Supporting Information

Molecular Packing of Surface Active Ionic Liquids in a Deep Eutectic Solvent:

A Small Angle X-ray Scattering (SAXS) Study

Qintang Li,*[a] Kun Tong,[b] Juan Qiu,[c] Minhao Yan,*[a] Qiang Tian, [a] Xiao Chen,[c] and
Xiu Yue*[d]

[a] State Key Laboratory of Environment-friendly Energy Materials, Southwest
University of Science and Technology, Mianyang 621000, China

[b] Beijing Institute of Aerospace Testing Technology; Beijing Key Laboratory of
Research and Application for Aerospace Green Propellants, Beijing 100074, China

[c] Key Laboratory of Colloid and Interface Chemistry, Shandong University,
Ministry of Education, Jinan 250100, China

[d] Laboratory of Environmental Sciences and Technology, Xinjiang Technical
Institute of Physics & Chemistry, Chinese Academy of Sciences; Key Laboratory of
Functional Materials and Devices for Special Environments, Chinese Academy of
Sciences, Urumqi 830011, China

Corresponding authors:

Qintang Li

E-mail: liqintangwind@sina.com

Minhao Yan

E-mail: yanminhao@swust.edu.cn

Xiu Yue

E-mail: yuexiu@ms.xjb.ac.cn

¹H NMR results (600MHz, DMSO)

C_{12}mimBr 0.86-0.90 (3H), 1.21-1.38 (18H), 2.09-2.32 (2H), 4.12-4.16 (3H), 4.30-4.35 (2H), 7.32-7.40 (1H), 7.45-7.55 (1H), 10.32-10.43 (1H).

C_{14}mimBr 0.86-0.90 (3H), 1.21-1.38 (22H), 2.00-2.10 (2H), 4.12-4.16 (3H), 4.30-4.35 (2H), 7.31-7.36 (1H), 7.43-7.51 (1H), 10.39-10.49 (1H).

C_{16}mimBr 0.87-0.91 (3H), 1.20-1.340 (26H), 1.96-2.00 (2H), 4.12-4.16 (3H), 4.31-4.35 (2H), 7.27-7.30 (1H), 7.37-7.43 (1H), 10.49-10.57 (1H).

SAXS analysis

Micelles

The scattering vector q is defined as

$$q = (4\pi/\lambda)sin\theta/2$$

in which λ is the wavelength of the X-ray and θ is the scattering angle. The scattering intensity $I(q)$ for monodisperse, homogeneous, and spherical particles is generally described by:

$$I(q) = nP(q)S(q)$$

Where n is the total number of particles, $P(q)$ and $S(q)$ are the form and structure factors.

Generalized indirect Fourier transformation (GIFT) method

For the GIFT method, it was done with the PCG software (version 4.05.12). The smeared data were used and desmearing process was included in the GIFT software. The pair distance distribution function (PDDF) $p(r)$ could be calculated by the Fourier transformation of $P(q)$, which is defined as

$$P(q) = 4\pi \int_0^\infty p(r)\frac{sin(qr)}{qr}dr$$

The size and shape of micelles could be obtained from PDDF curves.

For the electron density of the shell and the solvent is close, parameters obtained from PDDF curves correspond to the core of micelles, which is made of alkyl chains of surfactants. Considering the charge screening effects of ChG, a hard sphere $S(q)$ with Percus-Yevick closure relation would be good. No polydispersity was taken into consideration.

Model-fitting method

For the model-fitting method, it was done with the SASfit software (version 0.94.7). The data were desmeared with the beam length by the SAXSquant software

(version 4.1.1.8319). Several models like sphere, ellipsoid and cylinder have been tried and the ellipsoid model give good fitting results. The hard sphere structure factor with Percus-Yevick closure relation was adopted for the interaction between micelles. A constant was added in the background.

Calculation of the structural parameters of LLC

The H$_1$ phase

The lattice parameter (D) of the normal hexagonal liquid crystalline phase is obtained according to the equation.

$$D = \frac{4\pi}{\sqrt{3}q_1}$$

With the alkyl chains arranged inside the cylinders, i.e. the H$_1$ phase, the structural parameters are given by following equations.

$$R = D\sqrt{\frac{\sqrt{3}}{2\pi(1 + \frac{\rho_a}{\rho_s}\frac{1-\omega}{\omega})}}$$

$$S = \frac{2M_a}{\rho_a RN}$$

where ρ_a and ρ_s are the density of C$_n$mimBr and solvent ChG (ρ_a = 1.05, 1.04, 1.03 g/cm^3 for C$_{12}$mimBr, C$_{14}$mimBr, C$_{16}$mimBr, respectively; ρ_s = 1.18 g/cm^3 for ChG), R is the radius of the normal cylinder-like aggregates, S is the corresponding area per molecule of surfactants at the hydrophilic/hydrophobic interface, M$_a$ is the molar mass of surfactants (331.33, 359.38, 387.44 g/mol for C$_{12}$mimBr, C$_{14}$mimBr, C$_{16}$mimBr, respectively), ω is the weight fraction of surfactant in the binary system, N is the Avogadro's number (6.022*10^{23} mol^{-1}).

The V$_1$ phase

The lattice parameter (D) of the normal bicontinuous cubic liquid crystalline phase is obtained according to the equation.

$$D = \frac{2\pi\sqrt{h^2 + l^2 + k^2}}{q}$$

The structural parameters are given by following equations,

$$1 - \Phi_a = 2\sigma\left(\frac{l}{D}\right) + \frac{4}{3}\pi\chi(\frac{l}{D})^3$$

$$S = 2v_a \frac{\sigma D^2 + 2\pi\chi l^2}{\Phi_a D^3}$$

$$R = 0.248D - l \quad \text{(Ia3d)}$$

where Φ_a is the surfactant volume percentage, l is the solvent thickness, v_a is the volume of the surfactant, χ is Euler-Poincaré characteristic (-8 for Ia3d), σ is ratio of the minimal surface in a unit cell to the quantity (unit cell volume)$^{2/3}$ (3.091 for Ia3d), R is the radius of the solvophobic domains.

The L$_\alpha$ phase

The lattice parameter (D) of the lamellar liquid crystalline phase is obtained according to the equation.

$$D = \frac{2\pi}{q_1}$$

$$d_s = D(1 - \Phi_a)$$

$$d_a = D - d_s$$

$$S = \frac{v_a}{d_a}$$

where d_s and d_a is thickness of the solvent and solvophobic layer .
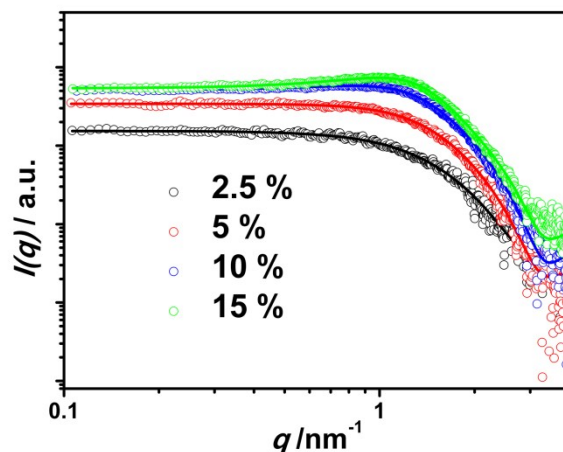
Fig. S1 SAXS results (model-fitting method) of the C_{12}mimBr/ChG system at 30 °C and different concentrations.
Open symbols for experimental and lines for fitting curves.

Table S1 Parameters of micelles in the C_{12}mimBr/ChG systems at 30 °C and different concentrations.

Concentration / %	a / nm	ε	R_{HS} / nm	φ
2.5	1.28	1.66	2.49	0.0175
5	1.27	1.73	2.12	0.0436
10	1.26	1.82	2.17	0.0910
15	1.25	1.92	2.15	0.129

a, the equal semi-axis; ε, the axis ratio, εa, the principle semi-axis; R_{HS}, hard sphere repulsion radius; φ, volume fraction.
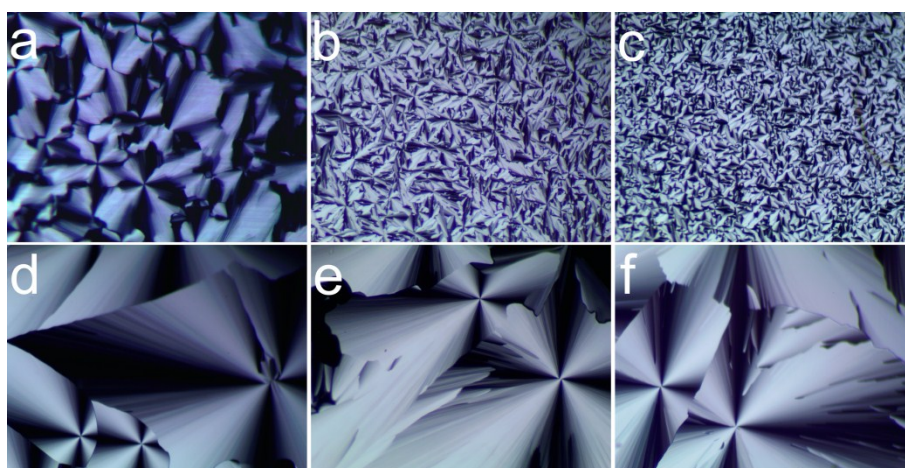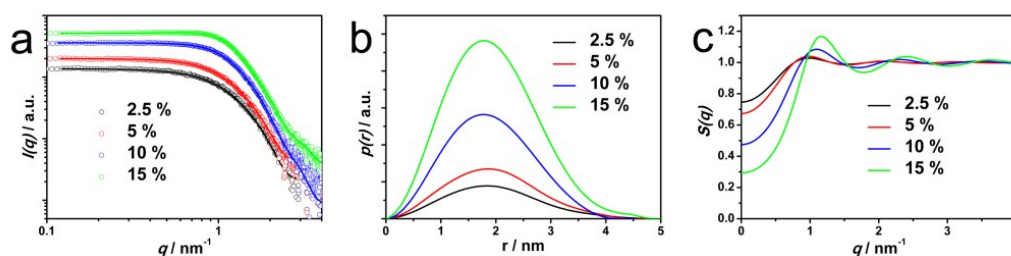

Fig. S2 POM images of C_{12}mimBr/ChG samples at 30 °C and different concentrations.
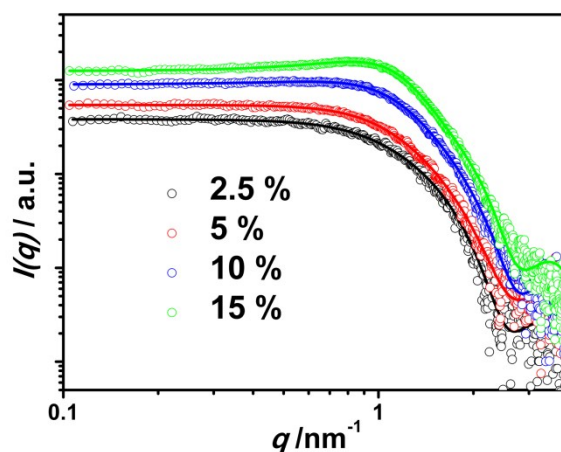a) 60 %; b) 65%; c) 70 %; d) 75 %; e) 80 %; f) 85%.

Table S2 Structure parameters of H_1 phases in the C_{12}mimBr/ChG system at 30 $^{\circ}$C and different concentrations.

Concentrations / %	D / nm	R / nm	d / nm	S / nm^2
60	4.37	1.82	0.73	0.577
65	4.22	1.82	0.58	0.575
70	4.15	1.85	0.45	0.565
75	4.08	1.88	0.32	0.557
80	3.97	1.88	0.21	0.556
85	3.86	1.88	0.10	0.557

Fig. S3 SAXS results (GIFT method) of the C_{14}mimBr/ChG system at 30 $^{\circ}$C and different concentrations.
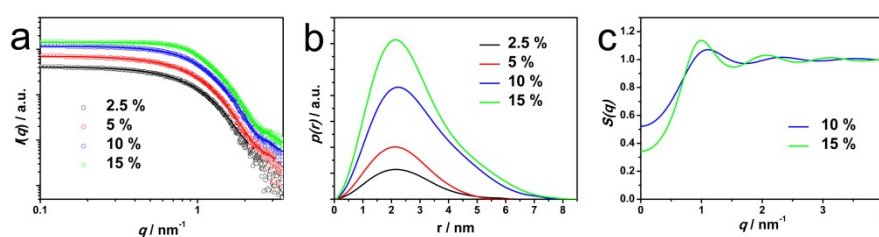a) SAXS curves, open symbols for experimental and lines for fitting curves; b) PDDF curves; c) $S(q)$ curves.

Fig. S4 SAXS results (model-fitting method) of the C_{14}mimBr/ChG system at 30 $^{\circ}$C and different concentrations.
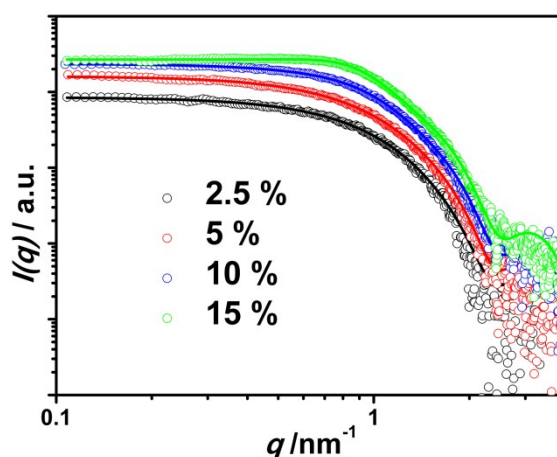Open symbols for experimental and lines for fitting curves.

Table S3 Parameters of micelles in the $C_{14}mimBr/ChG$ systems at 30 $^\circ C$ and different concentrations.

Concentration / %	a / nm	ε	R_{HS} / nm	φ
2.5	1.59	1.56	3.26	0.0224
5	1.57	1.79	2.86	0.0400
10	1.53	1.87	2.62	0.0791
15	1.51	2.32	2.55	0.144

Fig. S5 SAXS results (GIFT method) of the $C_{16}mimBr/ChG$ system at 30 $^\circ C$ and different concentrations.
a) SAXS curves, open symbols for experimental and lines for fitting curves; b) PDDF curves; c) *S(q)* curves.

Fig. S6 SAXS results (model-fitting method) of the $C_{16}mimBr/ChG$ system at 30 $^\circ C$ and different concentrations.
Open symbols for experimental and lines for fitting curves.

Table S4 Parameters of micelles in the $C_{16}mimBr/ChG$ systems at 30 °C and different concentrations.

Concentration / %	a / nm	ε	R_{HS} / nm	φ
2.5	1.76	1.93	-	-
5	1.73	2.07	-	-
10	1.70	3.24	3.02	0.0799
15	1.68	3.49	3.27	0.135

Table S5 Parameters of micelles in the $C_{n}mimBr/ChG$ systems at a 5% concentration and 30 °C.
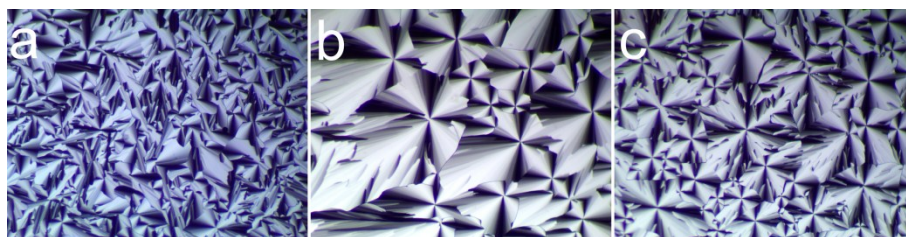
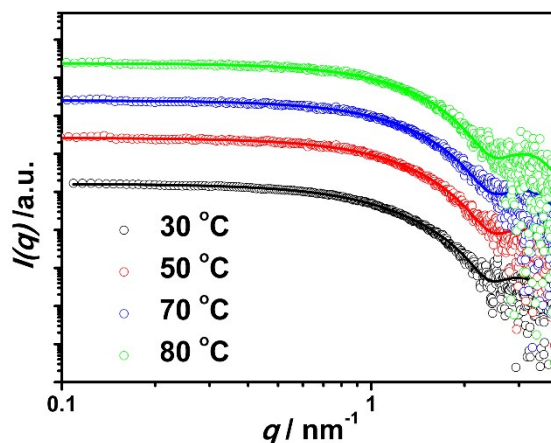| SAIL	a / nm	ε
$C_{12}mimBr$	1.27	1.73
$C_{14}mimBr$	1.57	1.79
$C_{16}mimBr$	1.73	2.07
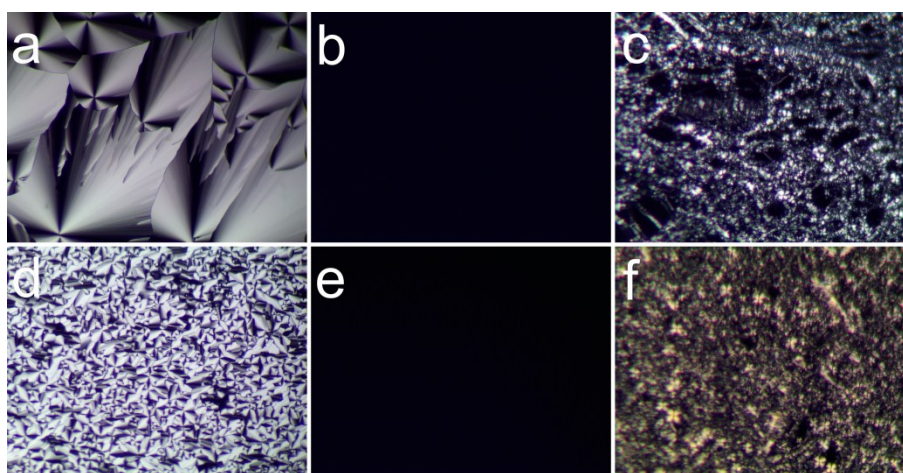
Fig. S7 Representative POM images of different samples.
a) $C_{14}mimBr/ChG$, 65 %, 30 °C; b) $C_{14}mimBr/ChG$, 80 %, 50 °C;
c) $C_{14}mimBr/ChG$, 90 %, 60 °C; d) $C_{16}mimBr/ChG$, 50 %, 50 °C;
e) $C_{16}mimBr/ChG$, 75 %, 50 °C; f) $C_{16}mimBr/ChG$, 90 %, 60 °C.

Fig. S8 POM images of 65 % $C_n$mimBr/ChG samples at 50 °C.
a) C_{12}mimBr; b) C_{14}mimBr; c) C_{16}mimBr.

**Fig. S9** SAXS results (model-fitting method) of the 5 % C_{16}mimBr/ChG sample at different temperatures.
Open symbols for experimental and lines for fitting curves.

**Table S6** Micellar Parameters of the 5 % C_{16}mimBr/ChG sample at different temperatures.

Temperature / °C	a / nm	ε
30	1.73	2.07
50	1.71	1.78
70	1.70	1.71
80	1.70	1.67

Table S7 Phase sequence of SAILs in different solvents.

| Solvent	C_{12}mimBr	C_{14}mimBr	C_{16}mimBr
ChG	$L_1/H_1/V_1$	$L_1/H_1/V_1/L_\alpha$	$L_1/H_1/V_1/L_\alpha$
water	$L_1/H_1/V_1/L_\alpha$	$L_1/H_1/V_1/L_\alpha$	$L_1/H_1/V_1/L_\alpha$
EAN	$L_1/H_1/V_1$	$L_1/H_1/V_1/L_\alpha$	$L_1/H_1/V_1/L_\alpha$
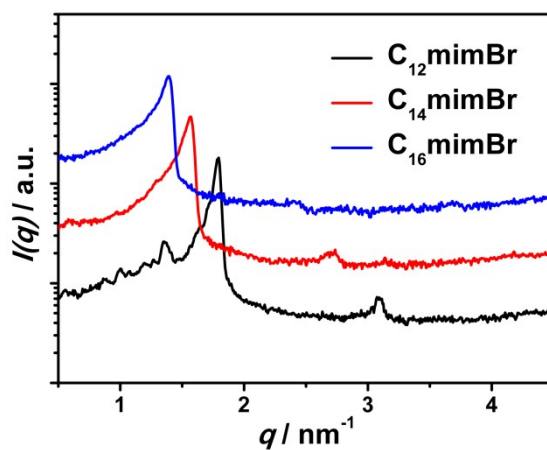
**Fig. S10** SAXS results of 65 % $C_n$mimBr/water samples at 50 °C.
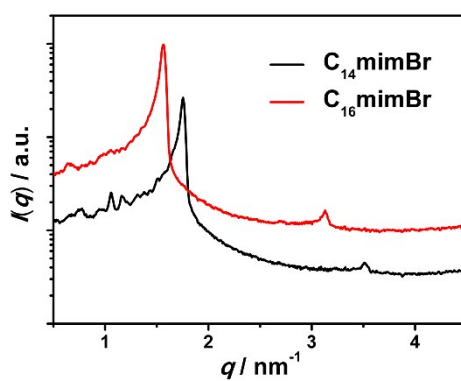
Fig. S11 SAXS results of 65 % $C_n$mimBr/EAN samples at 50 °C.

Table S8 Structure parameters of H_1 phases at 65 % and 50 °C.

Surfactant	Solvent	D / nm	R / nm	d / nm	S / nm²
C_{12}mimBr	water	4.03	1.69	0.65	0.620
C_{14}mimBr	water	4.60	1.93	0.74	0.595
C_{16}mimBr	water	5.16	2.17	0.82	0.576
C_{14}mimBr	EAN	4.12	1.79	0.54	0.640
C_{16}mimBr	EAN	4.62	2.01	0.60	0.621
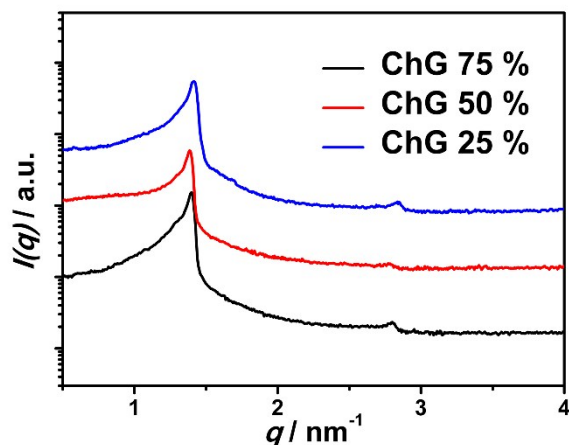
Fig. S12 SAXS results of 65 % C_{16}mimBr/solvent samples at 50 °C. ChG and water mixed solvents with different ChG weight percentage.
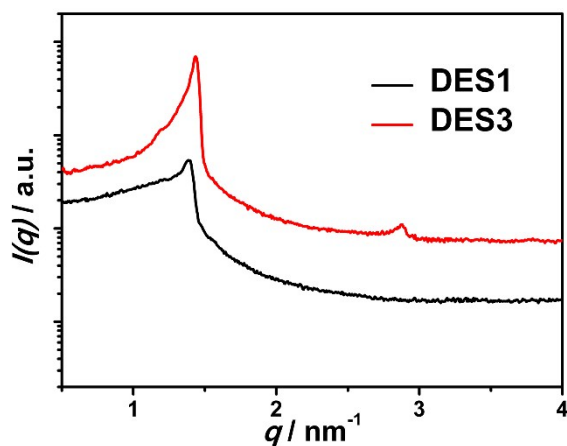
Fig. S13 SAXS results of 65 % C_{16}mimBr/DES samples at 50 °C. DES1, ChCl/G molar ratio 1/1; DES3, ChCl/G molar ratio 1/3.

Table S9 Structure parameters of 65 % C_{16}mimBr/solvent H_1 phases at 50 °C.

Solvent	D / nm	R / nm	d / nm	S / nm^2
ChG 75 %	5.16	2.22	0.72	0.563
ChG 50 %	5.19	2.21	0.77	0.565
ChG 25 %	5.15	2.18	0.79	0.569
DES1	5.17	2.23	0.71	0.561
DES3	5.01	2.17	0.67	0.575