Electronic Supplementary Material (ESI) for Soft Matter.

Lyotropic liquid crystal phase behavior of a cationic amphiphile in aqueous and non-stoichiometric protic ionic liquid mixtures

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Electronic Supplementary Information

Table S1. Thermal stability ranges for LLCPs of CTAB in EAN derived solvent systems

Solvent ID	molar ratio of water (mol of water/total mol)	acid-to-base molar ratio (mol of NO_3^- /mol of EA^+)	Thermal stability regions for LLCPs (°C)		
			Hexagonal (H_1)	Cubic (V_1)	Lamellar (Lα)
CTAB-water	1	0.0	31->100	48->100	53->100
CTAB-EAN neat	0.006	1.0	58->100	73->100	80->100
Base-rich compositions					
CTAB-EAN_1b	0.190	0.916	55->100	-	-
CTAB-EAN_2b	0.223	0.654	50->100	70->100	-
CTAB-EAN_3b	0.429	0.754	47->100	68->100	97->100
CTAB-EAN_4b	0.513	0.012	49-68	52-68	-
CTAB-EAN_5b	0.544	0.303	37->100	60->100	-
CTAB-EAN_6b	0.661	0.329	35->100	54->100	89->100
CTAB-EAN_7b	0.765	0.816	32->100	55->100	63-80
CTAB-EAN_8b	0.769	0.537	33->100	52->100	63-76
CTAB-EAN_9b	0.823	0.165	30-80	48-80	-
CTAB-EAN_10b	0.902	0.102	30->100	48->100	54-89
CTAB-EAN_11b	0.906	0.408	30->100	48-91	57-71
CTAB-EAN_12b	0.911	0.988	30->100	49-80	-
CTAB-EAN_13b	0.986	0.610	30->100	50-88	56-63
Acid-rich compositions					
CTAB-EAN_1a	0.338	1.067	40-85	59-85	70-85
CTAB-EAN_2a	0.498	1.290	30-49	-	-
CTAB-EAN_3a	0.529	1.868	-	-	-
CTAB-EAN_4a	0.589	1.594	30-47	42-47	-
CTAB-EAN_5a	0.630	1.712	30-45	42-45	-
CTAB-EAN_6a	0.686	1.158	30-62	51-62	-
CTAB-EAN_7a	0.711	1.605	30-51	42-51	-
CTAB-EAN_8a	0.809	1.484	30-60	46-60	-
CTAB-EAN_9a	0.829	1.810	30-52	45-52	-
CTAB-EAN_10a	0.862	1.233	30-70	48-70	59-70
CTAB-EAN_11a	0.874	1.438	30-62	48-62	-
CTAB-EAN_12a	0.951	1.925	30-75	48-75	57-73

Table S2. Thermal stability ranges for LLCPs of CTAB in EtAN derived solvent systems

Solvent ID	molar ratio of water (mol of water/total mol)	acid-to-base molar ratio (mol of NO_3^- /mol of EtA^+)	Thermal stability regions for LLCPs (°C)		
			Hexagonal (H_1)	Cubic (V_1)	Lamellar (Lα)
CTAB-water	1	0.0	31->100	48->100	53->100
CTAB-EtAN neat	0.024	1.0	62->100	73->100	76-98
Base-rich compositions					
CTAB_EtAN_1b	0.024	0.012	85->100	85->100	88->100
CTAB_EtAN_2b	0.070	0.654	66->100	76->100	85->100
CTAB_EtAN_3b	0.177	0.916	62->100	68->100	74->100
CTAB_EtAN_4b	0.409	0.754	55->100	63->100	67->100
CTAB_EtAN_5b	0.419	0.303	64->100	70->100	74->100
CTAB_EtAN_6b	0.619	0.329	50->100	64->100	67-96
CTAB_EtAN_7b	0.775	0.537	37->100	52->100	61-88
CTAB_EtAN_8b	0.783	0.816	37->100	49->100	55-90
CTAB_EtAN_9b	0.818	0.165	43->100	48->100	-
CTAB_EtAN_10b	0.905	0.102	35->100	52-90	-
CTAB_EtAN_11b	0.913	0.408	30->100	48->100	57-83
CTAB_EtAN_12b	0.921	0.988	30-95	50-75	-
CTAB_EtAN_13b	0.988	0.610	30->100	48->100	55-68
Acid-rich compositions					
CTAB_EtAN_1a	0.367	1.067	39-80	44-80	55-80
CTAB_EtAN_2a	0.527	1.290	30-57	35-57	46-57
CTAB_EtAN_3a	0.550	1.868	30-46	30-46	32-46
CTAB_EtAN_4a	0.615	1.594	30-54	35-54	38-54
CTAB_EtAN_5a	0.654	1.712	31-50	40-50	-
CTAB_EtAN_6a	0.714	1.158	41-72	53-72	-
CTAB_EtAN_7a	0.735	1.605	36-63	55-63	-
CTAB_EtAN_8a	0.828	1.484	30-66	48-66	-
CTAB_EtAN_9a	0.846	1.810	30-65	47-65	60-65
CTAB_EtAN_10a	0.877	1.233	31-87	37-87	-
CTAB_EtAN_11a	0.888	1.438	30-75	48-75	-
CTAB_EtAN_12a	0.957	1.925	30-77	48-77	-

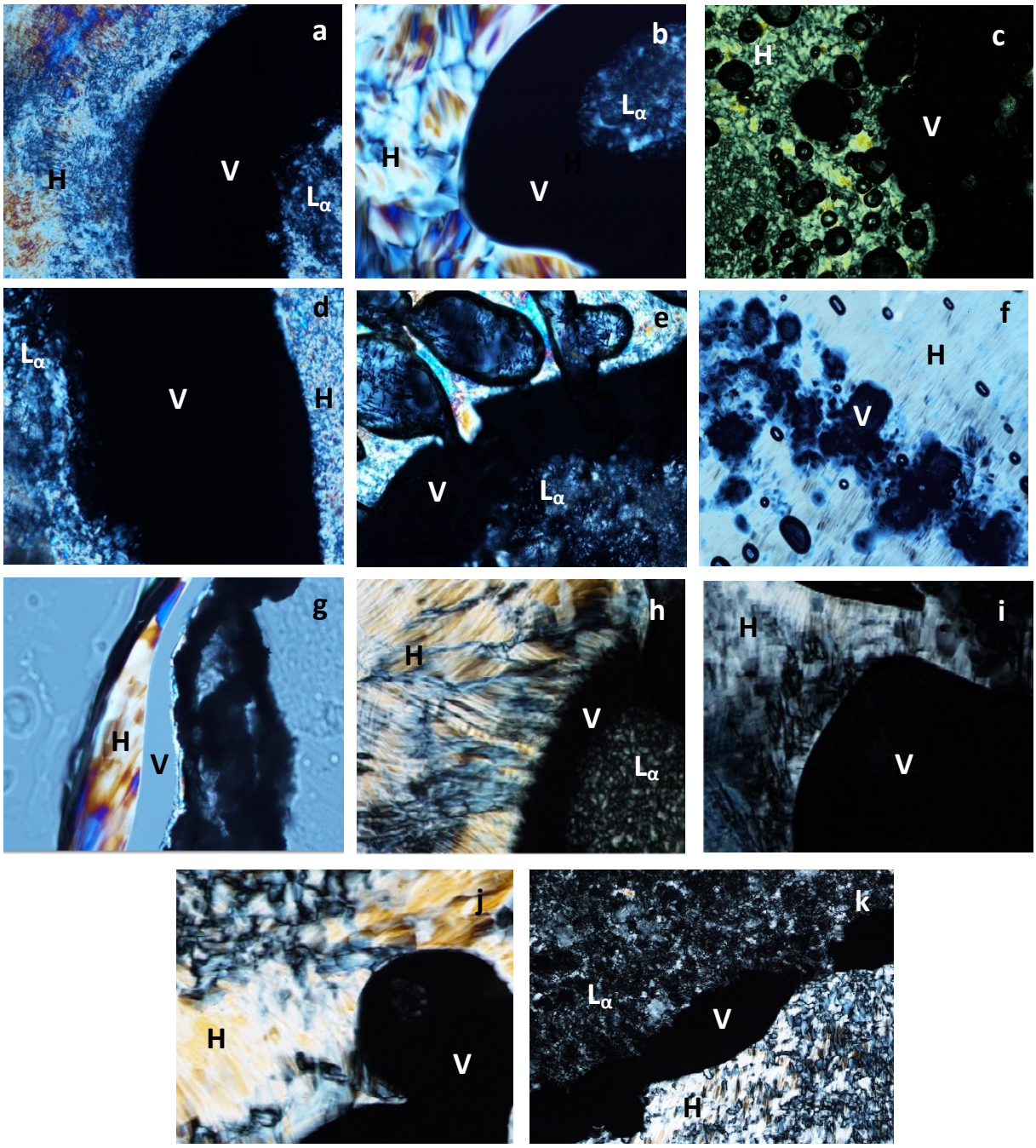


Figure S1. Representative CPOM images of selected CTAB-solvent combinations for a) CTAB-water at 59 °C, b) CTAB-EAN at 87 °C, c) CTAB-EtAN at 78 °C, d) CTAB-EAN_11a at 61 °C, e) CTAB-EAN_6a at 58 °C, f) CTAB-EAN_2b at 70 °C, g) CTAB-EAN_4b at 66 °C, h) CTAB-EtAN_11a at 75 °C, i) CTAB-EtAN_6a at 56 °C, j) CTAB-EtAN_2b at 80 °C, and k) CTAB-EtAN_4b at 70 °C. The symbols H, V and L_α denote hexagonal, isotropic cubic and lamellar phases, respectively.

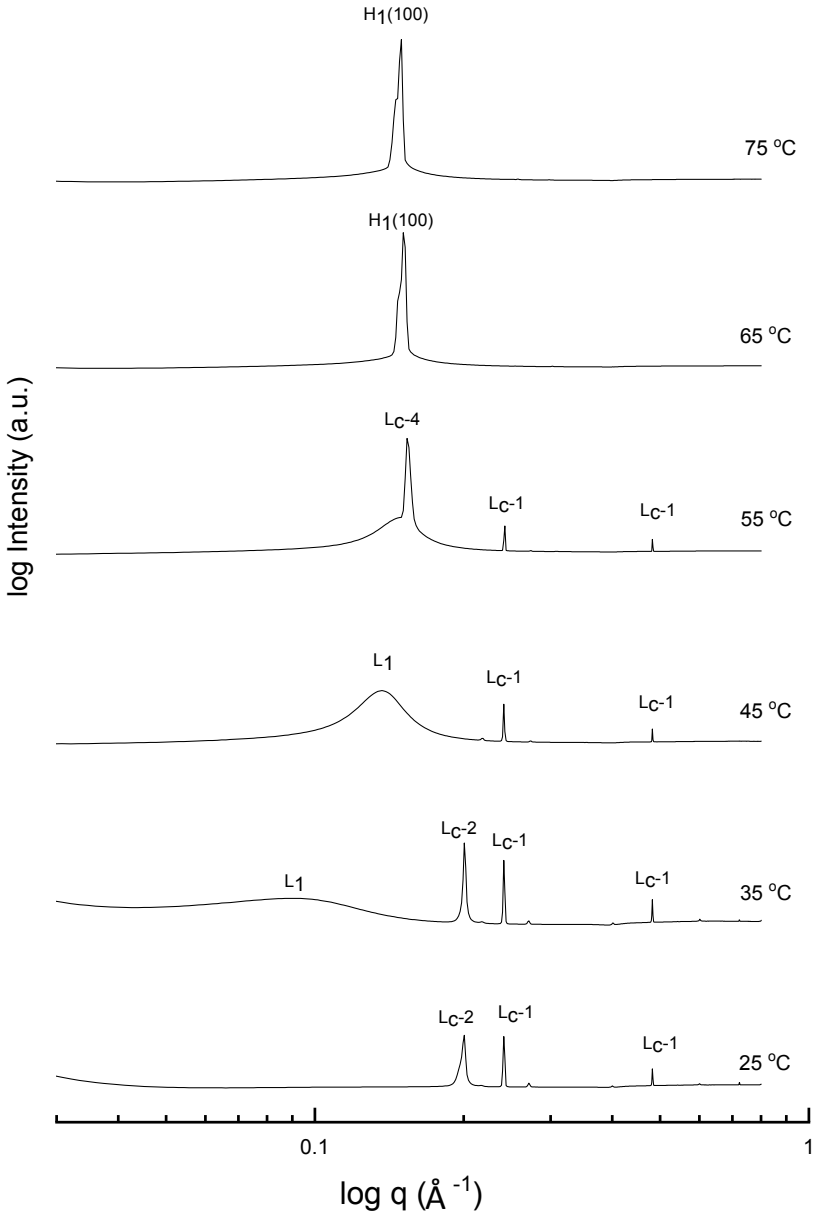


Figure S2. SAXS patterns of 50 wt% CTAB in neat EAN at temperatures between 25 to 75 °C. The symbols L_c-1 to L_c-4 denote the various forms of lamellar surfactant crystalline phases, L_1 refers to micellar and H_1 to normal hexagonal liquid crystal phases.

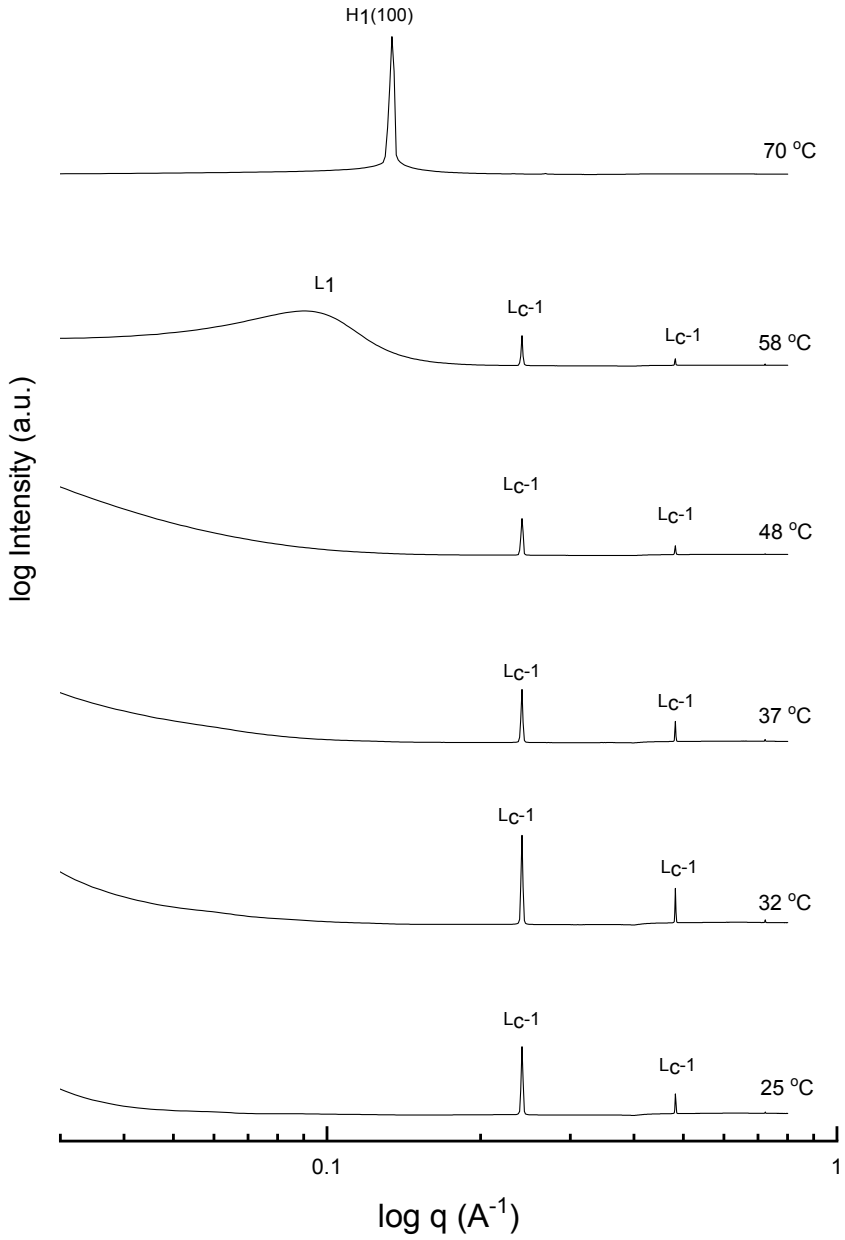


Figure S3. SAXS patterns of 50 wt% CTAB in neat EtAN at temperatures between 25 to 70 °C. The symbol L_c-1 denotes lamellar surfactant crystalline phase, and the liquid crystal phases are denoted as micellar (L_1) and normal hexagonal (H_1) liquid crystal phases.

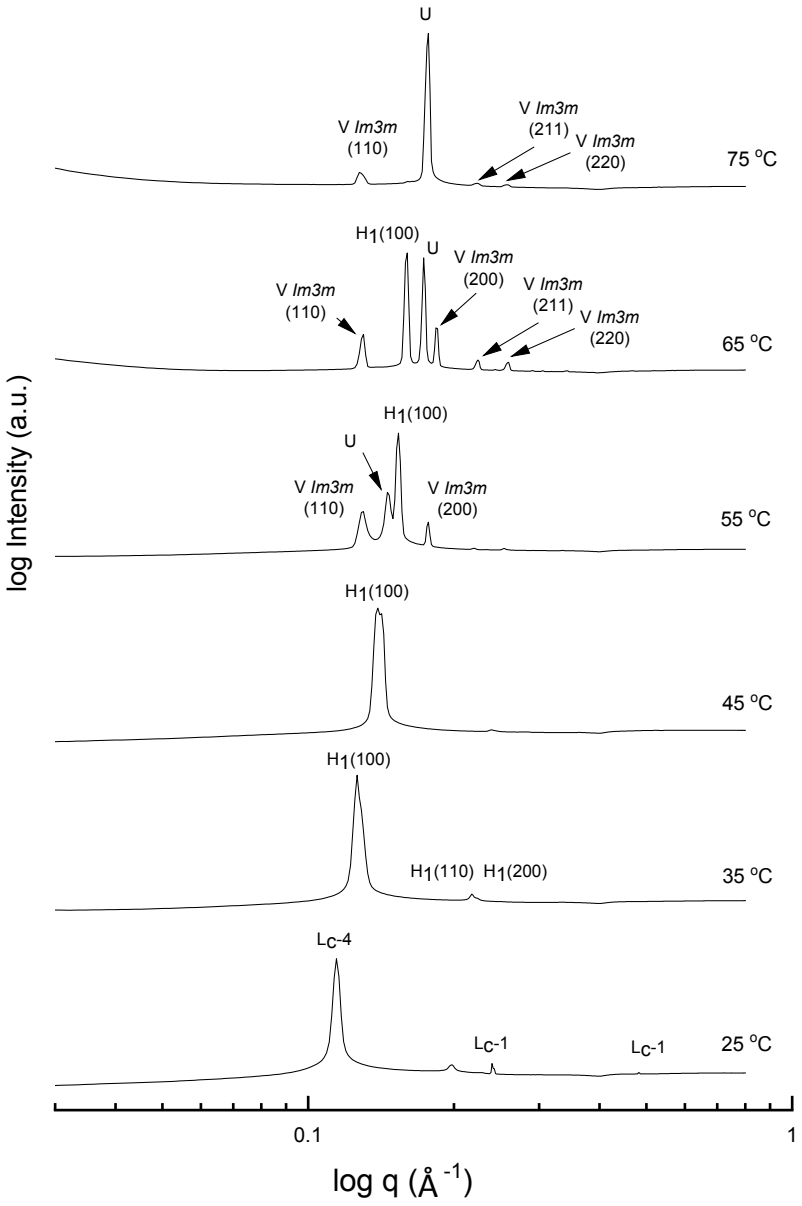


Figure S4. SAXS patterns of 50 wt% CTAB in neat water at temperatures between 25 to 75 °C. The symbols L_c-1 and L_c-4 denote lamellar surfactant crystalline phases, and the liquid crystal phases are denoted as normal hexagonal (H_1), normal primitive cubic (V_1 (*Im-3m*)), and unassigned transient (U) liquid crystal phases.

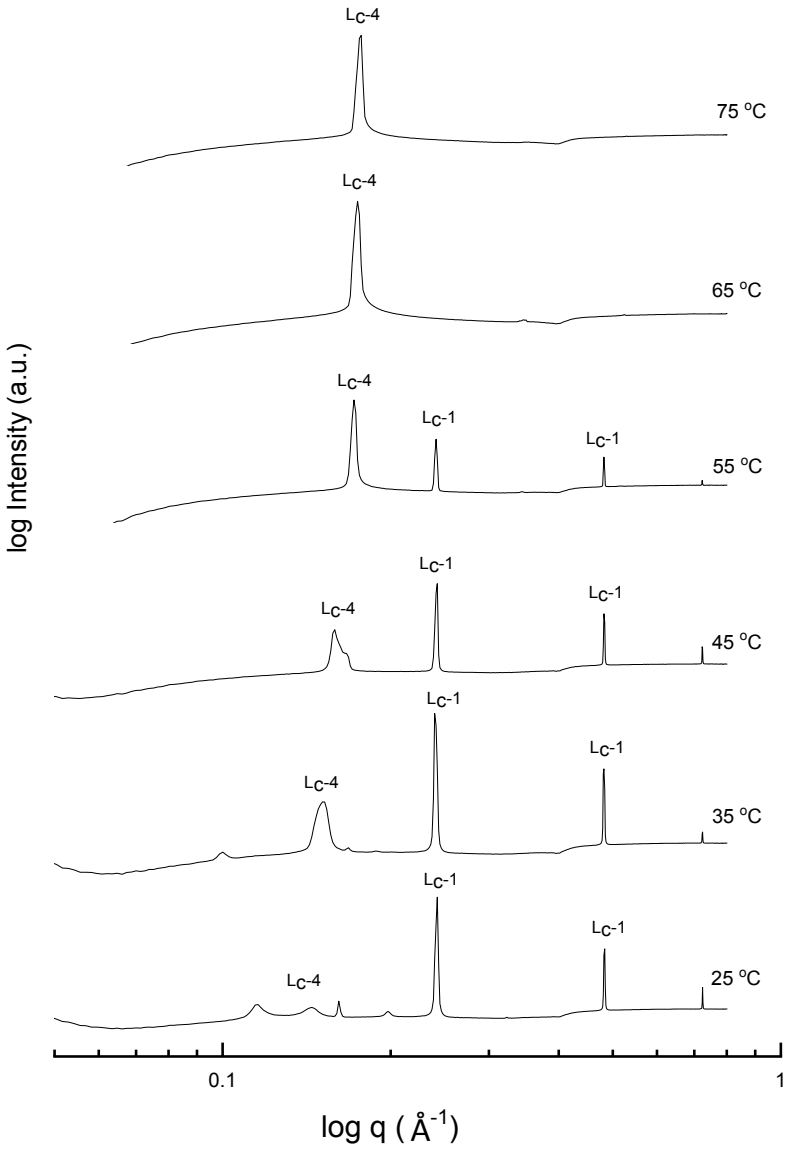


Figure S5. SAXS patterns of powder CTAB showing polymorphic transition from L_c-1 to L_c-4 with increasing temperature. The symbols L_c-1 and L_c-4 denote lamellar surfactant crystalline (major morphology) and lamellar surfactant crystalline (thermotropic) phases, respectively.

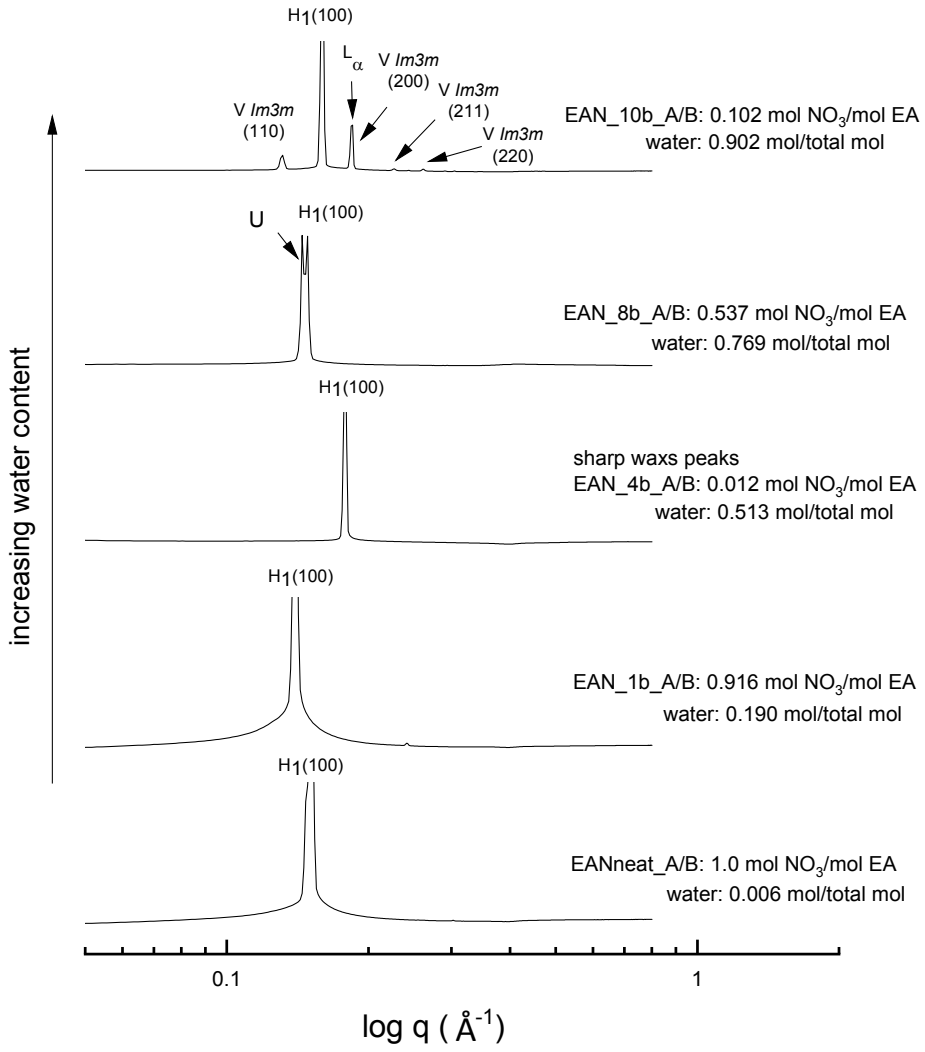


Figure S6. SAXS patterns of 50 wt% CTAB in selected base-rich EAN compositions. Data acquired at 65 °C for neat EAN while it was 70 °C for the others. The liquid crystal phases are denoted as normal hexagonal (H_1), normal primitive cubic (V_1 (*Im-3m*)), lamellar (L_α), and unassigned transient (U) liquid crystal phases.

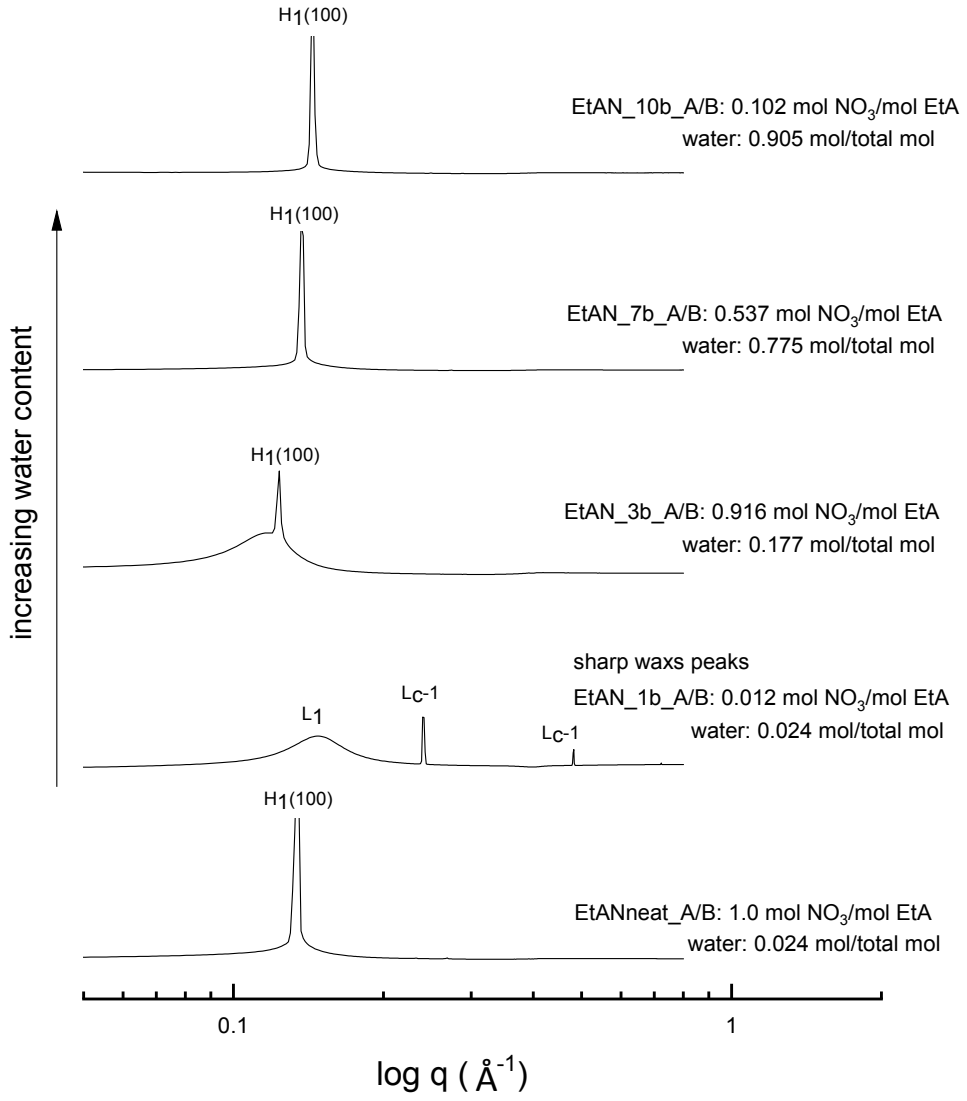


Figure S7. SAXS patterns of 50 wt% CTAB in selected base-rich EtAN compositions. Data acquired at 70 °C for all compositions. The symbol L_c-1 denotes lamellar surfactant crystalline phase, and the liquid crystal phases are denoted as micellar (L_1) and normal hexagonal (H_1) liquid crystal phases.

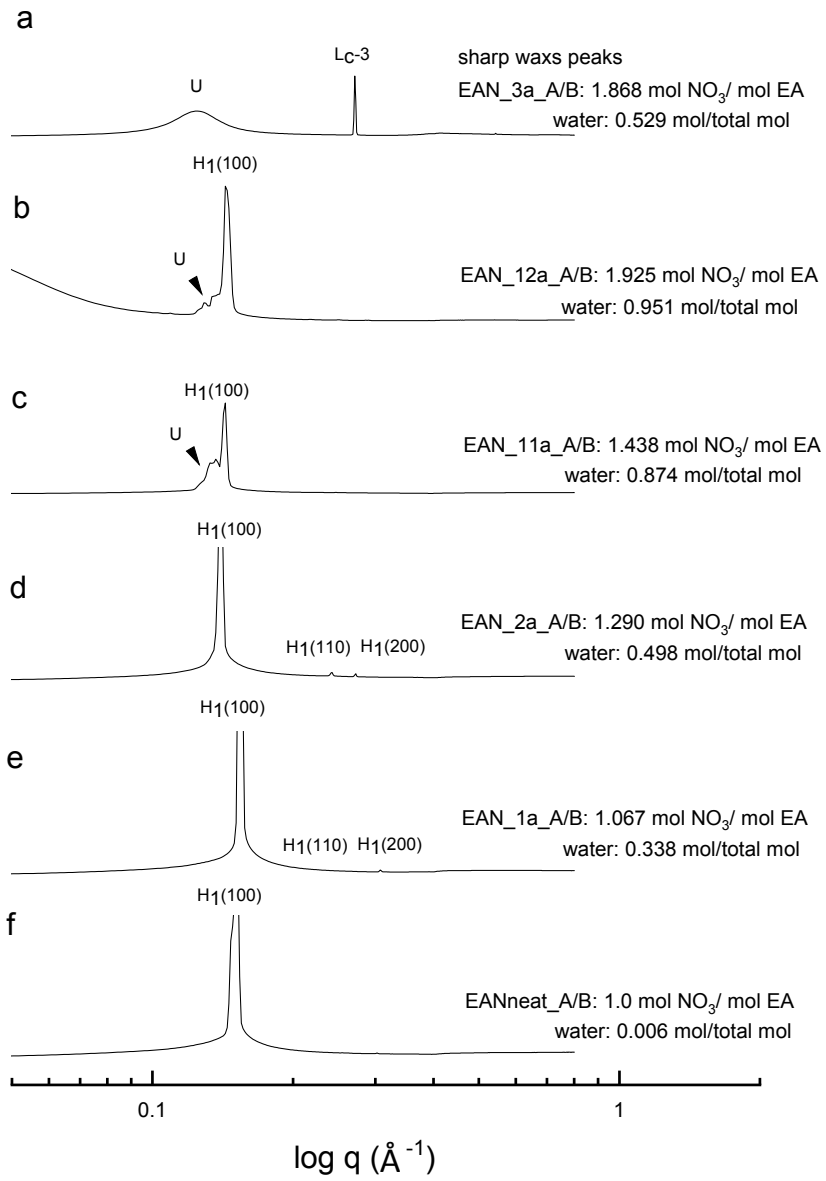


Figure S8. SAXS patterns of 50 wt% CTAB in selected acid-rich EAN compositions. Data acquired at 65 °C for neat EAN, EAN_1a and EAN_3a while it was 70 °C for the others. The symbol L_c-3 denotes lamellar surfactant crystalline phase, the liquid crystal phases are denoted as normal hexagonal (H_1), and unassigned transient (U) liquid crystal phases.

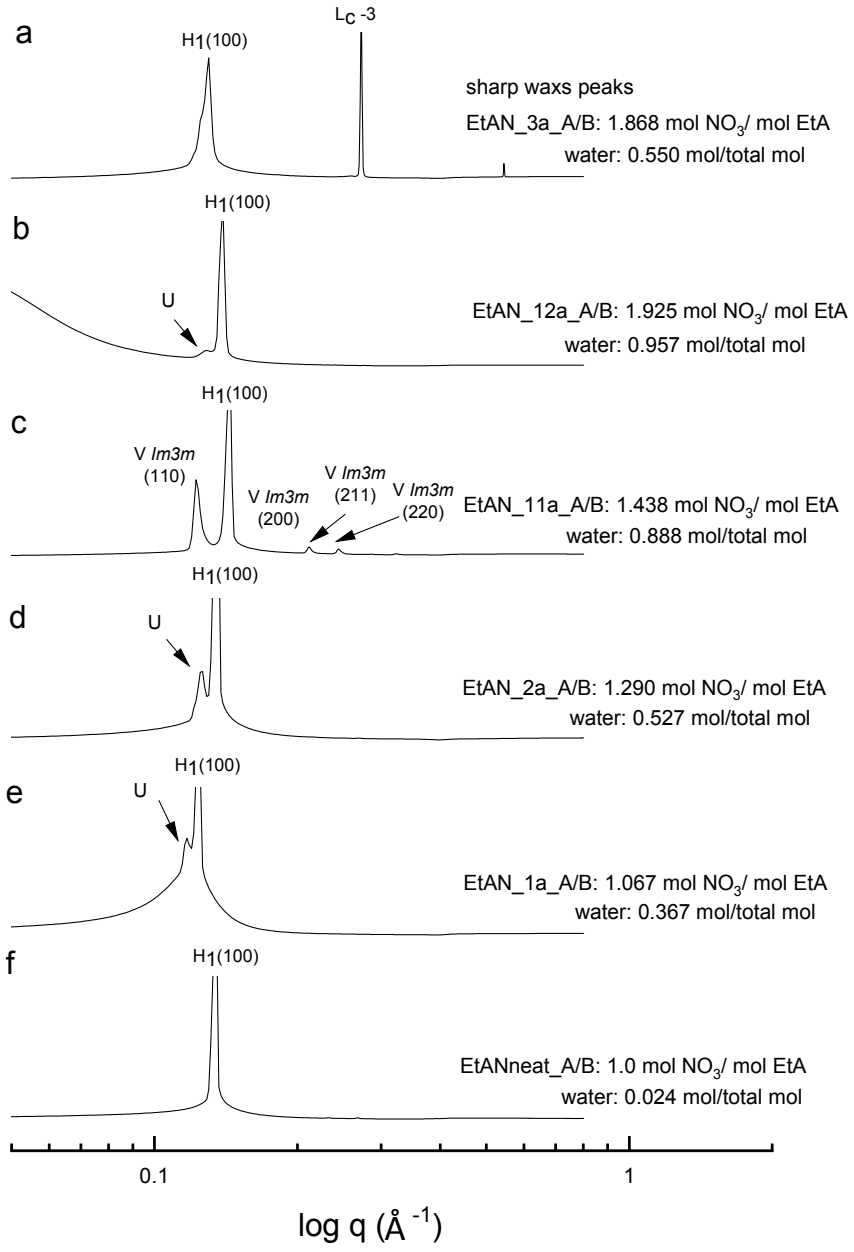
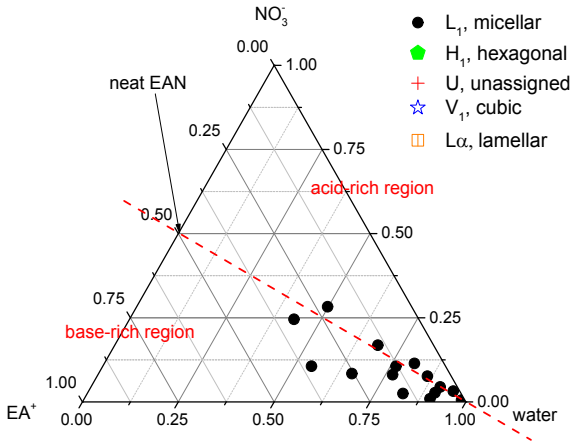
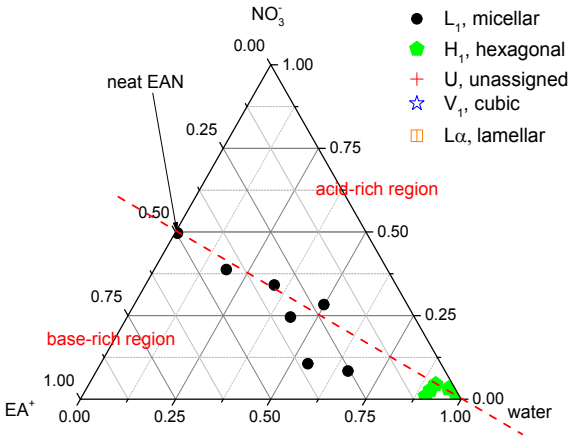


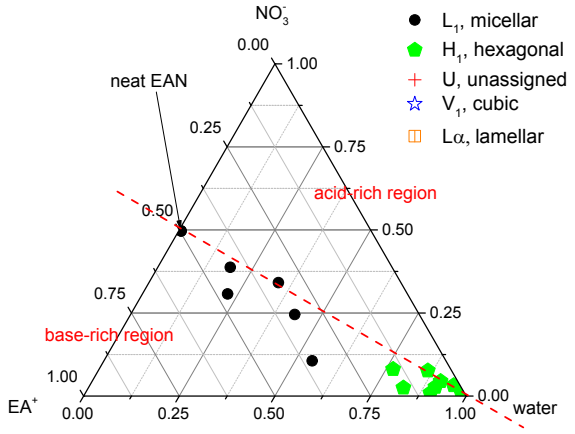
Figure S9. SAXS patterns of 50 wt% CTAB in selected acid-rich EtAN compositions. Data acquired at 70 °C for all compositions. The symbol L_c-3 denotes lamellar surfactant crystalline phase, the liquid crystal phases are denoted as normal hexagonal (H_1), normal primitive cubic (V_1 (*Im-3m*)), and unassigned transient (U) liquid crystal phases.

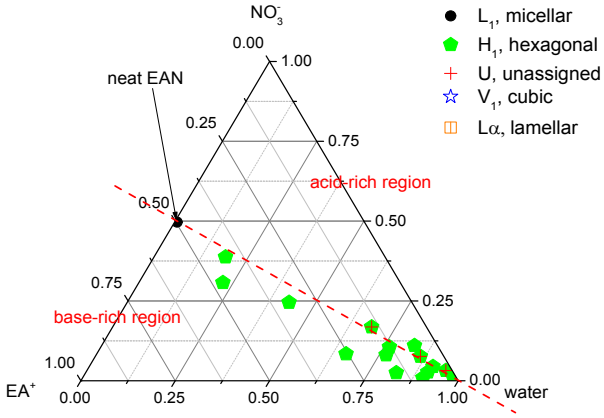


25 °C



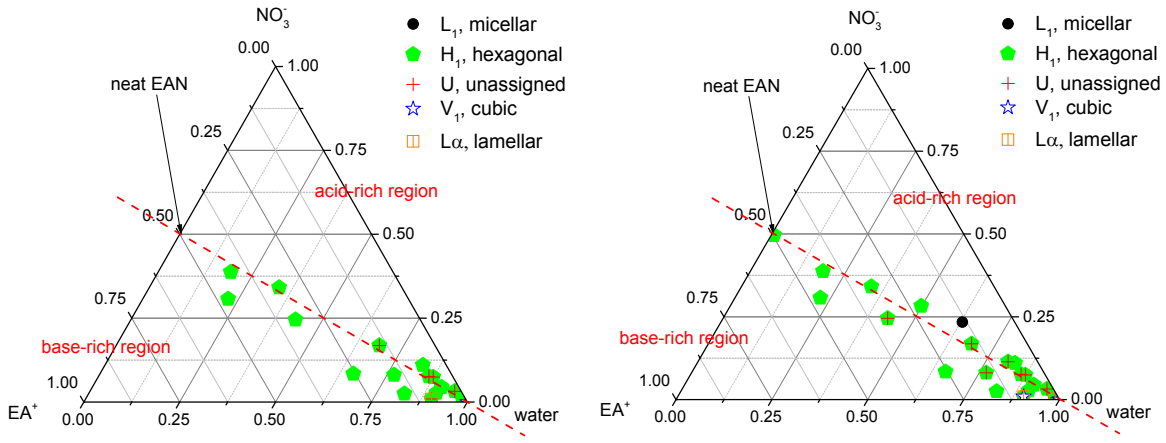
32 °C





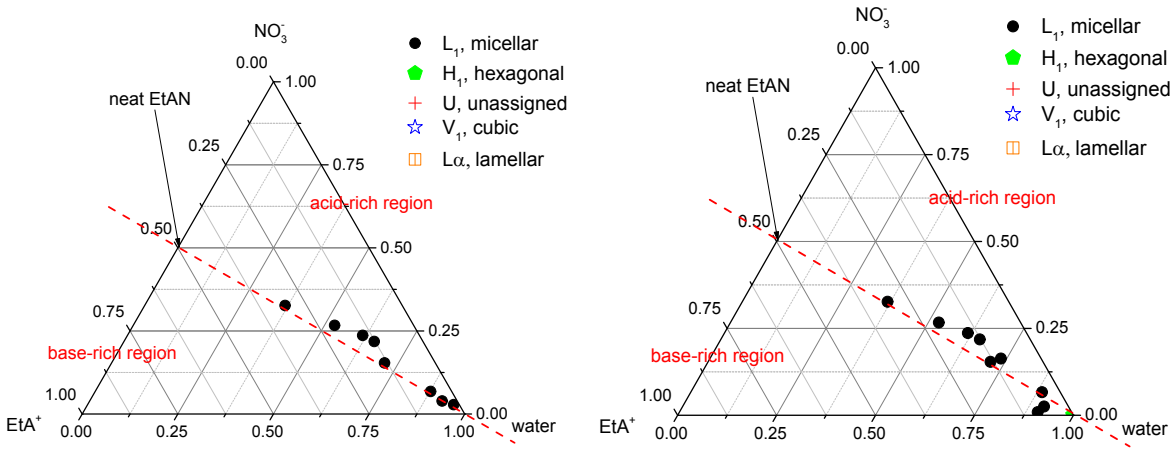
37 °C

48 °C

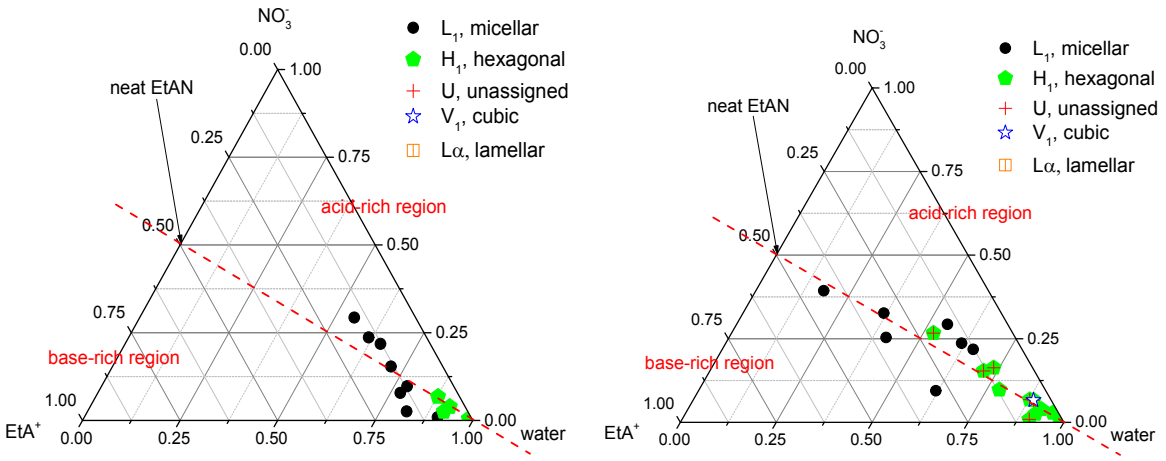


58 °C 70 °C

Figure S10. Partial phase diagrams for 50 wt% CTAB in EAN derived solvent compositions. Above the red dashed line represents the acid-rich region whereas under the red dashed line refers to the base-rich region.



25 °C 32 °C



37 °C 48 °C

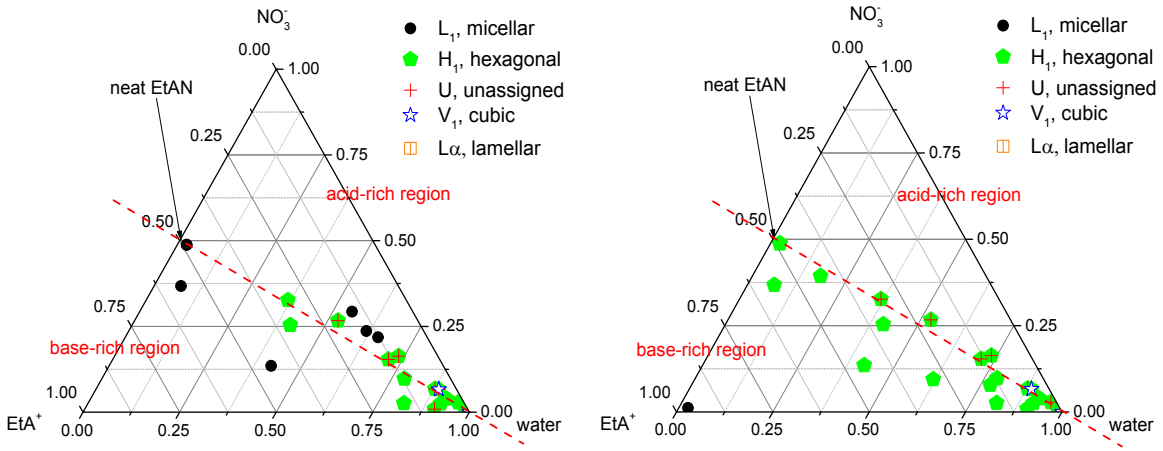
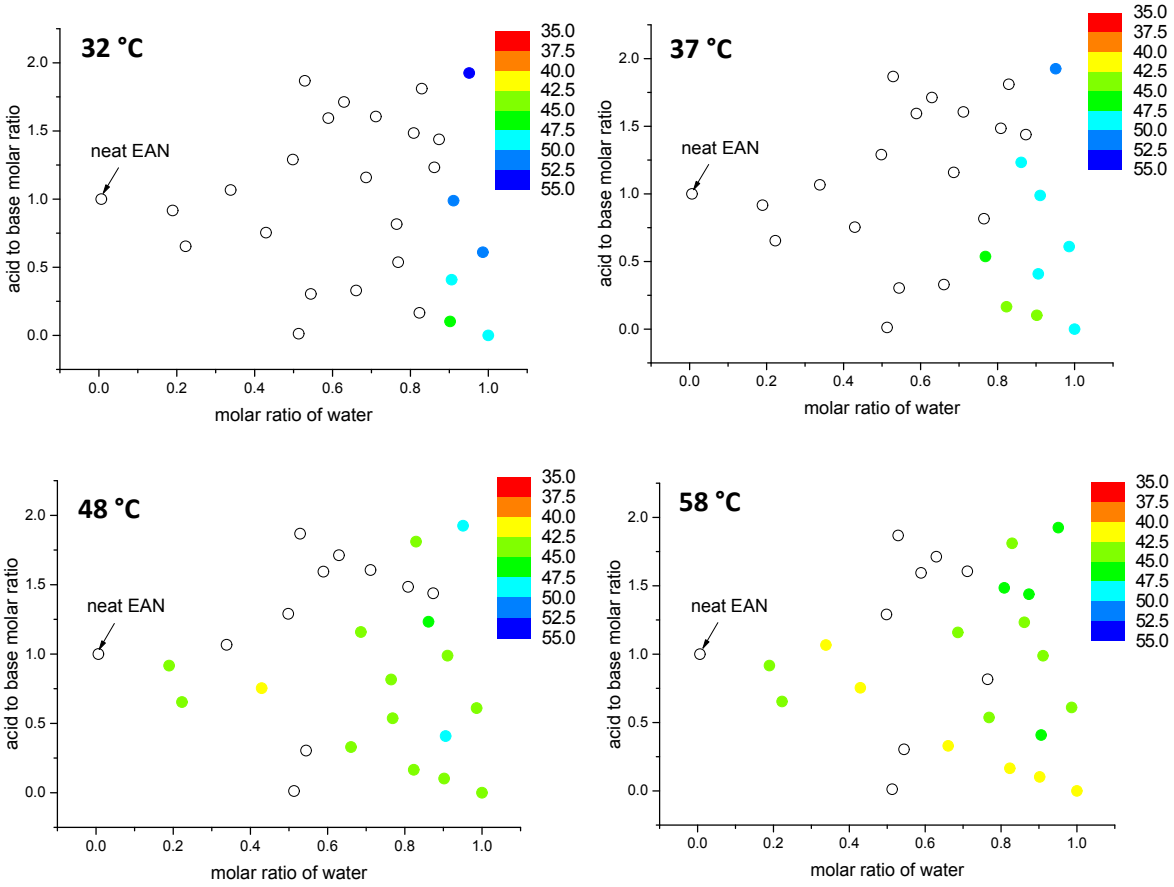


Figure S11. Partial phase diagrams for 50 wt% CTAB in EtAN derived solvent compositions. Above the red dashed line represents the acid-rich region whereas under the red dashed line refers to the base-rich region.



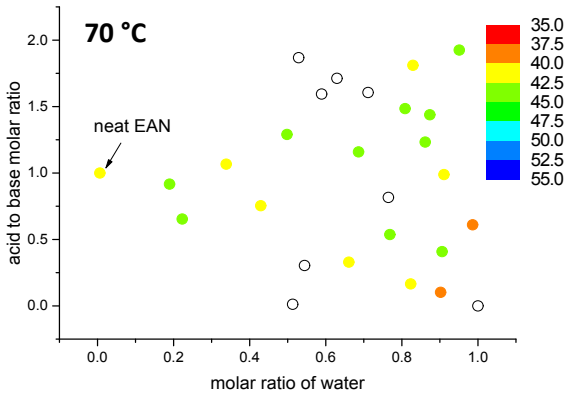
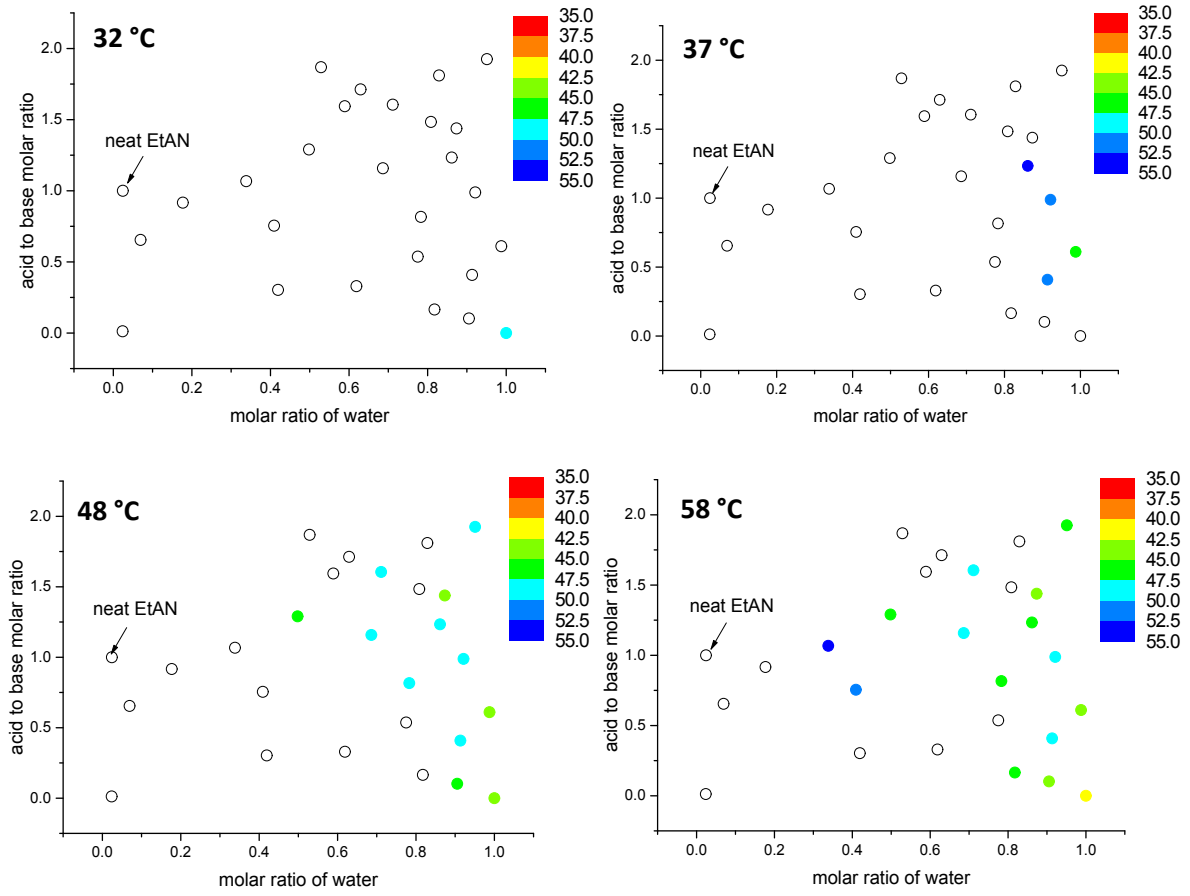


Figure S12. The change in lattice parameter values (Å) of the hexagonal phase (H_1) of 50 wt% CTAB in EAN derived solvent compositions as a function of temperature. Solid data points represent the sample compositions when the phase formation is supported while blank data points only denote sample compositions with this phase not observed.



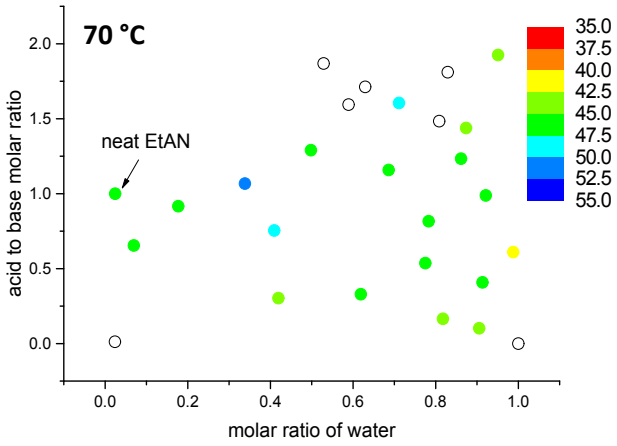


Figure S13. The change in lattice parameter values (Å) of the hexagonal phase (H_1) of 50 wt% CTAB in EtAN derived solvent compositions as a function of temperature. Solid data points represent the sample compositions when the phase formation is supported while blank data points only denote sample compositions with this phase not observed.

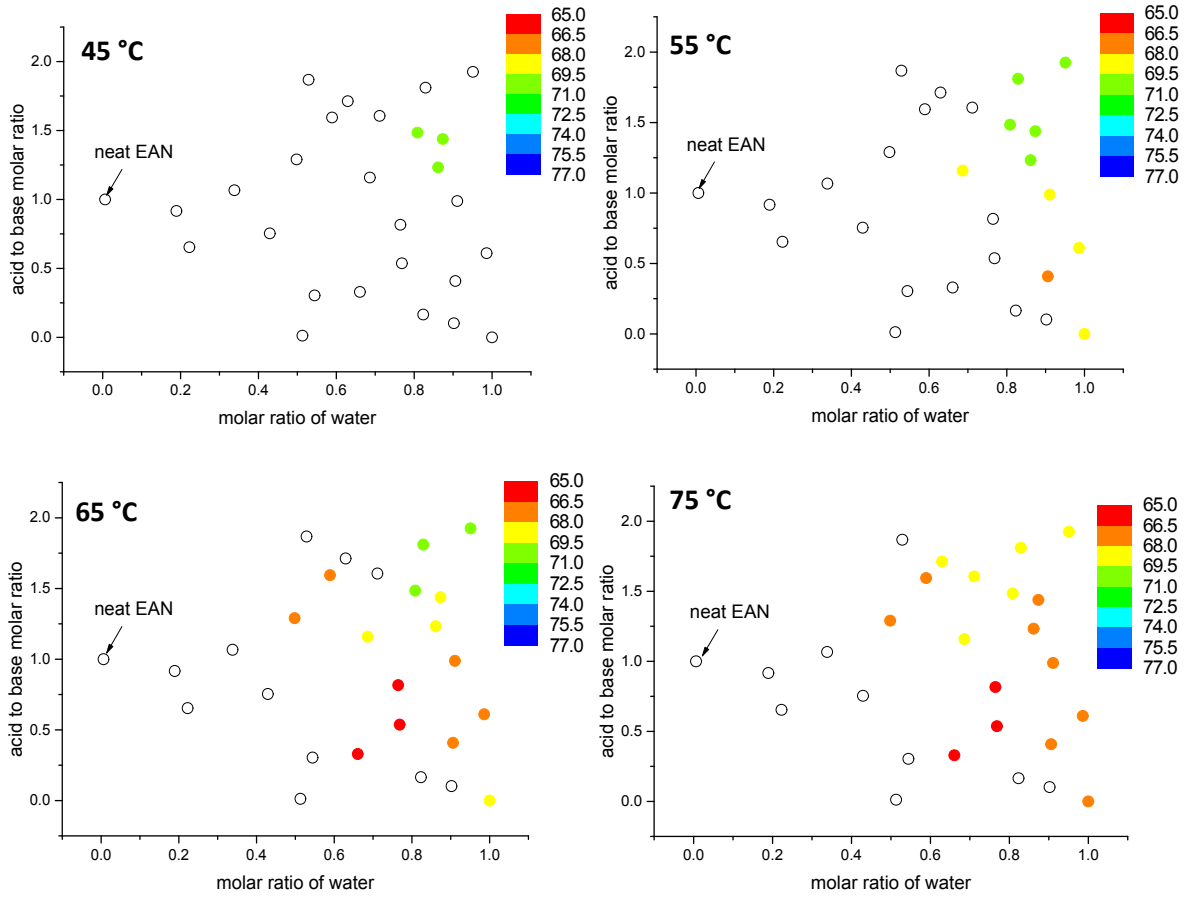


Figure S14. The change in lattice parameter values (Å) of the normal bicontinuous cubic phase (V_1) of 70 wt% CTAB in EAN derived solvent compositions as a function of temperature. Solid data points represent the sample compositions when the phase formation is supported while blank data points only denote sample compositions with this phase not observed.

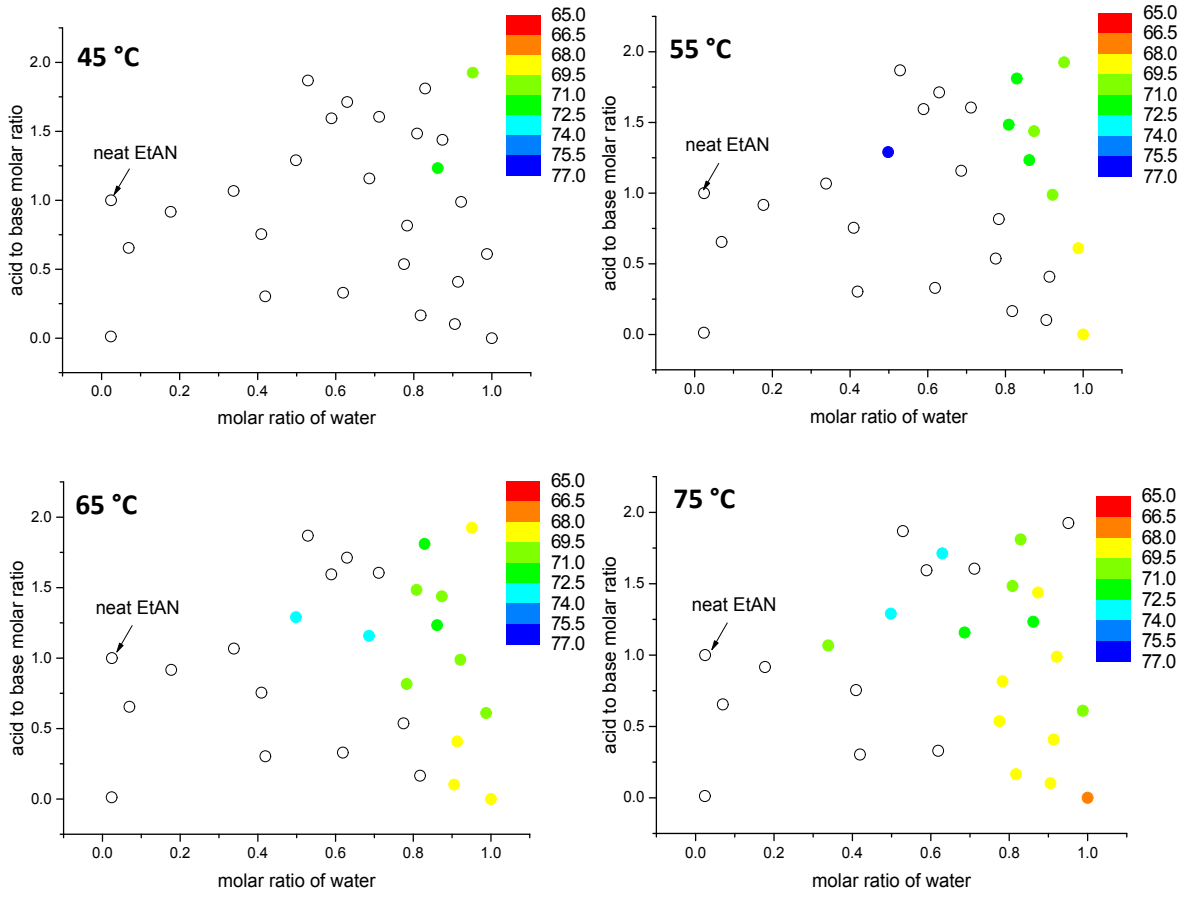


Figure S15. The change in lattice parameter values (Å) of the normal bicontinuous cubic phase (V_1) of 70 wt% CTAB in EtAN derived solvent compositions as a function of temperature. Solid data points represent the sample compositions when the phase formation is supported while blank data points only denote sample compositions with this phase not observed.

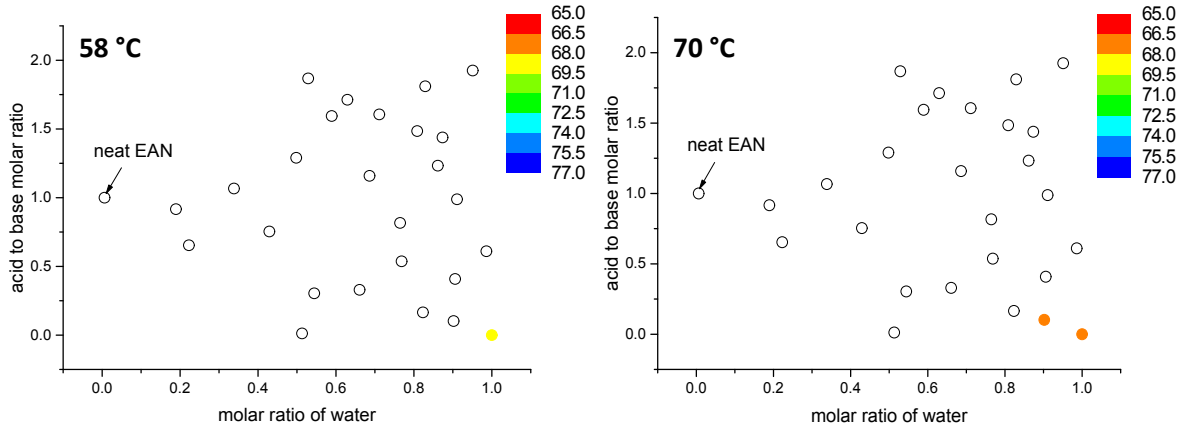
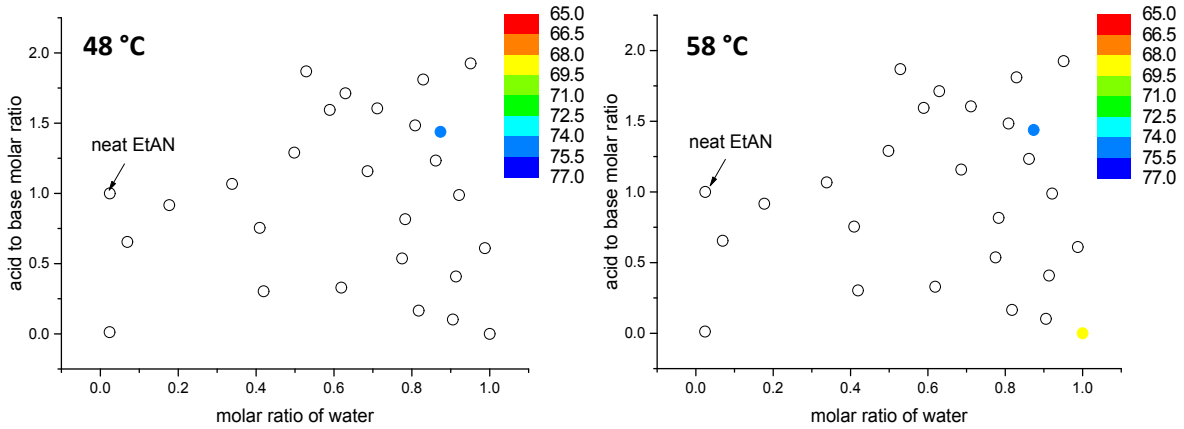


Figure S16. The change in lattice parameter values (Å) of the normal bicontinuous cubic phase (V_1) of 50 wt% CTAB in EAN derived solvent compositions as a function of temperature. Solid data points represent the sample compositions when the phase formation is supported while blank data points only denote sample compositions with this phase not observed.



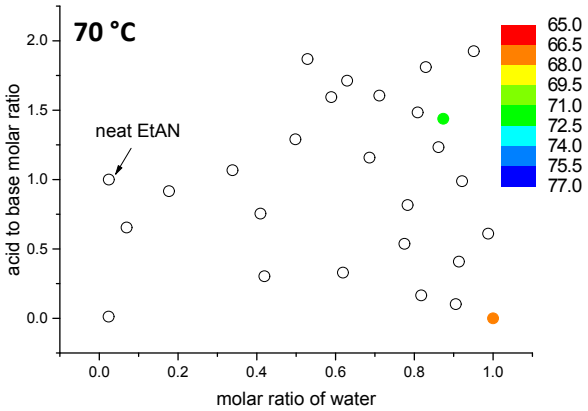


Figure S17. The change in lattice parameter values (Å) of the normal bicontinuous cubic phase (V_1) of 50 wt% CTAB in EtAN derived solvent compositions as a function of temperature. Solid data points represent the sample compositions when the phase formation is supported while blank data points only denote sample compositions with this phase not observed.

Table S3. The compositions and the Gordon parameters of EAN derived solvent systems

Solvent ID	**molar ratio of water (mol of water/total mol)**	**acid-to-base molar ratio (mol of NO_3^- /mol of EA^+)**	**Gordon parameter (J $mol^{1/3}/m^3$)**
CTAB-water	1	0.0	2.746
CTAB-EAN neat	0.006	1.0	1.264
Base-rich compositions			
CTAB-EAN_1b	0.190	0.916	1.292
CTAB-EAN_2b	0.223	0.654	1.209
CTAB-EAN_3b	0.429	0.754	1.362
CTAB-EAN_4b	0.513	0.012	0.806
CTAB-EAN_5b	0.544	0.303	1.112
CTAB-EAN_6b	0.661	0.329	1.243
CTAB-EAN_7b	0.765	0.816	1.640
CTAB-EAN_8b	0.769	0.537	1.525
CTAB-EAN_9b	0.823	0.165	1.391
CTAB-EAN_10b	0.902	0.102	1.545
CTAB-EAN_11b	0.906	0.408	1.760
CTAB-EAN_12b	0.911	0.988	1.666
CTAB-EAN_13b	0.986	0.610	2.474
Acid-rich compositions			
CTAB-EAN_1a	0.338	1.067	1.438
CTAB-EAN_2a	0.498	1.290	1.551
CTAB-EAN_3a	0.529	1.868	1.598
CTAB-EAN_4a	0.589	1.594	1.649
CTAB-EAN_5a	0.630	1.712	1.605

CTAB-EAN_6a	0.686	1.158	1.766
CTAB-EAN_7a	0.711	1.605	1.842
CTAB-EAN_8a	0.809	1.484	2.014
CTAB-EAN_9a	0.829	1.810	1.986
CTAB-EAN_10a	0.862	1.233	2.032
CTAB-EAN_11a	0.874	1.438	1.888
CTAB-EAN_12a	0.951	1.925	2.130

Table S4. The compositions and the Gordon parameters of EtAN derived solvent systems

Solvent ID	**molar ratio of water (mol of water/total mol)**	**acid-to-base molar ratio (mol of NO_3^- /mol of EtA^+)**	**Gordon parameter (J $mol^{1/3}/m^3$)**
CTAB-water	1	0.0	2.746
CTAB-EtAN neat	0.024	1.0	1.553
Base-rich compositions			
CTAB_EtAN_1b	0.024	0.012	1.199
CTAB_EtAN_2b	0.070	0.654	1.723
CTAB_EtAN_3b	0.177	0.916	1.647
CTAB_EtAN_4b	0.409	0.754	1.655
CTAB_EtAN_5b	0.419	0.303	1.493
CTAB_EtAN_6b	0.619	0.329	1.675
CTAB_EtAN_7b	0.775	0.537	2.003
CTAB_EtAN_8b	0.783	0.816	1.752
CTAB_EtAN_9b	0.818	0.165	1.646
CTAB_EtAN_10b	0.905	0.102	2.010
CTAB_EtAN_11b	0.913	0.408	1.871
CTAB_EtAN_12b	0.921	0.988	2.006
CTAB_EtAN_13b	0.988	0.610	2.263
Acid-rich compositions			
CTAB_EtAN_1a	0.367	1.067	1.942
CTAB_EtAN_2a	0.527	1.290	1.825
CTAB_EtAN_3a	0.550	1.868	1.891
CTAB_EtAN_4a	0.615	1.594	1.643
CTAB_EtAN_5a	0.654	1.712	1.625

CTAB_EtAN_6a	0.714	1.158	2.036
CTAB_EtAN_7a	0.735	1.605	1.980
CTAB_EtAN_8a	0.828	1.484	2.234
CTAB_EtAN_9a	0.846	1.810	2.095
CTAB_EtAN_10a	0.877	1.233	2.435
CTAB_EtAN_11a	0.888	1.438	2.279
CTAB_EtAN_12a	0.957	1.925	2.535