

## Supporting Information

### Non-Aqueous Lyotropic Liquid-Crystalline Phases Formed by Gemini Surfactants in a Protic Ionic Liquid

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#### 1. Calculation of the structural parameters of the hexagonal phase.

The lattice parameters (D) of the hexagonal liquid crystalline phase are obtained according to the equation:  $D=4\pi/\sqrt{3}q_{100}$ . With the alkyl chains arranged inside the cylinders ( $H_I$ ), the structural parameters are given by following equations.<sup>1,2</sup>

$$R_I = D \sqrt{\frac{\sqrt{3}}{2\pi \left(1 + \frac{v_w}{v_a} \frac{1-\omega}{\omega}\right)}} \quad (S1)$$

$$S_I = \frac{2M_a v_a}{R_I N} \quad (S2)$$

However, in the case of alkyl chains arranged outside the cylinders ( $H_{II}$ ), the structural parameters are given by different equations as following.<sup>1,2</sup>

$$R_{II} = D \sqrt{\frac{\sqrt{3}}{2\pi \left(1 + \frac{v_a}{v_w} \frac{\omega}{1-\omega}\right)}} \quad (S3)$$

$$S_{II} = \frac{2\pi R_{II} M_a v_a / N}{\sqrt{3} D^2 / 2 - \pi R_{II}^2} \quad (S4)$$

where,  $v_w$  &  $v_a$  are the specific volumes of the surfactant and EAN ( $v_w = 0.90 \text{ cm}^3/\text{g}$  for 12-2-12 estimated by pycnometric density measurements and similar to analogous molecule,<sup>2</sup>  $v_a = 0.83 \text{ cm}^3/\text{g}$  for EAN<sup>3</sup>).  $R_I$  &  $R_{II}$  are the radii of the normal and reverse cylinder-like aggregates.  $S_I$  &  $S_{II}$  are the corresponding areas per molecule of m-s-m at the hydrophilic/hydrophobic interface in the normal and reverse hexagonal phases.  $M_a$  is the molar mass of the Gemini-surfactant (614.67 g/mol for 12-2-12).  $\omega$  is the weight fraction of Gemini-surfactant in the binary system and  $N$  is the Avogadro's number ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ).

## 2. The effective headgroup area ( $a_o$ ) of the 12-2-12 molecule.

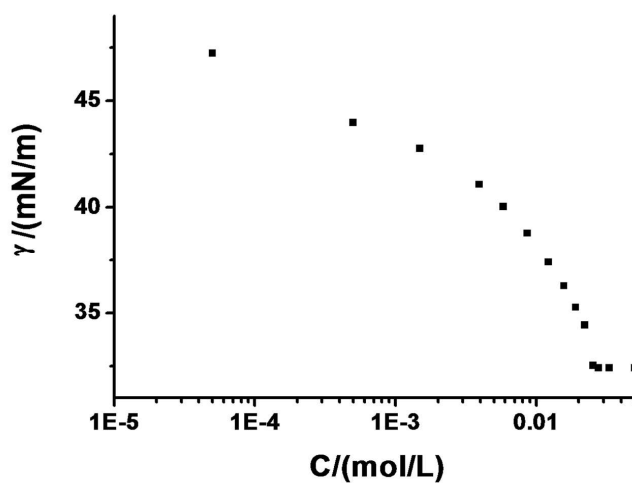
The maximum surface excess concentration  $\Gamma_{\max}$  and the effective headgroup area ( $a_o$ ) of 12-2-12 molecules can be calculated according to the Gibbs adsorption isotherm equation:<sup>4</sup>

$$\Gamma_{\max} = \frac{1}{nRT} \left( \frac{d\gamma}{d \ln C} \right) \quad (\text{S5})$$

$$a_o = \frac{1}{N_A \Gamma_{\max}} (\times 10^{23}) \quad (\text{S6})$$

where  $n$  is the number of solute species whose concentration at the interface changes with the surfactant concentration  $c$ ;  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ );  $T$  is the absolute temperature;  $\gamma$  represents the surface tension;  $d\gamma/d \ln c$  is the slope of the surface tension  $\gamma$  vs  $\ln c$  dependence when the concentration is near the cmc;  $N_A$  is Avogadro's number ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ). As an ionic liquid, the ionic nature of EAN causes a large degree of charge screening, which results in the value of  $n$  being taken as 1 in our system.

The measured surface tension change with the surfactant concentration is shown in Figure S1. Combining equations [S5] and [S6], the effective headgroup area of 12-2-12 molecules is calculated as  $81.8 \text{ \AA}^2$ .



**Figure S1.** Surface tension isotherm at 298 K as a function of 12-2-12 concentration in EAN solution.

#### References:

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