SUPPLEMENTARY MATERIAL

- **Determination of r_{hc} and a_s for a hexagonal structure**

Radius determination

Initially, the system was assumed as composed by two parts:

- hydrocarbon (hc) : containing the surfactant hydrocarbon chain (c) and oil (o), which is assumed to be insoluble in water;
- aqueous (aq) : containing water, the surfactant headgroup and the polyanion

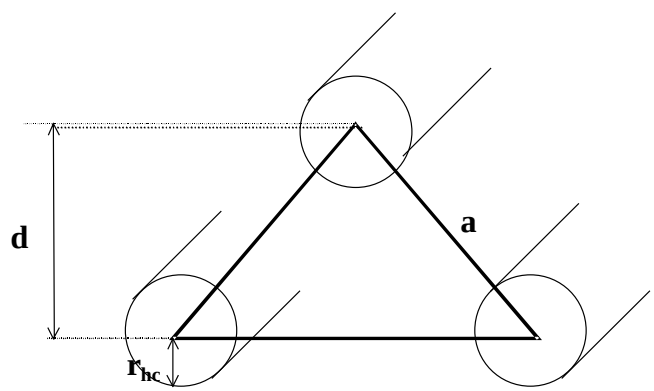


Figure 1. *Two-dimensional representation of a hexagonal phase indicating the parameters used in this calculation: a = cell parameter and d = distance between adjacent planes (d = 2π / q)*

In two dimensions, the volumetric fraction occupied by hydrocarbon can be related to the area occupied by the cylinders, A_{hc}, with respect to the total area of the triangle, A_{tot}, as follows:

$$\Phi_{hc} = \frac{A_{hc}}{A_{tot}} \qquad (1)$$

According to Fig. 1:

$$\sin 60° = \frac{d}{a} \longrightarrow \frac{\sqrt{3}}{2} = \frac{d}{a} \qquad (2)$$

$$a = \frac{2.d}{\sqrt{3}} \qquad (3)$$

Hence, the total area can be calculated as follows:

$$A_{tot} = \frac{d^2}{\sqrt{3}} \qquad (4)$$

And, from equations (1), (3) and (4), one obtains:

$$\phi_{hc} = \frac{\sqrt{3}\pi r_{hc}{}^2}{2d^2} \qquad (5)$$

The volumetric fraction occupied by hydrocarbon in the liquid crystalline system can be also calculated from its composition, using their mass fractions and density equal to 1 g cm^{-3}, as:

$$\phi_{hc} = \frac{V_{hc}}{V_{tot}} = \frac{V_c + V_o}{V_{tot}} = \frac{m_c / \delta_c + m_o / \delta_o}{m_{aq} / \delta_{aq} + m_c / \delta_c + m_o / \delta o_o} \qquad (6)$$

Using equation (5), one obtains:

$$\boxed{r_{hc} = \sqrt{\frac{\phi_{hc} 2d^2}{\sqrt{3}\pi}}} \qquad (8)$$

Determination of the area occupied per surfactant molecule (a_s) in a cylinder

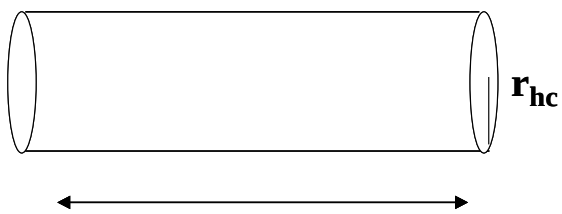


***Figure 2**: Schematic representation of a cylinder micelle*

A cylinder of length l contains

- n_s molecules of surfactant , each molecule with a hydrocarbon volume v_c
- n_o molecules of oil, each molecule with a volume v_o

The value of v_o can be estimated from the oil density and the volume of the surfactant hydrocarbon chain can be calculated from (11):

$$V = 0.027(n_c + n_{me}) \qquad (9)$$

Where n_c = number of carbon atoms and n_{me}= number of methyl groups.

The volume of this cylinder is defined as :

$$V_{hc} = \pi . r_{hc}^2 l = n_s . v_c + n_o v_o \quad \Longrightarrow \quad l = \frac{n_s v_c + n_o v_o}{\pi r_{hc}^2} \qquad (10)$$

The area per surfactant molecule can then be calculated dividing the total cylinder surface area by the number of molecules of surfactant:

$$a_s = \frac{2\pi r_{hc} l}{n_s} \qquad (11)$$

Using equations (10) and (11), it is possible to calculate a_s using :

$$\boxed{a_s = \frac{2}{r_{hc}}\left(v_c + \frac{n_o}{n_s}v_o\right)} \qquad (12)$$

- **Determination of d_{hc} and a_s for a lamellar structure**

Calculation of bilayer thickness (d_{hc})

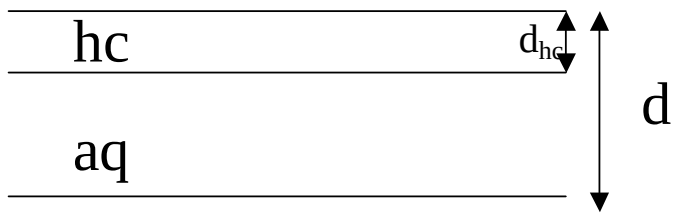


Figure 3. *Schematic two-dimensional representation of a lamellar structure : d_{hc} = bilayer thickness, d = repeating distance, hc and aq refer to hydrocarbon and aqueous parts of the lamellar.*

The system was assumed as composed by two parts :

- hydrocarbon (hc) : containing the surfactant hydrocarbon chain (c) and oil (o), which is assumed to be insoluble in water;
- aqueous (aq) : containing water, the surfactant headgroup and the polyanion

The volume fraction occupied by hydrocarbon can be calculated as:

$$\phi_{hc} = \frac{d_{hc}}{d} \qquad (13)$$

Hence,

$$\boxed{d_{hc} = d.\phi_{hc}} \qquad (14)$$

Determination of the área occupied per surfactant molecule(a_s) in a lamella

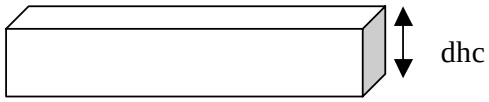


***Figure 4**: Schematic representation of a lamella*

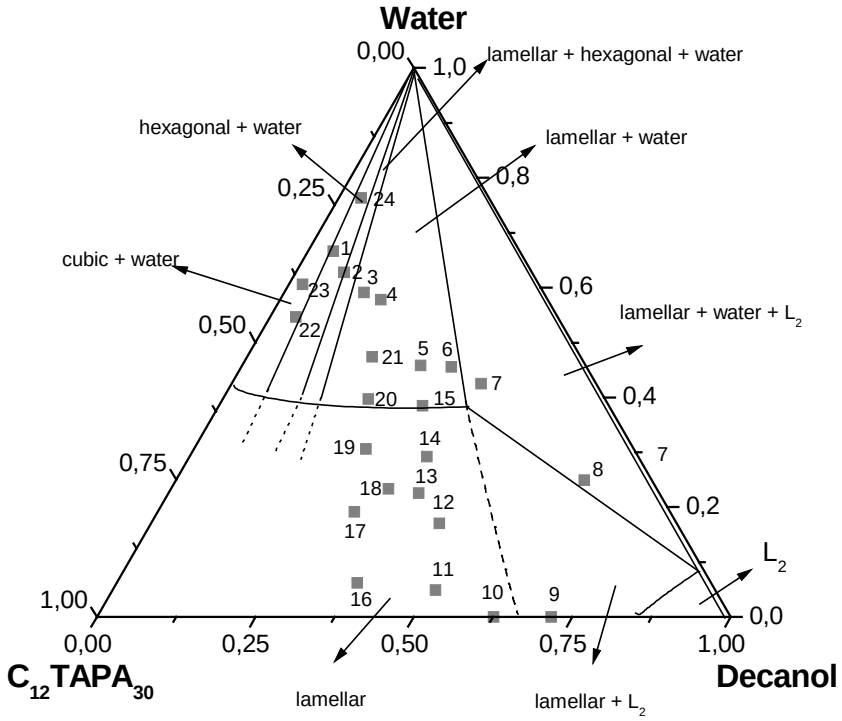
The volume of the hydrocarbon portion of a lamella can be calculated as :

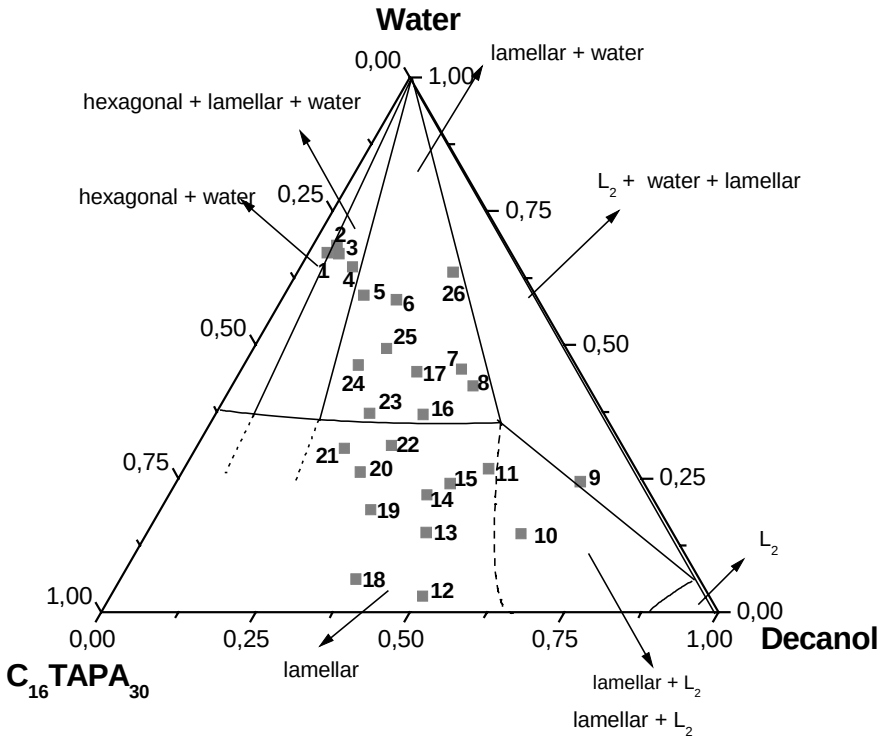
$$v_{hc} = n_S.v_S + n_O.v_O \qquad (15)$$

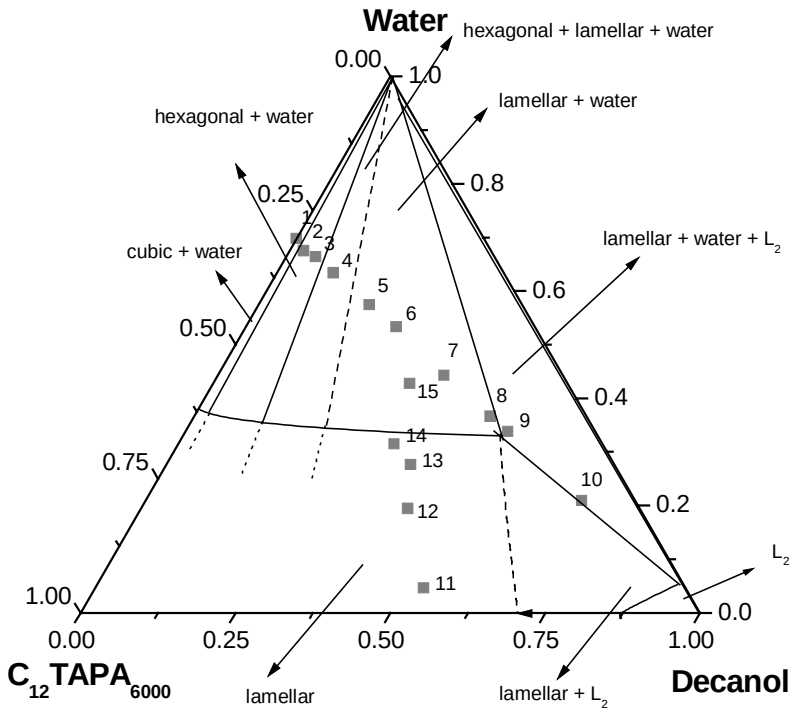
$$v_{hc} = d_{hc}.\ n_S.a_S/2 \qquad (16)$$

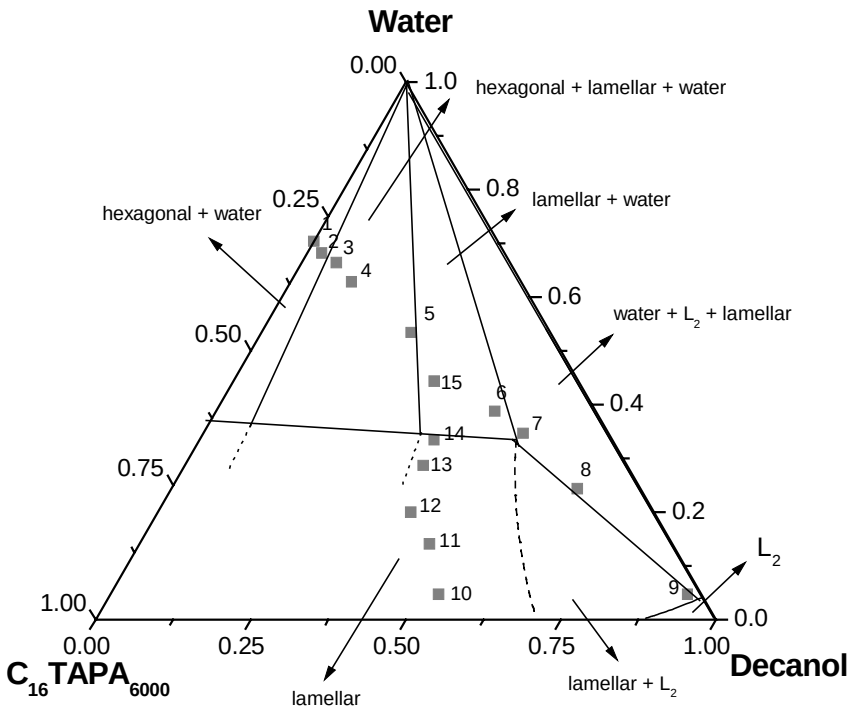
Combining equations (15) and (16), it is possible to calculate a_s as :

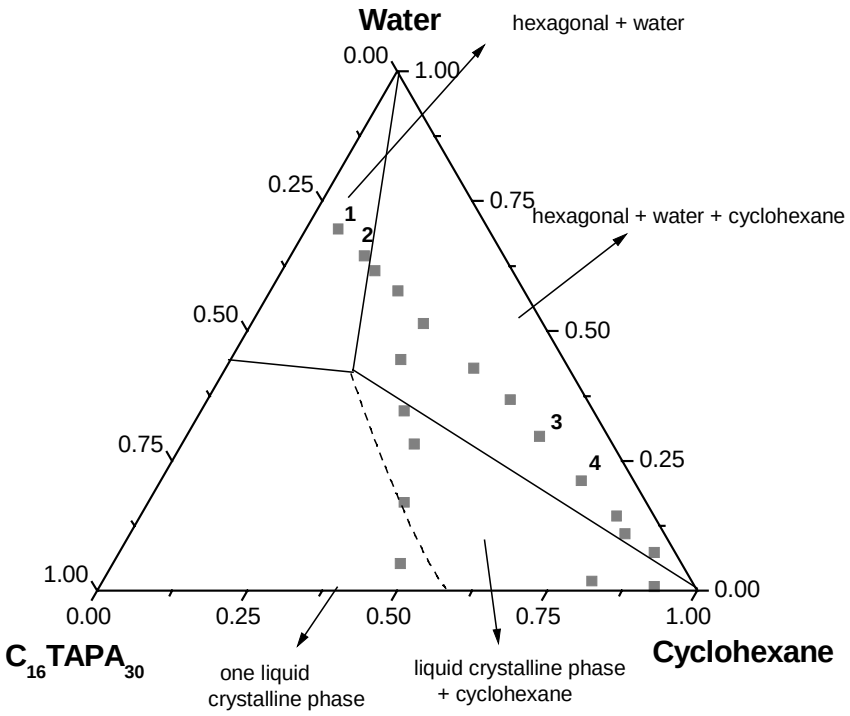
$$\boxed{a_S = (n_S.v_S + n_O.v_O).2/\ n_S.d_{hc}} \qquad (17)$$

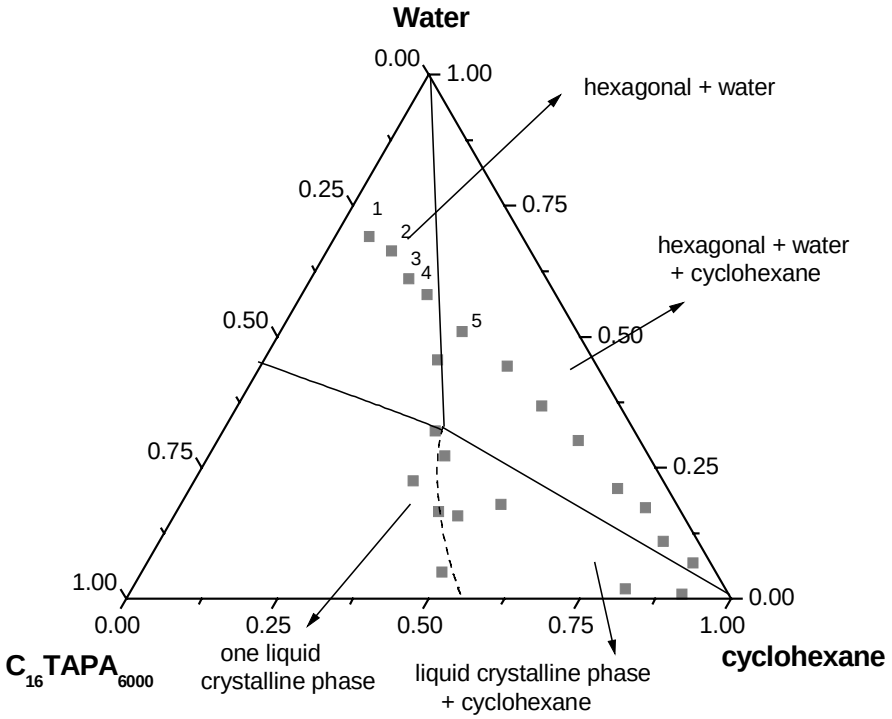

Water
0,00
1,0
lamellar + hexagonal + water
hexagonal + water
lamellar + water
0,8
0,25
cubic + water
0,6
lamellar + water + L2
0,50
0,4
0,75
0,2
L2
1,00
0,0
0,00
0,25
0,50
0,75
1,00
C12TAPA30
Decanol
lamellar
lamellar + L2


Water
0,00
1,00
lamellar + water
hexagonal + lamellar + water
hexagonal + water
0,25
L2 + water + lamellar
0,75
0,50
0,50
0,75
0,25
L2
1,00
0,00
0,00
0,25
0,50
0,75
1,00
Decanol
C16TAPA30
lamellar
lamellar + L2
lamellar + L2


Water
hexagonal + lamellar + water
lamellar + water
hexagonal + water
cubic + water
lamellar + water + L2
L2
lamellar
lamellar + L2
Decanol
C12TAPA6000
0.00
0.25
0.50
0.75
1.00
1.0
0.8
0.6
0.4
0.2
0.0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15


Water
hexagonal + lamellar + water
lamellar + water
hexagonal + water
water + L2 + lamellar
L2
lamellar
lamellar + L2
Decanol
C16TAPA6000
0.00
0.25
0.50
0.75
1.00
1.0
0.8
0.6
0.4
0.2
0.0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15


Water
hexagonal + water
hexagonal + water + cyclohexane
0.00
1.00
0.25
0.75
0.50
0.50
0.75
0.25
1.00
0.00
0.00
0.25
0.50
0.75
1.00
1
2
3
4
C16TAPA30
one liquid
crystalline phase
liquid crystalline phase
+ cyclohexane
Cyclohexane


Water
hexagonal + water
hexagonal + water
+ cyclohexane
0.00
1.00
0.25
0.75
0.50
0.50
0.75
0.25
1.00
0.00
0.00
0.25
0.50
0.75
1.00
1
2
3
4
5
C16TAPA6000
one liquid
crystalline phase
liquid crystalline phase
+ cyclohexane
cyclohexane

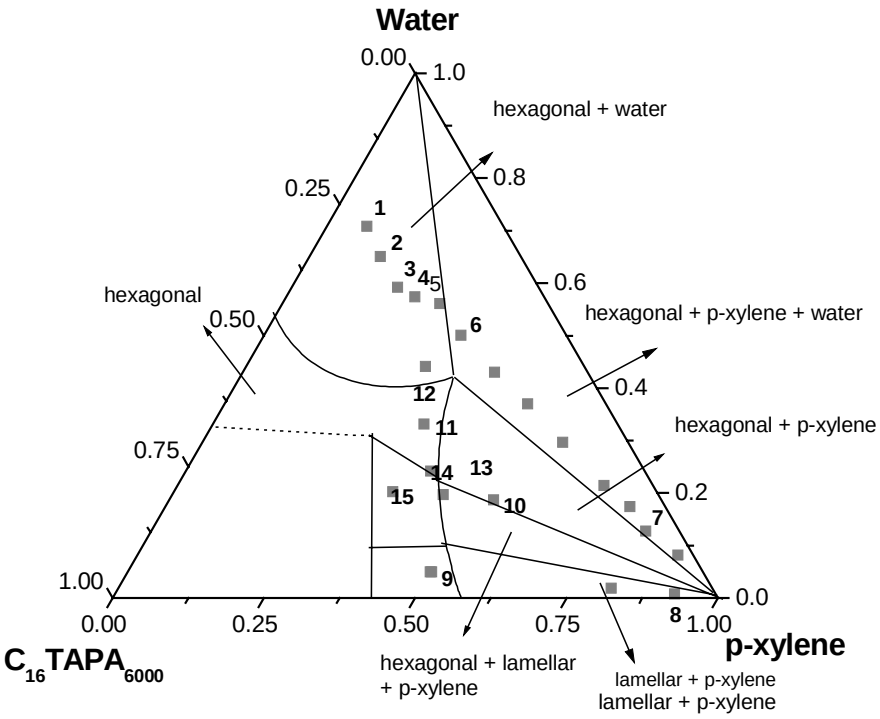

Water
0.00
1.0
hexagonal + water
0.25
0.8
1
2
3
4
5
0.6
hexagonal
0.50
hexagonal + p-xylene + water
6
0.4
12
11
hexagonal + p-xylene
0.75
14
13
15
10
0.2
7
1.00
9
0.0
8
0.00
0.25
0.50
0.75
1.00
p-xylene
C16TAPA6000
hexagonal + lamellar
+ p-xylene
lamellar + p-xylene
lamellar + p-xylene

Table A1. Structural parameters for liquid crystalline systems formed by the mixture decanol/$C_{12}TAPA_{30}$/water. Symbols: a represents the lattice parameter determined from SAXS spectra; d_{hc} is the lamellae thickness; R is the radius of the aggregate cylinder in hexagonal phases and a_s represents the area per surfactant headgroup.

Sample	Wt % decanol	Wt % water	Wt % $C_{12}TAPA_{30}$	Structure	a (Å)	dhc* (Å)	R (Å)	as (Å^2)
1	0.040	0.666	0.293	hexagonal	44.2	----------	14.2	62.7
2	0.076	0.628	0.296	hexagonal	45.2	----------	15.2	68.0
3	0.127	0.591	0.282	lamellar	38.2	17.3	----------	70.8
4	0.159	0.578	0.263	lamellar	38.2	18.4	----------	79.1
5	0.332	0.455	0.213	lamellar	41.4	22.7	----------	117.2
6	0.394	0.425	0.181	lamellar	43.7	24.5	----------	118.4
7	0.645	0.249	0.106	lamellar	43.9	24.7	----------	117.6
8	0.710	0.028	0.250	lamellar	40.1	34.9	----------	88.8
9	0.620	0.037	0.330	lamellar	40.0	33.5	----------	88.7
10	0.510	0.049	0.441	lamellar	39.5	30.9	----------	68.0
11	0.455	0.171	0.374	lamellar	41.5	28.9	----------	75.4
12	0.395	0.225	0.372	Two lamellae	d_1=41.0 d_2=39.5	----------	----------	----------
13	0.375	0.291	0.330	Two lamellae	d_1=42.2 d_2=40.7	----------	----------	----------
14	0.321	0.384	0.294	lamellar	43.2	22.4	----------	90.2
15	0.321	0.385	0.294	lamellar	41.6	21.6	----------	93.7
16	0.380	0.062	0.558	lamellar	39.4	28.2	----------	53.6
17	0.311	0.191	0.498	lamellar	37.7	23.3	----------	62.5
18	0.344	0.234	0.422	lamellar	39.3	24.0	----------	70.2
19	0.271	0.306	0.422	lamellar	38.9	20.1	----------	70.6
20	0.230	0.397	0.373	lamellar	39.1	17.9	----------	79.3
21	0.197	0.474	0.329	lamellar	39.1	17.9	----------	79.3
22	0.041	0.546	0.412	cubic	89.7	----------	----------	----------
23	0.022	0.607	0.371	hexagonal	40.1	----------	12.9	62.7
24	0.036	0.763	0.201	hexagonal		----------	14.2	60.9

Table A2. Structural parameters for liquid crystalline systems formed by the mixture decanol/$C_{16}TAPA_{30}$/water.

Sample	Wt % decanol	Wt % water	Wt % $C_{16}TAPA_{30}$	Structure	a (Å)	dhc* (Å)	R (Å)	as (Å^2)
1	0.030	0.672	0.297	hexagonal	50.7	----------	17.3	61.9
2	0.039	0.686	0.275	hexagonal + lamellar	dh=51.8 dl=41.8	----------	----------	----------
3	0.050	0.670	0.280	hexagonal + lamellar	dh=52.0 dl=4.2.0	---------	----------	---------
4	0.084	0.646	0.270	hexagonal + lamellar	dh=51.6 dl=42.6	---------	----------	---------
5	0.129	0.592	0.278	lamellar	42.4	20.9	----------	74.1
6	0.186	0.584	0.230	lamellar	42.0	23.7	----------	93.92
7	0.357	0.454	0.189	lamellar	48.2	28.8	----------	121.9
8	0.391	0.423	0.186	lamellar	47.4	28.6	----------	140.2
9	0.654	0.244	0.101	lamellar	48.1	29.6	----------	161.0
10	0.607	0.146	0.246	lamellar	46.6	31.6	----------	109.6
11	0.494	0.268	0.238	lamellar	45.2	30.5	----------	126.4
12	0.506	0.029	0.464	lamellar	45.1	36.9	----------	67.4
13	0,452	0.149	0.398	lamellar	46.0	33.5	----------	76.1
14	0,418	0.219	0.363	lamellar	46.5	31.4	----------	82.0
15	0,445	0.240	0.314	lamellar	46.6	31.4	----------	94.2
16	0.337	0.369	0.294	lamellar	47.9	26.4	----------	98.6
17	0.287	0.449	0.263	lamellar	48.8	26.9	----------	96.7
18	0.382	0.062	0.556	lamellar	45.8	34.5	----------	55.3
19	0.341	0.191	0.467	two lamellae	d_1=44.2 d_2=47.1	----------	----------	----------
20	0.289	0.261	0.449	lamellar	45.3	27.1	----------	68.2
21	0.242	0.306	0.452	lamellar	42.8	23.5	----------	71.7
22	0.314	0.312	0.374	lamellar	44.6	25.8	----------	82.6
23	0.249	0.372	0.379	lamellar	43.7	22.3	----------	84.2
24	0.186	0.462	0.352	lamellar	42.1	20.8	----------	82.1
25	0.216	0.493	0.291	lamellar	43.4	22.9	----------	90.0
26	0.252	0.636	0.112	lamellar	47.9	28.8	----------	138.7

Table A3. Structural parameters for liquid crystalline systems formed by the mixture decanol/$C_{12}TAPA_{6000}$/water.

Sample	Wt % decanol	Wt % water	Wt % $C_{12}TAPA_{6000}$	Structure	a (Å)	dhc* (Å)	R (Å)	as (Å^2)
1	0.000	0.697	0.303	cubic	83.6	----------	----------	----------
2	0.023	0.675	0.302	hexagonal	43.7	----------	13.9	53.3
3	0.048	0.664	0.288	hexagonal	39.4	----------	15.5	60.3
4	0.091	0.634	0.275	*				
5	0.179	0.574	0.247	lamellar	38.5	20.0	----------	78.4
6	0.243	0.533	0.223	lamellar	41.2	22.5	----------	83.8
7	0.365	0.443	0.192	lamellar	43.8	26.6	----------	107.8
8	0.478	0.367	0.155	lamellar	42.3	27.1	----------	172.5
9	0.521	0.338	0.141	lamellar	44.3	28.4	----------	164.7
10	0.704	0.209	0.086	lamellar	42.5	27.3	----------	171.7
11	0.530	0.047	0.423	lamellar	40.4	32.0	----------	69.3
12	0.431	0.195	0.375	lamellar	41.1	27.6	----------	75.7
13	0.395	0.276	0.329	lamellar	41.6	25.5	----------	84.3
14	0.349	0.315	0.336	*				
15	0.317	0.428	0.255	lamellar	42.1	23.5	----------	91.1

*** not identified**

Table A4. Structural parameters for liquid crystalline systems formed by the mixture decanol/$C_{16}TAPA_{6000}$/water.

Sample	Wt % decanol	Wt % water	Wt % $C_{16}TAPA_{6000}$	Structure	a (Å)	dhc* (Å)	R (Å)	as (Å^2)
1	0.000	0.703	0.266	Hexagonal	48.6	----------	16.0	57.4
2	0.023	0.681	0.294	Hexagonal	51.2	----------	17.4	61.5
3	0.056	0.664	0.279	Hexagonal + lamellar	dh=52.2 dl=42.9	----------	----------	----------
4	0.098	0.628	0.273	Hexagonal + lamellar	dh=50.8 dl=38.8	----------	----------	----------
5	0.242	0.534	0.223	two lamellae	d_1=43.5 d_2=47.1	----------	----------	----------
6	0.449	0.387	0.162	Lamellar	48.0	30.2	----------	168.2
7	0.516	0.346	0.137	Lamellar	48.0	30.6	----------	181.1
8	0.655	0.243	0.101	Lamellar	47.9	30.5	----------	181.4
9	0.931	0.046	0.022	Lamellar	47.9	30.5	----------	
10	0.529	0.047	0.423	Lamellar	45.0	31.9	----------	85.2
11	0.468	0.140	0.391	Lamellar	46.1	34.2	----------	77.4
12	0.408	0.199	0.391	Lamellar	46.5	31.8	----------	76.3
13	0.384	0.286	0.328	Lamellar	45.9	28.6	----------	91.2
14	0.378	0.333	0.287	Lamellar	48.4	28.7	----------	98.2
15	0.321	0.443	0.232	two lamellae	d_1=47.2 d_2=43.9	----------	----------	----------

Table A5. Structural parameters for liquid crystalline systems formed by the mixture cyclohexane/$C_{16}TAPA_{30}$/water.

Sample	Wt % cyclohexane	Wt % water	Wt % $C_{16}TAPA_{30}$	Structure	a (Å)	R (Å)	As (Å^2)
1	0.05	0.696	0.253	Hexagonal	65.6	21.8	64.1
2	0.121	0.649	0.229	Hexagonal	71.4	25.6	86.7
3	0.585	0.303	0.111	Hexagonal	70.1	25.4	101.0
4	0.695	0.221	0.083	Hexagonal	70.1	25.4	101.0

Table A6. Structural parameters for liquid crystalline systems formed by the mixture cyclohexane/$C_{16}TAPA_{6000}$/water.

Sample	Wt % cyclohexane	Wt % water	Wt % $C_{16}TAPA_{6000}$	Structure	a (Å)	R (Å)	As (Å^2)
1	0.054	0.692	0.252	Hexagonal	65.5	21.7	65.4
2	0.105	0.669	0.225	Hexagonal	71.1	25.1	85.0
3	0.158	0.613	0.228	Hexagonal	89.1	33.1	80.4
4	0.209	0.578	0.212	Hexagonal	89.4	35.2	99.6
5	0.299	0.507	0.507	Hexagonal	89.9	36.3	120.9

Table A7. Structural parameters for liquid crystalline systems formed by the mixture xylene /$C_{16}TAPA_{6000}$/water.

Sample	Wt % xylene	Wt % water	Wt % $C_{16}TAPA_{6000}$	Structure	a (Å)	R (Å)	as (Å^2)
1	0.063	0.709	0.226	Hexagonal	55.9	19.3	64.0
2	0.113	0.656	0.230	Hexagonal	62.7	24.3	64.1
3	0.166	0.596	0.237	Hexagonal	74.6	29.9	63.2
4	0.205	0.581	0.212	Hexagonal	73.1	29.7	75.1
5	0.256	0.567	0.177	Hexagonal	78.0	32.4	89.4
6	0.320	0.503	0.176	Hexagonal	77.9	30.0	100.2
7	0.817	0.128	0.054	Hexagonal	76.2	30.0	100.2
8	0.921	0.013	0.065	Lamellar	----	-----	----
9	0.498	0.055	0.446	Lamellar	----	------	-----
10	0.513	0.193	0.274	Hexagonal	78.6	33.2	72.1
11	0.345	0.334	0.320	Hexagonal	79.4	31.5	75.7
12	0.292	0.444	0.262	Hexagonal	77.1	29.5	84.1
13	0.452	0.189	0.358	Hexagonal + lamellar	----	-----	-----
14	0.403	0.245	0.351	Hexagonal + lamellar	----	-----	-----
15	0.359	0.202	0.438	Hexagonal + lamellar	----	-----	-----