift of characteristic bands corresponding to formate and C(2)H proton of imidazolium as a consequence of hydrogen bonding with ProC$_3$ is marked with arrow. Only a small shift is observed because of very low concentration of surfactant IL.

**References**

