Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

High throughput approach to investigating ternary solvents of aqueous non-stoichiometric protic ionic liquids

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Electronic Supplementary Information

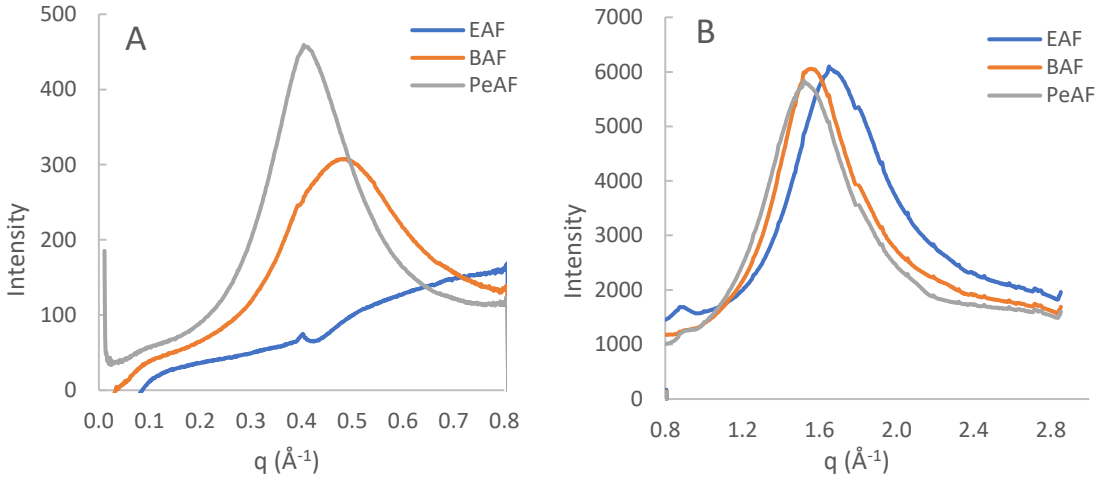

Figure S1. A) SAXS and B) WAXS patterns of PILs with the formate anion, EAF, BAF and PeAF.

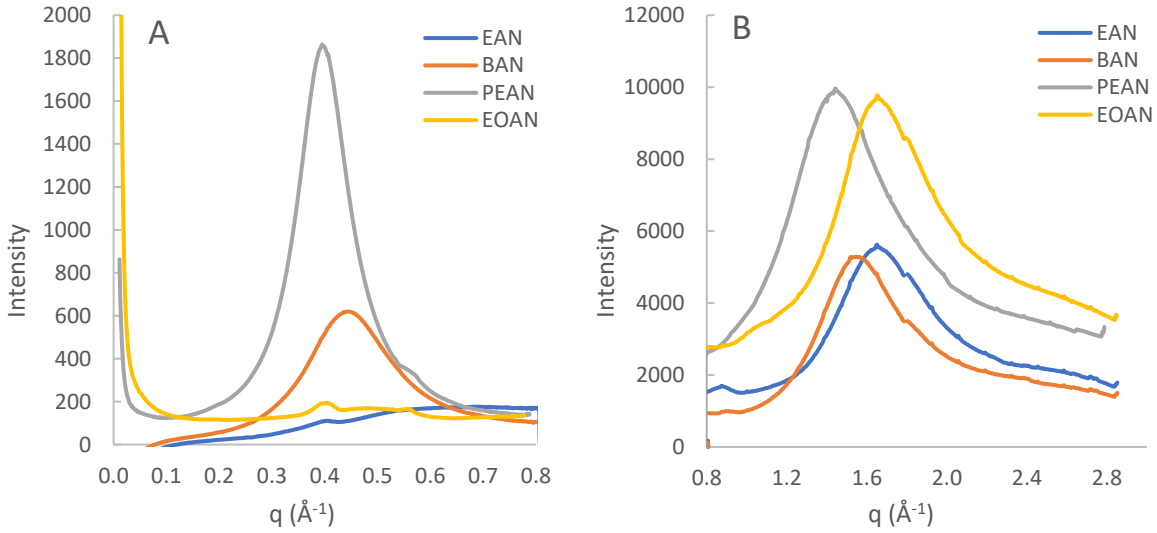

Figure S2. A) SAXS and B) WAXS patterns of PILs with the nitrate anion, EAN, BAN, PeAN and EOAN.

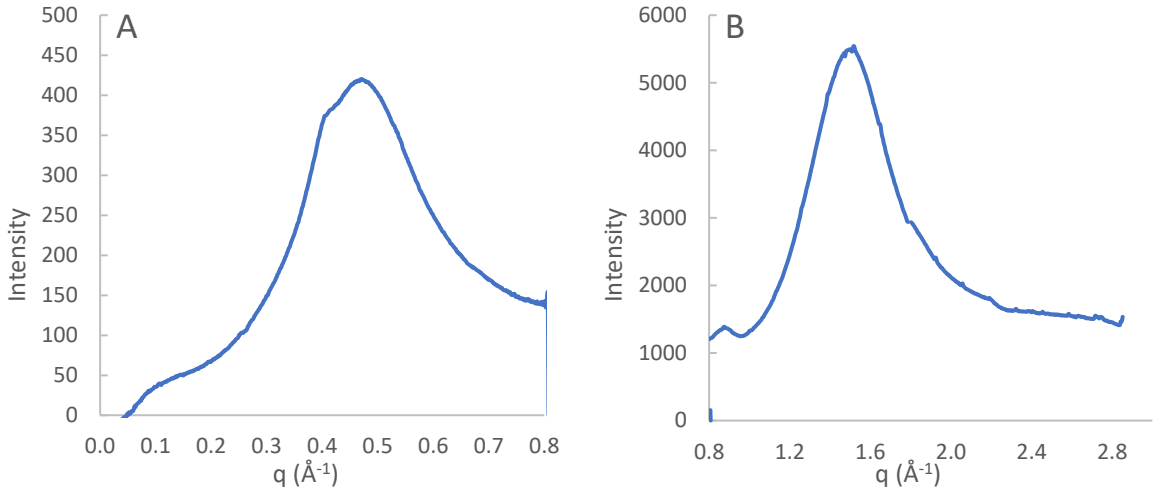

Figure S3. A) SAXS and B) WAXS patterns for the PIL, PeAA with an acetate anion.

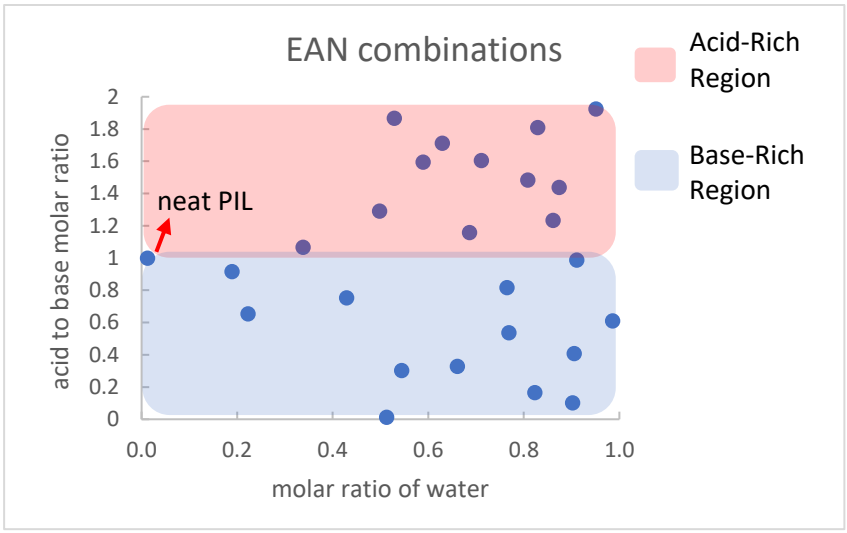

Figure S4. PIL-solvent combinations of EAN based samples according to the LHS design methodology.

Table S1. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of base-rich EAN combinations.

Base-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
EAN	0.012	1	47.6	-	0.69	1.65
EAN_1b	0.190	0.916	46.7	9.5[a]		1.65
EAN_2b	0.223	0.654	43.8	10.6[a]		1.82
EAN_3b	0.429	0.754	46.3	10.4		1.65
EAN_4b	0.513	0.012	27.8	13.8		1.82
EAN_5b	0.544	0.303	37.1	11.7		1.65
EAN_6b	0.661	0.329	39.5	11.6		1.82
EAN_7b	0.765	0.816	49.0	10.4		1.86
EAN_8b	0.769	0.537	45.8	11.1		1.85
EAN_9b	0.823	0.165	41.1	12.1		1.86
EAN_10b	0.902	0.102	43.6	12.3		1.93
EAN_11b	0.906	0.408	49.2	11.4		1.93
EAN_12b	0.911	0.988	46.1	9.2		1.93
EAN_13b	0.986	0.610	65.5	11.0		2.06

[a] Values provided for completeness where the water fractions were less than 0.4 mol.

Table S2. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of acid-rich EAN combinations.

Acid-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
EAN	0.012	1	47.6	-	0.69	1.65
EAN_1a	0.338	1.067	49.7	-0.9[a]		1.65
EAN_2a	0.498	1.290	50.8	-1.1		1.80
EAN_3a	0.529	1.868	51.3	-1.5		1.82
EAN_4a	0.589	1.594	52.1	-1.3		1.82
EAN_5a	0.630	1.712	49.9	-1.1		1.83
EAN_6a	0.686	1.158	54.2	-0.6		1.86
EAN_7a	0.711	1.605	55.6	-1.1		1.85
EAN_8a	0.809	1.484	58.4	-0.7		1.93
EAN_9a	0.829	1.810	56.9	-0.8		1.93
EAN_10a	0.862	1.233	57.6	-0.2		1.93
EAN_11a	0.874	1.438	53.1	-0.3		1.93
EAN_12a	0.951	1.925	57.4	-0.1		1.93

[a] Value provided for completeness where the water fractions were less than 0.4 mol.

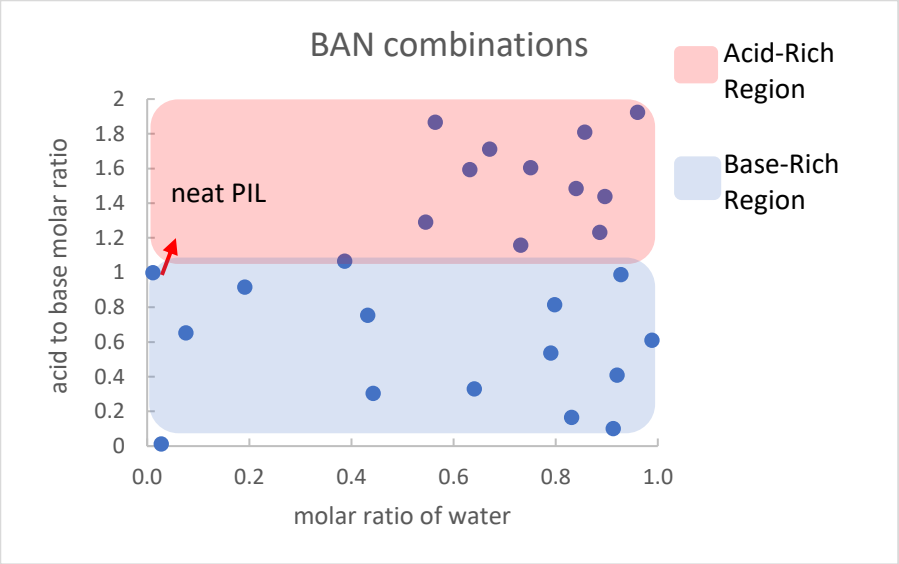

Figure S5. PIL-solvent combinations of BAN based samples according to the LHS design methodology.

Table S3. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of base-rich BAN combinations.

Base-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
BAN	0.011	1	34.3		0.45	1.54
BAN_1b	0.028	0.012	24.3	13.0[a]		1.43
BAN_2b	0.076	0.654	32.0	10.2[a]	0.45	1.52
BAN_3b	0.191	0.916	33.9	9.1[a]	0.44	1.55
BAN_4b	0.432	0.754	33.6	10.0	0.40	1.56
BAN_5b	0.442	0.303	28.4	11.4	0.39	1.52
BAN_6b	0.641	0.329	29.3	11.2	0.36	1.52
BAN_7b	0.791	0.537	32.3	10.7	0.32	1.83
BAN_8b	0.798	0.816	36.3	10.1		1.84
BAN_9b	0.831	0.165	28.8	11.6	0.27	1.86
BAN_10b	0.913	0.102	28.7	11.9	0.19	1.93
BAN_11b	0.920	0.408	31.3	11.2		1.93
BAN_12b	0.928	0.988	41.3	9.3		1.93
BAN_13b	0.989	0.610	51.3	10.9		2.06

[a] Values provided for completeness where the water fractions were less than 0.4 mol.

Table S4. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of acid-rich BAN combinations.

Acid-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
BAN	0.011	1	34.3		0.45	1.54
BAN_1a	0.387	1.067	36.1	-0.9[a]	0.43	1.58
BAN_2a	0.546	1.290	38.5	-1.1	0.44	1.65
BAN_3a	0.565	1.868	39.7	-1.4	0.45	1.65
BAN_4a	0.632	1.594	40.0	-1.2	0.47	1.65
BAN_5a	0.671	1.712	39.8	-1.1	0.50	1.65
BAN_6a	0.732	1.158	41.6	-0.4	0.49	1.82
BAN_7a	0.751	1.605	42.6	-0.8		1.83
BAN_8a	0.840	1.484	43.6	-0.5		1.86
BAN_9a	0.857	1.810	45.4	-0.6		1.93
BAN_10a	0.886	1.233	46.2	0.0		1.93
BAN_11a	0.896	1.438	47.3	-0.2		1.93
BAN_12a	0.961	1.925	57.9	0.0		1.93

[a] Value provided for completeness where the water fractions were less than 0.4 mol.

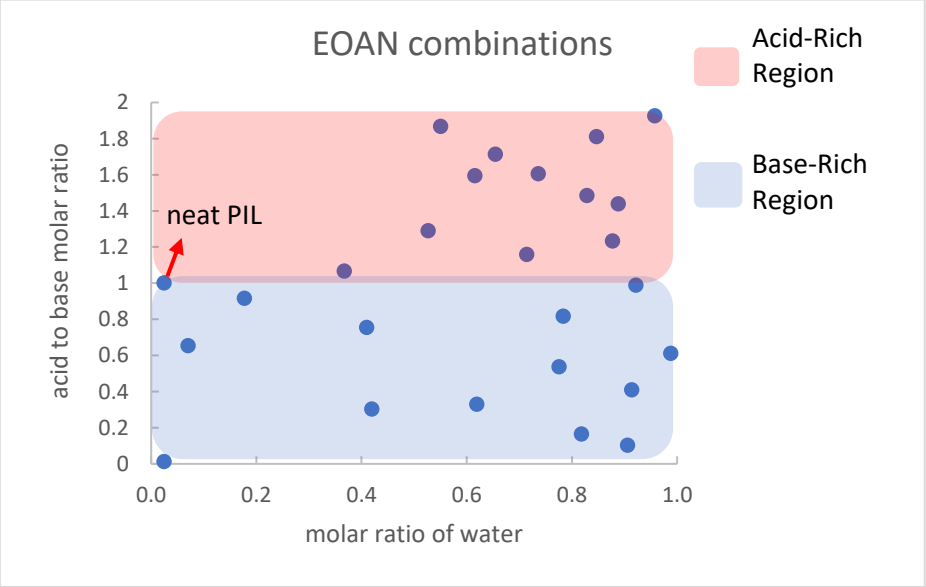

Figure S6. PIL-solvent combinations of EOAN based samples according to the LHS design methodology.

Table S5. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of base-rich EOAN combinations.

Base-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
EOAN	0.024	1	57.3			1.65
EOAN_1b	0.024	0.012	46.7	13.5[a]		1.65
EOAN_2b	0.070	0.654	63.7	9.9[a]		1.93
EOAN_3b	0.177	0.916	58.8	9.0[a]		1.52
EOAN_4b	0.409	0.754	55.8	9.7		1.65
EOAN_5b	0.419	0.303	51.1	11.0		1.82
EOAN_6b	0.619	0.329	53.4	10.7		1.93
EOAN_7b	0.775	0.537	59.4	10.1		1.65
EOAN_8b	0.783	0.816	51.5	9.4		1.86
EOAN_9b	0.818	0.165	48.3	11.0		1.65
EOAN_10b	0.905	0.102	56.2	11.1		1.65
EOAN_11b	0.913	0.408	51.8	10.3		1.93
EOAN_12b	0.921	0.988	55.0	8.9		1.86
EOAN_13b	0.988	0.610	59.8	9.8		1.82

[a] Values provided for completeness where the water fractions were less than 0.4 mol.

Table S6. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of acid-rich EOAN combinations.

Acid-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
EOAN	0.024	1	57.3			1.65
EOAN_1a	0.367	1.067	65.7	-0.8[a]		1.83
EOAN_2a	0.527	1.290	58.6	-1.1		1.81
EOAN_3a	0.550	1.868	598	-1.4		1.70
EOAN_4a	0.615	1.594	51.0	-1.2		1.86
EOAN_5a	0.654	1.712	49.7	-1.2		1.81
EOAN_6a	0.714	1.158	61.3	-0.5		1.93
EOAN_7a	0.735	1.605	58.8	-0.9		1.93
EOAN_8a	0.828	1.484	63.9	-0.6		1.84
EOAN_9a	0.846	1.810	59.3	-0.7		1.93
EOAN_10a	0.877	1.233	68.2	-0.1		1.93
EOAN_11a	0.888	1.438	63.4	-0.3		1.93
EOAN_12a	0.957	1.925	68.0	0		1.82

[a] Value provided for completeness where the water fractions were less than 0.4 mol.

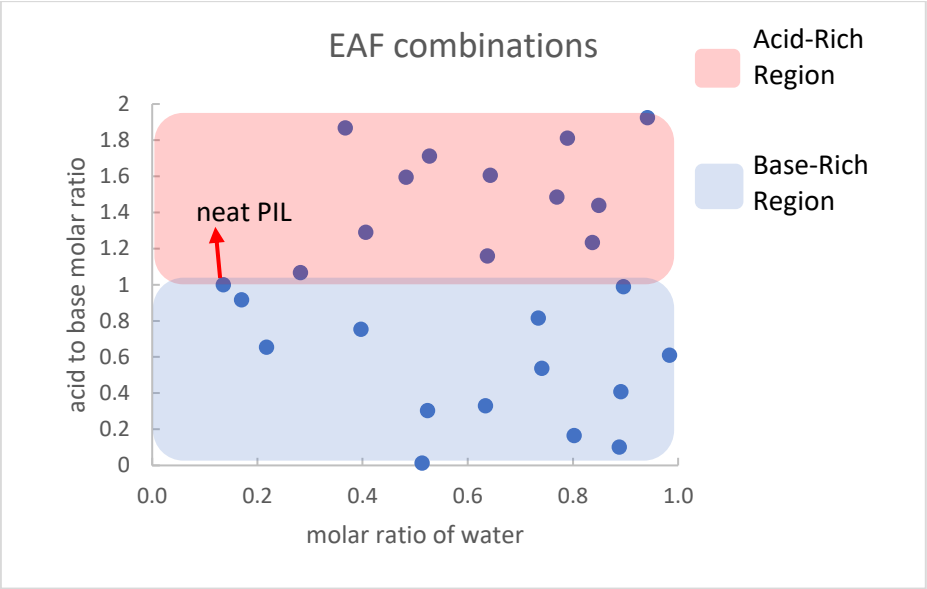

Figure S7. PIL-solvent combinations of EAF based samples according to the LHS design methodology.

Table S7. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of base-rich EAF combinations.

Base-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
EAF	0.135	1	46.9		0.78	1.65
EAF_1b	0.170	0.916	48.0	6.8[a]		1.65
EAF_2b	0.217	0.654	49.5	11.3[a]		1.65
EAF_3b	0.397	0.754	50.8	10.8[a]		1.70
EAF_4b	0.513	0.012	27.5	13.8		1.59
EAF_5b	0.523	0.303	36.5	12.2		1.65
EAF_6b	0.633	0.329	42.5	12.0		1.86
EAF_7b	0.734	0.816	57.2	10.5		1.86
EAF_8b	0.740	0.537	54.7	11.4		1.85
EAF_9b	0.802	0.165	47.2	12.3		1.87
EAF_10b	0.888	0.102	54.6	12.3		1.93
EAF_11b	0.891	0.408	59.0	11.5		1.93
EAF_12b	0.896	0.988	68.3	4.6		1.93
EAF_13b	0.984	0.610	69.6	10.9		2.06

[a] Values provided for completeness where the water fractions were less than 0.4 mol.

Table S8. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of acid-rich EAF combinations.

Acid-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
EAF	0.135	1	46.9		0.78	1.65
EAF_1a	0.282	1.067	47.2	5.9[a]		1.70
EAF_2a	0.367	1.868	49.7	4.1		1.81
EAF_3a	0.406	1.290	50.1	5.0		1.81
EAF_4a	0.483	1.594	50.5	4.4		1.82
EAF_5a	0.527	1.712	51.8	4.1		1.82
EAF_6a	0.637	1.158	54.0	4.9		1.85
EAF_7a	0.642	1.605	53.0	4.1		1.85
EAF_8a	0.769	1.484	56.4	4.0		1.93
EAF_9a	0.789	1.810	55.6	3.7		1.93
EAF_10a	0.837	1.233	60.2	4.2		1.93
EAF_11a	0.849	1.438	59.6	3.9		1.93
EAF_12a	0.941	1.925	65.4	3.4		1.93

[a] Value provided for completeness where the water fractions were less than 0.4 mol.

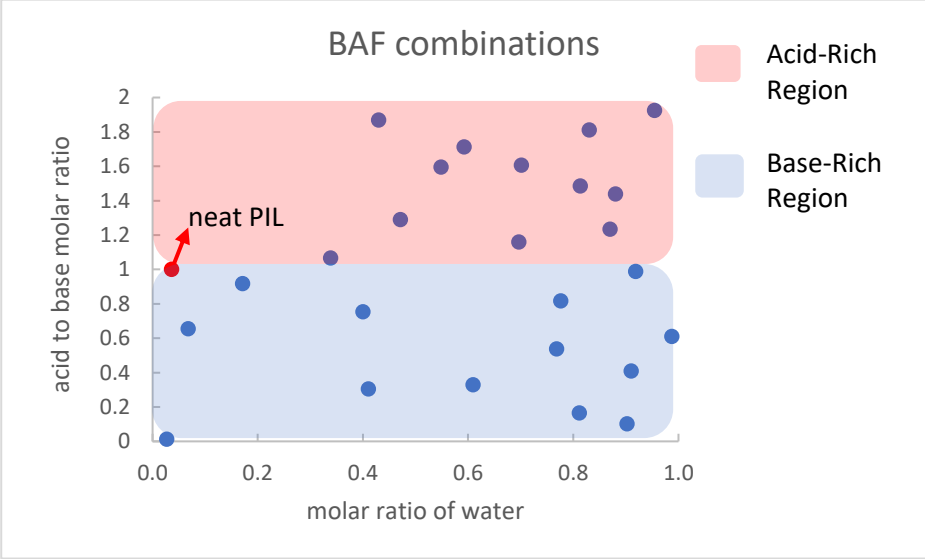

Figure S8. PIL-solvent combinations of BAF based samples according to the LHS design methodology.

Table S9. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of base-rich BAF combinations.

Base-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
BAF	0.037	1	37.2		0.49	1.55
BAF_1b	0.027	0.012	23.6	13.3[a]		1.39
BAF_2b	0.068	0.654	33.3	10.9[a]	0.44	1.52
BAF_3b	0.171	0.916	36.5	9.9[a]	0.47	1.57
BAF_4b	0.400	0.754	37.4	10.5	0.42	1.58
BAF_5b	0.410	0.303	31.0	11.6	0.38	1.52
BAF_6b	0.610	0.329	31.1	11.4	0.35	1.52
BAF_7b	0.768	0.537	35.0	10.9	0.31	1.82
BAF_8b	0.776	0.816	39.8	10.3	0.36	1.83
BAF_9b	0.812	0.165	29.7	11.7	0.27	1.83
BAF_10b	0.902	0.102	30.4	11.9	0.20	1.93
BAF_11b	0.910	0.408	34.3	11.2	0.19	1.93
BAF_12b	0.918	0.988	54.7	6.0		1.93
BAF_13b	0.987	0.610	54.1	11.0		2.06

[a] Values provided for completeness where the water fractions were less than 0.4 mol.

Table S10. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of acid-rich BAF combinations.

Acid-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
BAF	0.037	1	37.2		0.49	1.55
BAF_1a	0.339	1.067	37.7	6.2	0.47	1.59
BAF_2a	0.430	1.868	39.9	4.0	0.51	1.65
BAF_3a	0.472	1.290	39.6	5.1	0.47	1.65
BAF_4a	0.549	1.594	40.1	4.3	0.48	1.65
BAF_5a	0.593	1.712	41.4	4.1	0.47	1.81
BAF_6a	0.696	1.158	42.9	5.1	0.47	1.83
BAF_7a	0.701	1.605	43.5	4.2	0.53	1.82
BAF_8a	0.813	1.484	45.5	4.1		1.86
BAF_9a	0.830	1.810	46.5	3.8		1.93
BAF_10a	0.870	1.233	48.8	4.4		1.93
BAF_11a	0.880	1.438	48.6	4.0		1.93
BAF_12a	0.955	1.925	58.2	3.5		1.93

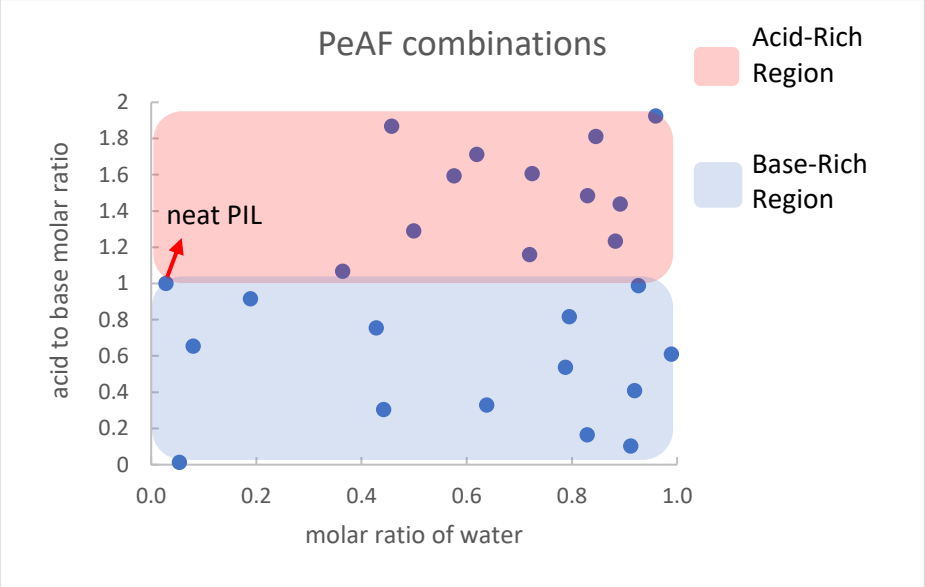

Figure S9. PIL-solvent combinations of PeAF based samples according to the LHS design methodology.

Table S11. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of base-rich PeAF combinations.

Base-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
PeAF	0.028	1	35.2		0.40	1.52
PeAF_1b	0.053	0.012	24.8	13.0[a]		1.43
PeAF_2b	0.080	0.654	32.2	10.7[a]	0.39	1.52
PeAF_3b	0.189	0.916	34.4	9.5[a]	0.39	1.52
PeAF_4b	0.428	0.754	32.3	10.3	0.36	1.52
PeAF_5b	0.442	0.303	29.5	11.4	0.34	1.52
PeAF_6b	0.637	0.329	27.4	11.1	0.31	1.52
PeAF_7b	0.788	0.537	30.4	10.6	0.27	1.81
PeAF_8b	0.795	0.816	34.6	9.9	0.30	1.81
PeAF_9b	0.829	0.165	28.3	11.3	0.24	1.52
PeAF_10b	0.912	0.102	27.7	11.6	0.17	1.86
PeAF_11b	0.919	0.408	28.7	10.9	0.16	1.93
PeAF_12b	0.926	0.988	41.4	5.3		1.93
PeAF_13b	0.989	0.610	43.2	11.0		1.93

[a] Values provided for completeness where the water fractions were less than 0.4 mol.

Table S12. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of acid-rich PeAF combinations

Acid-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
PeAF	0.028	1	35.2		0.40	1.52
PeAF_1a	0.364	1.067	35.0	5.9	0.38	1.52
PeAF_2a	0.457	1.868	36.7	4.0	0.38	1.65
PeAF_3a	0.499	1.290	35.5	4.9	0.37	1.65
PeAF_4a	0.576	1.594	36.3	4.2	0.37	1.65
PeAF_5a	0.619	1.712	37.9	4.0	0.36	1.65
PeAF_6a	0.719	1.158	37.3	4.9	0.35	1.82
PeAF_7a	0.724	1.605	38.0	4.0	0.34	1.81
PeAF_8a	0.829	1.484	40.9	4.0	0.34	1.86
PeAF_9a	0.845	1.810	41.4	3.6		1.93
PeAF_10a	0.882	1.233	42.0	4.3		1.93
PeAF_11a	0.891	1.438	41.2	4.0		1.93
PeAF_12a	0.959	1.925	47.5	3.5		1.93

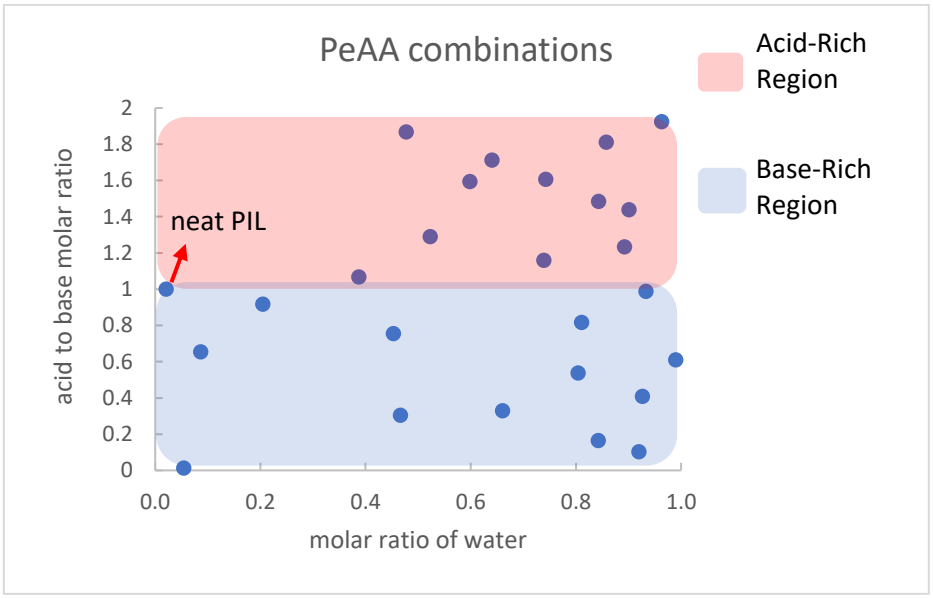

Figure S10. PIL-solvent combinations of PeAA based samples according to the LHS design methodology.

Table S13. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of base-rich PeAA combinations.

Base-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
PeAA	0.021	1	38.9		0.47	1.52
PeAA_1b	0.054	0.012	24.9	13.1[a]		1.44
PeAA_2b	0.087	0.654	34.0	10.7[a]	0.42	1.52
PeAA_3b	0.204	0.916	38.5	8.6[a]	0.45	1.52
PeAA_4b	0.452	0.754	34.4	10.3	0.39	1.52
PeAA_5b	0.466	0.303	28.8	11.5	0.34	1.52
PeAA_6b	0.660	0.329	29.8	11.2	0.31	1.52
PeAA_7b	0.804	0.537	31.7	10.6	0.28	1.65
PeAA_8b	0.811	0.816	37.0	9.8	0.33	1.81
PeAA_9b	0.842	0.165	27.9	11.3	0.23	1.65
PeAA_10b	0.919	0.102	27.6	11.5	0.16	1.87
PeAA_11b	0.926	0.408	30.1	10.9	0.17	1.87
PeAA_12b	0.933	0.988	39.6	6.3		1.88
PeAA_13b	0.990	0.610	38.8	10.9		1.93

[a] Values provided for completeness where the water fractions were less than 0.4 mol.

Table S14. Molar ratio of water, acid to base molar ratio, SAXS/WAXS peak positions, surface tension and apparent pH of acid-rich PeAA combinations.

Acid-Rich Samples						
Sample ID	Molar ratio of water	Acid to base molar ratio	Surface tension (mN/m) (± 0.5)	pH (± 0.2)	q_1 (Å^{-1}) (± 0.01)	q_2 (Å^{-1}) (± 0.001)
PeAA	0.021	1	38.9		0.47	1.52
PeAA_1a	0.387	1.067	34.8	7.0	0.43	1.52
PeAA_2a	0.477	1.868	34.0	5.4	0.44	1.52
PeAA_3a	0.523	1.290	34.4	6.2	0.40	1.52
PeAA_4a	0.598	1.594	34.5	5.7	0.40	1.58
PeAA_5a	0.640	1.712	34.3	5.5	0.40	1.59
PeAA_6a	0.739	1.158	35.8	6.1	0.36	1.65
PeAA_7a	0.743	1.605	35.6	5.4	0.35	1.65
PeAA_8a	0.843	1.484	37.4	5.3		1.85
PeAA_9a	0.858	1.810	38.5	5.0		1.86
PeAA_10a	0.892	1.233	38.7	5.3		1.93
PeAA_11a	0.901	1.438	39.6	5.1		1.93
PeAA_12a	0.963	1.925	40.8	4.6		1.93

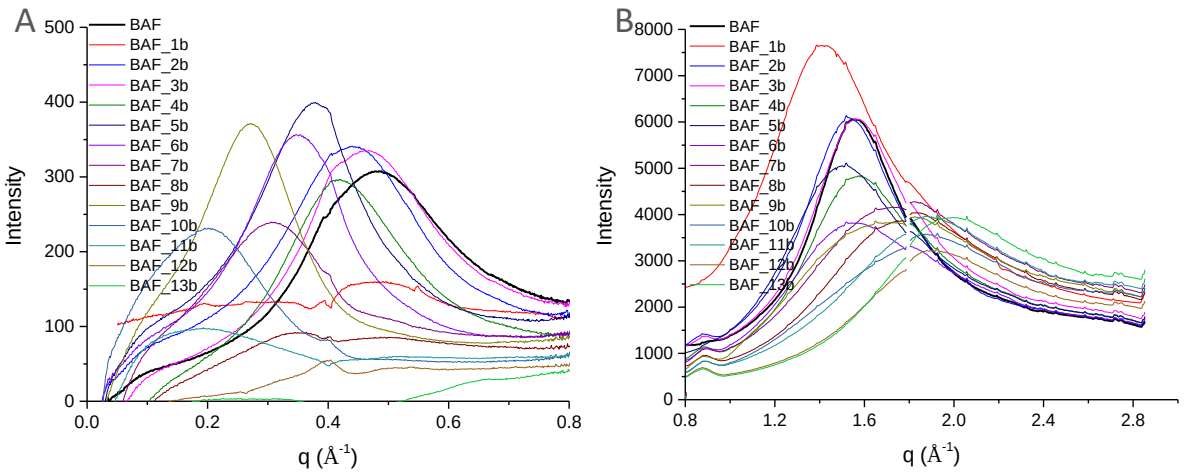

Figure S11. A) SAXS and B) WAXS patterns of base-rich BAF solvents.

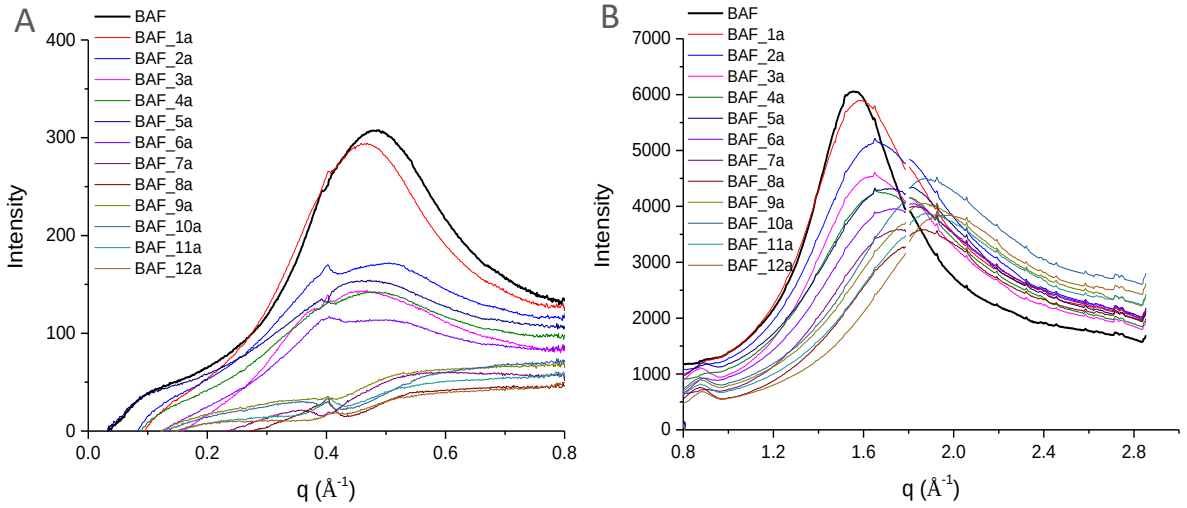

Figure S12. A) SAXS and B) WAXS patterns of acid-rich BAF solvents.

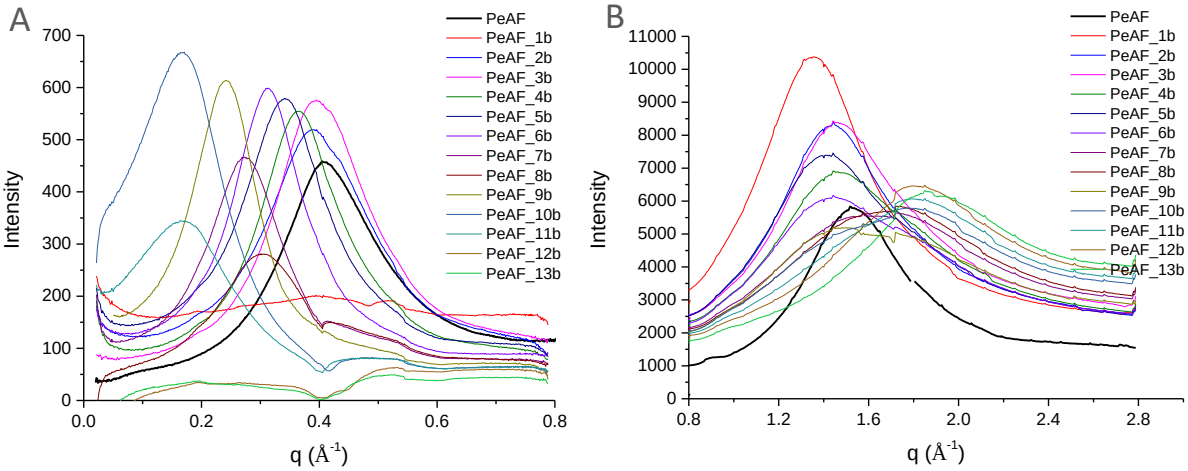

Figure S13. A) SAXS and B) WAXS patterns of base-rich PeAF solvents.

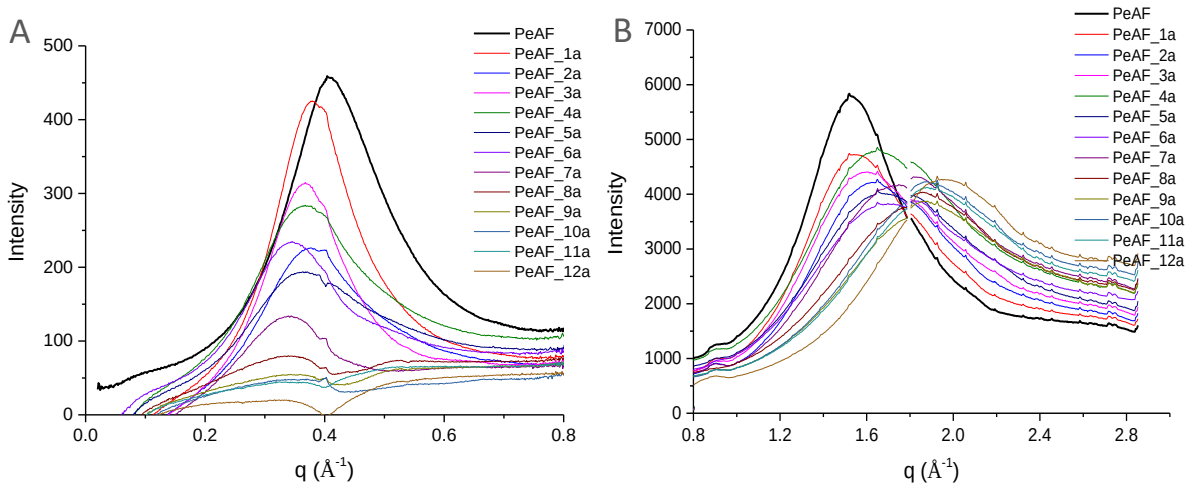

Figure S14. A) SAXS and B) WAXS patterns of acid-rich PeAF solvents.

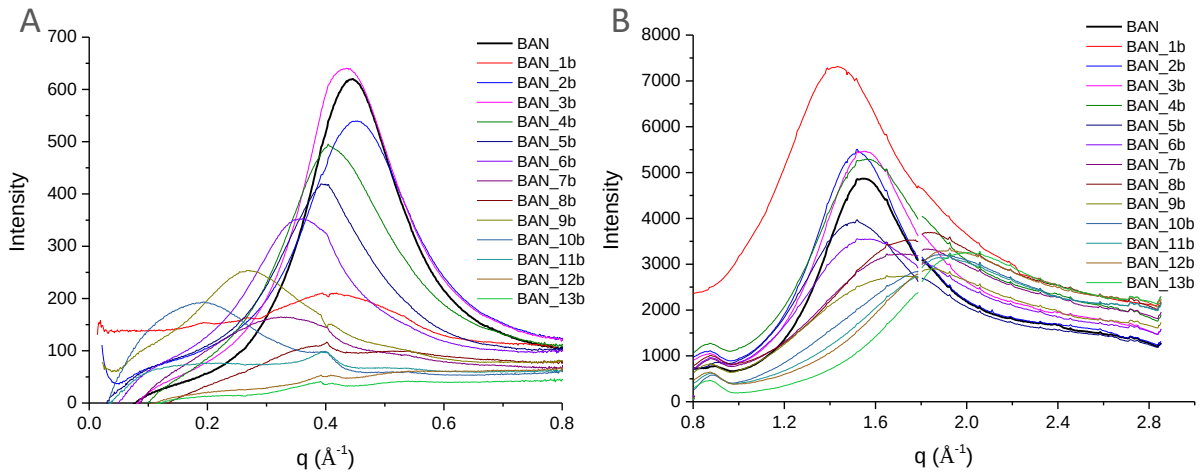

Figure S15. A) SAXS and B) WAXS patterns of base-rich BAN solvents.

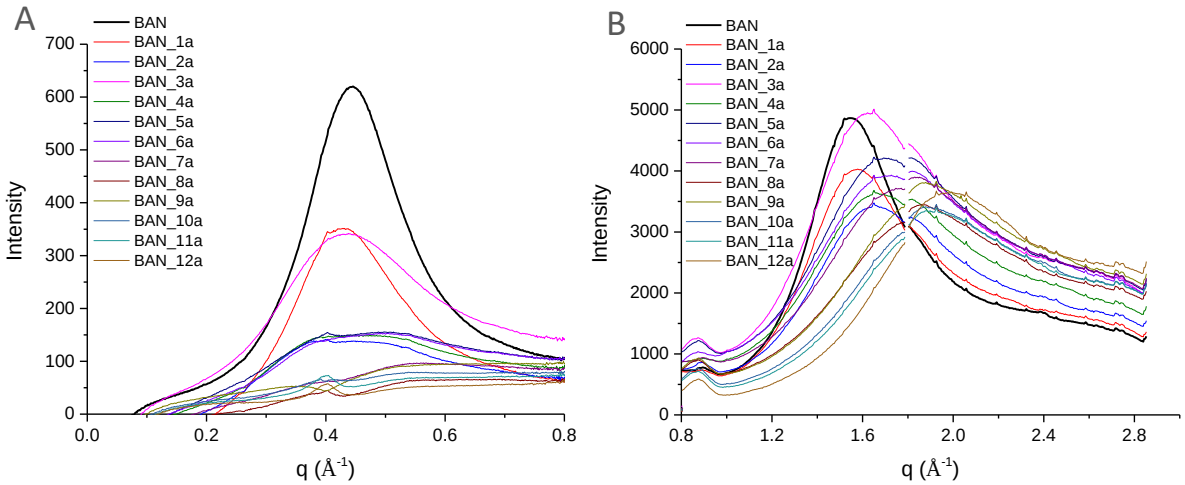

Figure S16. A) SAXS and B) WAXS patterns of acid-rich BAN solvents.

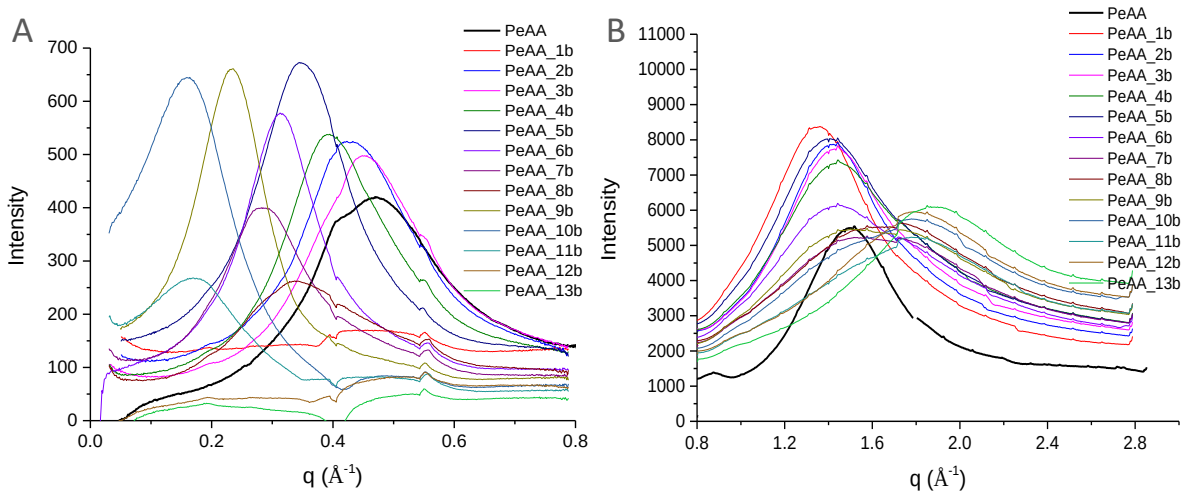

Figure S17. A) SAXS and B) WAXS patterns of base-rich PeAA solvents.

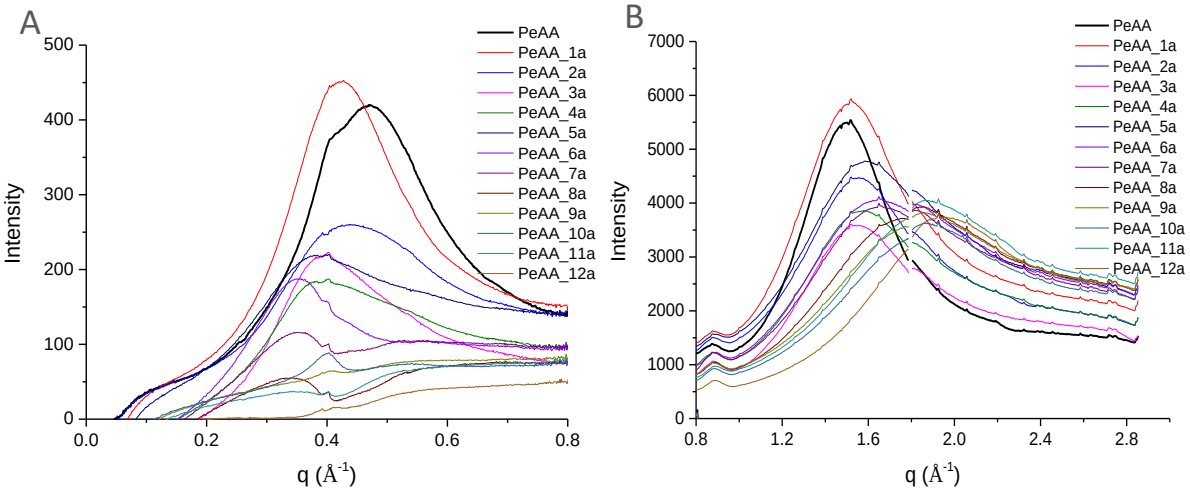

Figure S18. A) SAXS and B) WAXS patterns of acid-rich PeAA solvents.

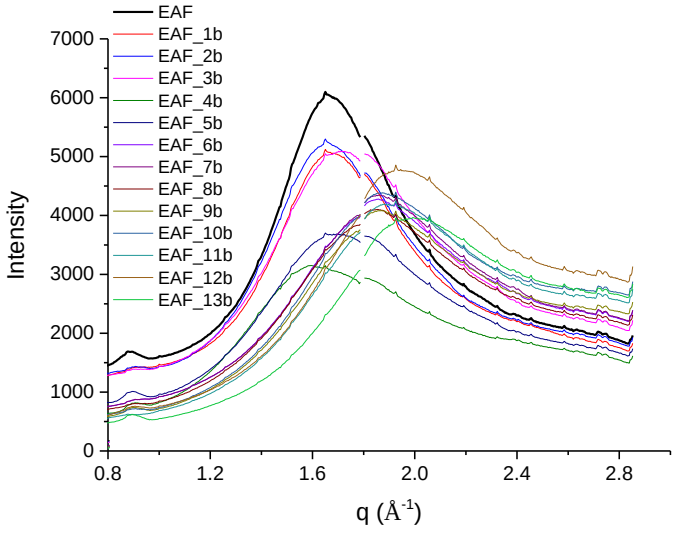

Figure S19. WAXS patterns of base-rich EAF combinations

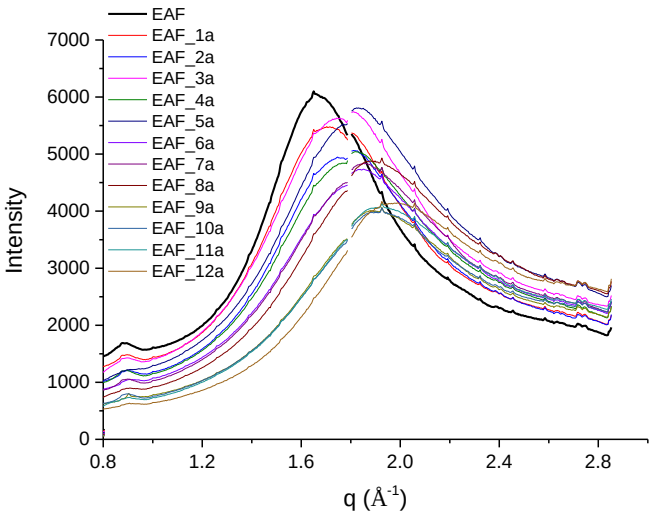

Figure S20. WAXS patterns of acid-rich EAF combinations

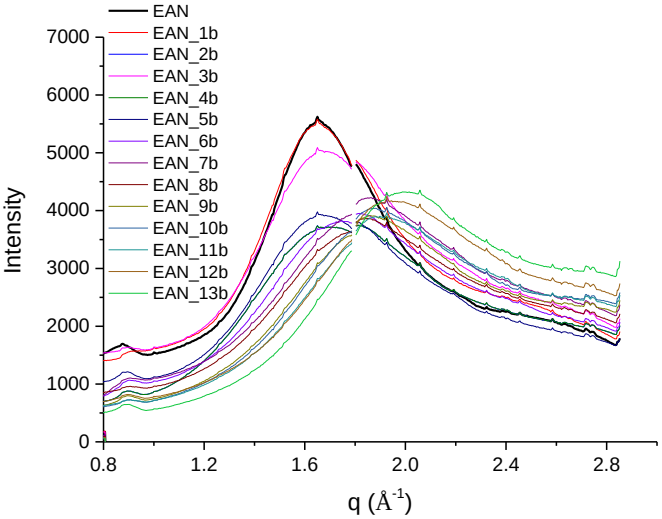

Figure S21. WAXS patterns of base-rich EAN solvents

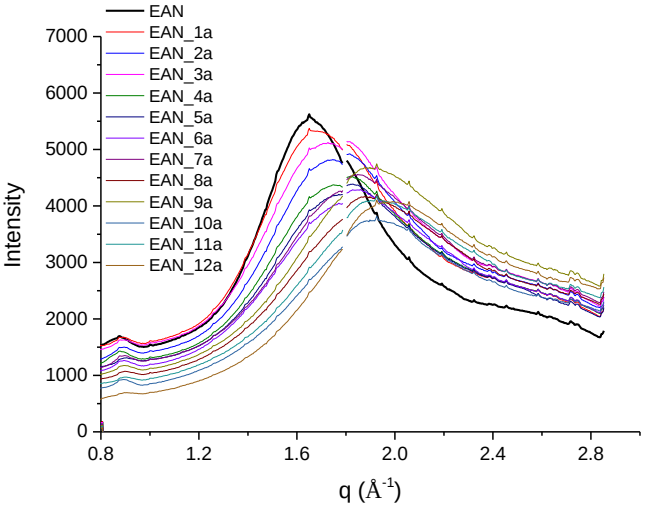

Figure S22. WAXS patterns of acid-rich EAN solvents

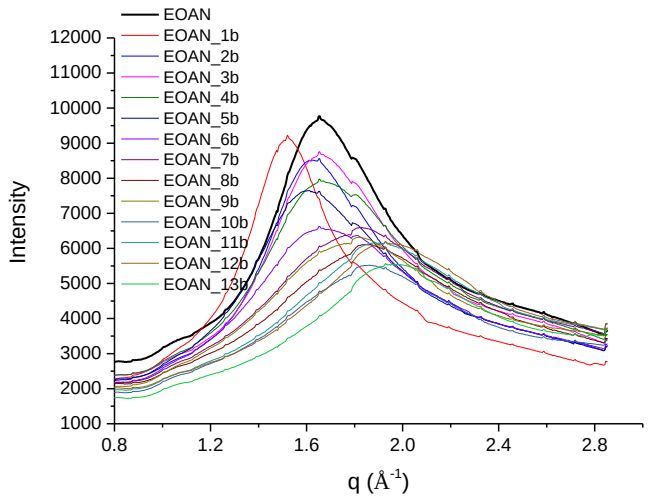

Figure S23. WAXS patterns of base-rich EOAN solvents

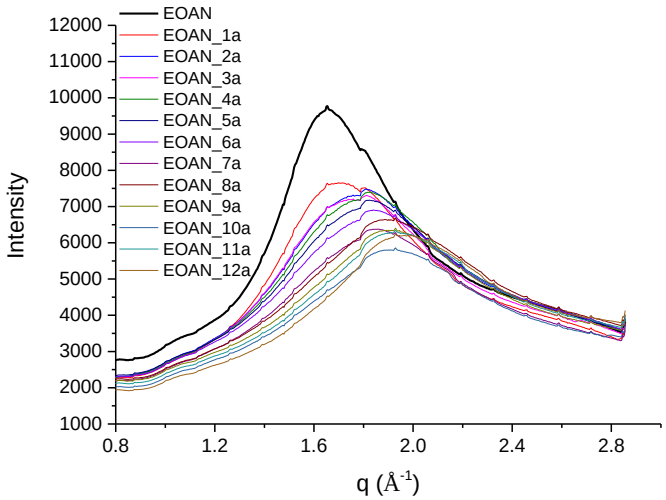

Figure S24. WAXS patterns of acid-rich EOAN solvents