

Supporting Information

PERFORMANCE OF TETRAALKYLAMMONIUM-BASED IONIC LIQUIDS AS CONSTITUENTS OF AQUEOUS BIPHASIC SYSTEMS IN THE EXTRACTION OF OVALBUMIN AND LYSOZYME

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Table S1. HPLC conditions used for the identification and quantification of ovalbumin and lysozyme.

	Ovalbumin	Lysozyme
Eluent	50 mM sodium phosphate buffer (NaH ₂ PO ₄ /Na ₂ HPO ₄), 0.3 M NaCl at pH 7.0	Solvent A = 100 : 38.4 (Stock solution I:Stock solution II), Solvent B = Stock solution II; Stock solution I = aq. 0.01% TFAA solution, Stock solution I = 0.01% TFAA in ACN solution
Eluting conditions	Isocratically	Gradient†
Run time	45 min	40 min
Flow rate	0.5 mL.min ⁻¹	1.0 mL.min ⁻¹

†expressed as proportion of solvent A: 0 – 20 min, 100%; 20 – 21 min, 100 – 50%; 21 – 22 min, 50%; 22– 23 min, 50 – 100%; 23 – 45 min, 100%

Table S2. Experimental weight fraction data for the binodal curves of the ABS formed by [N₄₄₄₄]Br (1) + K₂HPO₄/KH₂PO₄ (2) at (25 ± 3)°C and pH 7.

w₁	w₂	w₁	w₂	w₁	w₂
57.61	0.66	26.02	8.44	18.65	12.04
56.69	1.27	25.58	8.29	18.48	12.28
50.73	1.14	25.29	8.63	18.33	12.18
49.63	1.96	25.15	8.59	18.01	12.64
46.55	1.84	24.88	8.92	17.84	12.52
45.76	2.46	24.59	8.82	17.57	12.92
43.10	2.32	24.35	9.12	17.38	12.78
42.32	2.98	24.22	9.07	17.10	13.20
40.66	2.86	23.94	9.42	16.85	13.01
40.08	3.38	23.67	9.31	16.55	13.48
38.64	3.25	23.39	9.66	16.41	13.37
38.10	3.75	23.16	9.57	16.18	13.73
37.10	3.65	22.92	9.87	15.94	13.53
36.45	4.27	22.65	9.76	15.73	13.86
35.42	4.15	22.41	10.08	15.53	13.68
34.67	4.88	22.31	10.04	15.35	13.99
34.18	4.81	22.10	10.31	15.28	13.93
33.80	5.19	21.87	10.19	15.22	14.04
33.33	5.12	21.67	10.46	15.10	13.93
32.90	5.55	21.56	10.40	14.92	14.23
32.06	5.41	21.33	10.71	14.78	14.10
31.66	5.82	21.21	10.65	14.70	14.24
31.18	5.74	20.98	10.97	14.60	14.14
30.28	6.70	20.75	10.85	14.50	14.32
29.94	6.62	20.53	11.14	14.39	14.22
29.75	6.83	20.43	11.08	14.21	14.53
29.57	6.79	20.26	11.32	14.06	14.39
29.24	7.16	20.10	11.24	13.98	14.54
28.82	7.05	19.92	11.49	13.89	14.45
28.73	7.16	19.74	11.39	13.79	14.61
28.52	7.11	19.58	11.63	13.75	14.56
28.13	7.54	19.52	11.59	13.65	14.73
27.88	7.47	19.37	11.81	13.56	14.63
27.46	7.95	19.22	11.72	13.37	14.97
27.03	7.82	19.06	11.94	13.20	14.78
26.70	8.20	18.94	11.87		
26.32	8.08	18.77	12.12		

Table S3. Experimental weight fraction data for the binodal curves of the ABS formed by [N₄₄₄₄]Cl (1) + K₂HPO₄/KH₂PO₄ (2), at (25 ± 3)°C and pH 7.

w₁	w₂	w₁	w₂
41.64	2.16	19.73	10.70
40.93	2.79	19.56	10.61
39.36	2.68	19.19	11.13
38.68	3.31	18.85	10.93
37.26	3.19	18.23	11.85
36.65	3.77	18.03	11.71
35.43	3.65	17.72	12.17
34.83	4.25	17.57	12.06
33.67	4.11	17.30	12.46
33.21	4.58	17.11	12.32
32.30	4.46	16.61	13.10
31.78	5.01	16.48	13.00
31.28	4.93	16.23	13.39
30.82	5.43	16.11	13.29
30.31	5.34	16.07	13.35
29.89	5.79	15.91	13.22
29.05	5.63	15.21	14.36
28.67	6.07	15.11	14.26
27.83	5.89	14.89	14.62
27.26	6.57	14.80	14.53
26.88	6.48	14.63	14.81
26.25	7.25	14.53	14.70
25.58	7.07	14.27	15.12
24.97	7.82	14.22	15.06
24.35	7.63	13.99	15.44
23.81	8.32	13.91	15.36
23.51	8.21	13.64	15.81
23.00	8.87	13.55	15.71
22.77	8.78	13.30	16.14
22.17	9.58	13.21	16.03
21.53	9.31	12.88	16.60
21.41	9.48	12.71	16.39
21.25	9.41	12.34	17.04
20.97	9.81	12.26	16.94
20.75	9.71	11.90	17.59
20.33	10.29	11.83	17.48
20.10	10.17		

Table S4. Experimental weight fraction data for the binodal curves of the ABS formed by $[\text{N}_{444}(\text{C}_7\text{H}_7)]\text{Cl}$ (1) + $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (2), at $(25 \pm 3)^\circ\text{C}$ and pH 7.

w_1	w_2	w_1	w_2	w_1	w_2
57.64	0.69	27.04	8.07	18.64	12.70
56.69	1.32	26.77	7.99	18.10	13.47
53.05	1.24	26.45	8.36	17.97	13.37
51.90	2.05	26.16	8.27	17.72	13.74
47.07	1.86	25.88	8.60	17.59	13.64
46.40	2.39	25.58	8.50	17.30	14.06
44.65	2.30	25.30	8.83	17.19	13.97
43.91	2.91	25.05	8.75	16.91	14.38
42.30	2.80	24.78	9.07	16.79	14.28
41.49	3.49	24.52	8.98	16.53	14.66
39.48	3.32	24.28	9.27	16.42	14.56
38.89	3.86	24.03	9.18	16.22	14.84
37.75	3.74	23.62	9.69	16.12	14.75
37.27	4.19	23.39	9.60	15.86	15.13
36.67	4.13	23.12	9.94	15.77	15.03
36.09	4.68	22.91	9.85	15.54	15.37
35.11	4.55	22.68	10.15	15.46	15.29
34.43	5.22	22.49	10.07	15.30	15.54
33.43	5.07	22.05	10.63	15.25	15.49
32.92	5.60	21.86	10.54	15.03	15.83
32.44	5.52	21.66	10.81	14.95	15.75
31.99	5.98	21.46	10.71	14.85	15.91
31.52	5.89	21.04	11.27	14.76	15.81
31.09	6.35	20.87	11.18	14.45	16.29
30.33	6.20	20.66	11.45	14.39	16.22
29.96	6.60	20.48	11.35	14.19	16.54
29.61	6.52	20.10	11.86	14.10	16.43
29.31	6.85	19.95	11.76	13.93	16.69
28.95	6.77	19.77	12.00	13.86	16.60
28.33	7.46	19.61	11.90	13.60	17.01
28.03	7.38	19.23	12.42	13.52	16.91
27.70	7.76	19.09	12.32		
27.39	7.67	18.76	12.78		

Table S5. Experimental weight fraction data for the binodal curves of the ABS formed by $[N_{1118}]Br$ (1) + K_2HPO_4/KH_2PO_4 (2), at $(25 \pm 3)^\circ C$ and pH 7.

w_1	w_2	w_1	w_2
45.17	5.76	20.94	18.19
44.34	5.66	20.75	18.03
43.09	6.60	20.02	18.76
42.33	6.49	19.85	18.60
41.60	7.04	18.95	19.52
40.81	6.91	18.79	19.35
39.43	7.99	18.19	19.97
38.72	7.85	18.04	19.80
37.56	8.78	16.13	21.82
36.99	8.64	16.00	21.64
35.85	9.57	15.20	22.51
35.32	9.43	15.13	22.41
34.27	10.31	14.67	22.91
33.75	10.15	14.57	22.74
32.54	11.18	13.89	23.49
32.12	11.03	13.79	23.32
31.24	11.79	13.06	24.16
30.82	11.63	12.97	24.00
29.19	13.06	12.40	24.65
28.96	12.96	12.33	24.50
28.43	13.44	11.68	25.26
28.05	13.27	11.61	25.10
26.98	14.24	10.93	25.91
26.62	14.06	10.87	25.76
24.60	15.94	9.84	26.99
24.31	15.75	9.79	26.87
23.31	16.70	9.18	27.62
23.05	16.51	9.14	27.50
22.18	17.36	8.08	28.82
21.96	17.18	8.05	28.70

Table S6. Experimental weight fraction data for the binodal curves of the ABS formed by $[N_{111}(C_7H_7)]Cl$ (1) + K_2HPO_4/KH_2PO_4 (2), at $(25 \pm 3)^\circ C$ and pH 7.

w_1	w_2	w_1	w_2
55.90	1.47	36.20	7.28
54.39	2.48	35.69	7.17
51.52	2.35	34.25	8.45
50.23	3.26	33.41	8.24
48.17	3.13	31.50	10.00
47.00	3.99	31.13	9.88
44.64	3.79	30.20	10.75
43.67	4.56	29.85	10.62
43.00	4.49	28.45	11.95
42.05	5.24	28.12	11.81
40.71	5.08	26.87	13.02
39.85	5.79	26.59	12.88
39.24	5.70	24.67	14.76
38.55	6.29	24.49	14.65
37.99	6.20	21.63	17.49
37.24	6.84	21.42	17.32
36.79	6.76		

Table S7. Experimental weight fraction data for the binodal curves of the ABS formed by $[\text{N}_{222}(\text{C}_7\text{H}_7)]\text{Cl}$ (1) + $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (2), at $(25 \pm 3)^\circ\text{C}$ and pH 7.

w_1	w_2	w_1	w_2
53.15	0.89	26.37	10.51
50.76	2.59	25.51	11.44
46.34	2.37	25.24	11.32
45.41	3.10	24.45	12.18
43.06	2.94	24.21	12.06
41.69	4.09	23.50	12.85
40.34	3.95	23.27	12.73
39.65	4.55	22.28	13.84
39.03	4.48	22.06	13.70
38.39	5.04	21.07	14.83
37.26	4.89	20.90	14.70
36.64	5.45	19.92	15.84
36.05	5.36	19.78	15.73
35.52	5.86	18.93	16.73
35.00	5.77	18.87	16.68
34.45	6.30	17.60	18.17
33.98	6.21	17.54	18.10
32.94	7.21	16.73	19.07
32.46	7.10	16.61	18.94
31.99	7.55	15.49	20.29
31.56	7.45	15.39	20.16
30.69	8.32	14.04	21.80
30.30	8.21	13.96	21.67
29.93	8.58	12.97	22.89
29.58	8.48	12.90	22.76
28.72	9.36	11.66	24.31
28.38	9.25	11.61	24.21
27.67	9.99	10.54	25.56
27.35	9.87	10.51	25.47
26.65	10.62		

Table S8. Experimental weight fraction data for the binodal curves of the ABS formed by $[\text{N}_{222}(\text{C}_7\text{H}_7)]\text{Cl}$ (1) + $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (2), at $(25 \pm 3)^\circ\text{C}$ and pH 8.

w_1	w_2	w_1	w_2
67.52	4.67	20.48	14.53
39.36	4.66	20.10	14.75
37.49	5.23	19.50	15.31
35.81	5.87	19.20	15.41
34.19	6.43	18.67	15.92
32.87	6.97	18.23	16.29
31.98	7.55	17.80	16.65
30.69	7.97	17.37	17.10
29.84	8.44	17.08	17.27
28.98	8.95	16.75	17.52
28.20	9.48	16.36	17.89
27.44	9.88	15.96	18.25
26.68	10.27	15.58	18.62
26.03	10.66	15.23	18.97
25.38	11.01	14.89	19.28
24.81	11.40	14.70	19.40
24.22	11.80	14.39	19.71
23.67	12.16	14.08	19.99
23.16	12.50	13.79	20.25
22.67	12.79	13.52	20.48
22.24	13.08	13.25	20.79
21.60	13.66	13.00	21.01
21.19	13.88	12.78	21.18

Table S9. Experimental weight fraction data for the binodal curves of the ABS formed by $[\text{N}_{222}(\text{C}_7\text{H}_7)]\text{Cl}$ (1) + $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (2), at $(25 \pm 3)^\circ\text{C}$ and pH 9.

w₁	w₂	w₁	w₂
47.23	2.62	18.03	16.68
43.46	3.48	17.73	16.84
40.34	4.21	17.45	17.00
38.03	5.15	17.06	17.43
35.57	5.82	16.80	17.58
33.99	6.55	16.52	17.78
32.48	7.15	16.27	17.94
31.15	7.65	16.03	18.14
30.39	8.11	15.67	18.63
29.21	8.54	15.40	18.71
28.50	9.04	15.17	18.89
27.78	9.48	14.95	19.08
26.80	9.75	14.62	19.54
26.21	10.19	14.37	19.61
25.63	10.52	14.20	19.77
24.98	11.11	14.00	19.92
24.48	11.51	13.81	20.04
23.92	11.92	13.43	20.69
23.10	12.83	13.15	20.68
22.67	13.07	12.90	21.01
22.23	13.34	12.73	21.13
21.84	13.58	12.56	21.24
21.43	13.91	12.40	21.34
21.03	14.23	12.17	21.69
20.62	14.49	12.00	21.73
19.90	15.09	11.88	21.87
19.45	15.54	11.74	21.97
19.13	15.70	11.54	22.28
18.80	15.91	11.41	22.35
18.35	16.44	11.29	22.45

Table S10. Experimental weight fraction data for the binodal curves of the ABS formed by $[\text{N}_{222}(\text{C}_7\text{H}_7)]\text{Cl}$ (1) + $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ (2), at $(25 \pm 3)^\circ\text{C}$ and pH 13.

w_1	w_2	w_1	w_2
68.94	1.08	20.41	12.83
61.89	1.68	20.06	12.96
47.36	2.39	19.57	13.30
43.72	3.02	19.05	13.67
41.27	3.62	18.57	13.98
39.03	4.13	18.14	14.34
37.37	4.60	17.87	14.45
35.25	5.60	17.44	14.74
33.69	6.16	17.02	15.08
32.70	6.57	16.78	15.17
31.79	6.94	16.39	15.47
30.91	7.27	16.01	15.77
30.04	7.66	15.65	16.00
29.03	8.18	15.33	16.21
28.30	8.47	14.73	16.61
27.63	8.74	14.45	16.80
26.69	9.34	14.14	17.01
26.07	9.59	13.88	17.22
25.49	9.83	13.64	17.40
24.64	10.39	13.28	17.70
24.13	10.60	12.98	17.92
23.40	11.05	12.74	18.07
22.72	11.49	12.23	18.51
22.27	11.66	12.03	18.64
21.62	12.02	11.85	18.77
21.00	12.43	11.60	19.00

Table S11. Experimental weight fraction data for the binodal curves of the ABS formed by [N₂₂₂₂]Br (1) + K₂HPO₄/KH₂PO₄ (2), at (25 ± 3)°C and pH 7.

w₁	w₂	w₁	w₂
43.55	2.77	24.16	12.90
42.73	3.46	24.00	12.82
41.47	3.35	22.90	14.01
40.81	3.92	22.66	13.86
39.93	3.84	22.05	14.53
39.09	4.58	21.85	14.40
38.39	4.50	20.82	15.55
37.71	5.10	20.76	15.51
37.11	5.02	20.22	16.12
36.68	5.41	20.08	16.01
36.17	5.33	19.19	17.02
35.63	5.84	19.12	16.96
35.03	5.74	18.32	17.87
34.17	6.55	18.22	17.78
33.61	6.44	17.65	18.44
32.87	7.16	17.58	18.37
32.63	7.11	16.70	19.40
32.22	7.51	16.58	19.26
31.97	7.46	15.65	20.37
31.53	7.90	15.58	20.28
30.98	7.76	14.89	21.10
30.19	8.55	14.84	21.03
29.96	8.48	14.12	21.90
29.33	9.12	14.02	21.74
29.18	9.07	13.26	22.67
28.53	9.74	13.18	22.54
28.16	9.61	12.51	23.38
27.50	10.30	12.47	23.32
27.29	10.22	11.75	24.22
26.59	10.96	11.72	24.16
26.43	10.89	11.25	24.75
25.84	11.52	11.19	24.60
25.56	11.39		

Table S12. Experimental weight fraction data for the binodal curves of the ABS formed by [N₂₂₂₂]Br (1) + K₂HPO₄/KH₂PO₄ (2), at (25 ± 3)°C and pH 8.

w₁	w₂	w₁	w₂
67.11	1.56	22.45	14.35
46.77	2.31	21.54	14.82
43.78	3.29	20.80	15.51
41.29	3.92	20.10	16.14
38.82	4.72	19.45	16.71
36.76	5.50	18.90	17.22
34.83	6.09	17.84	18.15
33.65	6.76	17.22	18.45
32.50	7.37	16.77	18.83
30.02	9.10	16.23	19.43
29.13	9.60	15.81	19.80
28.37	10.09	15.44	20.13
27.56	10.58	14.76	20.72
26.87	11.02	14.42	20.98
26.20	11.45	13.98	21.46
25.63	11.80	13.54	21.74
24.61	12.70	13.26	21.97
23.78	13.35	12.98	22.21
23.22	13.65	12.72	22.46

Table S13. Experimental weight fraction data for the binodal curves of the ABS formed by [N₂₂₂₂]Br (1) + K₂HPO₄/KH₂PO₄ (2), at (25 ± 3)°C and pH 9.

w₁	w₂	w₁	w₂
74.69	1.15	19.96	15.29
49.15	2.03	19.48	15.87
46.04	3.07	19.00	16.41
41.80	3.79	18.60	16.48
39.48	4.55	18.29	16.71
37.35	5.25	17.97	16.94
35.72	5.73	17.67	17.14
34.15	6.33	17.26	17.61
33.23	6.81	17.01	17.79
32.16	7.26	16.75	17.99
31.32	7.85	16.35	18.52
30.22	8.18	15.86	18.85
29.59	8.58	15.51	19.30
28.89	9.03	15.08	19.63
28.15	9.60	14.79	19.65
27.53	10.03	14.60	19.78
27.01	10.40	14.41	19.92
26.45	10.71	14.22	20.05
25.92	11.05	14.02	20.25
25.38	11.44	13.84	20.38
24.79	11.80	13.60	20.74
24.28	12.15	13.41	20.87
23.79	12.51	12.97	21.76
23.40	12.76	12.74	21.75
22.98	13.03	12.59	21.87
22.54	13.28	12.44	21.95
21.86	14.04	12.29	22.05
21.49	14.24	12.07	22.35
21.08	14.48	11.94	22.48
20.71	14.72	11.80	22.58
20.33	15.01		

Table S14. Experimental weight fraction data for the binodal curves of the ABS formed by [N₂₂₂₂]Br (1) + K₂HPO₄/KH₂PO₄ (2), at (25 ± 3)°C and pH 13.

w₁	w₂	w₁	w₂
69.86	2.21	20.54	13.27
64.21	2.20	19.97	13.64
43.99	2.77	19.36	14.12
41.55	3.35	18.86	14.43
39.98	3.96	18.24	14.90
38.24	4.41	17.82	15.16
37.10	4.77	17.40	15.43
35.79	5.28	16.87	15.85
34.83	5.71	16.44	16.11
33.73	6.13	16.09	16.34
32.83	6.60	15.67	16.67
31.83	6.99	15.36	16.87
30.95	7.30	14.95	17.22
29.74	7.94	14.64	17.38
29.02	8.36	14.29	17.61
28.00	8.70	13.92	17.91
27.04	9.17	13.66	18.09
26.22	9.63	13.36	18.32
25.34	10.17	12.80	18.96
24.94	10.44	12.49	19.23
24.56	10.70	12.21	19.46
23.77	11.19	11.99	19.58
23.11	11.55	11.74	19.76
22.54	11.94	11.43	20.02
21.67	12.59	11.08	20.37
21.12	12.90		

Table S15. Experimental weight fraction data for the binodal curves of the ABS formed by [N₂₂₂₂]Cl (1) + K₂HPO₄/KH₂PO₄ (2), at (25 ± 3)°C and pH 7.

w₁	w₂	w₁	w₂
56.85	0.92	31.42	6.10
50.07	0.81	30.98	6.55
49.01	1.61	30.55	6.46
44.44	1.46	29.70	7.37
43.27	2.44	29.32	7.27
41.72	2.36	28.52	8.13
40.97	3.02	28.22	8.05
39.61	2.92	27.41	8.93
38.86	3.60	27.07	8.82
37.63	3.48	24.93	11.20
37.00	4.08	24.39	10.96
36.40	4.01	23.47	12.01
35.83	4.56	23.01	11.78
35.31	4.49	21.76	13.25
34.82	4.97	21.56	13.12
34.28	4.89	19.55	15.52
33.81	5.36	19.38	15.38
33.31	5.28	18.09	16.95
32.78	5.81	17.79	16.67
32.30	5.72	15.96	18.96
31.86	6.18	15.73	18.69

Table S16. Experimental weight fraction data for the binodal curves of the ABS formed by [N₂₂₂₂]Cl (1) + K₂HPO₄/KH₂PO₄ (2), at (25 ± 3)°C and pH 8.

w₁	w₂	w₁	w₂
56.35	2.14	19.66	15.26
40.10	3.05	19.02	15.80
37.36	4.10	18.29	16.63
34.94	5.15	17.57	17.36
32.98	5.82	17.24	17.59
30.36	7.58	16.73	18.24
28.08	9.08	15.97	19.13
25.65	10.27	15.46	19.62
24.02	11.26	14.55	20.90
22.87	12.40	12.72	23.61
21.47	13.36	11.86	24.80
20.50	14.38	11.24	25.72

Table S17. Experimental weight fraction data for the binodal curves of the ABS formed by [N₂₂₂₂]Cl (1) + K₂HPO₄/KH₂PO₄ (2), at (25 ± 3)°C and pH 9.

w₁	w₂	w₁	w₂
55.06	1.93	18.00	15.75
42.11	3.47	17.57	16.09
37.04	4.10	16.84	17.15
33.39	5.37	16.22	18.03
30.08	6.34	15.67	18.55
28.29	7.33	15.07	19.30
27.32	8.08	14.63	19.82
26.24	9.05	13.68	20.75
25.20	9.97	13.17	21.14
23.88	10.70	12.79	21.74
23.03	11.44	12.34	22.22
22.28	12.16	11.88	22.67
21.51	12.92	11.44	23.08
20.50	13.74	11.04	23.51
19.66	14.18	10.70	23.79
19.10	14.67	10.40	24.13
18.55	15.20	10.19	24.10

Table S18. Experimental weight fraction data for the binodal curves of the ABS formed by $[N_{2222}]Cl$ (1) + K_2HPO_4/KH_2PO_4 (2), at $(25 \pm 3)^\circ C$ and pH 13.

w_1	w_2	w_1	w_2
56.93	1.38	19.12	13.33
50.30	2.26	18.41	13.91
40.18	3.30	17.60	14.62
36.81	3.94	16.77	15.46
34.42	4.58	15.99	16.23
32.95	5.35	15.33	16.89
29.08	6.39	14.72	17.48
27.97	6.99	14.32	17.78
26.91	7.57	13.76	18.32
25.57	8.60	13.26	18.79
24.79	8.99	12.83	19.20
23.64	9.88	12.40	19.61
22.71	10.56	11.84	20.29
21.70	11.24	11.47	20.64
20.79	11.97	11.00	21.19
19.90	12.69		

For the determination of each TL, the following system of four equations (equations (S1)–(S4)) and four unknown parameters ($[IL]_T$, $[IL]_B$, $[Salt]_T$, $[Salt]_B$) was applied:

$$[IL]_T = A \exp[(B \times [Salt]_T^{0.5}) - (C \times [Salt]_T^3)] \quad (S1)$$

$$[IL]_B = A \exp[(B \times [Salt]_B^{0.5}) - (C \times [Salt]_B^3)] \quad (S2)$$

$$[IL]_T = \frac{[IL]_M}{\alpha} - \frac{1-\alpha}{\alpha} \times [IL]_B \quad (S3)$$

$$[Salt]_T = \frac{[Salt]_M}{\alpha} - \frac{1-\alpha}{\alpha} \times [Salt]_B \quad (S4)$$

where the subscripts M, T and B designate, respectively, the initial mixture, the top and bottom phases. The value α is the ratio between the mass of the top phase and the total mass of the mixture experimentally determined. Each tie-line length (TLL) was determined through the application of the following equation:

$$TLL = \sqrt{([Salt]_T - [Salt]_B)^2 + ([IL]_T - [IL]_B)^2} \quad (S5)$$

Table S19. Weight fraction compositions for the TLs and respective Tie-Line Lengths (TLLs), at the Top (T) and Bottom (B) phases, and at the initial biphasic composition of the mixture (M), composed of ILs and salts at $T = (25 \pm 3) \text{ }^\circ\text{C}$ and atmospheric pressure.

IL + [KH ₂ PO ₄ /K ₂ HPO ₄ at pH 7]	weight fraction composition/wt %							
	[IL] _T	[Salt] _T	[IL] _M	[Salt] _M	[IL] _B	[Salt] _B	TLS	TLL
[N ₁₁₁ (C ₇ H ₇)]Cl	35.16	7.90	27.99	16.13	9.86	36.97	-0.87	38.54
	39.48	6.08	31.08	16.09	6.96	44.84	-0.84	50.60
[N ₂₂₂ (C ₇ H ₇)]Cl	35.00	6.04	29.14	11.96	2.94	38.60	-0.98	45.83
	38.80	4.82	27.81	15.42	3.04	39.29	-1.04	49.67
[N ₂₂₂₂]Cl	33.13	5.74	27.90	14.92	5.27	37.39	-0.88	42.09
	40.18	3.80	31.35	14.72	1.14	43.22	-0.99	52.65
[N ₂₂₂₂]Br	34.13	6.74	26.90	13.92	4.27	36.39	-1.01	42.09
	39.18	4.80	30.35	13.72	2.14	42.22	-0.99	52.65
[N ₄₄₄ (C ₇ H ₇)]Cl	40.41	3.57	21.82	18.97	1.81	35.54	-1.21	50.12
	44.50	2.76	21.33	20.99	1.54	36.56	-1.27	54.67
[N ₄₄₄₄]Cl	28.88	5.87	23.15	11.99	1.80	34.74	-0.94	39.58
	38.27	3.36	29.13	11.62	1.89	36.25	-1.11	49.04
[N ₄₄₄₄]Br	38.63	3.71	30.04	9.03	2.37	26.54	-1.59	43.36
	45.93	2.17	29.67	11.74	1.49	28.33	-1.70	51.56
[N ₁₁₁₈]Br	51.48	3.81	33.04	15.99	3.16	35.72	-1.51	57.91
	45.21	5.60	30.15	15.96	4.19	33.85	-1.45	49.81

Table S20. Adjusted parameters and respective standard deviations obtained from the regression of equation (1) at (25 ± 3) °C and different pH values.

IL	pH	$A \pm \sigma$	$B \pm \sigma$	$10^5 (C \pm \sigma)$
[N ₁₁₁ (C ₇ H ₇)]Cl		90.02 ± 5.39	-0.334 ± 0.02	0.35 ± 0.62
[N ₂₂₂ (C ₇ H ₇)]Cl		80.53 ± 1.74	-0.337 ± 0.008	1.97 ± 0.22
[N ₂₂₂₂]Cl		70.11 ± 2.94	-0.317 ± 0.021	1.17 ± 1.64
[N ₂₂₂₂]Br	pH 7	73.88 ± 0.91	-0.298 ± 0.004	2.49 ± 0.14
[N ₄₄₄ (C ₇ H ₇)]Cl		88.70 ± 1.33	-0.415 ± 0.001	3.15 ± 0.42
[N ₄₄₄₄]Cl		79.40 ± 2.41	-0.414 ± 0.013	3.20 ± 0.88
[N ₄₄₄₄]Br		77.76 ± 1.83	-0.360 ± 0.012	10.2 ± 1.23
[N ₁₁₁₈]Br		93.37 ± 2.63	-0.304 ± 0.009	3.44 ± 1.79
[N ₂₂₂ (C ₇ H ₇)]Cl		81.97 ± 1.20	-0.340 ± 0.005	2.99 ± 0.13
[N ₂₂₂₂]Cl	pH 8	73.43 ± 3.16	-0.324 ± 0.015	1.43 ± 0.34
[N ₂₂₂₂]Br		71.27 ± 1.39	-0.280 ± 0.007	3.38 ± 0.20
[N ₂₂₂ (C ₇ H ₇)]Cl		79.26 ± 2.05	-0.329 ± 0.009	3.27 ± 0.24
[N ₂₂₂₂]Cl	pH 9	64.35 ± 3.30	-0.292 ± 0.017	2.59 ± 0.36
[N ₂₂₂₂]Br		76.51 ± 1.23	-0.313 ± 0.005	3.26 ± 0.16
[N ₂₂₂ (C ₇ H ₇)]Cl		78.60 ± 0.87	-0.337 ± 0.004	6.50 ± 0.20
[N ₂₂₂₂]Cl	pH 13	73.67 ± 3.03	-0.354 ± 0.016	2.62 ± 0.54
[N ₂₂₂₂]Br		75.88 ± 0.87	-0.323 ± 0.004	5.54 ± 0.18

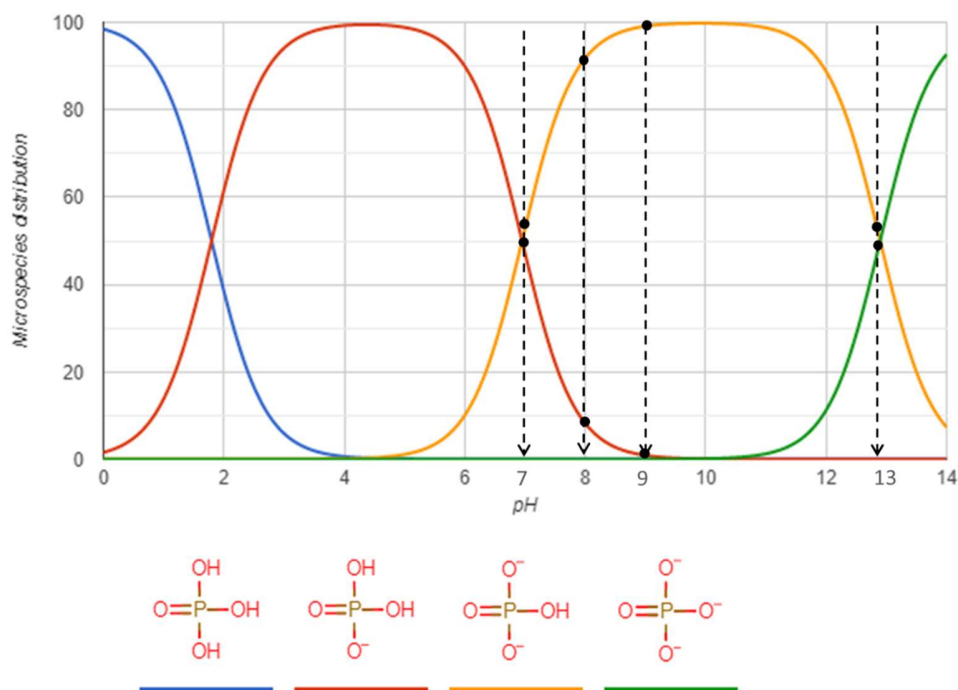


Figure S1. Anions distribution as function of the pH. The pH values studied in this work (7, 8, 9 and 13) are indicated. Information taken from the Chemspider database (www.chemspider.com).

Table S21. Extraction efficiencies ($EE\%$) and recovery yields ($RY\%$) of ovalbumin and lysozyme at pH 7 and respective mixture compositions.

Ionic liquid	weight fraction percentage / wt %		$EE_{Ova}\%$	$RY_{Ova}\%$	$EE_{Lys}\%$	$RY_{Lys}\%$
	[IL] _M	[Salt] _M				
[N ₁₁₁ (C ₇ H ₇)]Cl	31.08	16.09	100.0 ± 0.2	77.3 ± 1.1	100.0 ± 0.2	100.0 ± 0.2
[N ₂₂₂ (C ₇ H ₇)]Cl	27.81	15.42	100.0 ± 0.2	58.8 ± 0.9	100.0 ± 0.2	100.0 ± 0.2
[N ₂₂₂₂]Cl	31.35	14.72	100.0 ± 0.2	100.0 ± 0.2	100.0 ± 0.2	100.0 ± 0.2
[N ₂₂₂₂]Br	30.35	13.72	100.0 ± 0.2	100.0 ± 0.2	100.0 ± 0.2	100.0 ± 0.2
[N ₄₄₄ (C ₇ H ₇)]Cl	21.33	20.99	100.0 ± 0.2	33.3 ± 1.8	100.0 ± 0.2	100.0 ± 0.2
[N ₄₄₄₄]Cl	29.13	11.62	100.0 ± 0.2	56.7 ± 1.7	100.0 ± 0.2	100.0 ± 0.2
[N ₄₄₄₄]Br	29.67	11.74	100.0 ± 0.2	42.6 ± 2.3	100.0 ± 0.2	100.0 ± 0.2
[N ₁₁₁₈]Br	30.15	15.96	100.0 ± 0.2	36.0 ± 1.6	100.0 ± 0.2	100.0 ± 0.2

Table S22. Extraction efficiencies ($EE\%$) and recovery yields ($RY\%$) of lysozyme at different pH values and respective mixture compositions.

Ionic liquid	pH	weight fraction percentage / wt %		$EE_{Lys}\%$	$RY_{Lys}\%$
		$[IL]_M$	$[Salt]_M$		
$[N_{222}(C_{7H_7})]Cl$		27.81	15.42	100.0 ± 0.2	100.0 ± 0.2
$[N_{2222}]Cl$	pH7	31.35	14.72	100.0 ± 0.2	100.0 ± 0.2
$[N_{2222}]Br$		30.35	13.72	100.0 ± 0.2	100.0 ± 0.2
$[N_{222}(C_{7H_7})]Cl$		27.81	15.42	100.0 ± 0.2	100.0 ± 0.2
$[N_{2222}]Cl$	pH8	31.35	14.72	100.0 ± 0.2	100.0 ± 0.2
$[N_{2222}]Br$		30.35	13.72	100.0 ± 0.2	100.0 ± 0.2
$[N_{222}(C_{7H_7})]Cl$		27.81	15.42	100.0 ± 0.2	100.0 ± 0.2
$[N_{2222}]Cl$	pH9	31.35	14.72	100.0 ± 0.2	100.0 ± 0.2
$[N_{2222}]Br$		30.35	13.72	100.0 ± 0.2	100.0 ± 0.2
$[N_{222}(C_{7H_7})]Cl$		27.81	15.42	100.0 ± 0.2	36.7 ± 1.5
$[N_{2222}]Cl$	pH13	31.35	14.72	100.0 ± 0.2	78.8 ± 0.4
$[N_{2222}]Br$		30.35	13.72	100.0 ± 0.2	30.9 ± 1.9

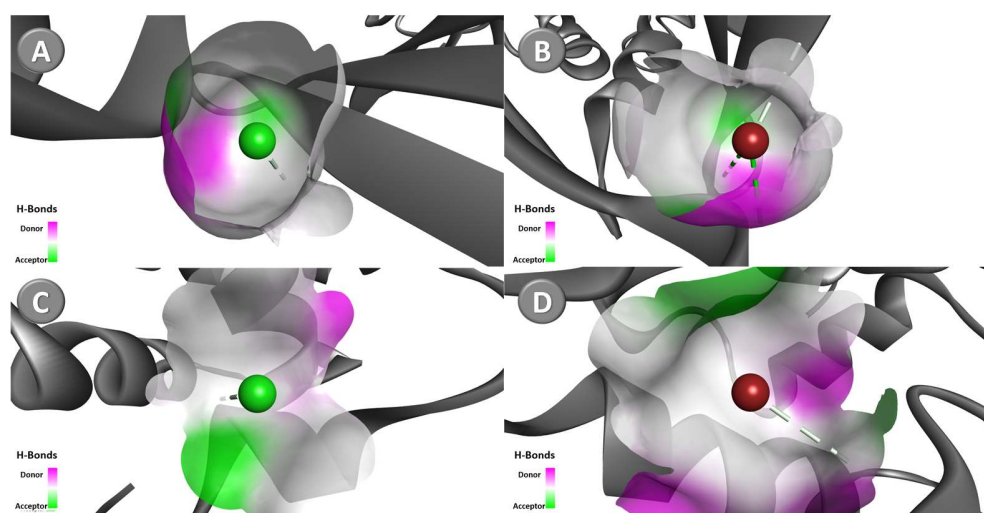


Figure S2. Docking pose with the lowest absolute value of affinity for ovalbumin: (A) Cl^- and (B) Br^- ; and lysozyme with: (C) Cl^- and (D) Br^- .

Table S23. Docking affinity energy and interacting amino acids residues predicted by AutoDock vina for Ovalbumin-IL ions.

IL ion	Affinity (kcal/mol)	Interacting nucleic acids	Type of interaction	From	To	Distance (Å)
[N ₁₁₁ (C _{7H7}) ⁺	-3.8	ARG290	Hydrophobic	[N ₁₁₁ (C _{7H7}) ⁺	ARG290	4.49
[N ₂₂₂₂] ⁺	-2.9	GLU27	Electrostatic	[N ₂₂₂₂] ⁺	GLU27	4.94
[N ₂₂₂ (C _{7H7}) ⁺	-4.4	VAL333	Hydrophobic	[N ₂₂₂ (C _{7H7}) ⁺	VAL333	3.95
[N ₄₄₄₄] ⁺	-3.6	ARG29	Hydrogen Bond	[N ₄₄₄₄] ⁺	ARG29	3.53
[N ₄₄₄ (C _{7H7}) ⁺	-3.6	LYS199	Hydrophobic	[N ₄₄₄ (C _{7H7}) ⁺	LYS199	3.61
		VAL347			VAL347	5.31
[N ₁₁₁₈] ⁺	-3.2	GLU122	Electrostatic	[N ₁₁₁₈] ⁺	GLU122	5.50
		ALA149	Hydrophobic	ALA149	[N ₁₁₁₈] ⁺	4.00
Cl ⁻	-1.2	PRO243	Hydrogen Bond	PRO243	Cl ⁻	2.72
Br ⁻	-1.3	GLU195	Hydrogen Bond	GLU195	Br ⁻	3.81
		LYS196		LYS196		3.00
		LEU242		LEU242		3.75

Table S24. Docking affinity energy and interacting amino acids residues predicted by AutoDock vina for Lysozyme-IL ions.

IL ion	Affinity (kcal/mol)	Interacting nucleic acids	Type of interaction	From	To	Distance (Å)
[N ₁₁₁ (C _{7H7})] ⁺	-4.3	ALA107	Hydrogen Bond	[N ₁₁₁ (C _{7H7})] ⁺	ALA107	3.57
		TRP108		TRP108	[N ₁₁₁ (C _{7H7})] ⁺	4.93
		ILE98	Hydrophobic	[N ₁₁₁ (C _{7H7})] ⁺	ILE98	5.16
		ALA107			ALA107	4.36
[N ₂₂₂₂] ⁺	-2.7	ASP52	Electrostatic	[N ₂₂₂₂] ⁺	ASP52	3.88
		ASP46			ASP46	3.66
		ASP52	Hydrogen Bond		ASP52	3.31
					ASP52	3.75
[N ₂₂₂ (C _{7H7})] ⁺	-3.8	ASP101	Electrostatic	[N ₂₂₂ (C _{7H7})] ⁺	ASP101	5.33
		ASP101		ASP101	4.51	
		TRP62	Hydrophobic	TRP62	[N ₂₂₂ (C _{7H7})] ⁺	4.02
					TRP62	3.72
[N ₄₄₄₄] ⁺	-3.1	TRP123	Electrostatic	[N ₄₄₄₄] ⁺	TRP123	4.92
			Hydrophobic			3.79
[N ₄₄₄ (C _{7H7})] ⁺	-3.6	GLU7	Electrostatic	[N ₄₄₄ (C _{7H7})] ⁺	GLU7	5.12
				GLU7	[N ₄₄₄ (C _{7H7})] ⁺	4.00
		ALA10	Hydrophobic	[N ₄₄₄ (C _{7H7})] ⁺	ALA10	5.43
		ALA11			ALA11	4.84
[N ₁₁₁₈] ⁺	-2.8	CYS76	Hydrogen Bond	[N ₁₁₁₈] ⁺	CYS76	3.55
		CYS76			3.47	
		LYS96	Hydrophobic		LYS96	4.67
Cl ⁻	-0.8	TRP123	Hydrogen Bond	TRP123	Cl ⁻	3.17

Br ⁻	-1.0	ILE58	Hydrogen Bond	GLU195	Br ⁻	3.89
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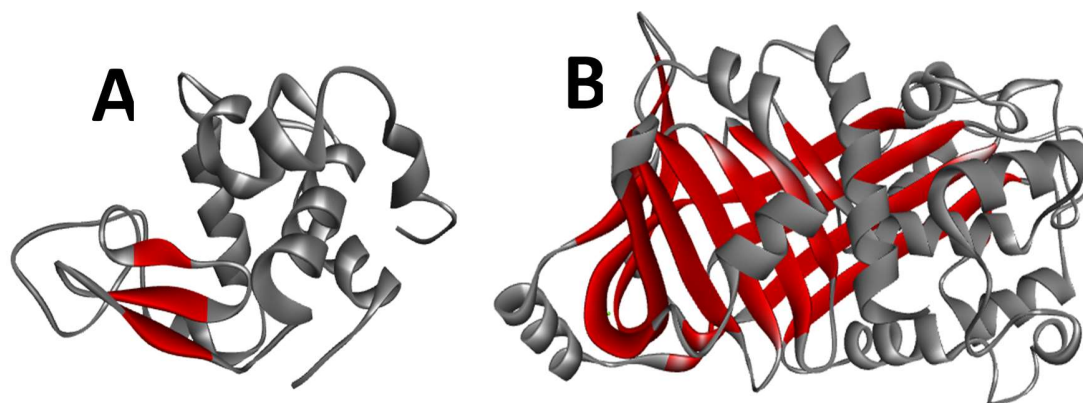


Figure S3. B-sheet content (in red) of lysozyme (A) and ovalbumin (B).

Table S25. Percentage recovery yield (*RY*%) of Lysozyme after the purification and precipitation steps the ABS composed of ILs + K₂HPO₄/KH₂PO₄ + H₂O at pH 7 and 8.

IL-rich phase	<i>RY</i> _{Lys} %
[N ₂₂₂ (C ₇ H ₇)]Cl pH7	80.76 ± 2.25
[N ₂₂₂₂]Cl pH7	99.04 ± 2.98
[N ₂₂₂₂]Br pH7	93.45 ± 3.45
[N ₂₂₂ (C ₇ H ₇)]Cl pH8	81.02 ± 1.67
[N ₂₂₂₂]Cl pH8	99.32 ± 2.72
[N ₂₂₂₂]Br pH8	96.68 ± 2.05

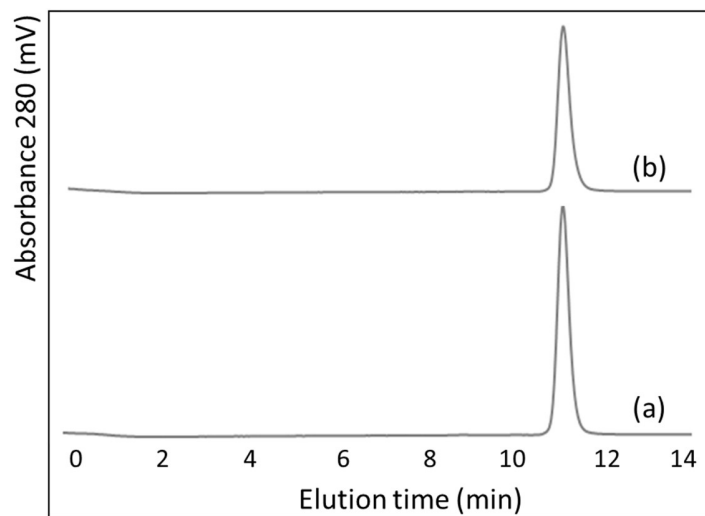


Figure S4. Size exclusion chromatograms of (a) lysozyme solution in PBS and (b) recovered lysozyme from the IL-rich phase of the ABS composed of $[N_{2222}]\text{Cl} + \text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4 + \text{H}_2\text{O}$ at pH 8.