First observation of rich lamellar structures formed by a single-tailed amphiphilic ionic liquid in aqueous solutions

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1. Materials and methods

Materials: 1-Methylimidazole (98%) was purchased from Sigma-Aldrich and distilled prior to use. 1-Bromododecane (97%) was purchased from Aladdin Reagent Company. β-Naphthalenesulfonic acid sodium salt (98%) was the product of TCI. CDCl 3 (99.96%) and D 2O (99.96%) were purchased from Sigma-Aldrich. Triply distilled water was used throughout the whole experiments. The ILs used in this study were synthesized in our laboratory and the purity of the products were ascertained by the 1H NMR spectrum in CDCl 3.

Synthesis of [C 12 mim]Br: 1-Methylimidazole (0.1 mol) and 1-bromododecane (0.12 mol) were dissolved in acetonitrile, and the mixture was stirred at 75-80 °C under nitrogen atmosphere for 48 h. The solvent was removed by evaporation under reduced pressure. The product was purified by recrystallization from ethyl acetate at least four times and then dried in vacuo for 48 h.

1H NMR (CDCl 3, δ/ppm): 0.75 (t, 3H, -CH 3), 1.18-1.29 (d, 18H, -(CH 2) 9 CH 3), 1.84 (t, 2H, -(CH 2)(CH 2) 9 CH 3), 3.91 (s, 3H, -NCH 3), 4.24 (t, 2H, -(CH 2)(CH 2) 10 CH 3), 7.52 (m, 2H, -NCHCHN-), 9.05 (s, 1H, -NCHN-).

Synthesis of [C 12 mim][Nsa]: β-Naphthalenesulfonic acid sodium salt (0.055mol) and [C 12 mim]Br (0.05mol) were dissolved in a minimal quantity of water separately. The two solutions were then mixed and stirred at room temperature for 24 h. The resulting white precipitate was then filtered off and dissolved in dichloromethane. The pure
solution was separated from excess salt, solvent was removed under reduced pressure, and the product was then dried in vacuo for 48 h.

\[^1\text{H NMR (CDCl}_3, \delta/\text{ppm): } 0.88 \ (t, 3\text{H}, -\text{CH}_3), \ 1.20-1.30 \ (d, 18\text{H}, -(\text{CH}_2)_9\text{CH}_3), \ 1.82 \ (t, 2\text{H}, -\text{CH}_2(\text{CH}_2)_9\text{CH}_3), \ 4.06 \ (s, 3\text{H}, -\text{NCH}_3), \ 4.21 \ (t, 2\text{H}, -\text{CH}_2(\text{CH}_2)_{10}\text{CH}_3), \ 7.15 \ (s, 1\text{H}, -\text{NCHCHN}-), \ 7.22 \ (s, 1\text{H}, -\text{NCHCHN}-), \ 7.47 \ (m, 2\text{H}, \text{arom. H}_{10}, H_{11}), \ 7.81-7.89 \ (m, 3\text{H}, \text{arom. H}_9, H_{12}, H_{13}), \ 7.99-8.01 \ (m, 1\text{H}, \text{arom. H}_{14}), \ 8.43 \ (s, 1\text{H}, \text{arom. H}_{15}), \ 10.10 \ (s, 1\text{H}, -\text{NCHN}-).\]

**Freeze fracture transmission electron microscope (FF-TEM) observations:** A small amount of sample solution was placed on a 0.1mm thick copper disk covered with a second copper disk. Then the copper sandwich with the sample was plunged into liquid propane cooled by liquid nitrogen. Fracturing and replication were carried out on a Balzers BAF-400D equipment at -150 °C. Pt/C was deposited at an angle of 45°. The replicas were examined on a JEOL JEM-1400 TEM operated at 120 kV. The images were recorded on a Gatan multiscan CCD and processed with digital micrograph.

**Small angle X-ray scattering measurements:** The structural characterizations of LLC phases were performed using Anton-paar SAX Sess mc² system with Ni-filtered Cu Kα radiation (0.154 nm) operating at 50 kV and 40 mA. The vesicle samples were held in a capillary and the lyotropic liquid samples were placed in stainless steel tank and sealed by a transparent film. The distance between the sample and detector was 264.5 mm. The temperature was controlled using a computer controlled Peltier heating system (Hecus MBraun Austria).

**^1\text{H NMR measurements:** The ^1H NMR spectra were run on a Bruker Advance 400 spectrometer equipped with a pulse field gradient module (Z-axis) using a 5 mm BBO probe. The instrument was operated at a frequency of 400.13 MHz.

**Polarized optical microscope observations:** A polarized optical microscope (Panasonic Super Dynamic II WV-CP460) equipped with cooled CCD (Evolution MP5.1RTV, Q-imaging, Canada) was used to observe textures of the vesicles and lyotropic liquid crystal phases. The temperature was controlled at 10 ± 0.1 °C with a Linkam THSME600 liquid crystal freezing and heating stage system with a TP94
temperature controller (Linkam Scientific Instrument Ltd., UK).

**Surface tension measurements:** The surface tension measurements were carried out on a Model JYW-200B tensiometer (Chengde Dahua Instrument Co., Ltd., accuracy ± 0.1 mN/m) using the ring method. Temperature was controlled at 10 ± 0.1 °C using a thermostatic bath.

**Fig. S1** SAXS curves for the samples with different concentrations of [C$_{12}$mim][Nsa] at 10 °C.

![SAXS curves for the samples with different concentrations of [C$_{12}$mim][Nsa] at 10 °C.](image)

**Fig. S2** (a) SAXS curves for the sample at 5 wt% at different temperatures; (b) FF-TEM image of the sample at 5 wt% at 25 °C.
Fig. S3 SAXS curves for the samples at 50 and 60 wt% at different temperatures.

Fig. S4 Surface tension of [C\textsubscript{12}mim][Nsa] aqueous solutions as a function of concentration at 10 °C.

Table S1 Structural parameters of LLC phase in the [C\textsubscript{12}mim][Nsa]/H\textsubscript{2}O system at 10 °C.

<table>
<thead>
<tr>
<th>[C\textsubscript{12}mim][Nsa] (wt%)</th>
<th>$d$ (Å)</th>
<th>$d_L$ (Å)</th>
<th>$d_W$ (Å)</th>
<th>$a_S$ (Å\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>44.0</td>
<td>22.1</td>
<td>21.9</td>
<td>32.0</td>
</tr>
<tr>
<td>60</td>
<td>38.9</td>
<td>23.4</td>
<td>15.5</td>
<td>30.2</td>
</tr>
<tr>
<td>70</td>
<td>34.8</td>
<td>24.4</td>
<td>10.4</td>
<td>28.3</td>
</tr>
</tbody>
</table>

Table S2 Surface properties and micellization parameters of [C\textsubscript{12}mim][Nsa] in aqueous solution at 10 °C.

<table>
<thead>
<tr>
<th>IL</th>
<th>CMC (mM)</th>
<th>$\gamma_{CMC}$ (mN/m)</th>
<th>$\Gamma_{\text{max}}$ (µmol/m\textsuperscript{2})</th>
<th>$A_{\text{min}}$ (Å\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C\textsubscript{12}mim][Nsa]</td>
<td>0.78</td>
<td>33.2</td>
<td>2.75</td>
<td>60.3</td>
</tr>
</tbody>
</table>
Theory for calculation of structural parameters of liquid crystalline phase

From the results of SAXS, several structural parameters characterizing the structure of the lamellar liquid crystalline phase could be calculated as follows.

The interlayer spacing $d$ of the lamellar liquid crystalline phase can be determined from

$$d = 2\pi/q_1$$  \hspace{1cm} (1)

where $q_1$ is the scattering vector of the first scattering peak.

Then the thickness of hydrophobic domain ($d_L$) could be obtained as

$$d_L = d \cdot \varphi_L$$  \hspace{1cm} (2)

where $\varphi_L$ is the volume fraction of hydrophobic domain, and can be calculated by

$$\varphi_L = \frac{w_S / \rho_S}{w_S / \rho_S + w_W / \rho_W}$$  \hspace{1cm} (3)

where $w_S$ and $w_W$ are the weight fraction of $[\text{C}_{12}\text{mim}][\text{Nsa}]$ and water, respectively, and $\rho_S$ and $\rho_W$ are the densities of $[\text{C}_{12}\text{mim}][\text{Nsa}]$ and water, respectively. The density of $[\text{C}_{12}\text{mim}][\text{Nsa}]$ is obtained using a pycnometer as reported previously, and the reference solvent is ethyl acetate ($\rho = 0.8944 \text{ g cm}^{-3}$). The density of $[\text{C}_{12}\text{mim}][\text{Nsa}]$ is 0.9935 g·cm$^{-3}$.

The thickness of the water layer ($d_W$) is given by

$$d_W = d - d_L$$  \hspace{1cm} (4)

Furthermore, the area per molecule for $[\text{C}_{12}\text{mim}][\text{Nsa}]$ in the hydrophobic/hydrophilic interface is given by

$$a_s = \frac{2v_L}{d_L}$$  \hspace{1cm} (5)

$v_L$ is the volume of the hydrophobic part of the surfactant, calculated according to the Tanford equation:

$$v_L (\text{Å}^3) = 27.4 + 26.9N$$  \hspace{1cm} (6)

References