Synthesis of purine-based ionic liquids and their applications

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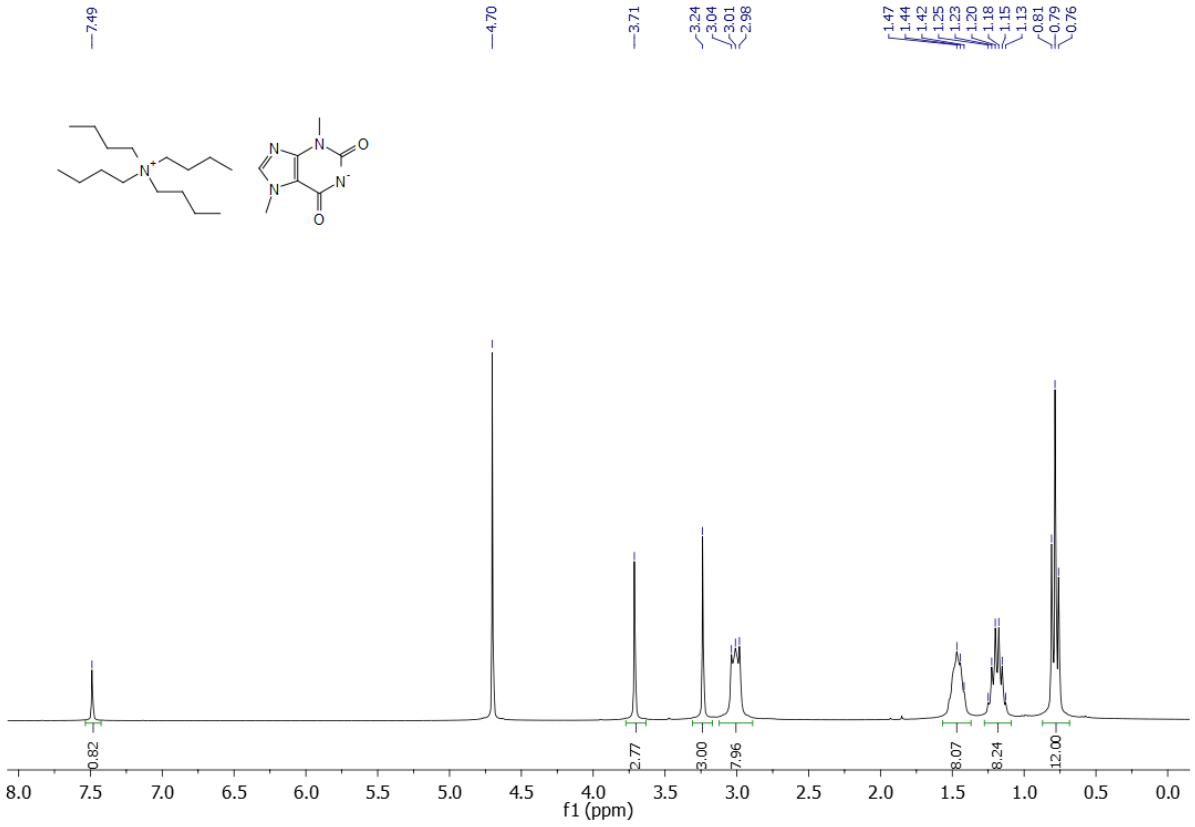
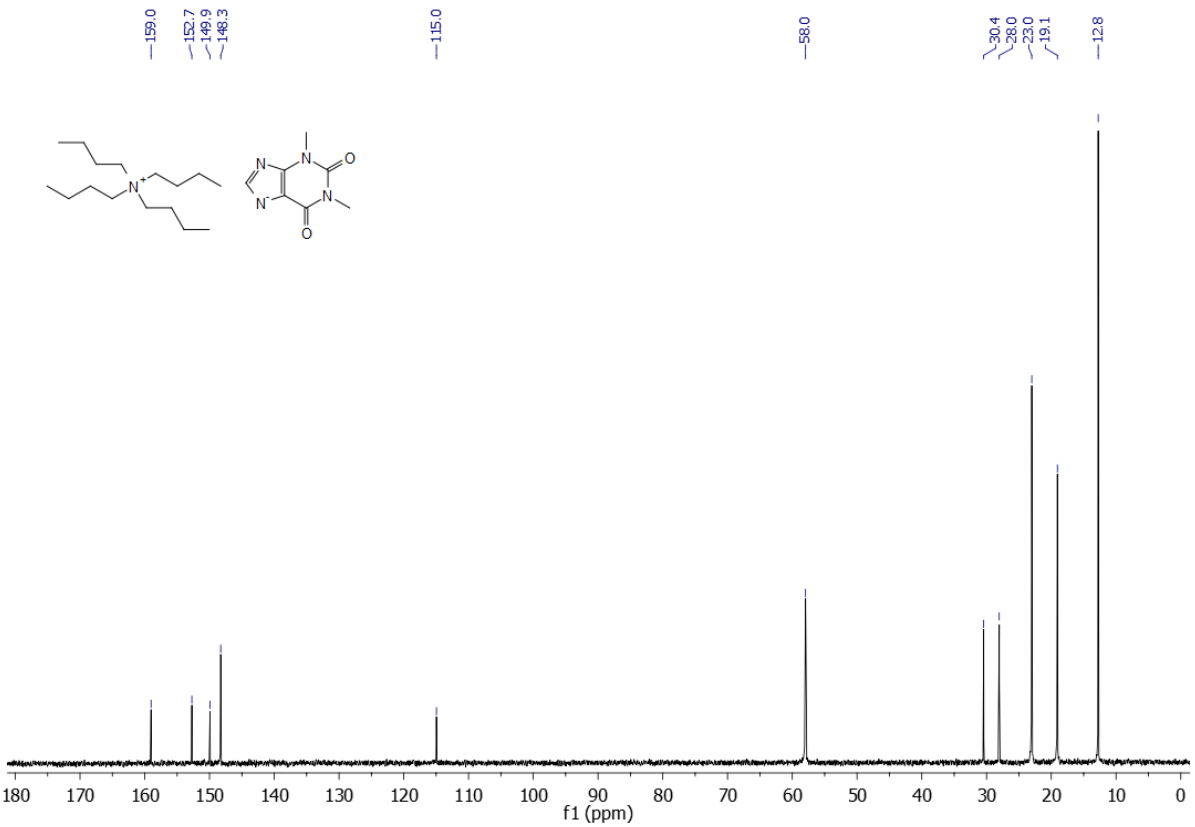
Nuclear magnetic resonance (NMR) characterization

Tetrabutylammonium theobrominate, [N_{4444}][Theob]:

^{1}H NMR (D_2O, 300 MHz, [ppm]): δ 0.78 (t, J_{HH} = 7.3 Hz, 12H, $N^+CH_2CH_2CH_2\boldsymbol{CH_3}$), 1.19 (sext, J_{HH} = 7.3 Hz, 8H, $N^+CH_2CH_2\boldsymbol{CH_2}CH_3$), 1.37 – 1.57 (m, 8H, $N^+CH_2\boldsymbol{CH_2}CH_2CH_3$), 2.89 – 3.12 (m, 8H, $N^+\boldsymbol{CH_2}CH_2CH_2CH_3$), 3.24 (s, 3H, -CONC$\boldsymbol{H_3}$-), 3.71 (s, 3H, -NCHC$\boldsymbol{H_3}$-), 7.49 (s, 1H, -NC$\boldsymbol{H}$N-). ^{13}C NMR ($D_2O$, 75.47 MHz, [ppm]): δ 12.8, 19.1, 23.0, 29.3, 33.2, 58.0, 109.6, 141.2, 149.9, 159.4, 165.1.



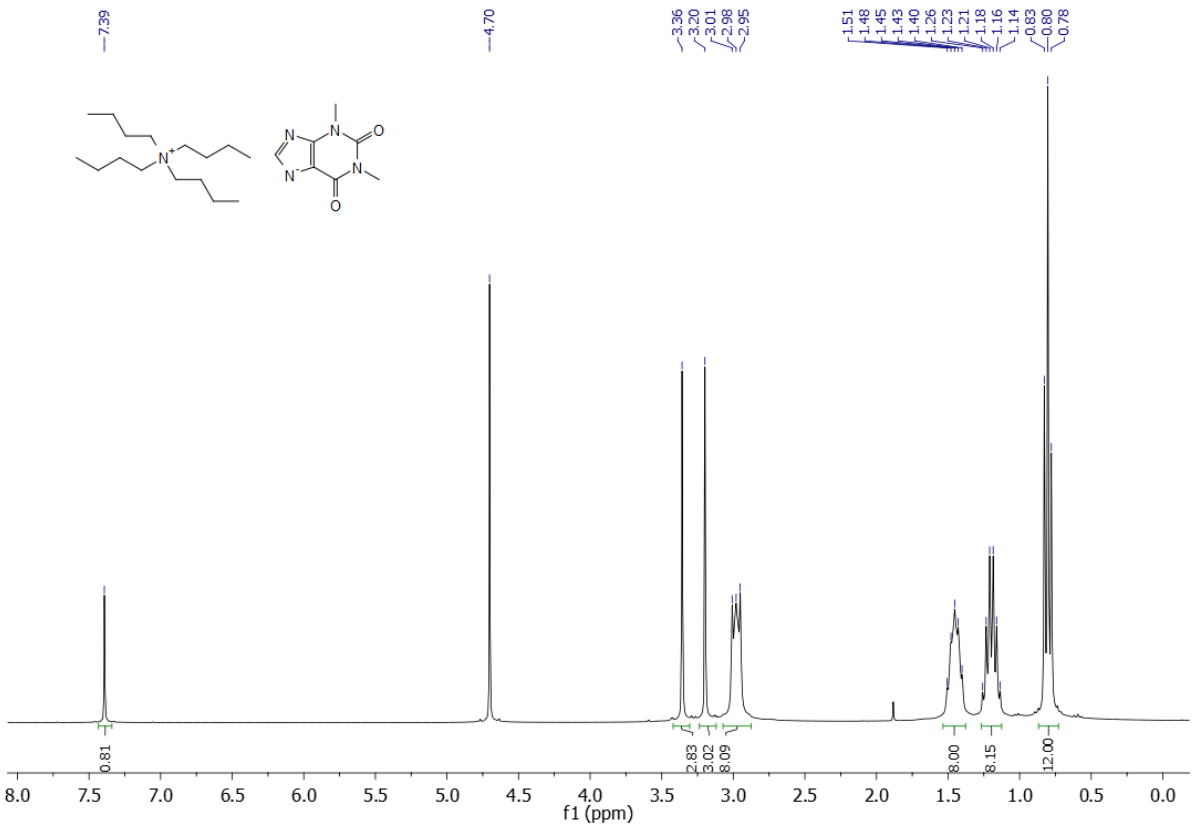
Spectrum S1. ^{1}H NMR spectra of [N_{4444}][Theob] (D_2O, 300 MHz).



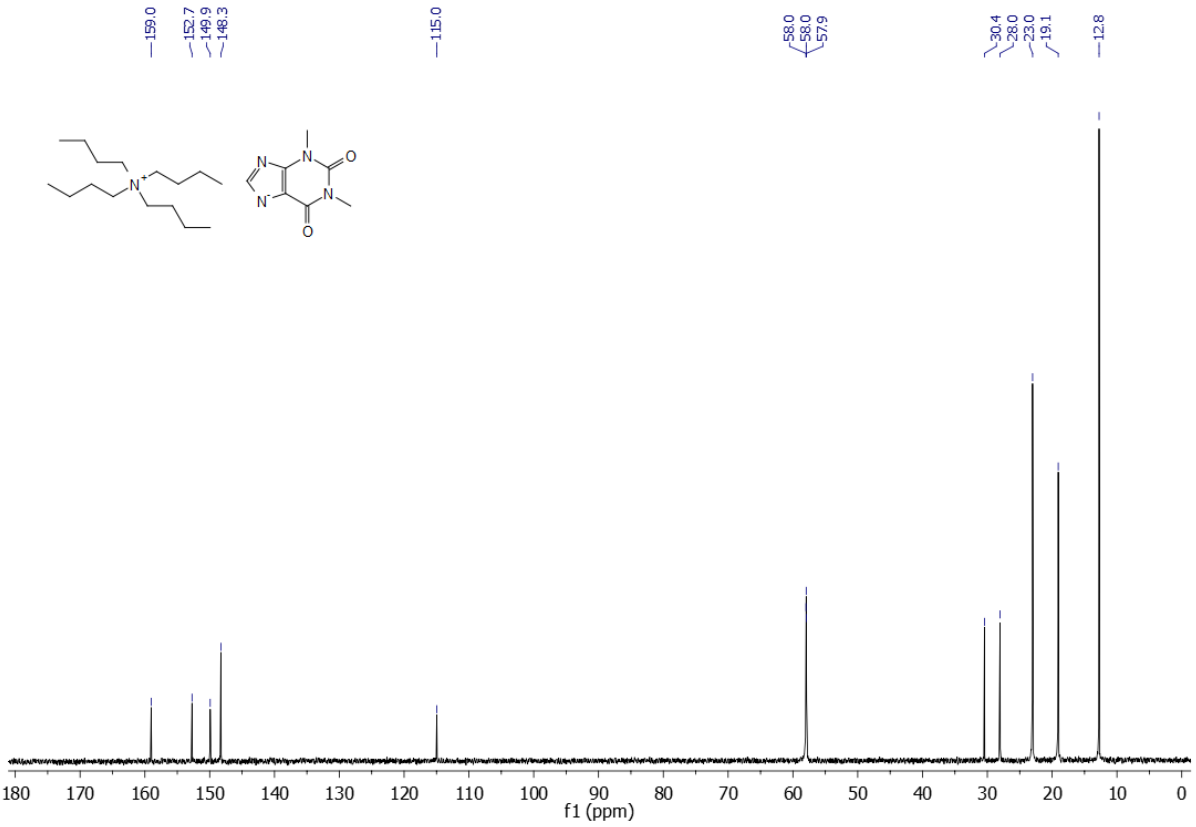
Spectrum S2. ^{13}C NMR spectra of [N_{4444}][Theob] (D_2O, 75.47 MHz).

Tetrabutylammonium theophillinate, [N_{4444}][Theop]:

^{1}H NMR (D_2O, 300 MHz, [ppm]): δ 0.80 (t, J_{HH} = 7.3 Hz, 12H, $N^+CH_2CH_2CH_2C\boldsymbol{H}_3$), 1.20 (sext, J_{HH} = 7.3 Hz, 8H, $N^+CH_2CH_2C\boldsymbol{H}_2CH_3$), 1.23 – 1.51 (m, 8H, $N^+CH_2C\boldsymbol{H}_2CH_2CH_3$), 2.95 – 3.01 (m, 8H, $N^+C\boldsymbol{H}_2CH_2CH_2CH_3$), 3.20 (s, 3H, -CON(C$\boldsymbol{H}_3$)CO-), 3.36 (s, 3H, -CON(C$\boldsymbol{H}_3$)C-), 7.39 (s, 1H, -NC$\boldsymbol{H}$N-). ^{13}C NMR (D_2O, 75.47 MHz, [ppm]): δ 12.8, 19.1, 23.0, 28.0, 30.4, 58.0, 115.0, 148.3, 149.9, 152.7, 159.0.



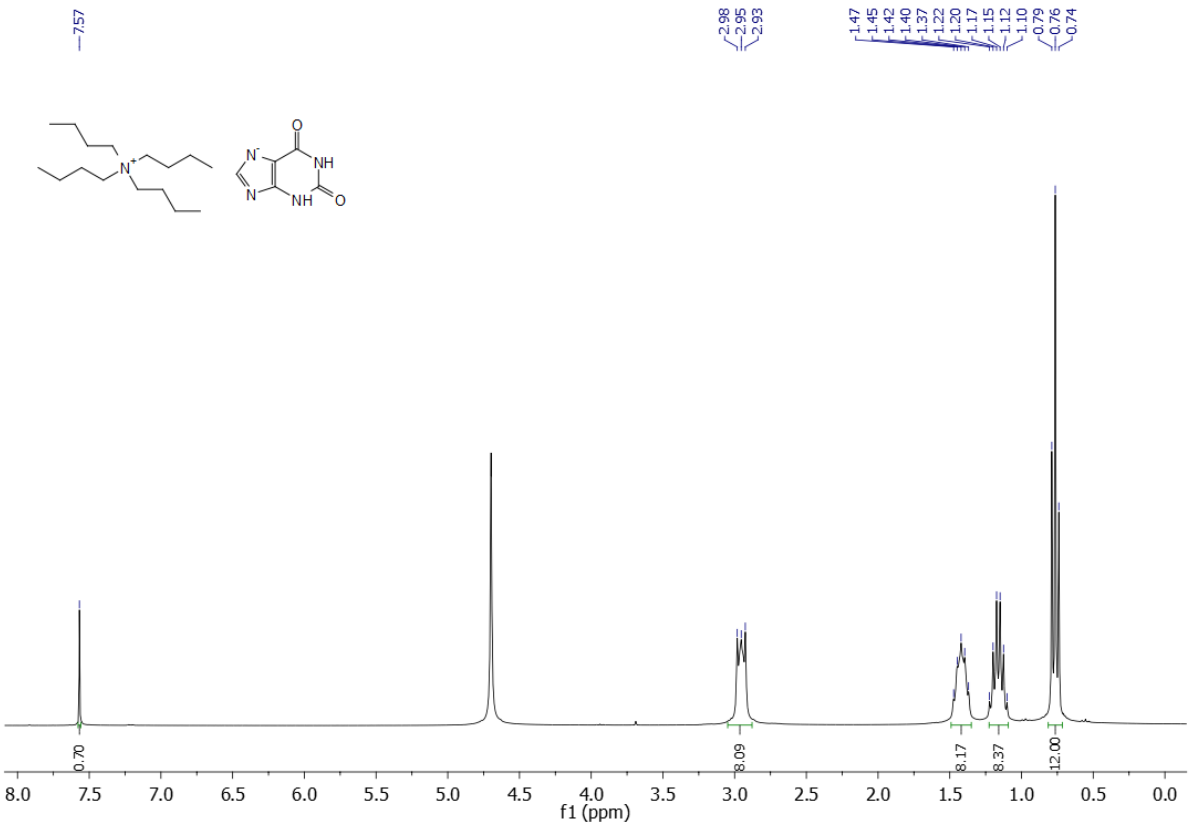
Spectrum S3. ^{1}H NMR spectra of [N_{4444}][Theop] (D_2O, 300 MHz).



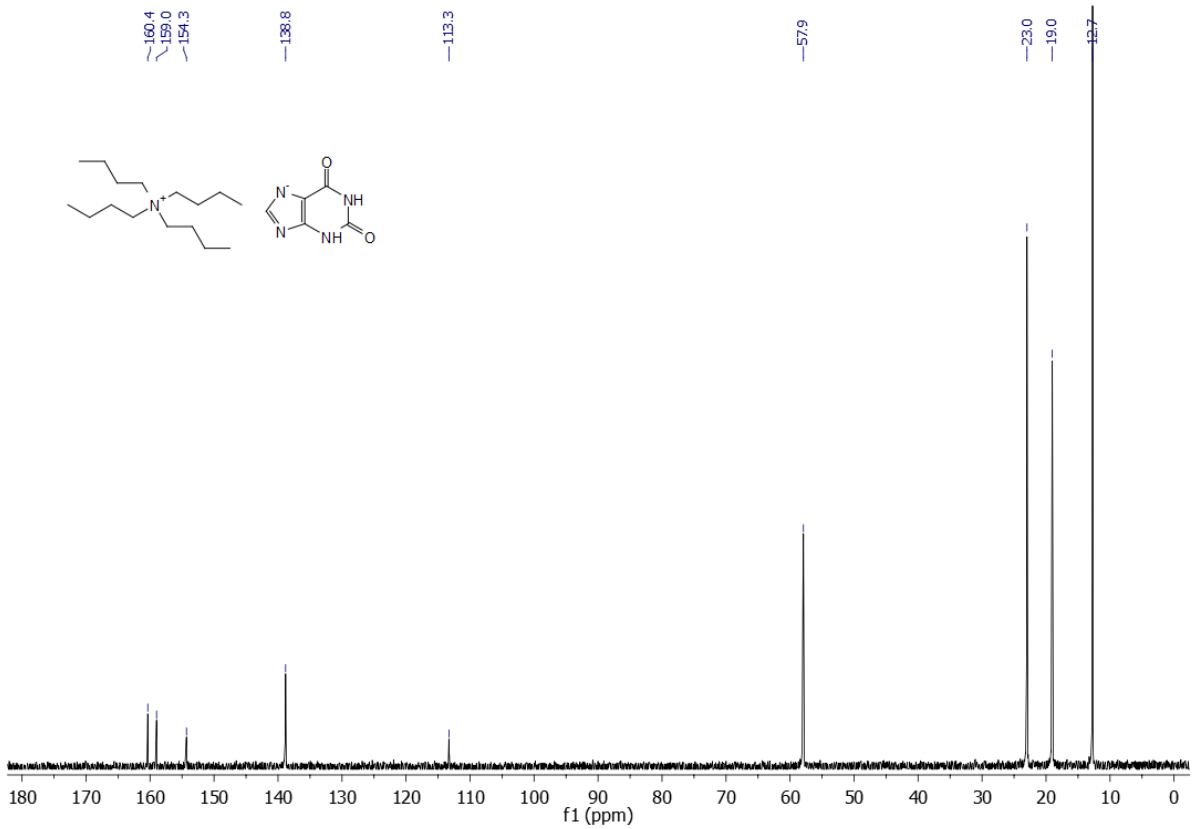
Spectrum S4. ^{13}C NMR spectra of [N_{4444}][Theop] (D_2O, 75.47 MHz).

Tetrabutylammonium xanthinate, [N_{4444}][Xan]:

^{1}H NMR (D_2O, 300 MHz, [ppm]): δ 0.76 (t, J_{HH} = 7.3 Hz, 12H, $N^+CH_2CH_2CH_2C\boldsymbol{H}_3$), 1.16 (sext, J_{HH} = 7.3 Hz, 8H, $N^+CH_2CH_2C\boldsymbol{H}_2CH_3$), 1.37 – 1.47 (m, 8H, $N^+CH_2C\boldsymbol{H}_2CH_2CH_3$), 2.93 – 2.98 (m, 8H, $N^+\boldsymbol{C}H_2CH_2CH_2CH_3$), 7.57 (s, 1H, -NC***H***N-). ^{13}C NMR (D_2O, 75.47 MHz, [ppm]): δ 12.7, 19.0, 23.0, 57.9, 113.3, 138.8, 154.3, 159.0, 160.4.



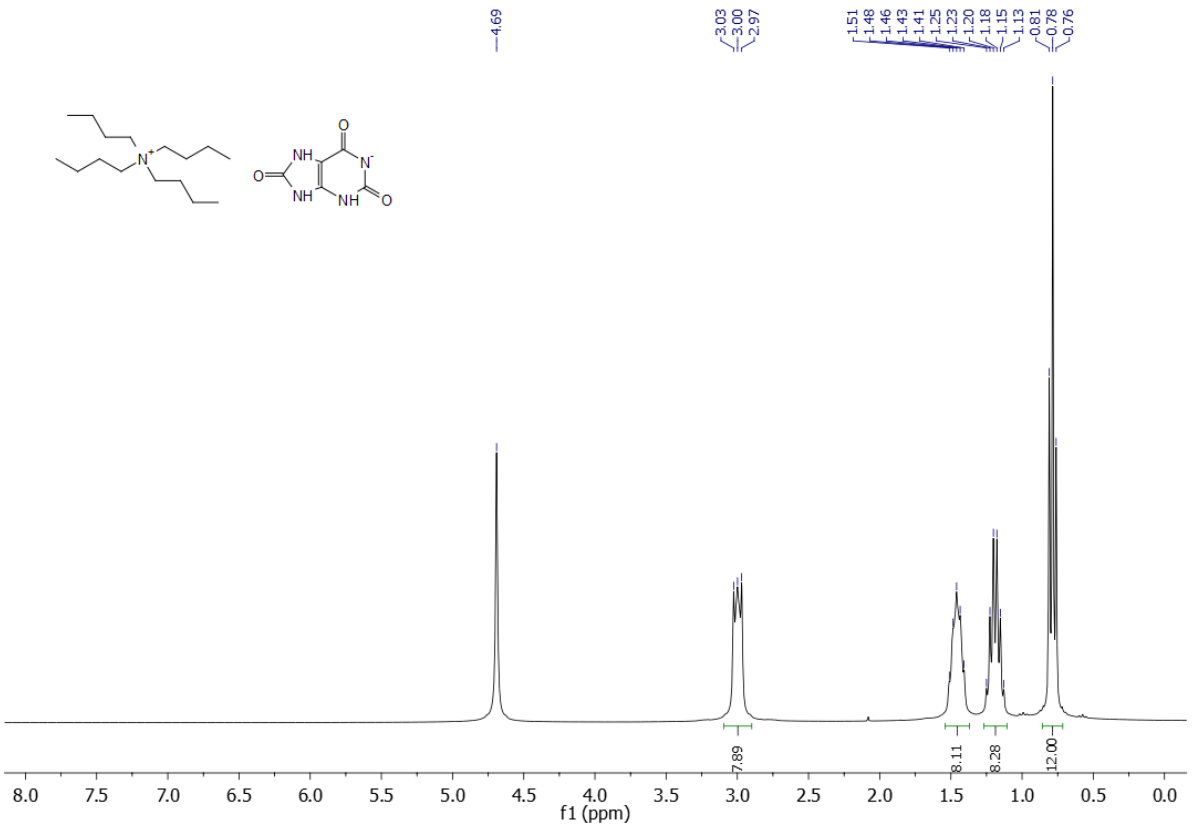
Spectrum S5. ^{1}H NMR spectra of [N_{4444}][Xan] (D_2O, 300 MHz).



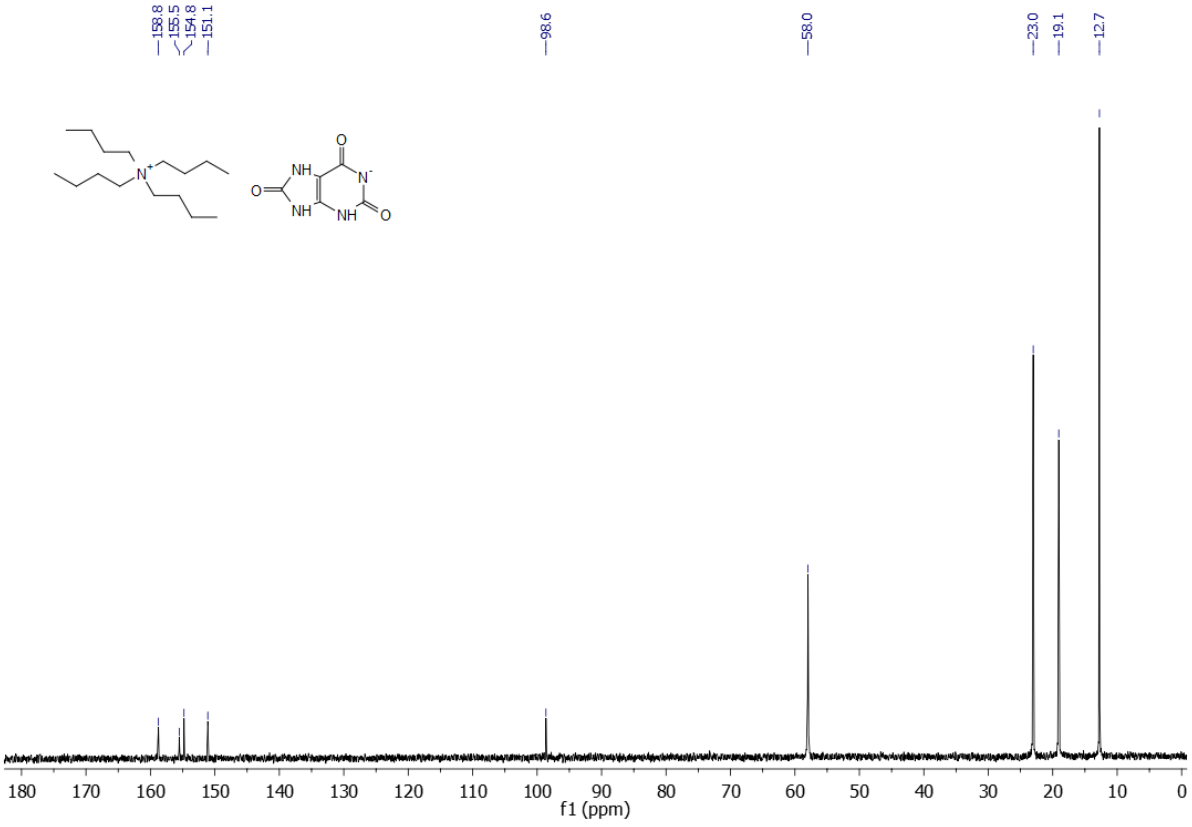
Spectrum S6. ^{13}C NMR spectra of [N_{4444}][Xan] (D_2O, 75.47 MHz).

Tetrabutylammonium urate, [N_{4444}][Ur]:

^{1}H NMR (D_2O, 300 MHz, [ppm]): δ 0.79 (t, J_{HH} = 7.3 Hz, 12H, $N^+CH_2CH_2CH_2C\mathbf{H}_3$), 1.16 (sext, J_{HH} = 7.2 Hz, 8H, $N^+CH_2CH_2C\mathbf{H}_2CH_3$), 1.46 (quint, J_{HH} = 15.4, 8.0 Hz, 8H, $N^+CH_2C\mathbf{H}_2CH_2CH_3$), 2.97 – 3.03 (m, 8H, $N^+C\mathbf{H}_2CH_2CH_2CH_3$). ^{13}C NMR ($D_2O$, 75.47 MHz, [ppm]): δ 12.7, 19.1, 23.0, 58.0, 98.6, 151.1, 154.8, 155.5, 158.8.



Spectrum S7. ^{1}H NMR spectra of [N_{4444}][Ur] (D_2O, 300 MHz).



Spectrum S8. ^{13}C NMR spectra of [N_{4444}][Ur] (D_2O, 75.47 MHz).

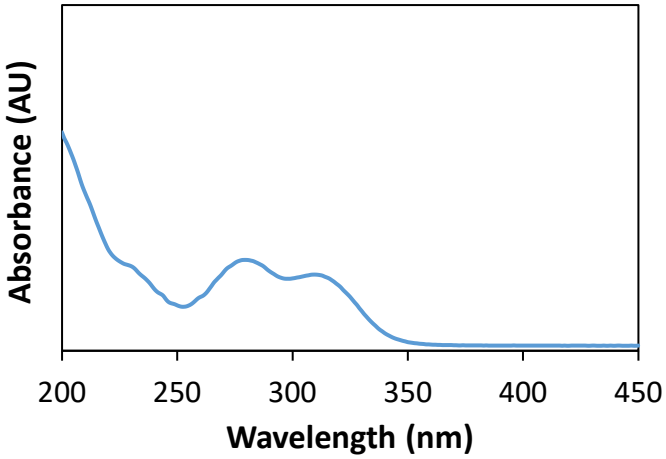


Figure S1. Ferulic acid absorbance spectrum in an aqueous solution of $[N_{4444}][Theob]$ at 0.5 mol·L^{-1}.

Table S1. Molar water-solubility (S) of the purine-based ILs, pH of the saturated IL solution at (298 ± 1) K and molar water-solubility of their respective purines (S_0).

IL	$S \pm \sigma$ (mol·L^{-1})	pH saturated	Purine	S_0 (mol·L^{-1})[a]
$[N_{4444}][Theob]$	1.59 ± 0.07	12.76	Theobromine	1.83×10^{-3} [b]
$[N_{4444}][Theop]$	2.2 ± 0.1	10.89	Theophylline	4.09×10^{-2} [b]
$[N_{4444}][Xan]$	0.17 ± 0.01	10.14	Xanthine	4.60×10^{-4} [c]
$[N_{4444}][Ur]$	0.096 ± 0.007	8.31	Uric acid	3.57×10^{-4} [d]

[a] Data from PubChem [1]. [b] Solubility measured at (298 ± 1) K. [c] Solubility determined at (289 ± 1) K. [d] Solubility determined at (293 ± 1) K.

Table S2. Molar solubility (S) of sodium theophyllinate in an aqueous solution of $[N_{4444}]Cl$ (1.0 mol·L^{-1}) and in pure water (S_0) and its molar aqueous solubility enhancement (S/S_0). The pH of the initial aqueous solution of $[N_{4444}]Cl$ and of the final saturated solution are also shown.

$S \pm \sigma$ (mol·L^{-1})	$S_0 \pm \sigma$ (mol·L^{-1})	S/S_0	pH initial	pH saturated
0.30 ± 0.02	0.26 ± 0.01	1.13	4.23	10.55

Table S3. EC_{50} values ($mg \cdot L^{-1}$) of the purine-based ILs and $[N_{4444}]Cl$, after 96 h of incubation with the microalgae *Raphidocelis subcapitata* and the logarithm function of their anion octanol-water partition coefficient, log (K_{ow}). The respective 95% confidence limits are presented in the parenthesis.

IL	**EC_{50} / ($mg \cdot L^{-1}$) (lower limit; upper limit)**	**log (K_{ow})[a]**
$[N_{4444}][Theob]$	2.6 (1.8; 3.3)	-3.17
$[N_{4444}][Theop]$	3.7 (1.4; 5.9)	-2.12
$[N_{4444}][Xan]$	0.8 (0.7; 1.0)	-1.49
$[N_{4444}][Ur]$	2.7 (1.6; 3.7)	-2.75
$[N_{4444}]Cl$	2.6 (2.0; 3.1)	0.96

[a] Data from Marvin 21.14 [2].

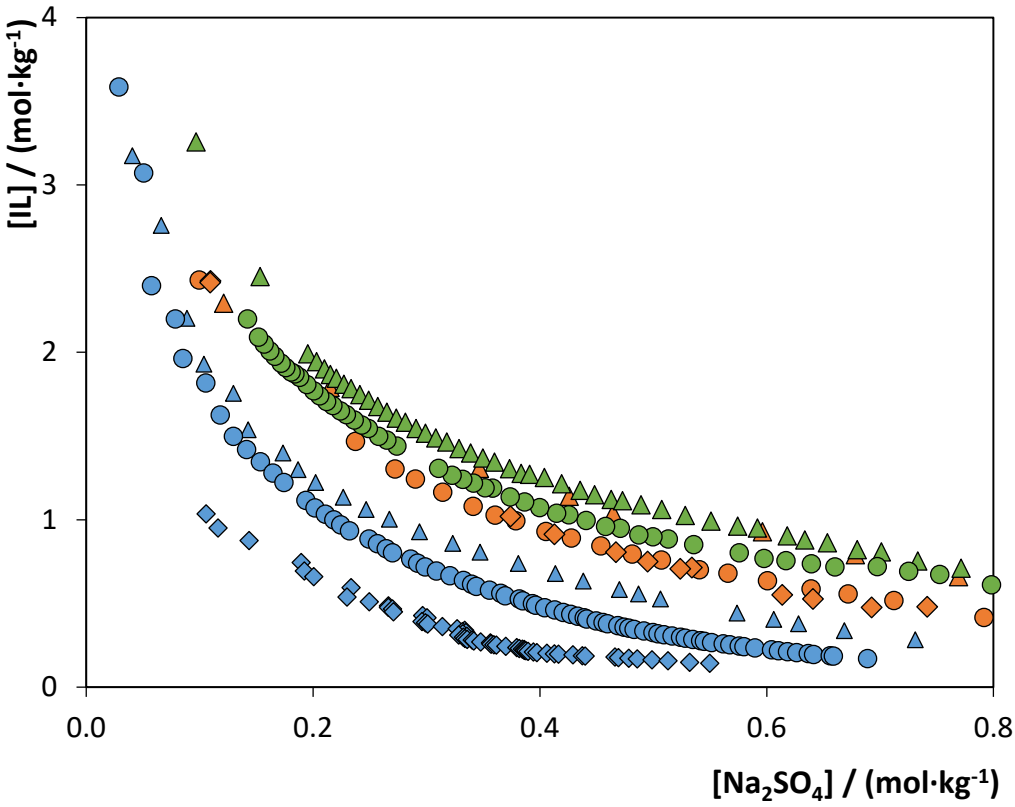


Figure S2. Binodal curves of the ternary systems composed of $[N_{4444}][Theop]$ (blue), $[N_{4444}][Theob]$ (orange) or $[N_{4444}]Cl$ (green), water and Na_2SO_4 at 298 K (Δ), 323 K (○) or 353 K (◇) (± 1 K) and atmospheric pressure (0.1 MPa). $[N_{4444}]Cl$ was not tested at (353 ± 1) K.

Table S4. Experimental weight fraction of the ternary systems composed of IL, water and Na_2SO_4 at (298 ± 1) K and atmospheric pressure (0.1 MPa).

[N_{4444}]Cl					
IL (wt%)	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**
47.51	1.36	29.65	4.07	23.25	6.50
40.54	2.13	29.27	4.19	22.76	6.72
35.63	2.70	28.92	4.32	22.19	6.98
35.08	2.80	28.38	4.46	21.59	7.25
34.56	2.89	28.00	4.59	21.08	7.54
34.17	2.97	27.55	4.73	20.89	7.75
33.90	3.04	27.21	4.86	20.07	8.07
33.46	3.13	26.62	5.03	19.64	8.25
33.13	3.21	26.18	5.16	19.31	8.49
32.68	3.31	26.09	5.26	18.59	8.80
32.27	3.41	25.83	5.42	18.32	9.06
31.79	3.52	25.25	5.62	17.31	9.43
31.35	3.63	24.61	5.82	16.48	9.88
30.88	3.74	24.21	5.99	16.32	10.39
30.55	3.84	23.75	6.17		
[N_{4444}][Theob]					
IL (wt%)	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**
49.16	1.69	30.46	6.19	20.45	10.44
43.02	2.96	28.10	7.81	18.05	11.36
35.51	4.69	25.01	8.79	17.09	11.98
32.45	5.70	21.76	9.85	15.88	12.68
[N_{4444}][Theop]					
IL (wt%)	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**
57.24	0.57	32.35	3.12	19.72	6.26
53.77	0.93	30.92	3.38	19.01	6.47
48.17	1.24	29.70	3.66	18.15	6.71
44.85	1.45	28.14	4.00	15.73	7.53
42.53	1.81	26.57	4.39	14.56	7.93
39.33	1.99	25.35	4.70	13.77	8.19
37.09	2.40	23.76	5.13	12.46	8.67
35.38	2.58	22.23	5.55	10.63	9.41
34.02	2.79	21.06	5.86		

Table S5. Experimental weight fraction of the ternary systems composed of IL, water and Na_2SO_4 at (323 ± 1) K and atmospheric pressure (0.1 MPa).

[N_{4444}]Cl					
IL (wt%)	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**
37.93	1.98	30.33	3.33	20.86	6.27
36.75	2.11	30.03	3.41	20.17	6.47
36.28	2.18	29.41	3.53	19.98	6.63
35.81	2.25	29.09	3.63	19.75	6.79
35.45	2.31	28.58	3.74	19.11	7.07

34.98	2.38	26.65	4.23	18.23	7.56
34.66	2.44	26.01	4.38	17.60	7.82
34.35	2.50	25.65	4.50	17.33	8.05
34.21	2.54	25.29	4.62	16.99	8.33
33.95	2.60	24.87	4.76	16.68	9.01
33.43	2.69	24.84	4.84	16.64	8.57
32.98	2.77	24.01	5.04	16.14	9.34
32.60	2.84	23.50	5.20	15.73	9.66
32.17	2.92	22.95	5.37	14.51	10.18
31.85	3.00	22.41	5.56	14.03	10.57
31.45	3.08	22.23	5.70	13.43	11.07
31.15	3.15	21.68	5.89		
30.71	3.24	21.07	6.11		
$[N_{4444}][Theob]$					
IL (wt%)	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**
50.64	1.40	28.17	5.44	19.84	8.32
38.22	3.26	27.28	5.73	18.99	8.71
35.46	3.72	26.23	6.05	17.88	9.19
34.38	3.96	25.08	6.40	14.94	10.11
32.92	4.27	24.22	6.72	13.81	10.69
31.27	4.62	22.83	7.13	12.44	11.33
30.21	4.87	22.27	7.44		
29.51	5.10	21.13	7.86		
$[N_{4444}][Theop]$					
IL (wt%)	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**
60.19	0.40	22.63	4.20	12.67	6.42
56.43	0.71	21.91	4.35	12.36	6.53
50.28	0.81	21.16	4.51	12.07	6.63
48.11	1.10	20.60	4.60	11.86	6.68
45.30	1.19	20.22	4.66	11.63	6.75
43.38	1.47	19.62	4.81	11.38	6.83
40.66	1.65	19.09	4.93	11.12	6.93
38.71	1.81	18.71	4.98	10.93	6.98
37.43	1.97	18.16	5.14	10.70	7.06
36.22	2.13	17.87	5.18	10.48	7.14
35.04	2.28	17.37	5.29	10.32	7.18
34.01	2.41	17.07	5.33	10.10	7.26
31.98	2.67	16.65	5.43	9.81	7.39
31.11	2.78	16.24	5.54	9.62	7.46
30.35	2.90	15.85	5.63	9.39	7.56
29.62	3.01	15.50	5.72	9.22	7.61
28.99	3.09	15.16	5.80	8.97	7.73
28.23	3.19	14.85	5.87	8.56	7.90
27.19	3.42	14.64	5.90	8.39	7.98
26.51	3.52	14.29	6.00	8.18	8.07
25.85	3.62	14.01	6.08	7.98	8.17
25.27	3.69	13.77	6.13	7.75	8.29
24.36	3.90	13.39	6.24	7.61	8.35
23.77	3.99	13.12	6.31	7.32	8.52

23.24	4.07	12.91	6.36	7.21	8.56

Table S6. Experimental weight fraction of the ternary systems composed of IL, water and Na_2SO_4 at (353 ± 1) K.

[N_{4444}][Theob]					
IL (wt%)	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**
50.57	1.53	22.93	6.92	11.01	11.29
50.47	1.53	23.14	7.05	6.14	12.55
30.07	5.04	18.83	8.02	4.60	13.40
27.80	5.54	18.18	8.34	1.80	15.24
25.35	6.22	16.71	8.96	0.78	16.98
24.03	6.57	16.81	9.53		
[N_{4444}][Theop]					
IL (wt%)	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**	**IL (wt%)**	**Na_2SO_4 (wt%)**
60.19	0.40	21.91	4.35	12.07	6.63
56.43	0.71	21.16	4.51	11.86	6.68
50.28	0.81	20.60	4.60	11.63	6.75
48.11	1.10	20.22	4.66	11.38	6.83
45.30	1.19	19.62	4.81	11.12	6.93
43.38	1.47	19.09	4.93	10.93	6.98
40.66	1.65	18.71	4.98	10.70	7.06
38.71	1.81	18.16	5.14	10.48	7.14
37.43	1.97	17.87	5.18	10.32	7.18
36.22	2.13	17.37	5.29	10.10	7.26
35.04	2.28	17.07	5.33	9.81	7.39
34.01	2.41	16.65	5.43	9.62	7.46
31.98	2.67	16.24	5.54	9.39	7.56
31.11	2.78	15.85	5.63	9.22	7.61
30.35	2.90	15.50	5.72	8.97	7.73
29.62	3.01	15.16	5.80	8.56	7.90
28.99	3.09	14.85	5.87	8.39	7.98
28.23	3.19	14.64	5.90	8.18	8.07
27.19	3.42	14.29	6.00	7.98	8.17
26.51	3.52	14.01	6.08	7.75	8.29
25.85	3.62	13.77	6.13	7.61	8.35
25.27	3.69	13.39	6.24	7.32	8.52
24.36	3.90	13.12	6.31	7.21	8.56
23.77	3.99	12.91	6.36	6.70	8.91
23.24	4.07	12.67	6.42		
22.63	4.20	12.36	6.53		

Table S7. Experimental weight fraction of the ternary systems composed of IL, water and $K_3C_6H_5O_7$ at (298 ± 1) K.

[N_{4444}][Theob]					
IL (wt%)	**$K_3C_6H_5O_7$ (wt%)**	**IL (wt%)**	**$K_3C_6H_5O_7$ (wt%)**	**IL (wt%)**	**$K_3C_6H_5O_7$ (wt%)**
53.97	5.53	34.98	13.12	18.96	23.48

53.10	5.44	33.07	14.58	18.87	23.35
51.23	6.66	32.67	14.40	17.63	24.44
49.87	6.48	32.13	14.82	17.56	24.35
48.08	7.68	31.82	14.68	16.78	25.05
47.39	7.57	30.32	15.87	16.67	24.89
46.58	8.13	30.11	15.76	15.15	26.26
45.95	8.01	28.83	16.78	15.08	26.14
44.56	8.98	28.52	16.60	14.03	27.10
43.90	8.84	25.99	18.66	13.97	26.99
42.39	9.92	25.80	18.53	13.07	27.83
41.72	9.76	24.42	19.68	13.02	27.73
39.96	11.03	24.20	19.51	12.07	28.62
39.42	10.88	21.90	21.45	12.02	28.51
37.74	12.12	21.80	21.35	10.90	29.58
37.20	11.95	20.90	22.12	10.85	29.46
35.43	13.28	20.74	21.94		
$[N_{4444}][Theop]$					
IL (wt%)	**$K_3C_6H_5O_7$ (wt%)**	**IL (wt%)**	**$K_3C_6H_5O_7$ (wt%)**	**IL (wt%)**	**$K_3C_6H_5O_7$ (wt%)**
59.93	0.82	17.98	11.66	10.85	15.10
55.87	1.77	17.72	11.80	10.75	15.16
49.96	2.53	17.38	11.90	10.60	15.31
45.22	3.17	17.02	12.19	10.50	15.37
42.63	3.77	16.68	12.13	10.37	15.48
39.83	4.30	16.38	12.32	10.23	15.55
37.83	4.83	16.14	12.42	10.11	15.61
36.10	5.20	15.70	12.67	10.10	15.69
35.05	5.59	15.38	12.70	10.00	15.71
33.54	5.94	15.14	12.84	9.86	15.83
32.60	6.33	14.92	12.97	9.78	16.05
31.25	6.60	14.70	13.08	9.34	16.32
30.46	6.89	14.51	13.16	9.02	16.59
29.67	7.26	14.31	13.25	8.79	16.83
28.54	7.53	14.10	13.37	8.60	17.09
27.86	7.82	13.92	13.47	8.23	17.38
27.20	8.10	13.73	13.58	8.07	17.86
26.47	8.32	13.48	13.60	7.86	18.33
25.85	8.62	13.31	13.70	7.59	18.87
25.04	8.78	13.08	13.93	7.27	19.28
24.48	9.05	12.93	14.00	6.85	19.70
23.59	9.40	12.62	14.17	6.48	20.11
22.68	9.75	12.48	14.25	6.28	20.66
22.17	9.88	12.33	14.34	6.04	21.41
21.75	10.09	12.20	14.41	5.63	21.88
21.32	10.30	11.96	14.55	5.43	22.48
20.76	10.41	11.70	14.69	5.05	23.04
20.31	10.71	11.57	14.75	4.33	23.61
19.69	11.06	11.45	14.82	2.16	26.10
19.03	11.32	11.33	14.89	1.94	29.74
18.58	11.39	11.10	15.02	1.71	38.53

18.27	11.52	10.96	15.04		

The experimental binodal curves were fitted according to Equation 1 [3]:

$$[\mathrm{CIL}] = A\exp[(B[\mathrm{salt}]^{0.5}) - (C[\mathrm{salt}]^{3})] \quad (1)$$

where [CIL] and [salt] are the fraction percentages of CIL and salt, respectively. *A*, *B*, and *C* correspond to the fitting parameters.

Table S8. Merchuk equation parameters (*A*, *B* and *C*) and the respective standard deviations (σ) for the ternary systems composed of IL, water and Na_2SO_4 at 298 K, 323 K and 353 K (± 1 K).

IL	(T ± 1) K	$A \pm \sigma$	$B \pm \sigma$	$10^5 (C \pm \sigma)$	R^2
[N_{4444}][Theob]	298	78 ± 5	-0.35 ± 0.04	18 ± 5	0.9975
	323	89 ± 2	-0.47 ± 0.01	26 ± 3	0.9993
	353	87 ± 6	-0.44 ± 0.04	48 ± 9	0.9969
[N_{4444}][Theop]	298	89 ± 3	-0.56 ± 0.02	46 ± 10	0.9982
	323	93 ± 2	-0.65 ± 0.01	124 ± 8	0.9982
	353	74 ± 11	-0.7 ± 0.1	355 ± 74	0.9805
[N_{4444}]Cl	298	82 ± 2	-0.50 ± 0.01	$5x10^{-9}$ ± 2	0.9963
	323	81 ± 1	-0.54 ± 0.01	$5x10^{-8}$ ± 2	0.9993

Table S9. Merchuk equation parameters (*A*, *B* and *C*) and the respective standard deviations (σ) for the ternary systems composed of IL, water and $K_3C_5H_6O_7$ at (298 ± 1) K.

IL	(T ± 1) K	$A \pm \sigma$	$B \pm \sigma$	$10^5 (C \pm \sigma)$	R^2
[N_{4444}][Theob]	298	105 ± 3	-0.285 ± 0.001	2.7 ± 0.2	0.9990
[N_{4444}][Theop]	298	94 ± 4	-0.42 ± 0.02	14 ± 1	0.9918

Table S10. Experimental TLs and TLLs of the ternary systems composed of ILs + Na_2SO_4 at 298 K or 323 K (± 1 K) and atmospheric pressure (0.1 MPa). No TLs were determined at (353 ± 1) K.

		Mixture point (wt %)		Top phase (wt %)			Bottom phase (wt %)			
IL	**(T ± 1) K**	**[IL]**	**[salt]**	**[IL]**	**[salt]**	**pH**	**[IL]**	**[salt]**	**pH**	**TLL**
$[N_{4444}][Theob]$	298	24.9	10.1	35.0	4.9	11.46	2.8	21.3	11.07	36.1
		25.0	12.0	41.3	3.2	11.47	0.9	25.0	10.98	45.9
	323	25.0	10.0	36.0	3.6	11.43	0.2	24.5	10.93	41.5
		25.0	12.0	41.7	2.6	11.49	0.1	26.0	11.02	47.7
$[N_{4444}][Theop]$	298	25.0	5.6	39.1	2.1	9.86	13.3	8.4	9.25	26.6
		24.7	8.1	47.9	1.2	9.81	2.3	14.8	9.32	47.6
	323	25.0	5.5	49.2	1.0	9.82	4.8	9.3	9.21	45.2
		25.1	8.0	57.9	0.5	9.79	0.4	13.7	9.26	59.1
$[N_{4444}]Cl$	298	25.0	10.0	33.4	3.2	5.00	6.8	24.7	4.88	34.2

Table S11. Experimental TLs and TLLs of the ternary systems composed of ILs + $K_3C_5H_6O_7$ at (298 ± 1) K and atmospheric pressure (0.1 MPa).

		Mixture point (wt%)		Top phase (wt%)			Bottom phase (wt%)			
IL	**(T ± 1) K**	**[IL]**	**[salt]**	**[IL]**	**[salt]**	**pH**	**[IL]**	**[salt]**	**pH**	**TLL**
$[N_{4444}][Theob]$	298	25.0	23.6	46.7	7.9	12.50	3.5	39.1	11.95	53.2
		25.0	28.5	59.4	4.0	12.70	1.2	45.4	12.02	71.4
$[N_{4444}][Theop]$	298	25.1	23.7	69.7	0.4	11.03	0.1	36.8	10.44	78.6
		24.9	14.1	56.2	1.5	11.20	1.6	23.5	10.65	58.9

Ferulic acid was used to perform a simplistic study of its partition in different ternary mixtures. To perform this study, the following mixture points were used: $[N_{4444}][Theob]/[N_{4444}]Cl–Na_2SO_4$ (25-10) wt%, and $[N_{4444}][Theob]/[N_{4444}][Theop]/[N_{4444}]Cl–K_3C_5H_6O_7$ (25-24) wt% at (298 ± 1) K. The water content of each mixture point was substituted by an aqueous solution of ferulic acid with a concentration of 0.6 $g{\cdot}L^{-1}$. The mixture points were centrifuged for 20 min at 3500 rpm and the phases of the mixture points were separated and individually weighed (± 10^{-4} g). The amount of ferulic acid in each phase was determined by UV-Vis spectroscopy. All the assays were performed in duplicates. The extraction efficiency (*EE*) was determined as follows:

$$EE\ \% = \frac{m_{Top}}{m_{total}} \times 100$$

where m_{Top} is the amount of ferulic acid in the top phase, and m_{total} is the total amount of ferulic acid in the ternary mixture, respectively.

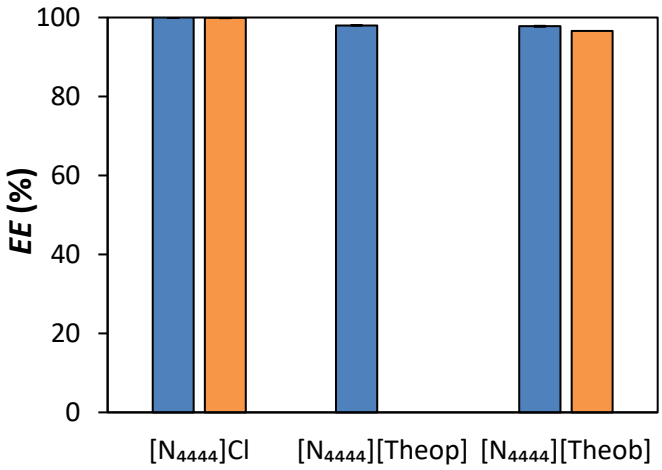


Figure S3. Extraction efficiency (*EE* %) of each ternary mixture at (289 ± 1) K and atmospheric pressure (0.1 MPa). Blue bars represent data from systems containing the salting-out agent $K_3C_5H_6O_7$ and orange bars represent ternary mixtures with Na_2SO_4 as the salting-out agent.

Table S12. Molar solubility (*S*) of ferulic acid in IL solutions with different concentrations.

ILs	[IL] / (mol·L^{-1})	($S \pm \sigma$) / (mol·L^{-1})
[N_{4444}][Theob]	0.05	0.0144 ± 0.0006
	0.1	0.0247 ± 0.0006
	0.25	0.12 ± 0.02
	0.5	0.23 ± 0.01
[N_{4444}][Theop]	0.05	0.0213 ± 0.0002
	0.1	0.063 ± 0.003
	0.25	0.237 ± 0.005
	0.5	0.46 ± 0.04
	1.0	0.60 ± 0.01
	1.5	0.38 ± 0.02
[N_{4444}]Cl	0.05	0.0040 ± 0.0001
	0.1	0.0047 ± 0.0001
	0.25	0.034 ± 0.001
	0.5	0.158 ± 0.003
	1.0	0.415 ± 0.009
	1.5	0.24 ± 0.01

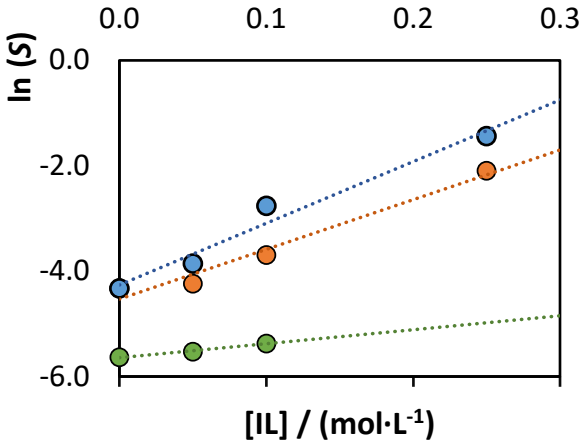


Figure S4. Fitted regression to the diluted region solubility data for the determination of the Setschenow constant. Different ILs are represented in different colors: [N_{4444}][Theop] (blue), [N_{4444}][Theob] (orange) and [N_{4444}]Cl (green).

Table S13. Setchenow constant for each IL, given by the slope of the fitted regression to the diluted region solubility data, and the respective coefficient of determination (R^2).

IL	Setschenow constant ($L \cdot mol^{-1}$)	R^2
[N_{4444}][Theob]	9.440	0.9714
[N_{4444}][Theop]	11.710	0.9681
[N_{4444}]Cl	2.657	0.9900

Table S14. Measured pH of the IL solutions before the addition of ferulic acid and after obtaining a saturated solution.

IL	[IL] / (mol·L^{-1})	Initial solution pH	Saturated solution pH
[N_{4444}][Theob]	0.05	10.85	5.36
	0.1	11.56	5.54
	0.25	11.80	8.51
	0.5	11.98	9.62
[N_{4444}][Theop]	0.05	8.91	5.30
	0.1	10.52	6.44
	0.25	10.81	6.56
	0.5	10.78	7.65
	1.0	11.06	8.63
	1.5	10.68	9.95
[N_{4444}]Cl	0.05	5.71	3.29
	0.1	6.31	2.89
	0.25	5.62	2.63
	0.5	4.26	2.36
	1.0	4.04	2.10
	1.5	4.20	2.26

Table S15. Ferulic acid water-solubility at different pH values.

Initial solution pH	Saturated solution pH	(Solubility ± σ) × 10^2 (mol·L^{-1})
2.46	2.45	0.355 ± 0.006
7.04	3.60	0.39 ± 0.02
11.63	4.70	0.94 ± 0.02
11.78	5.05	1.32 ± 0.04
12.59	5.78	7.3 ± 0.6
13.01	6.11	38 ± 1
13.16	7.93	35 ± 2
13.01	8.57	33 ± 1
13.16	9.16	31 ± 2

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