

Towards the differential diagnosis of prostate cancer by the pre-treatment of human urine using ionic liquids

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Supporting Information

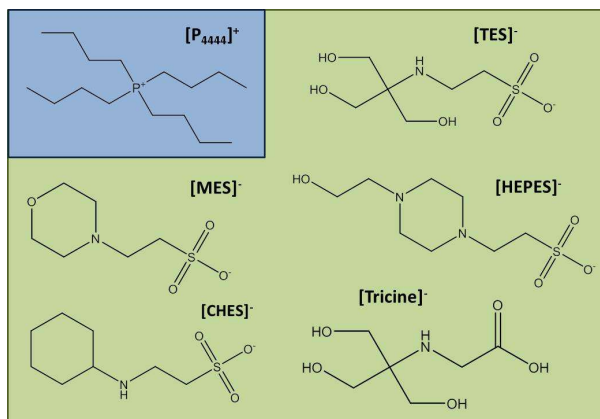


Figure S1. Chemical structures and abbreviations of the GB-ILs studied.

GB-ILs Characterization

[P₄₄₄₄][MES]: From the MES buffer (48.5 mmol), this compound was obtained as a white solid. Water content < 0.05 wt%. ¹H NMR (300 MHz, D₂O/TSP): 3.63 (t, 4H), 2.99 (t, 2H), 2.72 (t, 2H), 2.50 (t, 4H), 2.02 (m, 8H), 1.27-1.42 (m, 16H), 0.78 (t, 12H). ¹³C NMR (75.47 MHz, D₂O/TSP): 68.80, 55.44, 55.11, 50.02, 26.28, 20.80, 20.16, 15.44.

[P₄₄₄₄][TES]: From the TES buffer (45.1 mmol), this compound was obtained as a transparent viscous liquid. Water content < 0.05 wt%. ¹H NMR (300 MHz, D₂O/TSP): 3.31 (s, 6H), 2.82 (s, 2H), 2.57 (t, 2H), 2.10 (m, 8H), 1.29-1.49 (m, 16H), 0.79 (t, 12H). ¹³C NMR (75.47 MHz, D₂O/TSP): 60.65, 57.63, 51.58, 37.69, 26.28, 20.83, 20.17, 15.46.

[P₄₄₄₄][CHES]: From the CHES buffer (47.2 mmol), this compound was obtained as a transparent viscous liquid. Water content < 0.05 wt%. ¹H NMR (300 MHz, D₂O/TSP): 2.95 (m, 2H), 2.38-2.47 (m, 1H), 2.02 (m, 8H), 1.28-1.45 (m, 16H), 0.94 (m, 10H), 0.78 (t, 12H). ¹³C NMR (75.47 MHz, D₂O/TSP): 63.37, 63.09, 53.42, 39.56, 26.28, 26.08, 25.60, 20.30, 20.15, 15.43.

[P₄₄₄₄][HEPES]: From the HEPES buffer (44.3 mmol), this compound was obtained as a yellowish white solid. Water content < 0.05 wt%. ¹H NMR (300 MHz, D₂O/TSP): 3.59 (t, 4H), 2.97 (t, 2H), 2.94 (t, 2H), 2.67 (t, 2H), 2.46 (t, 8H), 2.03 (m, 8H), 1.28-1.45 (m, 16H), 0.79 (t, 12H). ¹³C NMR (75.47 MHz, D₂O/TSP): 61.59, 60.87, 55.02, 54.78, 54.19, 50.39, 26.29, 20.80, 20.16, 15.44.

[P₄₄₄₄][Tricine]: From the Tricine buffer (50.3 mmol), this compound was obtained as white solid. Water content < 0.05 wt%. ¹H NMR (300 MHz, D₂O/TSP): 3.37 (s, 6H), 3.12 (s, 2H), 2.00 (m, 8H), 1.27-1.44 (m, 16H), 0.77 (t, 12H). ¹³C NMR (75.47 MHz, D₂O/TSP): 182.71, 63.12, 62.97, 47.68, 26.28, 20.79, 20.15, 15.42.

Table S1. Correlation parameters of Equation (1) used to describe the experimental binodal data at 25°C.

IL + salt + water					
IL	Salt	$A \pm \sigma$	$B \pm \sigma$	$10^5 (C \pm \sigma)$	R^2
[P ₄₄₄₄][MES]	K ₃ C ₆ H ₅ O ₇	98.33 ± 0.54	-0.327 ± 0.022	3.96 ± 0.06	0.9996
[P ₄₄₄₄][CHES]		111.92 ± 2.49	-0.450 ± 0.009	10.50 ± 0.44	0.9929
[P ₄₄₄₄][HEPES]		105.17 ± 1.19	-0.295 ± 4.257	2.78 ± 0.08	0.9978
[P ₄₄₄₄][Tricine]		105.15 ± 5.10	-0.248 ± 0.016	1.71 ± 0.02	0.9992
[P ₄₄₄₄][TES]		99.63 ± 0.51	-0.356 ± 0.007	5.40 ± 0.29	0.9971

Table S2. Experimental TLs and TLLs of the ABS composed of IL + K₃C₆H₅O₇ + H₂O at 25°C.

Weight fraction composition / (wt %)							
IL + K ₃ C ₆ H ₅ O ₇ + water							
IL	[IL] _{IL}	[salt] _{IL}	[IL] _M	[salt] _M	[IL] _{salt}	[salt] _{salt}	TLL
[P ₄₄₄₄][MES]	65.71	1.51	29.42	20.48	2.89	34.36	70.89
	90.81	0.06	29.36	30.33	0.37	44.12	100.60
	94.29	0.01	30.21	39.87	0.27·10 ⁻³	58.64	111.04
[P ₄₄₄₄][CHES]	67.45	1.26	29.70	19.83	0.11	34.38	75.04
	75.58	0.76	29.64	30.25	0.17·10 ⁻⁴	49.27	89.81
	93.56	0.16	30.11	39.95	0.18·10 ⁻⁸	58.83	110.44
[P ₄₄₄₄][HEPES]	57.51	4.14	29.89	20.14	6.59	33.63	57.80
	83.11	0.63	30.24	29.49	0.95	46.00	93.84
	90.97	0.24	29.72	40.13	0.03	59.46	108.52
[P ₄₄₄₄][Tricine]	52.11	7.75	30.08	24.73	4.42	44.50	60.20
	70.02	2.64	30.45	29.71	2.53	48.78	81.75
	94.31	0.19	29.78	40.11	0.54	58.20	110.26
[P ₄₄₄₄][TES]	50.61	5.97	30.28	19.70	0.39	39.87	60.59
	93.58	0.05	30.69	29.89	0.08	44.32	103.45
	96.00	0.02	30.43	39.48	0.11·10 ⁻³	57.80	112.05

Table S3. Experimental weight fraction data for the ABS composed of IL (1) + K₃C₆H₅O₇ (2) + H₂O (3) at 25 °C and atmospheric pressure.

[P ₄₄₄₄][TES]		[P ₄₄₄₄][MES]		[P ₄₄₄₄][HEPES]	
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
76.71	0.96	62.37	1.95	79.05	1.21
70.87	1.36	55.07	3.07	57.38	3.82
68.27	2.17	46.15	5.21	54.39	4.36
65.19	2.44	38.99	7.55	52.99	4.88
61.73	2.92	35.53	9.45	51.00	5.21
59.35	3.82	32.17	10.43	49.78	5.79
57.40	4.38	29.24	12.18	48.55	6.45
55.12	4.67	25.01	14.22	46.85	6.80
51.18	5.62	24.37	14.94	45.84	7.21
48.08	6.76	23.45	15.59	44.92	7.54
45.45	7.58	22.73	15.99	43.94	8.03
44.36	8.01	22.10	16.27	43.08	8.33
43.30	8.31	21.05	17.21	42.24	8.63
41.47	9.27	20.19	17.49	41.06	9.46
39.38	10.12	19.88	17.71	40.29	9.76
37.71	10.70	19.30	18.08	39.61	9.99
36.76	11.09	18.82	18.32	38.78	10.41
35.71	11.69	18.48	18.78	38.09	10.79
34.46	12.49	17.96	19.05	37.15	11.51
33.18	12.85	17.56	19.34	36.51	11.87
32.30	13.27	17.16	19.51	35.92	12.10
31.34	13.85	16.73	19.90	35.09	12.68
30.81	13.98	16.30	20.01	34.58	12.88
29.88	14.51	15.93	20.21	33.99	13.09
29.46	14.56	15.77	20.58	33.20	13.63
28.66	14.96	15.05	21.16	32.72	13.81
27.96	15.39	14.78	21.34	31.98	14.39
27.22	15.82	14.47	21.49	31.54	14.60
26.42	15.92	14.02	21.86	31.09	14.79
25.57	16.33	13.60	22.21	30.50	15.29
24.21	16.84	13.35	22.44	30.07	15.47
23.85	16.93	13.12	22.55	29.44	15.97
23.30	17.33	12.86	22.75	29.03	16.18
22.99	17.35	12.62	22.89	28.48	16.60
22.38	17.80	12.33	23.10	28.11	16.77
21.60	18.21	12.13	23.25	27.54	17.25
21.33	18.26	11.94	23.41	27.16	17.43
20.90	18.58	11.64	23.79	26.77	17.63
20.47	18.89	11.41	23.87	26.26	18.10
20.22	18.89	11.19	24.14	25.91	18.23
19.77	19.19	10.81	24.41	25.55	18.44
19.25	19.37	10.64	24.57	25.09	18.84
18.93	19.56	10.26	25.32	24.76	19.04

18.65	19.78	10.05	25.33	24.43	19.19
18.28	20.02	9.90	25.44	24.13	19.35
17.65	20.34	9.76	25.58	23.85	19.47
17.44	20.36	9.49	25.92	23.56	19.66
17.12	20.62	9.35	26.10	23.14	20.09
16.97	20.76			22.88	20.22
16.55	21.14			22.60	20.41
16.16	21.25			22.37	20.51
15.95	21.33			22.09	20.67
15.78	21.37			21.74	21.01
15.56	21.32			21.49	21.16
15.14	21.59			21.23	21.33
14.97	21.66			20.99	21.51
14.68	21.95			20.76	21.65
14.35	22.09			20.50	21.80
14.21	22.12			20.17	22.17
14.06	22.17			19.95	22.32
13.81	22.43			19.74	22.44
13.46	22.70			19.53	22.58
13.30	22.75			19.33	22.70
13.00	23.11			19.13	22.81
12.87	23.18			18.93	22.94
12.66	23.37			18.74	23.05
12.36	23.56			18.56	23.13
12.12	23.69			18.37	23.28
11.86	23.81			18.18	23.40
11.66	23.92			17.99	23.56
11.44	24.04			17.80	23.71
11.15	24.30			17.64	23.81
10.94	24.38			17.47	23.90
10.68	24.58			17.31	23.99
10.50	24.64			17.06	24.27
10.28	24.80			16.91	24.34
9.98	25.04			16.76	24.43
				16.62	24.49
				16.46	24.55
				16.31	24.67
				16.16	24.83
				16.01	24.98
				15.89	25.08
				15.75	25.17
				15.61	25.27
				15.44	25.35
				15.25	25.43
				14.96	25.57
				14.78	25.57
				14.66	25.64

14.54	25.73
14.43	25.80
14.33	25.87
14.22	25.96
14.11	26.08
14.01	26.14
13.90	26.24
13.68	26.44
13.44	26.52
13.33	26.61
13.12	26.95
13.02	27.04
12.93	27.10
12.82	27.18
12.73	27.26
12.64	27.31
12.56	27.38
12.45	27.48
12.35	27.56
12.26	27.64
12.18	27.71
12.04	27.55
11.91	27.53
11.83	27.64
11.74	27.74
11.66	27.79
11.57	27.79
11.44	28.00
11.36	28.06
11.21	28.19
11.13	28.24
11.06	28.32
10.98	28.36
10.90	28.43
10.82	28.50
10.75	28.55
10.69	28.59
10.56	28.68
10.45	28.84
10.39	28.88
10.31	28.92
10.17	29.06
10.10	29.11
10.00	29.20
9.93	29.24
9.87	29.29
9.77	29.42

9.71	29.47
9.65	29.52
9.60	29.55
9.51	29.73
9.39	29.79
9.29	29.88
9.13	29.82
9.01	29.84
9.08	30.39
8.39	31.06
7.78	31.65
7.40	31.77
7.01	31.97
6.68	32.26
6.31	32.71
5.94	33.24
5.73	33.55
5.43	34.05
5.19	34.18
4.90	34.49
4.65	34.80
4.42	35.07
4.20	35.30
3.96	35.32
3.90	35.14
3.47	35.48
3.24	35.97
3.03	36.46
2.84	36.98
2.67	37.33
2.53	37.67
2.36	38.17
2.18	38.61
2.03	39.14
1.87	39.49
1.71	39.92
1.55	40.36
1.39	40.79
1.23	41.22
1.07	41.65
0.90	42.08
0.74	42.51
0.58	42.94
0.42	43.38
0.26	43.81
0.10	44.24

Table S4. Experimental weight fraction data for the ABS composed of IL (1) + K₃C₆H₅O₇ (2) + H₂O (3) at 25 °C and atmospheric pressure.

[P ₄₄₄₄][CHES]		[P ₄₄₄₄][Tricine]	
100 w ₁	100 w ₂	100 w ₁	100 w ₂
44.76	3.92	77.51	1.40
41.71	4.74	69.04	3.28
39.33	5.34	60.39	4.60
37.55	5.83	45.31	10.91
36.22	6.34	43.30	12.04
34.48	6.67	41.79	12.71
33.48	7.04	40.77	13.40
32.32	7.47	39.41	13.86
30.98	7.83	38.48	14.52
29.73	8.17	37.52	15.07
28.73	8.39	36.64	15.63
27.94	8.79	35.83	16.16
27.39	9.18	35.08	16.64
26.69	9.53	34.32	17.15
25.86	9.67	33.65	17.61
25.25	10.02	32.93	18.09
24.53	10.24	32.27	18.52
23.96	10.60	31.59	18.97
23.32	10.72	30.98	19.39
22.79	10.83	30.45	19.68
22.46	11.16	29.86	20.06
21.96	11.28	29.33	20.41
21.47	11.46	28.80	20.78
21.06	11.73	27.97	21.61
20.53	11.92	27.50	21.99
20.03	12.05	27.05	22.29
19.69	12.25	26.61	22.58
19.27	12.36	26.18	22.80
18.95	12.57	25.52	23.47
18.58	12.67	25.11	23.75
18.27	12.86	24.71	23.98
17.91	12.90	24.29	24.15
17.61	13.14	23.95	24.37
17.24	13.19	23.41	24.94
16.95	13.38	23.08	25.13
16.60	13.53	22.78	25.31
16.27	13.70	21.98	25.95
15.94	13.83	21.69	26.17
15.64	13.97	21.24	26.63
15.35	14.12	20.99	26.78
15.08	14.19	20.71	26.95
14.87	14.13	20.26	27.41
14.62	14.20	20.04	27.47

14.36	14.23	19.66	27.85
14.17	14.41	19.44	28.02
13.93	14.57	19.21	28.17
13.71	14.61	18.90	28.45
13.49	14.73	18.61	28.74
13.32	14.86	18.30	29.02
13.10	14.96	18.11	29.14
12.89	15.07	17.78	29.48
12.69	15.11	17.58	29.57
12.53	15.23	17.41	29.75
12.36	15.28	17.19	29.88
12.18	15.41	16.93	30.15
11.96	15.35	16.67	30.38
11.87	15.52	16.51	30.52
11.73	15.61	16.25	30.77
11.61	15.71	16.09	30.87
11.47	15.78	15.86	31.06
11.33	15.81	15.61	31.28
11.22	15.89	15.36	31.53
11.11	15.94	15.22	31.58
11.01	16.05	14.99	31.80
10.89	16.07	14.77	32.00
10.78	16.18	14.54	32.24
10.59	16.16	14.27	32.41
10.50	16.22	14.09	32.60
10.40	16.32	13.97	32.64
10.30	16.38	13.78	32.85
10.18	16.43	13.64	32.97
10.05	16.65	13.47	33.15
9.90	16.63	13.27	33.23
9.81	16.70	13.10	33.42
9.73	16.76	12.88	33.71
9.65	16.83	12.77	33.76
9.55	16.88	12.49	33.98
9.46	16.96	12.03	34.02
9.37	16.94	11.87	34.18
9.28	17.00	11.71	34.36
9.17	17.17	11.58	34.49
9.04	17.35	11.43	34.66
8.88	17.45	11.31	34.79
7.88	19.13	11.16	34.83
7.59	19.32	11.03	35.00
7.24	19.86	10.89	35.17
6.97	19.88	10.81	35.17
6.67	20.18	10.70	35.31
6.39	20.24	10.46	35.57
6.16	20.70	10.62	35.21

5.89	20.61	10.23	35.74
5.59	21.35	9.84	36.26
5.27	21.22	9.45	36.79
5.05	21.46	9.06	37.32
4.85	21.89	8.68	37.85
4.64	22.17	8.29	38.37
4.44	22.21	7.90	38.91
4.28	22.48	7.51	39.43
4.15	22.83	7.12	39.95
3.98	23.02	6.72	40.44
3.80	23.28	6.36	41.05
3.67	23.42	5.95	41.44
3.52	23.64	5.55	42.03
3.42	23.80	5.36	42.28
3.30	23.90	5.07	42.55
3.22	24.19	4.87	42.87
3.11	24.21	4.75	42.71
3.00	24.53	4.50	43.09
2.90	25.13	4.30	43.28
2.79	25.33	4.08	43.58
2.71	25.53	3.86	43.86
2.62	25.68	3.73	43.88
2.62	24.71	3.61	43.81
2.45	24.16	3.42	44.21
2.38	24.30	3.28	44.45
2.31	24.53	3.13	44.73
2.25	24.62	2.98	45.05
2.16	24.77	2.86	45.34
2.08	25.04	2.74	45.59
2.00	25.34	2.59	45.88
1.91	25.76	2.48	46.17
1.83	25.92	2.33	46.53
1.75	26.28	2.23	46.67
1.67	26.45	2.13	46.91
1.60	26.74	1.99	47.40
1.52	26.98	1.89	47.13
1.46	27.28	1.74	47.23
1.39	27.59		
1.31	27.82		
1.23	28.19		
1.17	28.53		
1.10	28.85		
1.04	29.09		
0.99	29.39		

Table S5. Extraction efficiency ($EE_{\text{PSA}}\%$) and recovery efficiencies ($RY_{\text{PSA}}\%$) of PSA at 25° C in the ABS composed of ILs and $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$.

IL	Weight fraction composition / (wt %)		$EE_{\text{PSA}}\%$	$RY_{\text{PSA}}\%$
	[IL]IL	[salt]IL		
[P4444][MES]	30.35 ± 0.15	30.84 ± 0.53	100	96.32 ± 1.05
	30.01 ± 0.04	40.03 ± 0.14	100	95.97 ± 0.96
[P4444][CHES]	30.13 ± 0.25	30.54 ± 0.63	100	97.96 ± 0.90
	29.94 ± 0.13	40.12 ± 0.57	100	98.53 ± 1.13
[P4444][HEPES]	30.16 ± 0.35	30.44 ± 0.29	100	9.88 ± 1.79
	30.09 ± 0.34	39.97 ± 0.27	100	10.51 ± 1.12
[P4444][Tricine]	30.90 ± 0.28	30.70 ± 0.31	100	6.58 ± 1.09
	30.37 ± 0.17	39.98 ± 0.07	100	7.08 ± 0.45
[P4444][TES]	29.95 ± 0.24	30.08 ± 0.69	100	31.77 ± 1.68
	30.63 ± 0.37	39.85 ± 0.17	100	32.01 ± 0.96

Table S6. Experimental data for the CF of the systems composed of [P₄₄₄₄][GB] + K₃C₆H₅O₇ + water at 25°C.

[P ₄₄₄₄][MES]							
CF	5	20	50	100	150	200	250
w IL / g	0.1538	0.8746	0.9034	0.4669	0.608	0.3206	0.2578
w Salt/ g	0.4907	11.1844	28.8004	29.0330	58.2693	40.8537	40.8927
w H ₂ O/ g	0.3556	7.9404	20.3765	20.5313	41.1231	28.8267	28.8521
w Top/ g	0.0783	0.4023	0.4108	0.2064	0.2603	0.1476	0.1166
w Bottom/ g	0.8099	18.7884	48.9843	46.2209	98.9366	69.2375	69.1359
Real CF	4.54	19.74	49.60	99.47	157.98	195.30	247.45

[P ₄₄₄₄][CHES]							
CF	5	20	50	100	150	200	250
w IL / g	0.1546	0.8718	0.896	0.4543	0.3079	0.317	0.2541
w Salt/ g	0.4918	11.2273	28.8647	29.1384	29.2327	40.9848	41.0242
w H ₂ O/ g	0.3553	7.9012	20.2728	20.4156	20.4793	28.7043	28.7221
w Top/ g	0.0855	0.4322	0.3842	0.2101	0.1319	0.1406	0.1174
w Bottom/ g	0.8246	17.8944	48.8542	49.2884	49.1391	68.4552	69.6864
Real CF	4.16	18.28	52.77	97.17	155.26	204.16	244.65

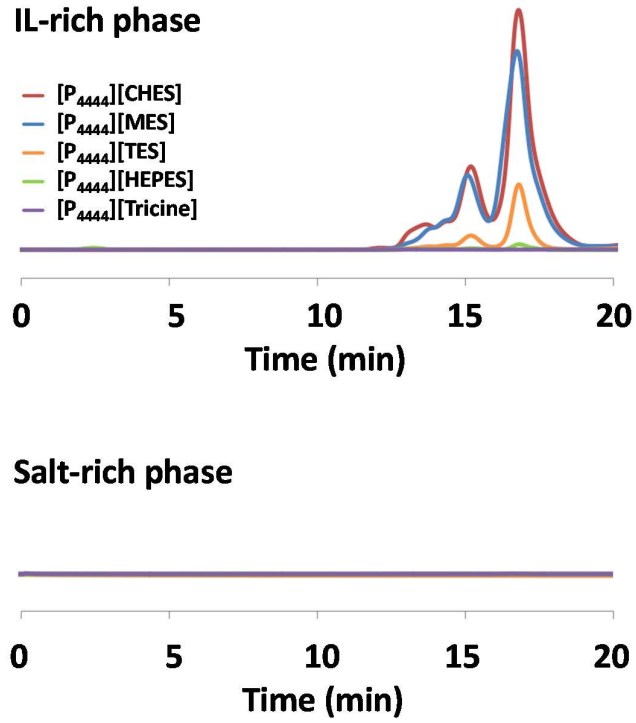


Figure S2. SE-HPLC profiles of ABS composed of [P₄₄₄₄][GB] + salt + PSA aqueous solution (150 ng.mL⁻¹).