

Supporting information for the paper:

*Self- assembly of polyion-surfactant ion complex salts in mixtures
with water and n-alcohols*

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1. Tabulated structural parameters

In the tables S1 - S8 below, the samples marked with asterisks (*) were analyzed in a different experimental set up of the SAXS beamline. The values of their cell parameters are slightly, but consistently, lower than those previously obtained, thus these SAXS results were only used to elucidate the structure of liquid crystalline phases, but their numerical information was not used.

Table S1: Structural parameters for liquid crystalline systems formed by the mixture octanol/CTAPA₃₀/water. Symbols: d_{hc} is the lamellae thickness; r_{hc} is the hydrophobic radius of the aggregate cylinder in hexagonal phases; r_{aq} is the hydrophilic radius of the aggregate in reversed hexagonal phases and a_s represents the area per surfactant headgroup.

Sample	Octanol wt %	Water wt %	CTAPA ₃₀ Wt %	Structure	Cell Parameter (Å)	r_{hc}/r_{aq} (Å)	a_s (Å ²)
1	4	73	23	Hexagonal	H: 51.3	r_{hc} : 15.3	H: 71.7
2	5	69	26	Hexagonal + Lamellar	H: 56.7 L: 43.6	r_{hc} : 17.8 d_{hc} : 18.9	H: 68.2 L: 84.5
3	7	69	24	Hexagonal + Lamellar	H: 51.2 L: 40.1	r_{hc} : 16.1 d_{hc} : 17.3	H: 75.5 L: 91.8
4	12	63	25	Lamellar	L: 41.5	d_{hc} : 16.1	L: 146.9
5	14	62	24	Lamellar	L: 44.4	d_{hc} : 19.4	L: 122.1
6	21	57	22	Lamellar + rev. Hexagonal	L: 41.4 H: 42.0	d_{hc} : 20.5 r_{aq} : 14.7	L: 115.6 H: -----
7	28	53	19	Lamellar + rev. Hexagonal	L: 44.3 H: 44.6	d_{hc} : 22.2 r_{aq} : 15.6	L: 97.0 H: -----
8	41	42	16	Rev.Hexagonal	H: 44.3	r_{aq} : 14.7	-----
9*	44	40	16	Rev.Hexagonal	H: 40.6	r_{aq} : 13.5	-----
10*	47	34	19	Rev.Hexagonal	H: 39.4	-----	-----
11	51	5	44	Rev.Hexagonal	H: 36.0	-----	-----
12	43	18	39	Lamellar + rev. Hexagonal	L: 40.2 H: 38.5	-----	-----
13	37	29	34	Lamellar + rev. Hexagonal	L: 42.8 H: 42.6	-----	-----
14	37	33	30	Lamellar + rev. Hexagonal	L: 41.3 H: 41.9	-----	-----
15*	38	34	28	Lamellar + rev. Hexagonal	L: 38.9 H: 40.0	-----	-----
16	29	45	26	Lamellar + rev. Hexagonal	L: 44.3 H: 44.4	d_{hc} : 22.2 r_{aq} : 15.5	L: 97.0 H: -----

Table S2: Structural parameters for liquid crystalline systems formed by the mixture hexanol/CTAPA₃₀/water. Symbols: d_{hc} is the lamellae thickness; r_{hc} is the radius of the aggregate cylinder in hexagonal phases and a_s represents the area per surfactant headgroup.

Sample	Hexanol wt %	Water wt %	CTAPA ₃₀ wt %	Structure	Cell Parameter (Å)	rhc/ dhc (Å)	As (Å ²)
1	7	65	28	Hexagonal + Lamellar	H: 60.2 L: 45.4	r_{hc} : 19.2 d_{hc} : 21.1	H: 61.2 L: 74.1
2	12	59	29	Hexagonal + Lamellar	H: 60.6 L: 46.0	r_{hc} : 19.3 d_{hc} : 21.4	H: 60.8 L: 73.1
3	21	54	25	Lamellar	L: 44.5	d_{hc} : 23.4	L: 101.0
4	28	49	23	Lamellar	L: 46.3	d_{hc} : 25.1	L: 94.4
5	40	41	19	Lamellar	L: 44.9	d_{hc} : 24.3	L: 97.4
6	46	14	40	Lamellar	L: 43.7	-----	-----
7	38	24	38	Lamellar	L: 45.2	-----	-----
8*	40	24	36	Lamellar	L: 34.6	-----	-----
9*	37	37	36	Lamellar	L: 36.5	d_{hc} : 19.0	L: 101.4

Table S3: Structural parameters for liquid crystalline systems formed by the mixture butanol/CTAPA₃₀/water. Symbols: d_{hc} is the lamellae thickness; r_{hc} is the radius of the aggregate cylinder in hexagonal phases and a_s represents the area per surfactant headgroup.

Sample	Butanol wt %	Water wt %	CTAPA ₃₀ wt %	Structure	Cell Parameter (Å)	rhc/ dhc (Å)	As (Å ²)
1	6	65	29	Hexagonal	H: 59.2	r_{hc} : 18.8	H: 62.3
2	12	60	28	Hexagonal + Lamellar	H: 56.5 L: 42.6	r_{hc} : 18.7 d_{hc} : 17.7	H: 69.6 L: 77.1
3*	14	62	24	Lamellar	L: 36.4	d_{hc} : 15.6	L: 92.6
4	27	48	25	Lamellar	L: 44.3	d_{hc} : 18.9	L: 76.1
5*	28	17	55	Lamellar	L: 31.4	d_{hc} : 20.3	L: 82.0
6*	21	20	59	Lamellar	L: 31.8	d_{hc} : 19.1	L: 75.2

Table S4: Structural parameter for liquid crystalline systems formed by the mixture ethanol/CTAPA₃₀/water.

Sample	Ethanol wt %	Water wt %	CTAPA ₃₀ wt %	Structure	Cell Parameter (Å)
1*	4	69	27	Cubic	C: 145.0
2*	9	66	25	Hexagonal	H: 46.8
3*	15	61	24	Hexagonal	H: 44.3
4*	16	62	22	Hexagonal	H: 45.0
5*	20	59	21	Hexagonal	H: 44.0
6*	26	55	19	Hexagonal	H: 43.8
7*	55	15	30	Elongated Micelle	L ₂ : 28.8
8*	35	17	48	Elongated Micelle	L ₂ : 28.5
9*	30	26	44	Elongated Micelle	L ₂ : 31.5
10*	23	31	46	Hexagonal	H: 39.2
11*	16	35	49	Hexagonal	H: 43.5
12*	24	45	31	Hexagonal	H: 43.4
13*	12	36	52	Hexagonal	H: 46.1
14*	9	47	44	Hexagonal	H: 46.6

Table S5: Structural parameters for liquid crystalline systems formed by the mixture octanol/CTAPA₆₀₀₀/water. Symbols: d_{hc} is the lamellae thickness; r_{hc} is the radius of the aggregate cylinder in hexagonal phases; r_{aq} is the hydrophilic radius of the aggregate in reversed hexagonal phases and a_s represents the area per surfactant headgroup.

Sample	Octanol wt %	Water wt %	CTAPA ₆₀₀₀ wt %	Structure	Cell Parameter (Å)	$r_{hc}/$ d_{hc}/r_{aq} (Å)	a_s (Å ²)
1	1	74	24	Hexagonal	H: 49.9	r_{hc} : 15.6	H: 63.3
2	6	70	24	Hexagonal + Lamellar	H: 51.1 L: 38.3	r_{hc} : 16.2 d_{hc} : 16.0	H: 64.9 L: 87.8
3	5	69	26	Hexagonal + Lamellar	H: 56.0 L: 43.1	r_{hc} : 17.8 d_{hc} : 18.0	H: 59.2 L: 78.0
4	13	64	23	Lamellar	L: 43.6	d_{hc} : 17.8	L: 132.6
5	18	60	22	Lamellar	L: 44.3	d_{hc} : 20.1	L: 117.6
6	30	50	20	Lamellar + Rev.Hexagonal	L: 44.5 H: 42.7	d_{hc} : 21.5 r_{aq} : 14.7	L: 110.2 H: 74.1
7	49	39	12	Rev.Hexagonal	H: 42.7	r_{aq} : 14.9	-----
8	67	27	6	Rev.Hexagonal	H: 39.3	r_{aq} : 13.7	-----
9	80	4	16	Rev.Hexagonal	H: 34.3	-----	-----
10*	61	24	15	Rev.Hexagonal	H: 38.6	-----	-----
11*	56	33	11	Rev.Hexagonal	H: 38.5	-----	-----
12*	42	25	33	Lamellar + Rev.Hexagonal	L: 38.0 H: 36.7	-----	-----
13*	38	34	28	Lamellar + Rev.Hexagonal	L: 39.3 H: 38.3	-----	-----
14	37	33	30	Lamellar + Rev.Hexagonal	L: 44.6 H: 42.5	-----	-----
15	32	37	31	Lamellar + Rev.Hexagonal	L: 41.5 H: 39.6	-----	-----
16	29	44	27	Lamellar + Rev.Hexagonal	L: 42.2 H: 42.2	-----	-----

Table S6: Structural parameters for liquid crystalline systems formed by the mixture hexanol/CTAPA₆₀₀₀/water. Symbols: d_{hc} is the lamellae thickness; r_{hc} is the radius of the aggregate cylinder in hexagonal phases; r_{aq} is the hydrophilic radius of the aggregate in reversed hexagonal phases and a_s represents the area per surfactant headgroup.

Sample	Hexanol wt %	Water wt %	CTAPA ₆₀₀₀ wt %	Structure	Cell Parameter (Å)	$r_{hc}/$ d_{hc}/r_{aq} (Å)	a_s (Å ²)
1	7	64	29	Hexagonal + Lamellar	H: 62.3 L: 46.5	r_{hc} : 20.1 d_{hc} : 20.7	H: 50.5 L: 67.3
2	11	60	29	Lamellar	L: 45.9	d_{hc} : 21.7	L: 72.3
3	21	54	25	Lamellar + rev. Hexagonal	L: 46.3 H: 45.7	d_{hc} : 19.9 r_{aq} : 17.4	L: 118.9 H: -----
4	28	50	22	Lamellar + rev. Hexagonal	L: 46.5 H: 46.4	d_{hc} : 20.0 r_{aq} : 17.7	L: 118.4 H: -----
5	38	42	20	Rev.Hexagonal	H: 47.2	r_{aq} : 16.4	-----
6	41	42	17	Rev.Hexagonal	H: 46.8	r_{aq} : 16.3	-----
7*	46	13	41	Lamellar + rev. Hexagonal	L: 45.9 H: 39.6	-----	-----
8*	44	17	39	Rev.Hexagonal	H: 40.4	-----	-----
9*	40	24	36	Lamellar + rev. Hexagonal	L: 44.9 H: 42.7	-----	-----
10*	35	36	29	Lamellar + rev. Hexagonal	L: 46.0 H: 46.7	-----	-----
11*	30	46	24	Lamellar + rev. Hexagonal	L: 46.0 H: 46.1	d_{hc} : 19.8 r_{aq} : 17.6	L: 119.7 H: -----

Table S7: Structural parameters for liquid crystalline systems formed by the mixture butanol/CTAPA₆₀₀₀/water. Symbols: d_{hc} is the lamellae thickness; r_{hc} is the radius of the aggregate cylinder in hexagonal phases and a_s represents the area per surfactant headgroup.

Sample	Butanol wt %	Water wt %	CTAPA ₆₀₀₀ wt %	Structure	Cell Parameter (Å)	$r_{hc}/d_{hc}/(\text{Å})$	$a_s (\text{Å}^2)$
1	5	67	28	Hexagonal	H: 60.3	r_{hc} : 20.8	H: 54.3
2*	18	60	22	Lamellar	L: 34.2	d_{hc} : 17.6	L: 115.4
3	22	53	25	Lamellar	L: 39.6	d_{hc} : 20.4	L: 107.7
4	27	51	22	Lamellar	L: 43.6	d_{hc} : 23.1	L: 108.4
5*	32	18	50	Lamellar	L: 31.8	d_{hc} : 23.3	L: 138.8
6*	22	32	46	Lamellar	L: 33.0	d_{hc} : 17.8	L: 91.1

Table S8: Structural parameter for liquid crystalline systems formed by the mixture ethanol/CTAPA₆₀₀₀/water.

Sample	Ethanol wt %	Water wt %	CTAPA ₆₀₀₀ wt %	Structure	Cell Parameter (Å)
1*	4	70	26	Hexagonal	H: 44.8
2*	16	62	22	Hexagonal	H: 43.9
3*	33	50	17	Hexagonal	H: 39.6
4*	16	34	50	Hexagonal	H: 43.4
5*	10	44	46	Hexagonal	H: 44.8
6*	23	34	43	Hexagonal	H: 45.4
7*	16	45	39	Hexagonal	H: 43.1

2. Phase diagrams

Figures S1 - S8 below show phase diagrams of all investigated mixtures. Each point represents an experimental sample prepared; those indicated in blue were investigated by SAXS.

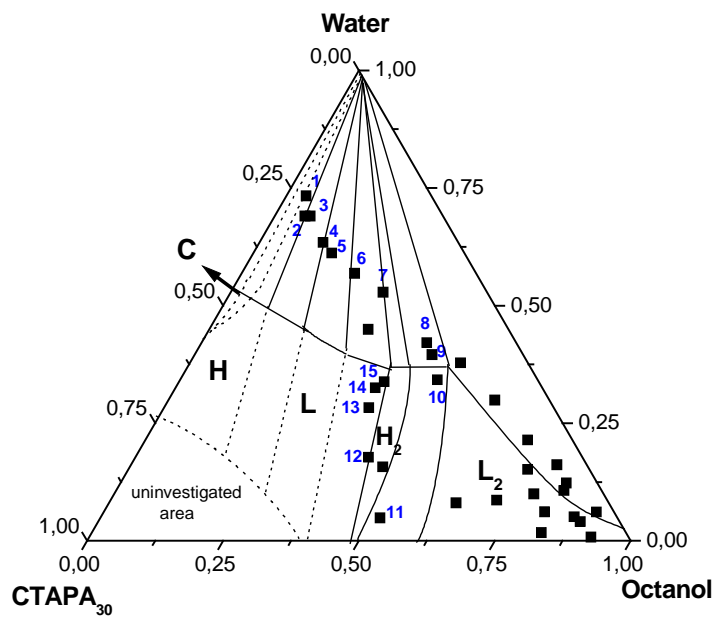


Fig. S1 Samples prepared along the ternary phase diagram
(octanol+ water + $C_{16}TAPA_{30}$)

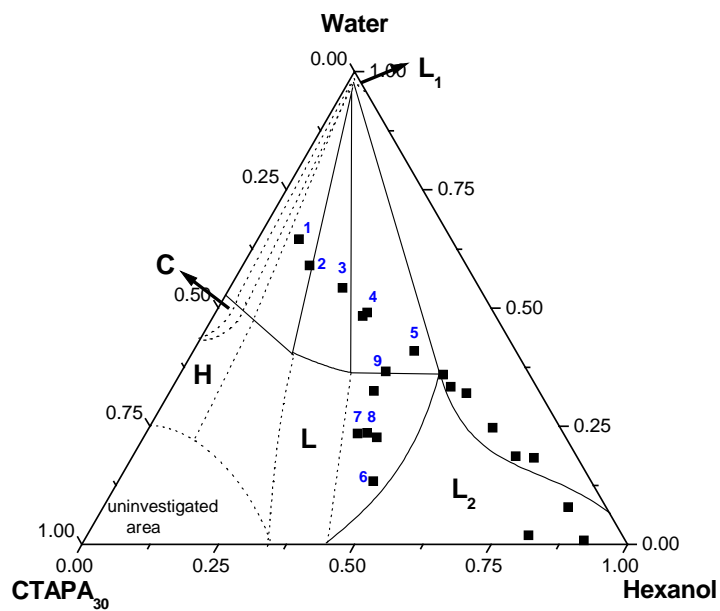


Fig. S2 Samples prepared along the ternary phase diagram
(hexanol+ water + $C_{16}TAPA_{30}$)

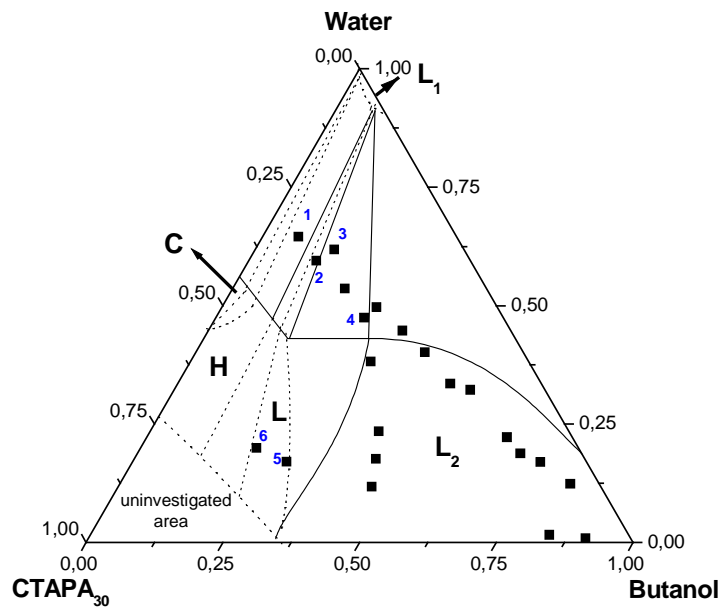


Fig. S3 Samples prepared along the ternary phase diagram
(butanol+ water + $C_{16}TAPA_{30}$)

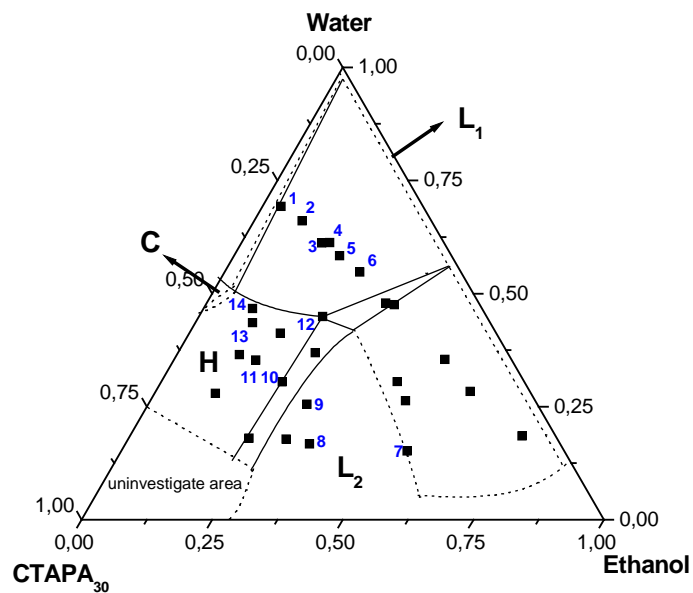


Fig. S4 Samples prepared along the ternary phase diagram
(ethanol+ water + $C_{16}TAPA_{30}$)

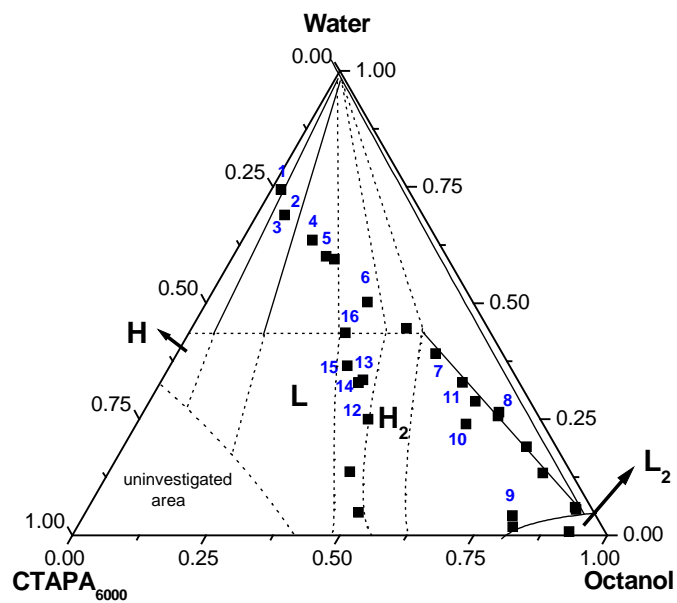


Fig. S5 Samples prepared along the ternary phase diagram
(octanol+ water + C₁₆TAPA₆₀₀₀)

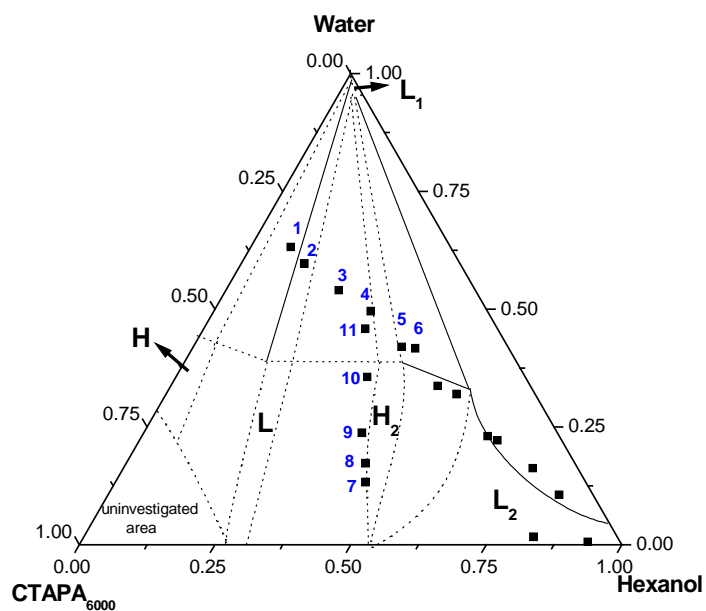


Fig. S6 Samples prepared along the ternary phase diagram
(hexanol+ water + C₁₆TAPA₆₀₀₀)

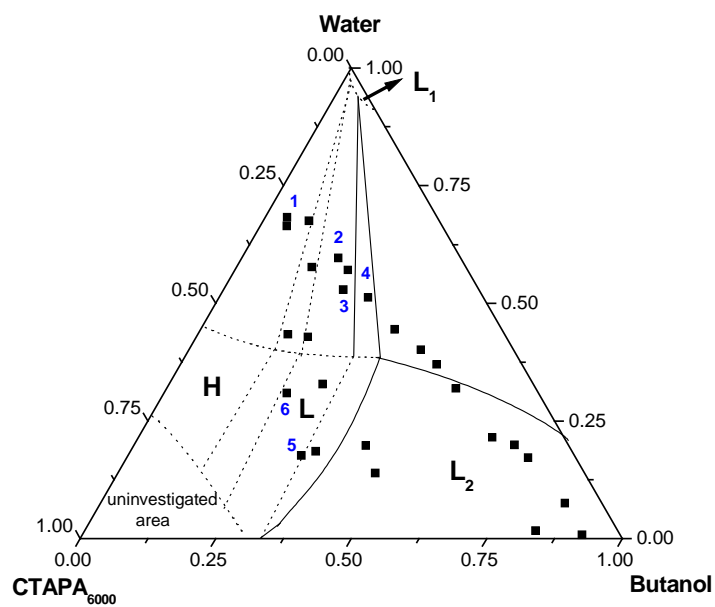


Fig. S7 Samples prepared along the ternary phase diagram
(butanol+ water + C₁₆TAPA₆₀₀₀)

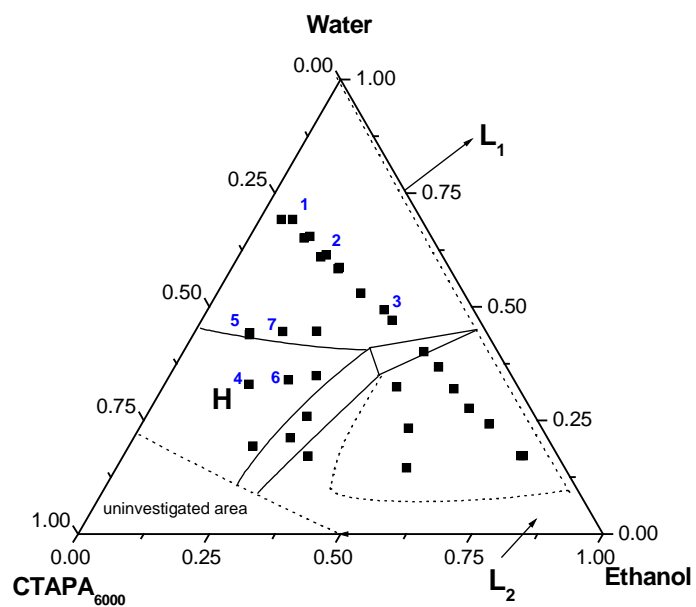


Fig. S8 Samples prepared along the ternary phase diagram
(ethanol+ water + C₁₆TAPA₆₀₀₀)