SUPPLEMENTARY INFORMATION

The pH effect on the formation of deep-eutectic-solvent-based aqueous biphasic systems

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Table S1. Experimental binodal weight fraction (wt %) data for the systems composed of $K_3C_6H_5O$ or $K_3C_6H_5O$/ $C_6H_8O_7$ (1) + $[N_{4444}]Cl$ (2) + H_2O (3) at 298.15 K and atmospheric pressure.

pH 5		**pH 7**		**pH 9**	
*w*1	*w*2	*w*1	*w*2	*w*1	*w*2
4.50	54.48	5.45	47.02	3.08	53.89
5.08	51.33	6.27	43.50	4.50	49.98
8.09	45.63	7.44	39.98	6.48	42.88
10.95	40.26	8.67	37.43	7.53	40.32
13.46	36.30	10.84	33.06	9.31	36.04
15.32	32.67	12.08	30.91	12.15	31.22
17.05	30.13	13.91	27.79	13.51	29.08
20.36	26.01	16.36	24.29	16.04	25.44
23.39	22.43	17.33	23.04	17.70	23.42
26.43	18.96	18.52	21.36	18.82	21.83
30.57	15.66	19.75	19.99	21.47	18.79
32.63	13.12	20.75	18.62	22.63	17.49
32.65	13.51	21.43	17.82	23.65	16.32
34.58	11.58	22.65	16.41	24.72	15.26
36.72	9.60	23.46	15.48	26.74	13.16
39.08	7.45	24.48	14.29	27.54	12.35
		25.50	12.76	28.19	11.70
		26.40	11.93	29.16	10.81
		27.33	11.06	29.98	10.07
		28.76	9.60	31.23	8.99
		30.04	8.42	32.00	8.36
		30.82	7.71		
		32.20	7.12		
		34.25	6.43		

Table S2. Experimental binodal weight fraction (wt %) data for the systems composed of $K_3C_6H_5O$ or $K_3C_6H_5O$/ $C_6H_8O_7$ (1) + $[N_{4444}]$Cl:ethanol (2:1) (2) + H_2O (3) at 298.15 K and atmospheric pressure.

pH 5		**pH 7**		**pH 9**	
*w*1	*w*2	*w*1	*w*2	*w*1	*w*2
9.77	46.90	6.22	49.91	4.83	46.23
11.10	41.58	7.74	43.59	5.52	42.69
14.78	34.43	11.46	35.23	9.22	36.44
18.70	28.20	12.84	32.15	9.91	34.77
24.21	21.25	18.01	24.02	11.82	31.65
29.50	15.51	20.48	21.00	13.04	29.88
		22.53	18.13	14.06	28.35
		24.51	16.07	15.80	25.58
		25.69	14.51	17.05	24.00
		25.91	14.12	18.14	22.59
		27.42	12.59	19.31	21.09
		28.88	11.04	20.58	19.65
		30.62	9.66	21.37	18.59
		31.15	9.11	23.24	16.49
				23.71	15.91
				24.45	15.06
				25.09	14.34
				25.71	13.67
				26.45	12.97
				27.66	11.74

Table S3. Experimental binodal weight fraction (wt %) data for the systems composed of $K_3C_6H_5O$ or $K_3C_6H_5O$/ $C_6H_8O_7$ (1) + $[N_{4444}]$Cl:ethanol (1:1) (2) + H_2O (3) at 298.15 K and atmospheric pressure.

pH 5		**pH 7**		**pH 9**	
*w*1	*w*2	*w*1	*w*2	*w*1	*w*2
6.84	50.49	4.57	49.45	3.39	51.91
10.87	41.97	7.45	42.97	4.73	46.12
14.12	35.90	9.74	35.66	5.97	42.41
19.10	28.83	11.36	31.92	7.88	38.33
26.63	20.11	13.33	28.72	11.57	32.86
36.02	10.69	15.77	25.64	12.32	31.50
		17.56	22.84	14.03	28.37
		20.77	18.98	16.17	25.60
		23.53	15.86	20.18	20.33
		24.97	14.41	22.21	18.37
		26.04	13.14	23.00	17.46
		27.79	11.23	24.16	16.27
		28.77	10.10	24.90	15.45
		29.75	9.30	25.57	14.65
		30.26	8.77	26.03	14.05

Table S4. Experimental binodal weight fraction (wt %) data for the systems composed of $K_3C_6H_5O$ or $K_3C_6H_5O$/ $C_6H_8O_7$ (1) + $[N_{4444}]$Cl:ethanol (1:2) (2) + H_2O (3) at 298.15 K and atmospheric pressure.

pH 5		**pH 7**		**pH 9**	
*w*1	*w*2	*w*1	*w*2	*w*1	*w*2
8.20	48.87	2.37	56.36	4.46	47.96
12.31	40.46	5.41	47.44	5.66	45.08
21.08	28.30	10.06	36.90	7.98	41.28
25.97	22.50	14.35	29.92	8.64	38.07
31.94	15.92	17.33	26.05	9.56	36.18
		20.17	22.53	12.59	31.27
		21.42	20.62	13.88	29.28
		22.57	19.01	16.51	25.61
		23.92	17.22	17.32	24.27
		25.56	15.07	19.62	21.52
		26.50	14.03	21.56	19.06
		27.24	13.41	22.61	17.86
		27.98	12.50	24.01	16.23
		29.31	11.28	25.39	14.71
		30.06	10.67	26.68	13.32
		30.85	9.88	27.31	12.67
				27.96	11.99
				29.18	10.85
				29.97	10.12
				31.05	9.19
				32.45	8.09

Table S5. Experimental binodal weight fraction (wt %) data for the systems composed of $K_3C_6H_5O$ or $K_3C_6H_5O$/ $C_6H_8O_7$ (1) + ethanol (2) + H_2O (3) at 298.15 K and atmospheric pressure.

pH 5		**pH 7**		**pH 9**	
*w*1	*w*2	*w*1	*w*2	*w*1	*w*2
42.45	11.75	46.64	6.56	1.36	63.43
33.69	17.19	40.66	8.82	2.36	55.32
27.61	22.85	35.16	11.47	3.23	51.84
25.30	24.62	28.37	16.08	4.18	49.47
21.51	28.35	25.26	19.10	6.15	44.73
19.36	30.77	21.65	23.82	7.48	41.55
17.59	32.60	20.82	24.77	8.74	39.52
15.40	35.18	19.77	25.86	11.62	34.80
14.27	36.24	19.19	26.64	12.91	32.78
12.87	38.13	17.99	28.18	14.36	30.83
11.72	40.12	17.27	29.49	15.65	28.99
10.84	41.10	14.81	31.99	16.79	27.41
10.73	41.48	12.73	34.73	17.71	26.10
9.84	42.87	11.67	35.71	19.74	23.49
9.27	43.42	10.69	37.63	20.50	22.49
8.57	44.43	10.13	38.22	21.42	21.34
8.17	45.31	9.13	40.68	22.21	20.33
		8.91	40.82	23.89	18.32
		8.44	41.85	24.74	17.35
		7.45	43.65	25.73	16.29
		7.27	44.04	26.61	15.25
		6.40	45.55	27.57	14.24
		5.96	46.63	28.87	13.13
				30.43	11.80

Table S6. Experimental binodal weight fraction (wt %) data for the systems composed of $K_3C_6H_5O$ or $K_3C_6H_5O$/ $C_6H_8O_7$ (1) + $[N_{4444}]Cl$:*n*-propanol (2:1) (2) + H_2O (3) at 298.15 K and atmospheric pressure.

pH 5		**pH 7**		**pH 9**	
*w*1	*w*2	*w*1	*w*2	*w*1	*w*2
5.97	52.18	3.54	54.93	4.42	48.99
11.24	42.05	6.75	47.36	5.75	44.76
12.37	39.15	9.27	40.32	7.30	40.53
16.07	33.02	13.62	30.89	8.87	38.03
22.54	24.68	16.16	26.06	9.78	35.57
25.69	20.80	17.08	24.58	11.72	32.00
29.09	16.75	20.59	20.12	13.32	29.58
33.25	12.42	21.16	19.41	14.31	28.15
47.35	0.70	23.49	16.15	15.98	25.56
		24.11	15.11	23.34	16.90
		26.09	12.88	24.60	15.14
		26.89	11.94	25.65	13.75
		27.60	11.18	25.92	13.21
		28.62	10.33	26.49	12.53
		29.12	9.61	27.24	11.79
		29.81	9.00	28.74	10.61
				29.06	9.99
				29.92	9.31
				31.28	8.36
				32.63	7.31
				32.90	6.88
				34.33	6.05

Table S7. Experimental binodal weight fraction (wt %) data for the systems composed of $K_3C_6H_5O$ or $K_3C_6H_5O$/ $C_6H_8O_7$ (1) + $[N_{4444}]Cl$:*n*-propanol (1:1) (2) + H_2O (3) at 298.15 K and atmospheric pressure.

pH 5		**pH 7**		**pH 9**	
*w*1	*w*2	*w*1	*w*2	*w*1	*w*2
5.59	53.09	3.36	53.96	3.69	54.69
8.90	45.18	6.19	45.11	5.66	45.21
12.33	38.32	8.75	39.87	7.85	40.02
14.13	34.76	10.35	34.07	9.60	36.14
17.59	29.17	14.52	27.65	11.91	31.51
20.45	25.38	15.46	25.60	13.00	28.82
21.06	22.78	17.29	22.89	14.56	25.63
24.40	18.89	18.41	21.04	16.72	23.08
26.94	15.84	19.95	18.71	19.38	19.69
30.35	12.73	21.08	17.15	21.20	17.17
		21.96	15.99	23.38	14.73
		23.14	14.70	24.67	12.66
		23.84	13.80	26.02	11.31
		24.08	13.28	26.94	10.40
		25.08	12.27	27.62	9.76
		25.77	11.76	29.65	8.07
		26.62	10.70	30.06	7.70
		27.62	9.66	30.71	7.21
				31.19	6.83
				32.47	6.00
				34.11	5.06
				34.44	4.80

Table S8. Experimental binodal weight fraction (wt %) data for the systems composed of $K_3C_6H_5O$ or $K_3C_6H_5O$/ $C_6H_8O_7$ (1) + $[N_{4444}]Cl$:*n*-propanol (1:2) (2) + H_2O (3) at 298.15 K and atmospheric pressure.

pH 5		**pH 7**		**pH 9**	
*w*1	*w*2	*w*1	*w*2	*w*1	*w*2
6.33	52.21	3.22	54.08	26.80	9.47
8.45	45.80	6.38	44.43	25.1	10.7
11.41	38.95	7.32	38.53	23.4	12.1
13.63	34.33	10.77	32.02	22.4	13.1
16.79	29.22	13.20	26.86	22.0	13.6
19.53	24.84	14.14	25.00	21.6	14.2
21.47	21.94	16.02	22.55	20.6	15.4
23.03	19.78	18.16	19.09	20.4	15.8
25.04	17.32	18.56	18.03	19.6	16.6
26.15	15.81	19.51	16.83	18.4	18.5
28.26	13.71	20.31	15.75	17.8	19.7
28.83	13.07	21.18	14.73	16.64	21.97
29.57	12.14	22.21	13.40	14.94	24.66
30.39	11.40	22.99	12.64	13.6	26.0
32.47	9.50	23.63	12.01	13.0	27.2
		24.06	11.40	11.39	30.03
		24.53	10.65	9.3	33.1
		25.71	9.57	7.88	37.21
				6.7	39.6
				5.7	44.5
				4.1	54.4

Table S9. Experimental binodal weight fraction (wt %) data for the systems composed of $K_3C_6H_5O$ or $K_3C_6H_5O$/ $C_6H_8O_7$ (1) + *n*-propanol (2) + H_2O (3) at 298.15 K and atmospheric pressure.

pH 5		**pH 7**		**pH 9**	
*w*1	*w*2	*w*1	*w*2	*w*1	*w*2
46.43	3.48	47.64	4.55	26.21	5.28
38.45	5.35	36.94	6.02	20.27	7.23
33.70	6.86	25.69	7.17	18.68	7.84
28.94	8.26	22.25	9.07	17.60	8.62
25.07	11.11	20.73	9.66	16.61	9.18
22.24	13.03	15.76	11.56	15.75	9.63
19.79	15.55	13.11	14.10	15.25	10.04
18.32	18.53	11.65	16.03	14.26	11.12
17.08	21.29	11.00	16.78	12.79	12.49
16.41	23.03	10.04	18.31	12.48	13.26
15.10	26.20	9.11	19.83	11.51	14.07
13.90	29.24	8.86	20.40	11.31	15.18
12.55	32.64	8.25	21.46	10.32	16.23
11.58	34.72	7.85	22.66	10.12	16.99
10.81	37.13	7.47	23.82	9.35	18.56
9.34	41.92	7.01	25.13	8.58	19.83
8.94	42.91	6.68	26.33	8.15	21.62
8.10	44.95	6.25	28.16	7.49	23.11
		6.13	28.52	7.13	24.87
		5.80	30.07	6.83	26.59
		5.50	31.16	5.81	30.00
		5.25	32.35	5.57	33.17
		4.32	34.80	4.20	39.41
		3.72	37.96	3.26	46.77
		3.22	41.00	2.20	52.70
				1.18	58.29

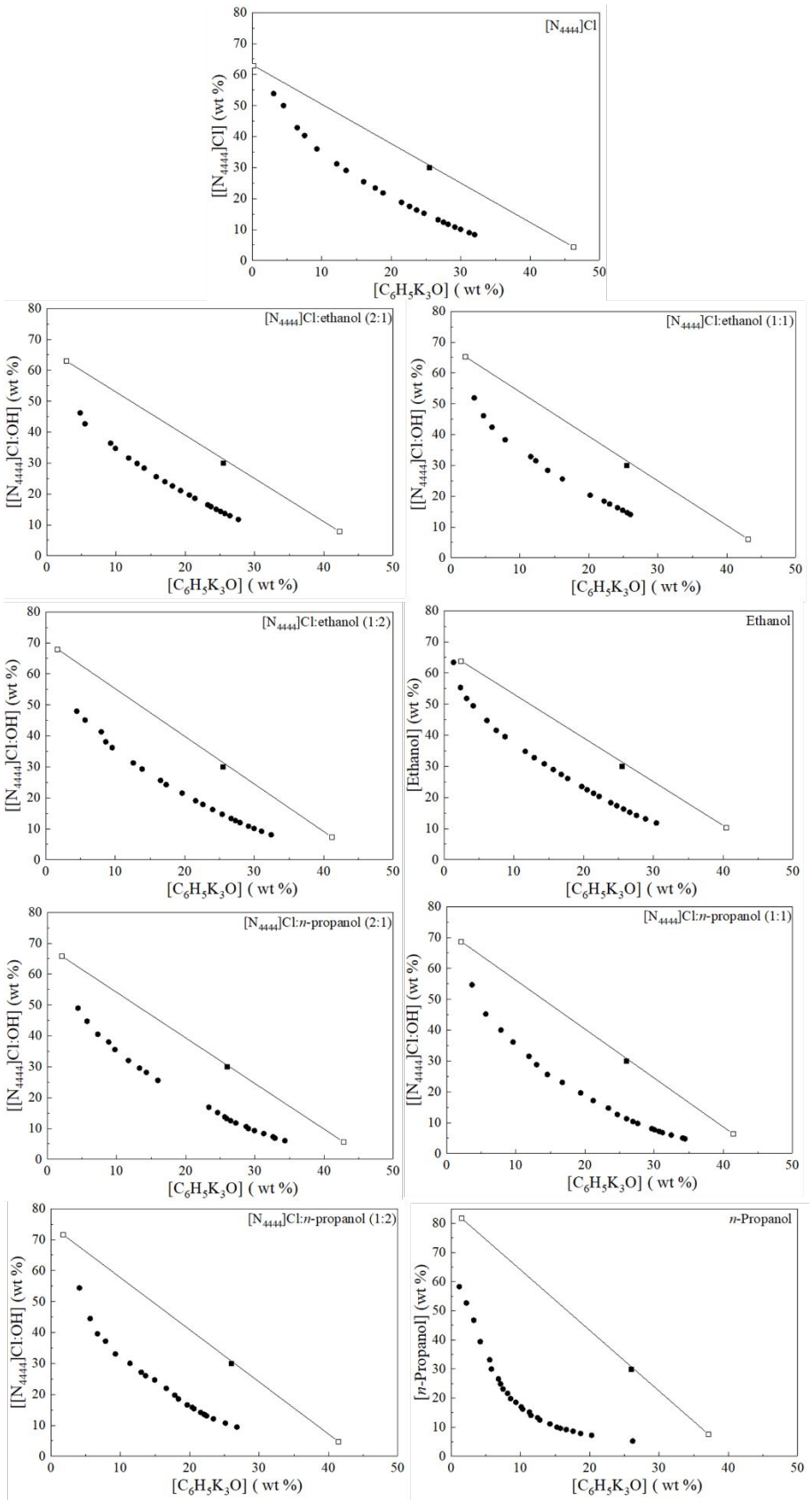

Figure S1. Phase diagrams for the ternary systems composed of: $K_3C_6H_5O$ + $[N_{4444}]Cl$ / ethanol/ *n*-propanol + water and the quaternary systems composed of: $K_3C_6H_5O$ + $[N_{4444}]Cl$ + ethanol/ *n*-propanol + water at 298 K and atmospheric pressure. Binodal curve (●), tie-line overall composition (■), and tie-line phases composition (□).

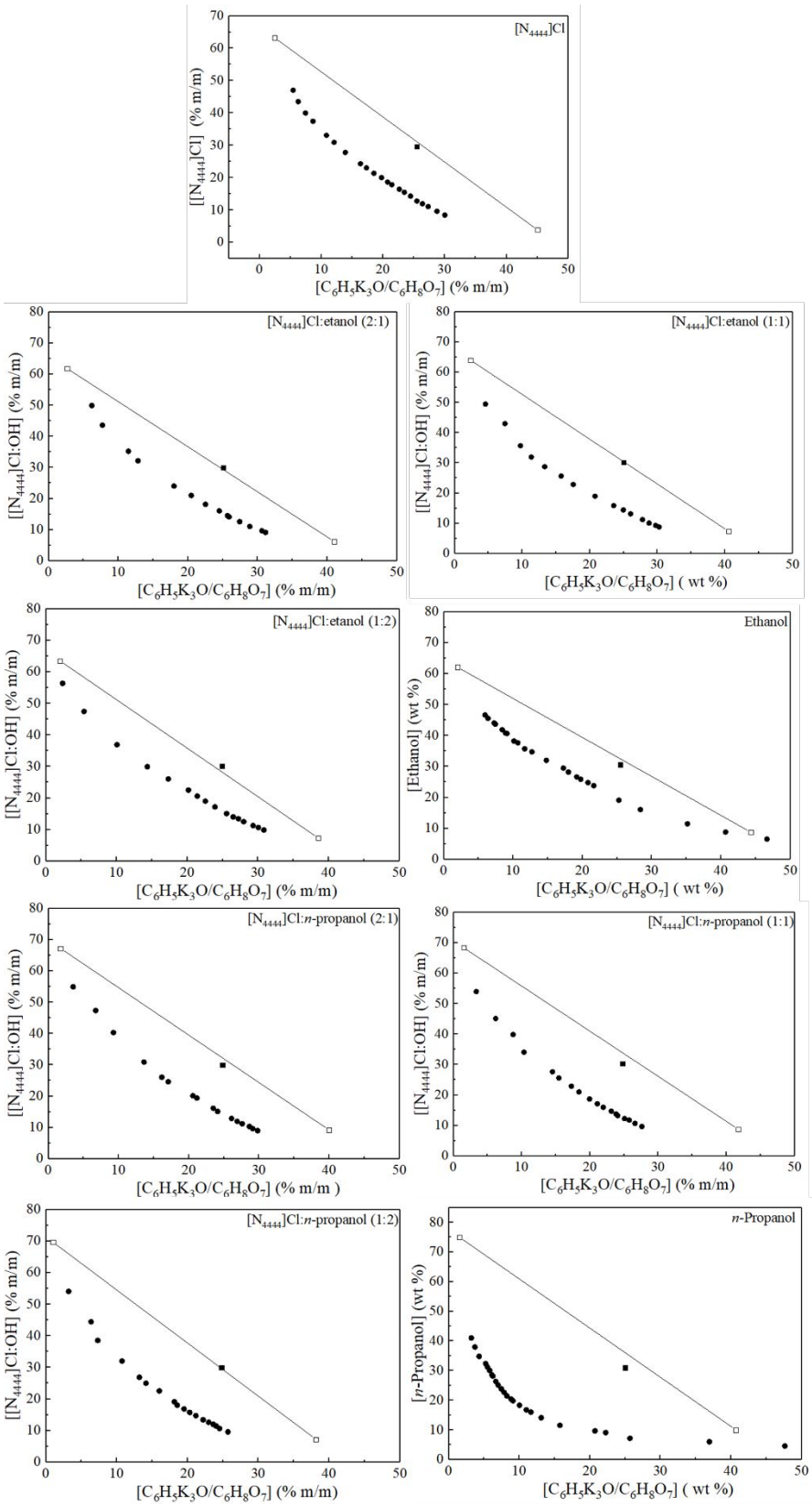

Figure S2. Phase diagrams for the ternary systems composed of $K_3C_6H_5O/C_6H_8O_7$ + $[N_{4444}]Cl$ / ethanol/ *n*-propanol + water and the quaternary systems composed of $K_3C_6H_5O/C_6H_8O_7$ + $[N_{4444}]Cl$ + ethanol/ *n*-propanol + water at pH 7, 298 K and atmospheric pressure. Binodal curve (●), tie-line overall composition (■), and tie-line phases composition (□).

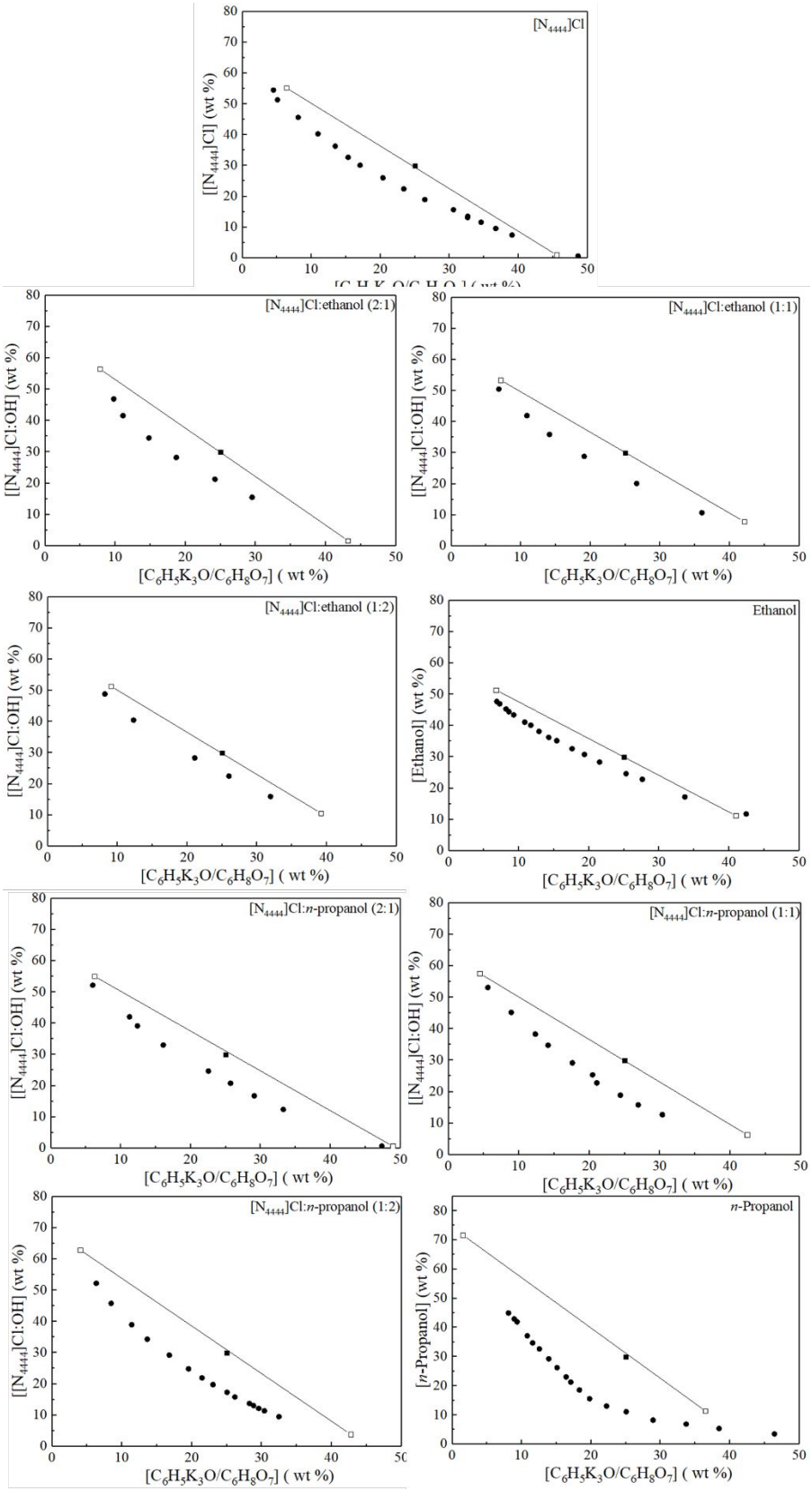

Figure S3. Phase diagrams for the ternary systems composed of $K_3C_6H_5O/C_6H_8O_7$ + $[N_{4444}]Cl$ / ethanol/ *n*-propanol + water and the quaternary systems composed of $K_3C_6H_5O/C_6H_8O_7$ + $[N_{4444}]Cl$ + ethanol/ *n*-propanol + water at pH 5, 298 K and atmospheric pressure. Binodal curve (●), tie-line overall composition (■), and tie-line phases composition (□).

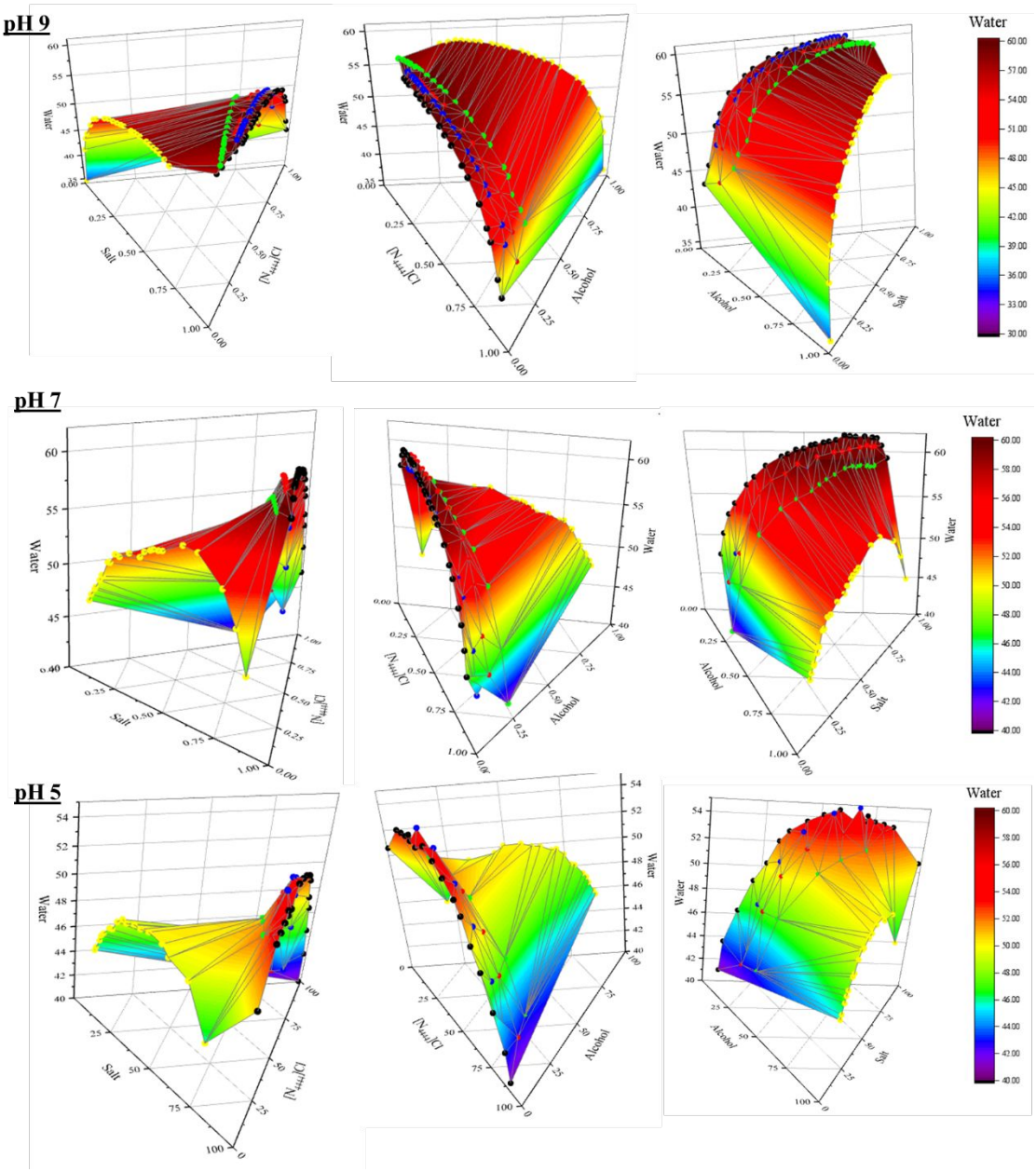

Figure S4. Phase diagrams at 298 K and atmospheric pressure of ABS composed of $[N_{4444}]Cl$: ethanol + $K_3C_6H_5O_7$ or $K_3C_6H_5O_7$ /$C_6H_8O_7$ + H_2O at different molar ratio of $N_{4444}Cl$: ethanol - 2:1 (●), 1:1 (■), 1:2 (▲); $[N_{4444}]Cl$ + $K_3C_6H_5O_7$ + H_2O (■) and ethanol + $K_3C_6H_5O_7$ + H_2O (◆).

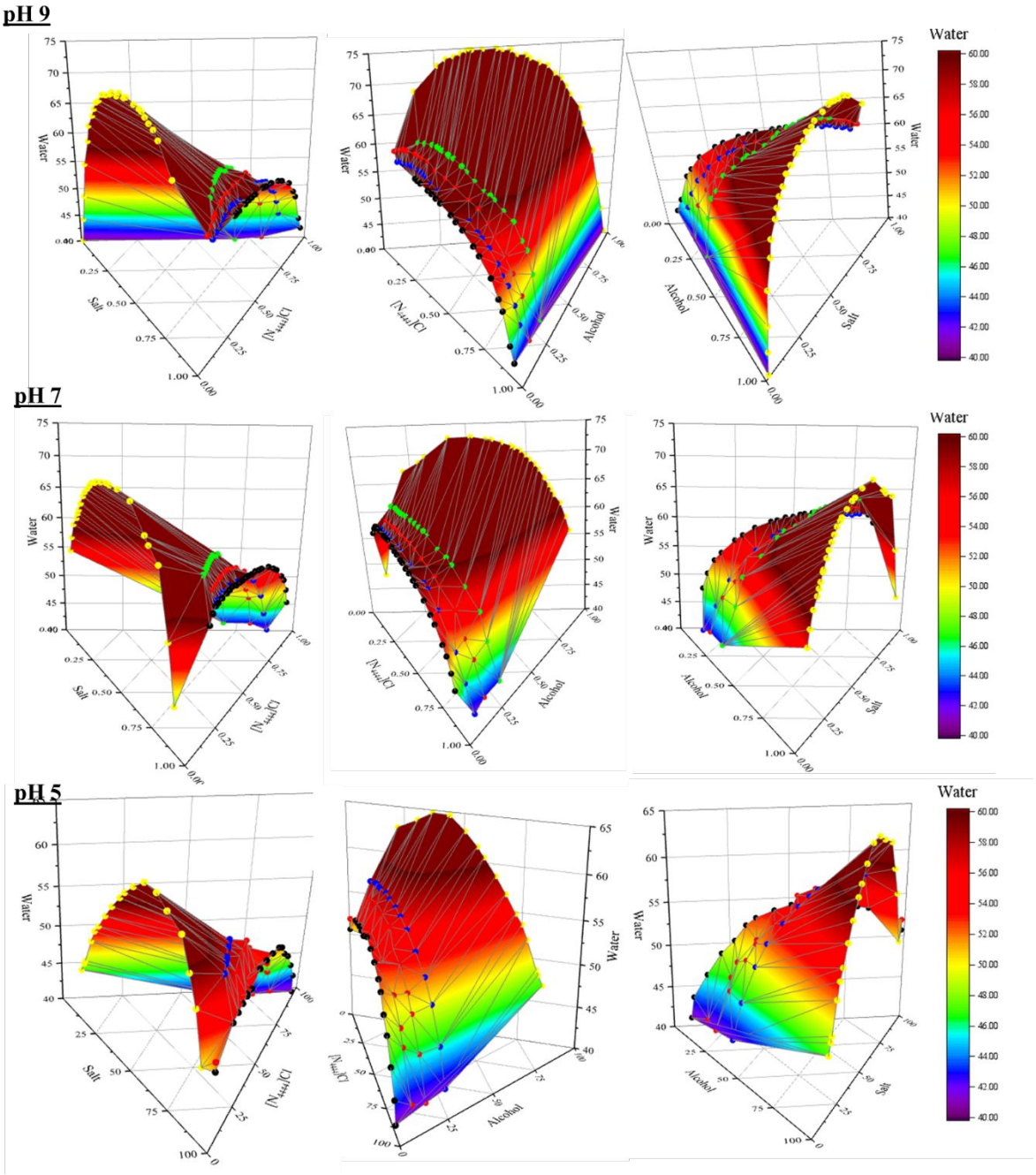

Figure S5. Phase diagrams at 298 K and atmospheric pressure of ABS composed of $[N_{4444}]Cl$:*n*-propanol + $K_3C_6H_5O_7$ or $K_3C_6H_5O_7$ /$C_6H_8O_7$ + H_2O at different molar ratio of $N_{4444}Cl$:*n*-propanol - 2:1 (●), 1:1 (■), 1:2 (▲); $[N_{4444}]Cl$ + $K_3C_6H_5O_7$ + H_2O (■) and *n*-propanol + $K_3C_6H_5O_7$ + H_2O (◆).

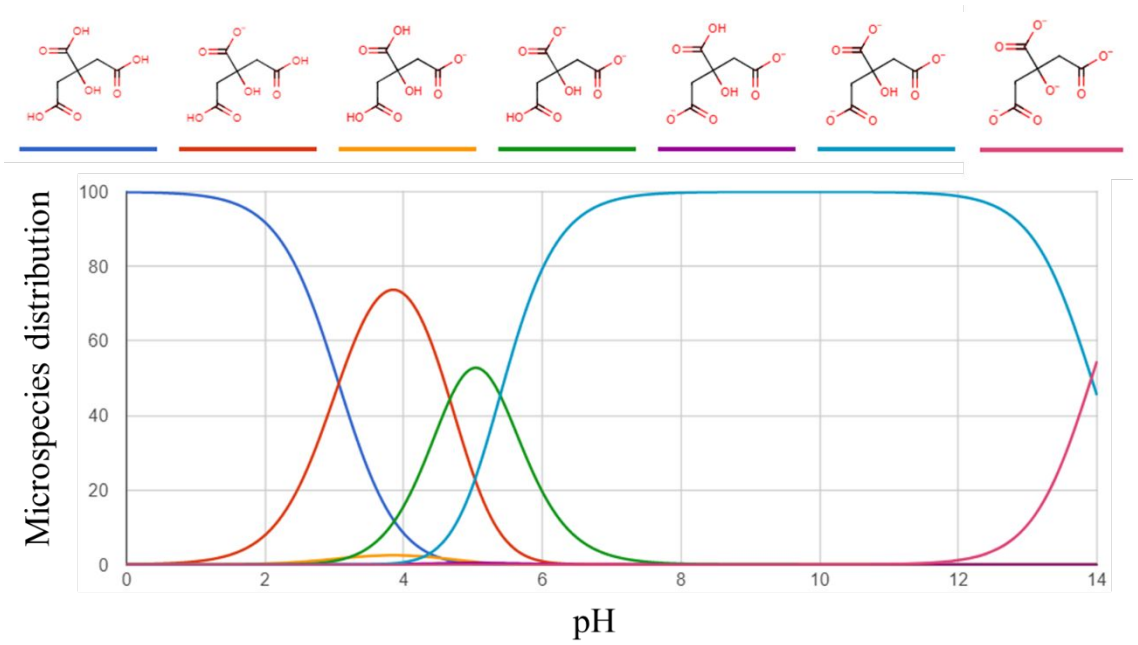

Figure S6. Chemical Speciation of $K_3C_6H_5O_7$ salt. [1]

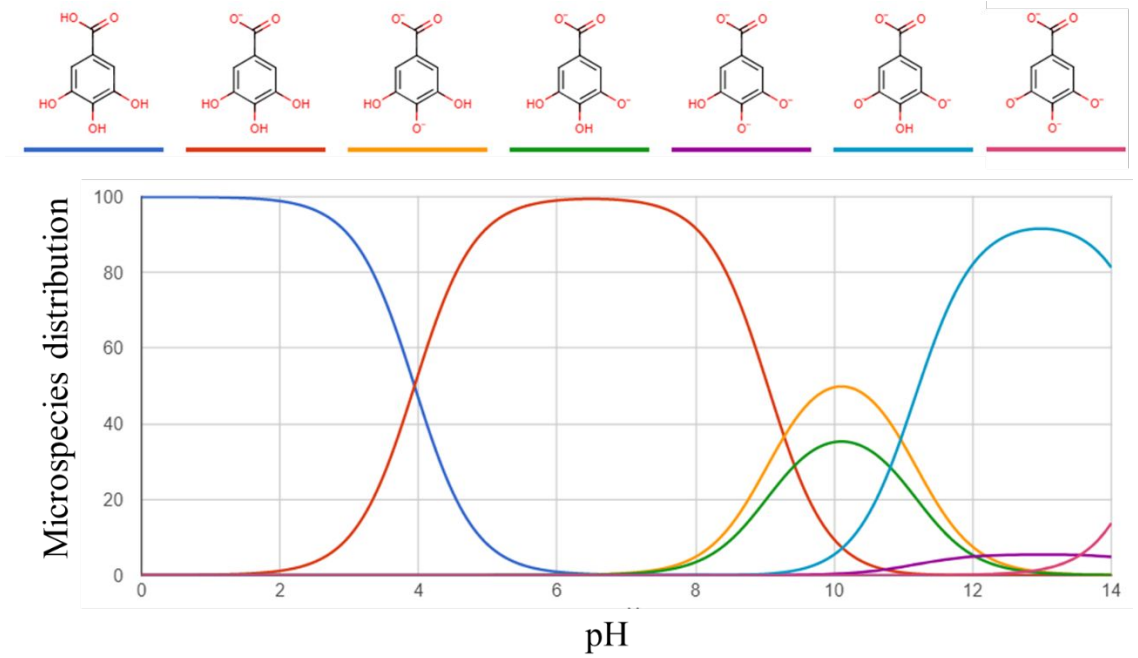

Figure S7. Chemical Speciation of gallic acid [1]

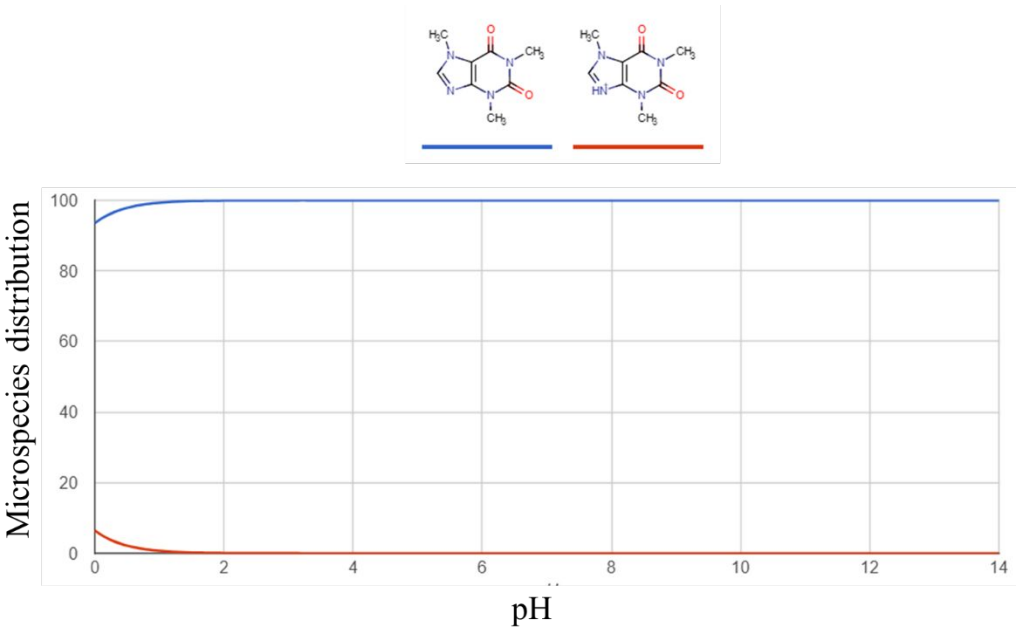

Figure S8. Chemical Speciation of caffeine. [1]

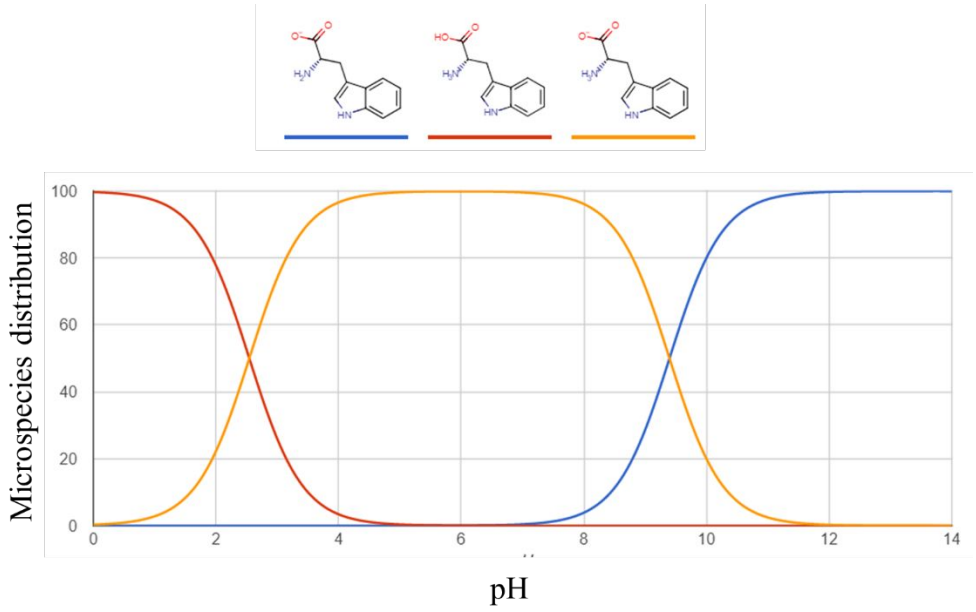

Figure S9. Chemical Speciation of L-tryptophan.[1]

Table S10. Biomolecules partition coefficient (*K*) and extraction efficiency percentage (*EE* %) to the top phase of ABS composed of $[N_{4444}]Cl$:OH + $K_3C_6H_5O_7$ or $K_3C_6H_5O_7/C_6H_8O_7$ + H_2O

OH molar fraction	*K*	*EE* %	*K*	*EE* %
Gallic Acid				
Ethanol	pH 9		pH 5	
0.0	20.2 ± 0.8	93.7 ± 0.2	20.5 ± 2.1	97.2 ± 0.4
0.33	21.7 ± 1.1	93.61 ± 0.3	19.2 ± 1.2	97.3 ± 0.2
0.50	23.4 ± 3.0	94.0 ± 0.8	19.6 ± 0.3	97.5 ± 0.1
0.67	22.2 ± 1.9	92.9 ± 0.6	16.1 ± 1.1	96.9 ± 0.2
1.0	0.7 ± 0.1	28.5 ± 2.4	1.0 ±0.3	70.1 ± 1.0
n-Propanol	pH 9		pH 5	
0.0	20.2 ± 0.8	93.7 ± 0.2	20.5 ± 2.1	96.7 ± 0.6
0.33	25.4 ± 1.9	94.5 ± 0.6	23.7 ± 0.2	96.4 ± 0.1
0.50	26.4 ± 1.0	94.7 ± 0.2	20.1 ± 1.5	94.8 ± 0.4
0.67	20.9 ± 2.0	92.5 ± 1.0	13.9 ± 0.2	91.7 ± 0.1
1.0	1.4 ± 0.1	44.6 ± 1.0	1.2 ± 0.2	33.1 ± 2.0
Caffeine				
Ethanol	pH 9		pH 5	
0.0	21.1 ± 0.3	93.9 ± 0.1	11.6 ± 0.2	93.3 ± 0.1
0.33	20.4 ± 0.2	93.3 ± 0.1	12.9 ± 0.0	93.4 ± 0.1
0.50	25.8 ± 0.3	94.5 ± 0.1	10.9 ± 0.1	91.7 ± 0.1
0.67	27.0 ± 0.6	94.1 ± 0.1	10.7 ± 0.0	91.4 ± 0.2
1.0	16.8 ± 0.9	90.7 ± 0.4	8.1 ± 0.0	87.6 ± 0.1
n-Propanol	pH 9		pH 5	
0.0	21.1 ± 0.3	93.9 ± 0.1	11.6 ± 0.2	93.3 ± 0.1
0.33	22.7 ± 0.5	93.8 ± 0.1	11.1 ± 0.2	92.3 ± 0.1
0.50	16.7 ± 0.2	91.0 ± 0.1	13.1 ± 0.4	92.2 ± 0.2
0.67	20.0 ± 0.1	92.3 ± 0.0	9.8 ± 0.2	88.5 ± 0.2
1.0	23.0 ± 0.1	90.8 ± 0.1	8.5 ± 0.1	78.7 ± 0.1
L-Tryptophan				
Ethanol	pH 9		pH 5	
0.0	21.3 ± 1.6	94.0 ± 0.4	5.0 ± 0.2	89.3 ± 0.3
0.33	19.5 ± 1.8	93.0 ± 0.6	5.9 ± 0.1	91.7 ± 0.1
0.50	21.7 ± 1.5	93.6 ± 0.4	5.2 ± 0.1	91.3 ± 0.2
0.67	24.5 ± 0.3	93.7 ± 0.1	3.6 ± 0.6	87.3 ± 1.7
1.0	3.9 ± 0.0	69.3 ± 0.1	1.1 0.2	71.4 ± 3.3
n-Propanol	pH 9		pH 5	
0.0	22.0 ± 0.5	94.2 ± 0.1	2.5 ± 0.1	75.0 ± 0.7
0.33	14.5 ± 2.0	90.7 ± 1.2	5.2 ± 0.8	85.5 ± 1.9
0.50	15.1 ± 1.2	91.0 ± 0.6	5.6 ± 0.4	83.5 ± 1.0
0.67	11.2 ± 0.7	86.9 ± 0.8	3.9 ± 0.3	75.5 ± 1.2
1.0	2.9 ± 0.0	62.8 ± 0.1	1.6 ± 0.9	49.3 ± 0.2

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