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Electronic Supporting Information

Designing the thermal behaviour of aqueous biphasic systems composed of ammonium-based zwitterions

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1. Materials

The reagents used in the zwitterions (ZIs) synthesis were 1,3-propanesultone (≥ 99 wt % pure), 1,4-butanesultone (≥ 99 wt % pure), triamylamine (≥ 98 wt % pure), tripropylamine (≥ 98 wt % pure), triethylamine (≥ 99 wt % pure) and trimethylamine (*ca.* 13 % v/v in acetonitrile) from Tokyo Chemical Industry Co. The following organic solvents, purchased from Kanto Chemical Co., Inc, were also used: acetonitrile (≥ 99.5 wt % pure), diethyl ether (≥ 99 wt % pure), ethyl acetate (≥ 99.5 wt % pure), hexane (≥ 96 wt % pure) and methanol (≥ 99.8 wt % pure). Deuterium oxide, D_2O (99.8 atom % D) from ACROS Organics was used in nuclear magnetic resonance (NMR) experiments.

To prepare aqueous biphasic systems (ABS) the following salts were used: dipotassium hydrogenphosphate, K_2HPO_4 (≥ 99 wt % pure), tripotassium citrate monohydrate, $K_3C_6H_5O_7{\cdot}H_2O$ (≥ 99 wt % pure), tripotassium phosphate, K_3PO_4 (≥ 95 wt % pure), potassium carbonate, K_2CO_3 (≥ 99.5 wt % pure), potassium dihydrogenphosphate, KH_2PO_4 (≥ 99 wt% pure) and trisodium citrate, $Na_3C_6H_5O_7$ (≥ 99 wt% pure), all from Wako Pure Chemical Industries, Ltd, and sodium dihydrogenphosphate dihydrate, $NaH_2PO_4{\cdot}2H_2O$ (≥ 99 wt% pure) from Kanto Chemical Co., Inc.

L-Tryptophan (purity 99 wt %) and glycine (purity > 99 wt %) were acquired from Acros Organics. The quantification of aliphatic amino acids was carried out using the ninhydrin reagent (2 % solution) from Sigma.

2. Experimental Procedure

Synthesis of zwitterions. Five ZIs were prepared. For the synthesis of *N*,*N*,*N*-tripentyl-3-sulfonyl-1-propaneammonium, N_{555}C3S, and *N*,*N*,*N*-tripropyl-3-sulfonyl-1-propaneammonium, N_{333}C3S, trialkylamine and 1,3-propanesultone were dissolved in acetonitrile, and the resulting solution was mixed under a dry nitrogen gas atmosphere. The obtained solution was stirred for two days at 80 °C. After the removal of acetonitrile by evaporation, the residual liquid was repeatedly washed with excess amounts of anhydrous diethyl ether. The resultant solid was purified by recrystallization with ethyl acetate/methanol, and the obtained white powder was dried in vacuum at 60 °C for 24 h. For the synthesis of *N*,*N*,*N*-triethyl-3-sulfonyl-1-propaneammonium, N_{222}C3S, trialkylamine and 1,3-propanesultone were dissolved in acetonitrile, and the resulting solution was mixed under a dry nitrogen gas atmosphere. The obtained solution was stirred for 5h at 80 °C. The white powder obtained was repeatedly washed with excess amounts of anhydrous diethyl

ether, and then dried in vacuum at 60 °C for 24 h, without the need of a recrystallization step. The same procedure was used in the synthesis of *N*,*N*,*N*-trimethyl-3-sulfonyl-1-propaneammonium, $N_{111}C3S$, and *N*,*N*,*N*-trimethyl-4-sulfonyl-1-butaneammonium, $N_{111}C4S$. However, the reaction temperature was of 0 °C to avoid the evaporation of trimethylamine. The chemical structure and purity of the synthesized ZIs were confirmed by ^{1}H NMR spectroscopy and elemental analysis.

Differential scanning calorimetry. Differential scanning calorimetry (DSC) was performed with a Hitachi DSC7000X at a heating rate of 2 °C/min.

Thermogravimetric analysis. Thermogravimetric analyses (TGA) were performed with an EXSTAR TG/DTA 7200 system (Seiko Instruments, Inc.) at a heating rate of 10 °C/min under nitrogen atmosphere.

Determination of the ABS phase diagrams. The binodal curves were determined through the cloud point titration method, previously described by us,[1] at 25, 35, and 45 °C (± 1 °C) and atmospheric pressure. Aqueous solutions of salt at 20-50 wt % and aqueous solutions of each ZI with concentrations ranging from 50 to 70 wt % were prepared and used. Repetitive drop wise addition of the aqueous salt solution to the aqueous solution of ZI was carried out under constant stirring until the detection of a cloudy (biphasic) solution, followed by the drop wise addition of ultrapure water until the finding of a monophasic region (clear and limpid solution). Whenever necessary, and to better characterize the solubility curves, the addition of the ZI aqueous solution to the salt aqueous solution also was carried out. The ternary system compositions were determined by weight quantification within ± 10^{-3} g.

Partition of amino acids. Aqueous solutions of amino acids were prepared at 1 g·dm^{-3} (4.9 x 10^{-3} mol·dm^{-3}) for L-tryptophan and at 0.75 g·dm^{-3} (1.0 x 10^{-2} mol·dm^{-3}) for glycine. The following mixtures compositions were used to carry out the separation of amino acids: 30 wt % of $N_{555}C3S$ + 4 wt % of K_3PO_4 and 19.5 wt % of $N_{111}C3S$ + 19.5 wt % of K_3PO_4. The extractions were carried out at 45 °C and 25 °C in $N_{555}C3S$- and $N_{111}C3S$-based ABS, respectively. Each mixture was vigorously stirred and left to equilibrate for at least 12 h, a time established in previous optimizing experiments, to achieve the complete partitioning of each amino acid between the coexisting phases. After a careful separation of both phases, the quantification of L-tryptophan was carried by UV-spectroscopy, using a BioTeck Synergy

HT microplate reader, at a wavelength of 279 nm. To quantify the glycine present in each phase, 75 µL of ninhydrin reagent was added to 100 µL of an adequately diluted sample of each ABS phase. After incubation at 80 °C during 30 min, ethanol at 50 % (v/v) was added to stop the reaction. Then glycine was quantified by UV-spectroscopy at a wavelength of 570 nm.[2] At least three individual systems were prepared in order to determine the average in the amino acids partition coefficients and extraction efficiencies, as well as the respective standard deviations. Possible interferences of the ZI and K_3PO_4 with the analytical method were taking into account, and control samples were always prepared at the same weight fraction composition, using pure water instead of the amino acid aqueous solution. The partition coefficients of L-tryptophan (K_{Try}) and glycine (K_{Gly}) are defined as the ratio of the concentration of the each amino acid in the ZI-rich phase to that in the salt-rich phase. The selectivity is defined as the ratio between the partition coefficient of L-tryptophan and the partition coefficient of glycine. The percentage extraction efficiency of L-tryptophan (EE_{Try}%) and glycine (EE_{Gly}%) are defined as the percentage ratio between the amount of amino acid in the ZI-rich aqueous phase or salt-rich phase and that in the total mixture.

3. Results

Synthesis of zwitterions. $N_{555}C3S$: δ_H (400 MHz; D_2O; δ/ppm relative to TMS): 0.77 (9H, t, J =7.00), 1.22 (12H), 1.52 (6H), 2.01 (2H), 2.83 (2H, t, J =7.00), 3.10 (6H), 3.25 (2H). Elemental analysis (%) for $C_{18}H_{39}NO_3S$: Found: C, 61.37; H, 11.67; N, 3.76; C/N, 16.32. Calculated: C, 61.85; H, 11.25; N, 4.01; C/N, 15.42.

$N_{333}C3S$: δ_H (400 MHz; D_2O; δ/ppm relative to TMS): 0.83 (9H, t, J =7.30), 1.55 (6H), 1.98 (2H), 2.83 (2H t, J =7.00), 3.06 (6H), 3.26 (2H). Elemental analysis (%) for $C_{12}H_{27}NO_3S$: Found: C,53.22; H, 10.50; N, 44.89; C/N, 10.89. Calculated: C, 54.31; H, 10.25; N, 45.28; C/N, 10.29.

$N_{222}C3S$: δ_H (400 MHz; D_2O; δ/ppm relative to TMS): 1.16 (9H, t, J =7.30), 2.01 (2H), 2.86 (2H t, J =7.10), 3.22 (8H). Elemental analysis (%) for $C_9H_{21}NO_3S$: Found: C, 47.77; H, 9.55; N, 5.92; C/N, 8.07. Calculated: C, 48.4; H, 9.48; N, 6.27; C/N, 7.72.

$N_{111}C3S$: δ_H (400 MHz; D_2O; δ/ppm relative to TMS): 2.12 (2H), 2.86 (2H, t, J =7.30), 3.03 (9H), 3.37 (2H). Elemental analysis (%) for $C_6H_{15}NO_3S$: Found: C, 39.60; H, 8.51; N, 7.38; C/N, 5.36. Calculated: C, 39.76; H, 8.34; N, 7.73; C/N, 5.14.

$N_{111}C4S$: δ_H (400 MHz; D_2O; δ/ppm relative to TMS): 1.68 (2H), 1.82 (2H), 2.85 (2H, t, J =7.30), 3.00 (9H), 3.25 (2H). Elemental analysis (%) for $C_7H_{17}NO_3S$: Found: C, 41.19; H, 8.93; N,6.48; C/N, 6.35. Calculated: C, 39.42; H, 8.98; N, 6.57; C/N, 6.00.

Table S1 Thermal properties of the synthesised ZIs: T_m – melting temperature. T_d – decomposition temperature.

ZI	T_m (°C)	T_d (°C)
N_{555}C3S	170	268
N_{333}C3S	228	282
N_{222}C3S	186	300
N_{111}C3S	195	368
N_{111}C4S	185	353

Determination of the ABS phase diagrams.

Table S2 Experimental weight fraction data for the systems composed of N_{555}C3S (1) + salt (2) + H_2O (3) at 25 °C and atmospheric pressure.

K_3PO_4		KH_2PO_4		K_2HPO_4		K_2CO_3	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
53.89	0.78	67.81	1.04	68.61	0.84	33.17	3.57
50.06	1.44	62.93	1.34	60.23	1.07	10.29	7.12
46.98	1.54	59.87	1.63	53.44	1.24	8.12	8.19
43.93	2.42	56.28	1.89	50.56	1.46	5.77	9.29
27.24	4.60	53.97	2.12	49.73	1.46	5.57	9.69
24.89	5.07	51.63	2.35	47.02	1.78	3.89	10.51
23.96	5.22	48.72	2.91	43.46	2.11	2.52	11.47
23.17	5.40	46.08	3.44	28.01	5.02	2.03	11.81
22.54	5.59	43.79	3.79	26.22	5.27	1.66	12.78
21.68	5.69	41.73	4.14	23.99	5.78	1.22	14.71
20.90	5.73	39.02	4.71	22.36	6.11		
20.13	5.89	36.56	5.24	21.12	6.40		
19.45	6.02	33.90	5.89	20.44	6.58		
19.00	6.21	31.37	6.54	18.77	6.88		
18.40	6.33	27.78	7.46	17.34	7.28		
17.77	6.41	25.33	8.17	16.68	7.49		
17.65	6.03	23.05	8.82	15.60	7.84		
16.94	6.69	21.31	9.35	14.69	8.10		
14.60	6.78	20.54	9.56	13.70	8.45		
13.33	7.12	19.71	9.78	12.82	8.76		
12.56	7.36	16.88	10.81	12.16	8.96		
11.75	7.66			11.35	9.30		
10.87	7.96			10.51	9.68		
8.74	8.75			9.83	9.98		
7.86	9.14			9.17	10.30		
6.92	9.47			8.79	10.44		
6.25	9.87			8.13	10.72		
5.74	10.10			7.40	11.20		
5.51	10.32			6.83	11.57		
4.95	10.57			6.14	12.07		
4.38	11.07						
3.00	12.95						
2.28	13.93						
2.06	15.70						

Table S3 Experimental weight fraction data for the systems composed of N_{555}C3S (1) + salt (2) + H_2O (3) at 25 °C and atmospheric pressure.

$K_3C_6H_5O_7$		$Na_3C_6H_5O_7$		NaH_2PO_4			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
70.74	1.56	41.18	3.64	63.44	1.15	17.45	9.08
57.13	2.56	36.36	4.09	60.18	1.58	17.00	9.20
50.14	3.33	33.49	4.58	55.37	1.95	16.44	9.39
45.04	3.91	31.09	5.02	51.56	2.26	15.98	9.55
41.57	4.43	28.19	5.87	49.12	2.61	15.50	9.72
38.63	4.91	26.46	6.24	46.57	2.85	14.99	9.93
36.13	5.29	25.06	6.44	44.78	3.10	14.58	10.07
34.23	5.75	23.11	7.03	43.00	3.34	14.20	10.20
32.66	6.18	19.61	7.82	41.18	3.62	13.84	10.33
31.15	6.57	18.42	8.17	39.66	3.80	13.49	10.46
29.64	6.86	17.26	8.57	37.78	4.23	13.18	10.57
28.49	7.16	16.27	8.90	36.54	4.43	12.87	10.69
21.03	8.83	15.44	9.16	34.94	4.77	12.59	10.81
18.33	9.58	14.48	9.53	34.14	4.93	12.24	10.96
15.96	10.32	13.80	9.75	32.61	5.27	11.83	11.17
15.21	10.62	12.99	10.08	31.78	5.43	11.44	11.36
13.88	11.06	12.08	10.51	30.47	5.75	11.04	11.57
12.86	11.62	11.33	10.77	29.62	5.90	10.68	11.76
11.12	12.40	10.75	11.05	28.43	6.19	10.18	12.03
9.55	13.19	10.09	11.34	27.32	6.45	9.76	12.28
8.97	13.91	9.43	11.74	26.23	6.70		
8.11	14.83	8.33	12.40	24.97	7.02		
4.65	17.27	7.38	12.99	24.17	7.21		
3.21	18.99	6.05	14.18	23.17	7.52		
2.66	20.15	2.93	15.91	22.47	7.69		
2.54	19.26	2.44	19.32	21.81	7.84		
2.32	20.56			20.98	8.11		
1.97	21.47			20.38	8.25		
1.57	23.56			19.62	8.48		
1.50	22.61			19.09	8.61		
1.38	24.45			18.47	8.79		
0.77	26.97			17.87	8.99		

Table S4 Experimental weight fraction data for the systems composed of $N_{333}C3S$ (1) + salt (2) + H_2O (3) at 25 °C and atmospheric pressure.

K_3PO_4		K_2HPO_4		K_2CO_3		$K_3C_6H_5O_7$	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
57.59	0.96	55.23	1.07	44.91	4.17	64.88	3.11
48.70	1.48	47.42	1.85	38.43	6.55	59.52	4.15
44.69	2.79	40.25	3.50	33.73	8.24	52.93	6.45
40.40	3.75	36.85	4.20	30.12	9.72	47.74	8.18
37.77	4.38	36.13	4.44	26.89	11.08	43.36	10.76
34.92	5.11	35.20	4.74	20.66	13.26	41.09	12.02
33.14	5.99	34.69	4.93	19.04	14.29	38.79	13.34
31.60	6.81	33.78	5.24	15.68	15.77	34.79	16.13
29.53	7.33	33.14	5.48	14.79	16.27	32.14	17.98
28.34	7.88	32.47	5.76	14.06	16.55	29.95	19.52
27.24	8.29	31.70	6.10	13.33	16.94	27.62	21.24
26.29	8.80	30.73	6.49	12.68	17.13	25.42	22.97
24.88	9.78	29.68	6.92	12.09	17.43	22.80	24.99
24.02	10.15	28.92	7.32	11.54	17.69	21.29	26.14
23.27	10.49	27.71	7.89	11.15	18.16	19.78	27.33
22.54	10.73	26.67	8.41	10.62	18.35	18.94	27.99
21.94	11.17	25.99	8.85	10.16	18.57	17.68	28.99
21.43	11.38	24.94	9.46	9.77	18.76	16.49	29.94
20.82	11.71	23.50	10.18	9.52	19.01	15.55	30.74
19.91	12.42	22.71	10.84	9.18	19.20	14.87	31.37
19.38	12.70	21.53	11.37	8.84	19.18	13.92	32.23
18.86	12.94	20.41	12.21	8.62	19.40	12.20	33.85
18.44	13.14	18.85	13.19	8.41	19.61	11.35	34.70
17.93	13.39	17.10	14.43	8.21	19.86		
17.18	14.03	15.34	15.79	7.93	19.89		
16.76	14.07	14.42	16.71	7.76	20.15		
16.32	14.27	11.93	18.38	7.42	20.63		
15.69	14.77	9.02	20.49	7.05	20.76		
15.32	14.88	7.24	22.43	6.78	21.04		
14.77	15.31			6.59	21.06		
14.48	15.49			6.33	21.42		
14.18	15.65			6.16	21.44		
13.88	15.82			6.02	21.41		
13.56	15.96			5.91	21.62		
13.32	16.07			5.80	21.76		
13.05	16.28			5.66	21.77		
12.76	16.44			5.56	21.91		
12.22	16.68			5.46	22.05		
11.86	16.96			5.34	22.02		
11.20	17.31			5.25	22.13		

11.00	17.45		5.18	22.26	
10.48	17.48		5.01	22.53	
10.13	18.12		4.87	22.73	
9.90	18.06		4.69	22.83	
9.44	18.27		4.55	23.01	
9.07	18.51		4.42	23.12	
8.79	19.00		4.30	23.28	
8.49	18.97		4.15	23.62	
8.20	19.20		4.02	23.64	
8.00	19.57		3.87	23.84	
7.73	19.73				
7.51	19.91				
7.27	20.10				

Table S5 Experimental weight fraction data for the systems composed of $N_{333}C3S$ (1) + salt (2) + H_2O (3) at 25 °C and atmospheric pressure.

$Na_3C_6H_5O_7$		**NaH_2PO_4**	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**
59.89	1.00	59.10	1.13
56.37	1.88	54.34	2.08
51.89	2.53	46.13	6.41
48.06	3.08	42.94	8.16
44.33	4.40	40.08	9.63
42.40	4.91	37.85	10.82
39.61	5.90	34.97	12.57
36.93	6.95		
33.16	8.64		
29.55	10.43		
24.36	13.31		
20.63	15.56		
16.31	18.18		

Table S6 Experimental weight fraction data for the systems composed of $N_{222}C3S$ (1) + salt (2) + H_2O (3) at 25 °C and atmospheric pressure.

K_3PO_4		K_2HPO_4		K_2CO_3	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
59.14	0.84	54.56	4.12	54.97	2.68
46.60	2.76	40.00	5.64	43.70	4.00
40.41	4.10	34.66	7.34	29.84	6.89
36.71	5.62	31.74	9.01	27.81	7.72
32.52	7.86	28.58	10.04	15.94	11.82
28.76	9.62	23.46	13.05	15.34	12.00
26.00	11.40	22.35	14.16	14.77	12.22
24.60	12.08	21.04	14.82	14.20	12.40
22.73	13.27	20.11	15.45	13.45	12.93
21.11	14.30	18.53	17.07	12.61	13.24
19.56	15.09	17.74	17.59	11.89	13.56
18.26	15.87	17.00	17.89	11.23	13.75
17.23	16.62	15.99	18.90	10.76	14.15
16.23	17.24	15.37	19.27	10.33	14.11
15.35	17.84	14.79	19.59	9.95	14.46
14.53	18.46	14.30	19.90	9.46	14.61
13.83	18.92	13.58	20.84	8.90	14.98
13.23	19.30	13.12	21.08	8.39	15.33
12.64	19.65	12.68	21.33	7.61	16.10
11.96	20.16	12.10	21.89	4.66	18.94
11.51	20.44	11.72	22.15	54.97	2.68
11.04	20.82	11.23	22.72	43.70	4.00
10.65	21.09	10.90	22.88	29.84	6.89
10.26	21.32	10.62	23.09	27.81	7.72
9.78	21.81	10.20	23.60	15.94	11.82
9.43	22.04	9.81	24.00		
9.07	22.38	9.53	24.16		
8.80	22.51	9.24	24.38		
8.56	22.67	8.98	24.66		
8.22	23.00	8.68	25.05		
7.92	23.27	8.40	25.40		
7.64	23.57	8.06	25.43		
7.43	23.66	7.77	25.74		
7.17	23.87	7.49	26.14		
6.93	24.10	7.29	26.36		
6.75	24.24	7.10	26.57		
6.52	24.44	6.78	26.91		
6.32	24.65	6.61	27.12		
6.13	24.88	6.36	27.33		
5.95	25.09	6.21	27.50		
5.79	25.27				
5.68	25.60				
5.52	25.42				

Table S7 Experimental weight fraction data for the systems composed of $N_{111}C4S$ (1) + salt (2) + H_2O (3) at 25 °C and atmospheric pressure.

K_3PO_4		K_2HPO_4		K_2CO_3	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
58.16	2.52	53.33	5.86	32.38	8.43
45.92	4.27	42.07	9.15	25.61	10.97
39.55	5.74	33.00	12.67	18.65	13.68
35.87	7.40	29.83	13.82	13.01	16.09
31.20	10.18	27.71	15.45	7.71	18.69
27.66	12.12	25.85	16.62	5.94	20.36
24.93	13.85	24.33	17.84	3.78	23.16
22.68	15.37	22.93	18.51		
20.82	16.57	21.74	19.31		
18.70	18.13	20.79	20.08		
17.41	18.86	19.14	21.81		
16.02	19.98	18.28	22.21		
15.07	20.57	17.46	22.84		
13.83	21.56	16.08	24.07		
12.91	22.29	15.54	24.61		
12.02	22.93	15.00	25.23		
11.11	23.67	14.04	26.12		
10.51	24.18	13.63	26.39		
9.93	24.65	12.90	27.00		
9.43	25.01	12.58	27.30		
9.00	25.37	12.23	27.57		
8.45	25.93	11.88	27.75		
7.93	26.46	11.38	28.41		
7.52	26.80	10.77	29.16		
7.09	27.35	9.85	29.84		
6.71	27.72	9.62	29.92		
6.37	28.03	9.44	30.16		
6.13	28.28	9.06	30.66		
5.82	28.35	8.87	30.73		
5.50	28.77	8.58	31.16		
5.25	29.11	8.27	31.42		
4.92	29.57	8.00	31.80		
		7.75	32.14		
		7.46	32.21		
		7.34	32.32		
		7.12	32.75		
		6.95	33.13		
		6.78	33.31		
		6.52	33.65		
		6.28	33.97		
		6.03	34.29		
		5.83	34.50		
		5.69	34.64		
		5.56	34.79		

	5.44	34.98	
	5.34	35.06	
	5.12	35.44	
	4.94	35.66	

Table S8 Experimental weight fraction data for the systems composed of $N_{111}C3S$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

K_3PO_4		K_2HPO_4		K_2CO_3	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
46.56	5.85	39.90	9.29	24.36	14.12
38.97	8.05	36.08	11.23	12.54	19.46
33.31	10.88	32.89	13.11	3.29	28.28
28.38	13.94	28.97	16.52		
23.63	16.46	26.99	17.65		
20.35	17.67	24.28	20.04		
17.93	19.50	22.82	20.84		
15.94	21.16	20.78	22.69		
14.23	22.39	19.18	24.09		
12.49	23.95	17.76	25.38		
11.28	25.19	16.58	26.31		
10.21	26.30	15.59	27.25		
9.37	27.31	14.70	28.10		
8.65	28.37	13.83	28.71		
7.08	30.06	12.85	29.85		
5.78	31.59	12.18	30.47		
5.14	32.86	11.60	30.96		
2.22	37.89	10.88	31.86		
		10.44	32.26		
		9.84	33.00		
		9.50	33.35		
		9.13	33.63		
		8.70	34.30		
		8.29	34.87		
		7.87	35.19		
		7.57	35.56		
		7.25	35.94		
		6.95	36.28		
		6.69	36.63		
		6.38	37.12		
		6.22	37.18		
		5.97	37.63		
		5.76	37.94		
		5.63	38.05		
		5.45	38.27		
		5.30	38.54		

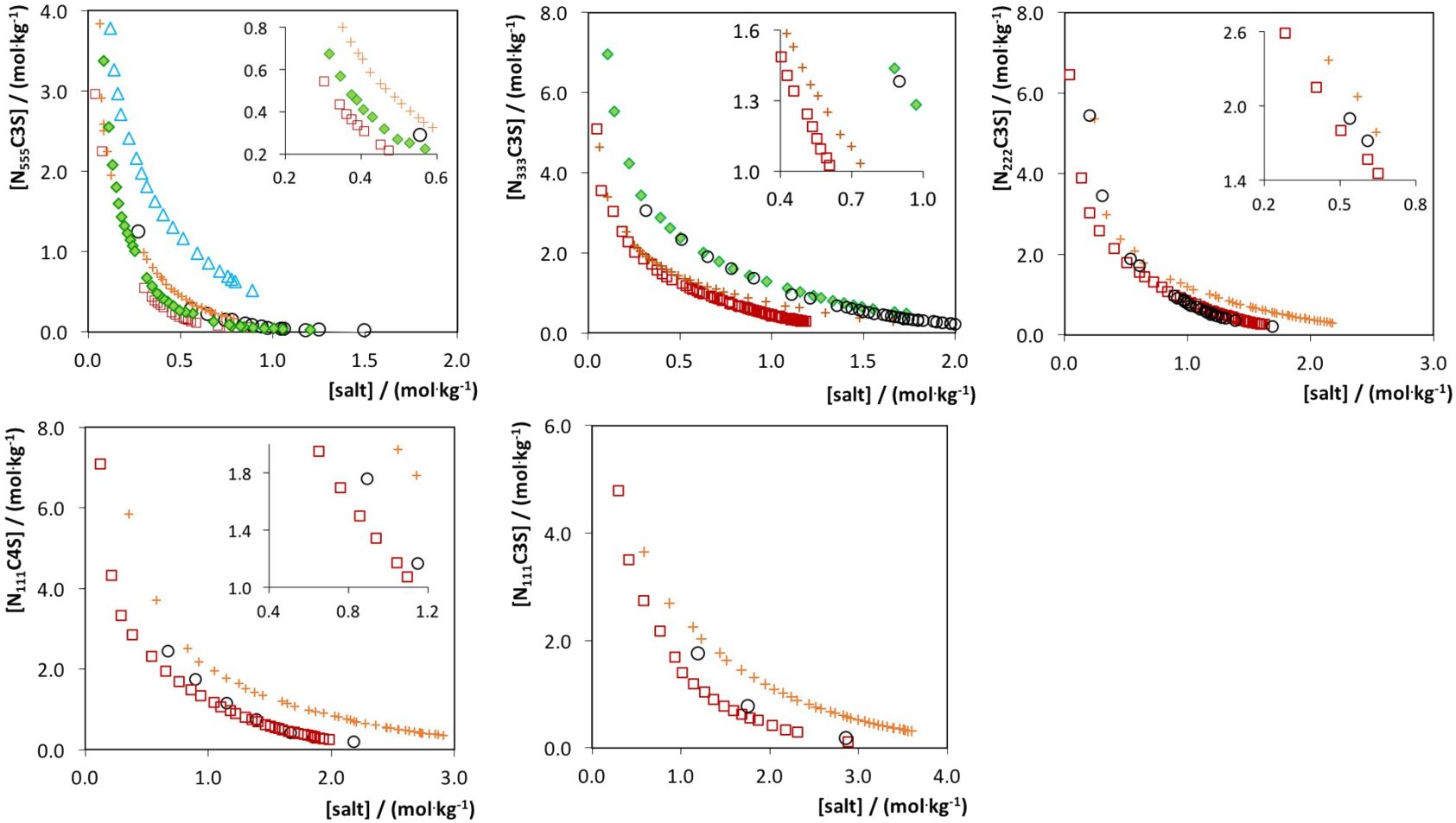

Fig. S1 Salt anion effect in the phase diagrams of ternary systems composed of water, ZIs, and the following potassium-based salts: K_3PO_4 (□), $K_3C_6H_5O_7$ (◆), K_2CO_3 (⛓), K_2HPO_4 (+) and KH_2PO_4 (❐).

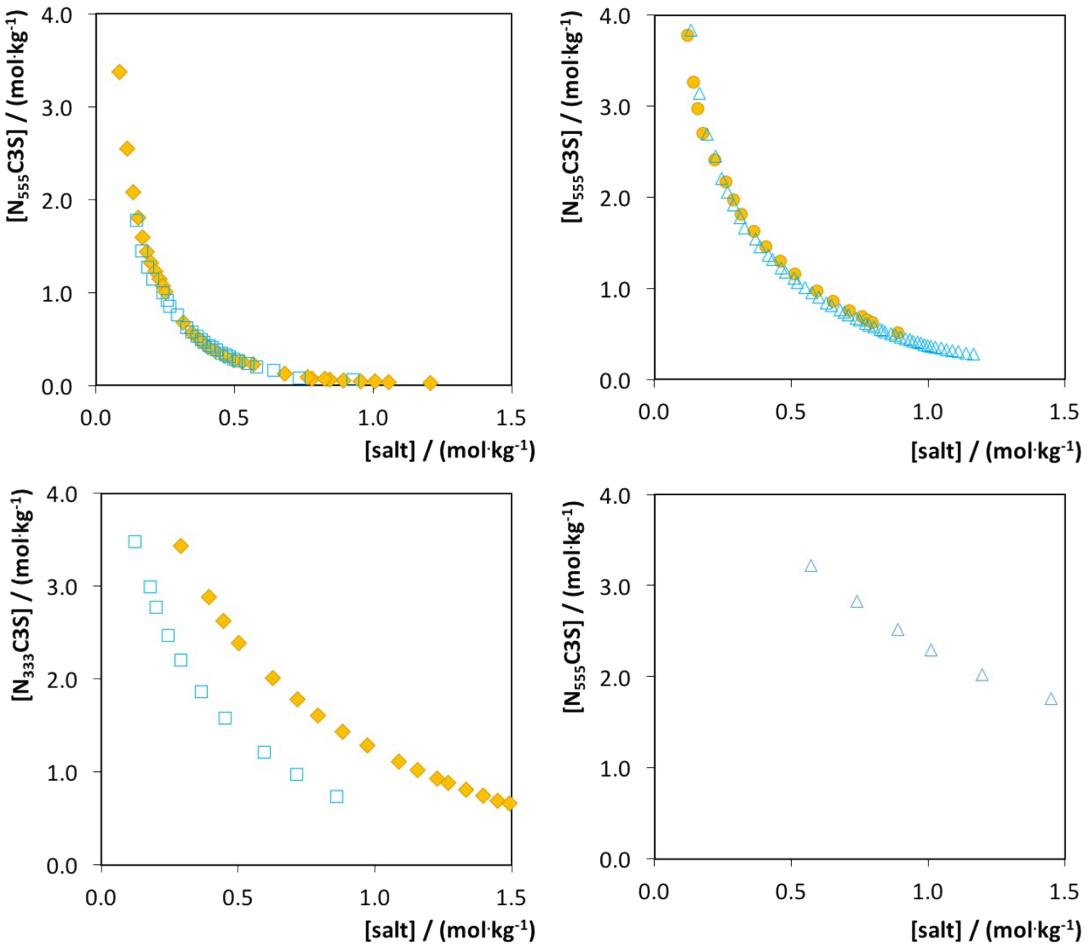

Fig. S2 Cation salt effect in the phase diagrams of ternary systems composed of water, ZIs, and the following salts: $Na_3C_6H_5O_7$ (□), $K_3C_6H_5O_7$ (◆), NaH_2PO_4 (❐) and KH_2PO_4 (ᘐ).

Table S9 Experimental weight fraction data for the systems composed of ZI (1) + K_3PO_4 (2) + H_2O (3) at 35 °C and 45 °C and atmospheric pressure.

$N_{555}C3S$				$N_{333}C3S$			
35 °C		45 °C		35 °C		45 °C	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
45.40	2.09	45.96	1.77	49.55	2.01	57.81	0.98
38.13	2.70	35.71	2.41	39.28	3.72	50.93	1.87
29.22	3.68	31.21	2.86	36.10	5.09	40.96	3.42
25.11	4.22	27.20	3.44	32.62	6.15	38.42	4.04
21.65	4.69	24.88	4.05	32.06	6.30	36.05	4.55
19.13	5.27	17.74	4.98	30.02	7.15	33.06	5.78
17.70	5.59	16.60	5.26	29.07	7.90	30.47	6.93
16.42	5.90	15.81	5.38	28.77	7.73	28.34	7.68
13.40	6.71	14.52	5.74	27.21	8.48	25.42	9.29
12.73	7.04	12.83	5.93	25.94	9.42	24.11	9.67
12.12	7.18	10.57	6.77	25.64	9.19	22.12	10.68
11.43	7.33	9.72	6.85	24.44	9.81	19.88	12.16
10.45	7.64	9.08	7.27	23.15	10.74	18.14	13.17
10.18	7.85	8.28	7.43	22.20	11.16	16.90	13.73
9.38	8.16	7.69	7.48	20.41	12.04	15.49	14.64
8.85	8.47	7.32	7.93	18.92	12.85	14.41	15.24
8.32	8.77	6.99	7.82	17.73	13.40	13.44	15.81
7.77	8.90	6.68	8.20	17.09	13.80	12.51	16.41
7.44	9.23	6.35	8.45	16.55	14.07	11.71	16.92
7.16	9.13	5.89	8.75	15.93	14.42	11.01	17.41
6.98	9.33	5.55	9.08	15.46	14.68	10.25	17.93
6.71	9.40	5.27	9.11	14.80	15.24	9.73	18.19
6.53	9.47	5.11	9.30	14.36	15.42	9.06	18.67
6.38	9.56	4.85	9.32	13.94	15.57	8.64	18.83
6.18	9.88	4.68	9.55	13.60	15.79	8.48	18.85
5.89	10.11			13.14	15.89	7.97	19.34
5.65	10.05			12.47	16.29	7.55	19.62
5.47	10.22			12.22	16.34	6.95	20.20
5.26	10.45			11.90	16.61	6.59	20.46
				11.48	16.75	6.46	20.50
				11.08	17.31	5.53	21.50
				10.80	17.22		
				10.65	17.35		
				10.24	17.66		
				10.09	17.73		
				9.91	17.86		
				9.59	18.07		
				9.26	18.30		

		8.97	18.46	
		8.69	18.55	
		8.33	18.81	
		8.14	19.02	
		8.06	19.05	
		7.84	19.17	
		7.50	19.46	
		7.43	19.46	
		7.34	19.49	
		7.21	19.62	
		7.07	19.73	
		7.00	19.79	

Table S10 Experimental weight fraction data for the systems composed of ZI (1) + K_3PO_4 (2) + H_2O (3) at 35 °C and 45 °C and atmospheric pressure.

$N_{222}C3S$				$N_{111}C4S$			
35 °C		45 °C		35 °C		45 °C	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
56.67	2.51	44.99	4.14	54.55	2.59	47.95	4.17
38.52	5.61	40.40	5.46	45.20	5.18	40.44	5.64
35.58	6.85	37.02	6.46	40.37	7.13	35.35	8.54
33.03	7.95	34.64	7.49	33.63	9.66	31.26	10.57
29.85	9.86	32.72	8.40	29.62	12.02	29.41	11.28
28.10	10.56	30.81	9.29	25.44	14.91	25.39	14.02
25.77	12.10	29.45	9.87	23.09	16.31	22.14	16.14
23.84	13.46	28.00	10.45	21.03	17.43	19.34	18.39
22.75	13.79	25.32	12.56	18.82	18.86	17.52	19.78
20.67	15.33	23.83	12.82	17.01	20.12	16.05	20.87
19.71	15.66	22.92	13.23	15.49	21.21	14.66	21.85
18.05	16.95	21.61	14.28	14.25	22.03	12.91	23.35
16.95	17.46	20.89	14.62	13.64	22.22	12.54	23.38
16.23	17.69	19.60	15.60	11.83	24.07	11.47	24.41
15.14	18.61	18.66	16.22	11.30	24.31	10.79	24.88
14.05	19.28	18.08	16.30	10.54	24.90	9.70	26.09
12.95	19.64	17.20	17.02	9.74	25.58	9.21	26.39
12.29	20.51	16.79	17.18	9.31	25.83	7.92	27.96
12.01	20.57	16.16	17.49	8.68	26.36	7.67	28.00
11.67	20.65	15.34	18.23	8.18	26.80	7.07	28.62
11.03	21.11	14.66	18.35	7.51	27.56	6.45	29.37
10.60	21.55	13.92	19.02			6.11	29.65
10.26	21.80	13.31	19.29			5.75	30.03
10.05	21.79	13.01	19.40				
9.45	22.59	12.29	20.26				
9.26	22.56	11.81	20.38				
8.83	23.06	11.14	20.87				
8.68	23.06	10.38	21.51				
8.52	23.06	10.10	21.45				
8.29	23.13	9.53	22.03				
7.81	23.88	9.02	22.37				
7.54	23.88	8.56	22.84				
		7.96	23.15				

Table S11 Experimental weight fraction data for the systems composed of $N_{111}C3S$ (1) + K_3PO_4 (2) + H_2O (3) at 35 °C and 45 °C and atmospheric pressure.

35 °C		45 °C	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**
50.05	4.95	49.83	5.37
39.60	8.45	43.03	7.25
32.80	10.90	38.41	9.11
27.25	14.79	35.25	10.40
23.43	16.98	30.76	13.10
20.30	19.16	25.44	16.84
17.60	21.33	22.76	18.50
15.28	22.98	19.28	21.23
12.87	24.99	16.62	23.18
11.10	26.54	14.79	24.46
9.09	28.57	13.27	25.44
7.10	30.71	12.00	26.41
6.52	31.21	10.62	27.56
		8.79	29.33
		7.87	30.17
		6.60	31.56

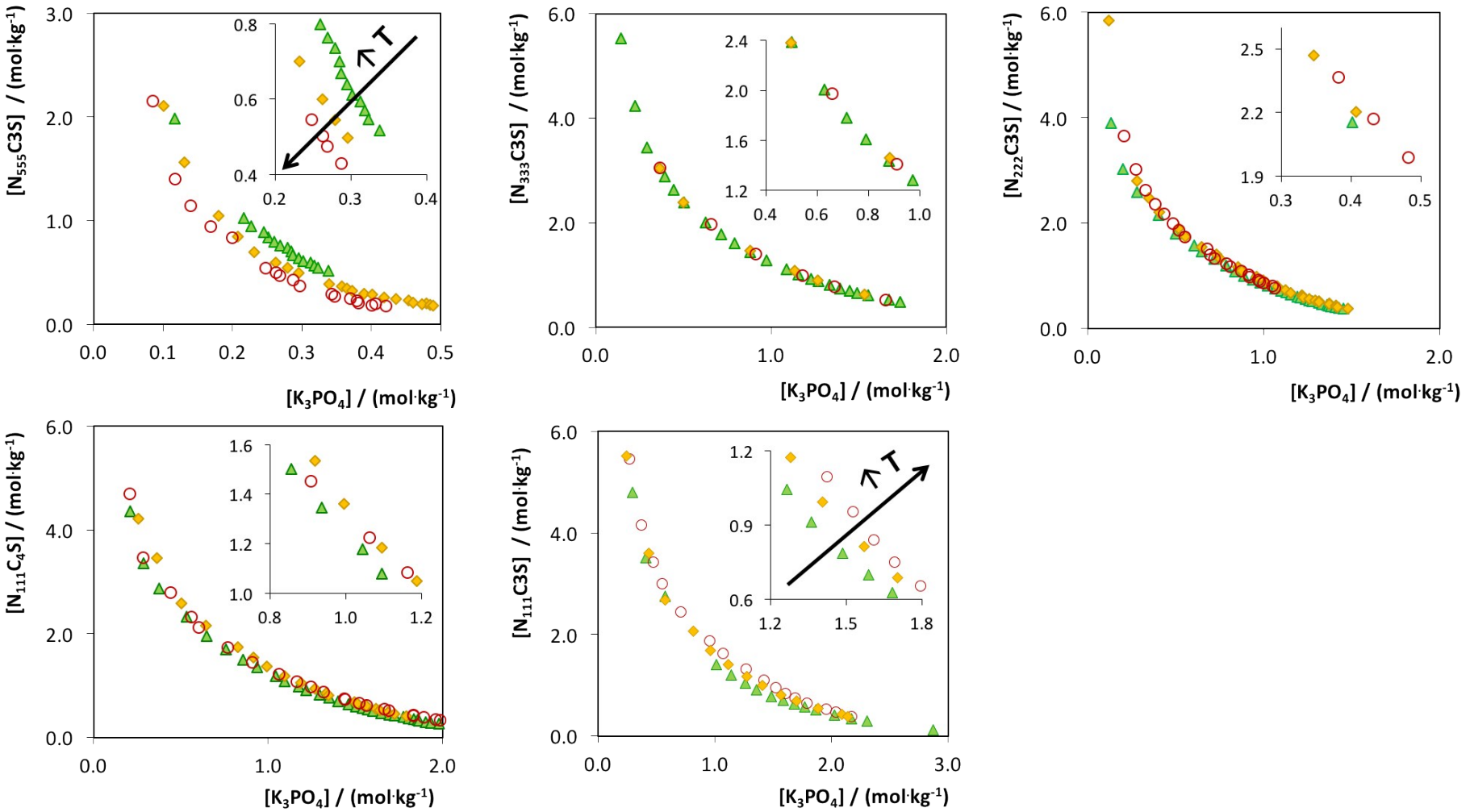

Fig. S3 Temperature effect in the phase diagrams of the ternary systems composed of ZI + K_3PO_4 + water at 25 ˚C (□), 35 ˚C (✹), and 45 ˚C (○).

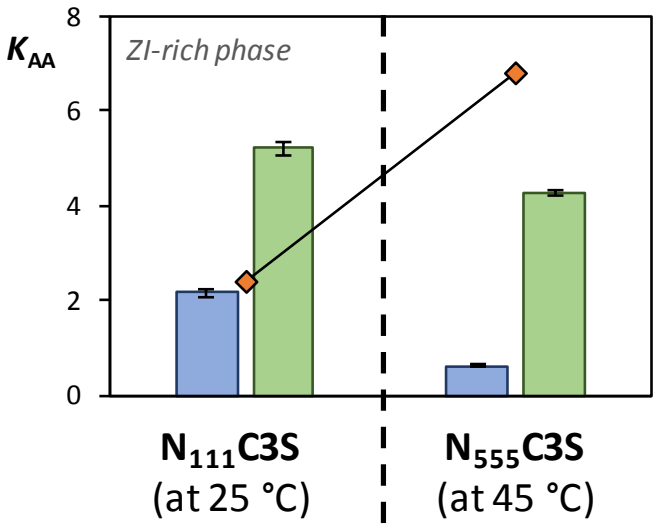

Fig. S4 Partition coefficient (K_{AA}) of L-tryptophan (green bars) and glycine (blue bars) in N_{111}C3S- and N_{555}C3S-based ABS at 25 °C and 45 °C, respectively, and selectivity (◆).

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