

## Supporting information

To explore the inner structure of lyotropic liquid crystal formed in ternary systems of [C<sub>8</sub>mim]Cl, water, and different alcohols, derived dimensions of L<sub>α</sub> phases are calculated.<sup>1-3</sup>

The volume fraction of the hydrophobic components ([C<sub>8</sub>mim]Cl and alcohol),  $\phi_a$ , is represented as the following:

$$\phi_a = \frac{\frac{W_s + W_o}{\rho_s + \rho_o}}{\frac{W_s + W_o + W_w}{\rho_s + \rho_o + \rho_w}} \quad (1)$$

where,  $W_s$ ,  $W_o$ , and  $W_w$  are the weight fractions of [C<sub>8</sub>mim]Cl, alcohol, and H<sub>2</sub>O;  $\rho_s$ ,  $\rho_o$ , and  $\rho_w$  are the densities of [C<sub>8</sub>mim]Cl (1.01 g·cm<sup>-3</sup>), alcohol (C<sub>6</sub>H<sub>13</sub>OH, 0.81 g·cm<sup>-3</sup>; C<sub>8</sub>H<sub>17</sub>OH, 0.82 g·cm<sup>-3</sup>; C<sub>10</sub>H<sub>21</sub>OH, 0.83 g·cm<sup>-3</sup>; C<sub>12</sub>H<sub>25</sub>OH, 0.83 g·cm<sup>-3</sup>), and H<sub>2</sub>O (1.00 g·cm<sup>-3</sup>).

Similarly, the volume fractions of alcohol ( $\phi_o$ ) and H<sub>2</sub>O ( $\phi_w$ ) can be obtained.

The molar volume of the [C<sub>8</sub>mim]Cl hydrocarbon chain can be calculated from:

$$V = 0.027 \times (n_c + n_{me}) \quad (2)$$

where,  $n_c$  and  $n_{me}$  are the numbers of carbon atoms and methyl groups, respectively.

In the ternary system, the volume fraction of the hydrophobic domain (the hydrophobic carbon chains of [C<sub>8</sub>mim]Cl and alcohol),  $\phi_c$ , is given by:

$$\phi_c = \frac{\frac{W_s}{M_s} \times V}{\frac{W_s}{\rho_s} + \frac{W_o}{\rho_o} + \frac{W_w}{\rho_w}} + \phi_o \quad (3)$$

where,  $M_s$  is the molecular weight of [C<sub>8</sub>mim]Cl (230.8 g·mol<sup>-1</sup>).

The thickness of the hydrophobic domain,  $d_c$ , in the L<sub>α</sub> phase is calculated using:

$$d_c = d \times \phi_c \quad (4)$$

where,  $d$  is the lattice spacing, given by the SAXS determination.

The area per polar group at the hydrophilic/hydrophobic interface ( $S$ ) is obtained using

$$S = \frac{2V}{d_c} \times \frac{\phi_c}{\phi_c - \phi_o} \quad (5)$$

Derived dimensions of  $L_\alpha$  phases formed in the four ternary systems are listed in Table 1-4.

#### References

- (1) Fontell, K.; Khan, A.; Lindstrom, B.; Maciejewska, D.; Puang-Ngern, S. *Colloid Polym. Sci.* **1991**, *269*, 727.
- (2) Yamashita, Y.; Kunieda, H.; Oshimura, E.; Sakamoto, K. *Langmuir* **2003**, *19*, 4070.
- (3) Bernardes, J.B.; Norrman, J.; Piculell, L.; Loh, W. *J. Phys. Chem. B* **2006**, *110*, 23433.

Table 1. Derived dimensions of L <sub>$\alpha$</sub>  phase formed in the [C<sub>8</sub>mim]PF<sub>6</sub>-C<sub>6</sub>H<sub>13</sub>OH-H<sub>2</sub>O ternary system.

Composition (%)	R	$\Phi_c$	d (nm)	$d_c$ (nm)	S (nm <sup>2</sup> )
65-20-15	0.69	0.633	2.77	1.75	0.444
60-20-20	0.75	0.602	2.80	1.68	0.477
55-20-25	0.82	0.572	2.91	1.66	0.500
60-25-15	0.94	0.654	2.76	1.80	0.489
50-25-25	1.13	0.594	2.95	1.75	0.548
55-30-15	1.23	0.675	2.71	1.83	0.548
45-25-30	1.25	0.563	3.10	1.74	0.581
50-30-20	1.35	0.645	2.80	1.81	0.582
35-25-40	1.61	0.503	3.48	1.75	0.664
40-30-30	1.69	0.585	3.01	1.76	0.679
30-25-45	1.88	0.472	3.75	1.77	0.720
35-30-35	1.94	0.555	3.25	1.80	0.721
30-30-40	2.26	0.525	3.48	1.83	0.783
25-25-50	2.26	0.442	4.16	1.84	0.778

Table 2. Derived dimensions of L <sub>$\alpha$</sub>  phase formed in the [C<sub>8</sub>mim]PF<sub>6</sub>-C<sub>8</sub>H<sub>17</sub>OH-H<sub>2</sub>O ternary system.

Composition (%)	R	$\Phi_c$	d (nm)	$d_c$ (nm)	S (nm <sup>2</sup> )
55-20-25	0.64	0.570	3.23	1.84	0.449
50-20-30	0.71	0.540	3.37	1.82	0.472
40-20-40	0.89	0.478	3.72	1.78	0.536
45-30-25	1.18	0.613	3.24	1.99	0.557
30-20-50	1.18	0.417	5.04	2.10	0.528
40-30-30	1.33	0.583	3.41	1.99	0.596
20-15-65	1.33	0.300	7.39	2.22	0.535
30-30-40	1.77	0.523	3.98	2.08	0.683
25-25-50	1.77	0.440	4.86	2.14	0.664
20-20-60	1.77	0.356	6.13	2.18	0.652
15-20-65	2.36	0.325	7.32	2.38	0.728

Table 3. Derived dimensions of L <sub>$\alpha$</sub>  phase formed in the [C<sub>8</sub>mim]PF<sub>6</sub>-C<sub>10</sub>H<sub>21</sub>OH-H<sub>2</sub>O ternary system.

Composition (%)	R	$\Phi_c$	d (nm)	$d_c$ (nm)	S (nm <sup>2</sup> )
60-25-15	0.60	0.652	3.26	2.12	0.411
58.4-25.0-16.6	0.62	0.642	3.26	2.09	0.422
53.8-23.1-23.1	0.62	0.594	3.33	1.98	0.446
50-25-25	0.73	0.591	3.33	1.97	0.481
50.0-33.4-16.6	0.97	0.676	3.33	2.25	0.490
46.1-30.8-23.1	0.97	0.627	3.51	2.20	0.501
45-30-25	0.97	0.612	3.91	2.39	0.461
42.8-28.6-28.6	0.97	0.584	3.84	2.24	0.492
37.5-25.0-37.5	0.97	0.514	4.66	2.40	0.459
40-30-30	1.09	0.582	3.84	2.23	0.528
38.4-38.5-23.1	1.45	0.658	3.53	2.32	0.609
35.7-35.7-28.6	1.45	0.614	3.80	2.33	0.605
31.2-31.3-37.5	1.45	0.542	4.30	2.33	0.606
30-30-40	1.45	0.521	4.44	2.31	0.610
27.8-27.8-44.4	1.45	0.485	5.14	2.49	0.566
25.0-25.0-50.0	1.45	0.438	5.38	2.36	0.597

Table 4. Derived dimensions of L <sub>$\alpha$</sub>  phase formed in the [C<sub>8</sub>mim]PF<sub>6</sub>-C<sub>12</sub>H<sub>25</sub>OH-H<sub>2</sub>O ternary system.

Composition (%)	R	$\Phi_c$	d (nm)	$d_c$ (nm)	S (nm <sup>2</sup> )
50-25-25	0.62	0.591	3.68	2.17	0.437
45-25-30	0.69	0.560	3.93	2.20	0.454
50-30-20	0.74	0.642	3.48	2.23	0.466
45-30-25	0.82	0.612	3.92	2.40	0.459
35-25-40	0.88	0.499	4.71	2.35	0.488
40-30-30	0.93	0.582	4.08	2.37	0.497
45-35-20	0.96	0.662	3.56	2.36	0.510
30-25-45	1.03	0.469	5.46	2.56	0.491
40-35-25	1.08	0.632	4.00	2.53	0.512
40-40-20	1.24	0.682	3.77	2.57	0.548
30-30-40	1.24	0.521	4.92	2.56	0.551
20-20-60	1.24	0.354	7.46	2.64	0.534
30-35-35	1.44	0.572	4.54	2.60	0.602
35-45-20	1.59	0.702	3.73	2.62	0.639
30-40-30	1.65	0.623	4.32	2.69	0.639
25-35-40	1.73	0.542	4.88	2.64	0.674
20-30-50	1.85	0.461	5.73	2.64	0.709
15-25-60	2.06	0.378	7.06	2.67	0.758