Factors driving metal partition in ionic liquid-based acidic aqueous biphasic systems

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Table S1. Experimental weight fraction data obtained for the different AcABS at (298.0 ± 0.1) K and atmospheric pressure (0.10 ± 0.01) MPa.

[P_{44414}][HSO_4] + HCl + H_2O			
[P_{44414}][HSO_4] (wt %)	HCl (wt %)	[P_{44414}][HSO_4] (wt %)	HCl (wt %)
43.75	16.29	10.11	21.76
39.26	16.72	9.79	21.82
35.77	17.17	9.54	21.84
32.02	17.55	9.29	21.84
29.63	17.79	8.76	22.02
27.88	18.03	8.28	22.57
25.69	18.50	7.67	22.64
23.93	18.90	7.20	22.76
22.60	19.12	6.67	22.99
21.09	19.40	6.25	23.02
19.91	19.67	5.85	23.09
18.76	19.99	5.47	23.29
18.05	19.96	5.22	23.25
16.86	20.31	4.94	23.25
16.02	20.47	4.65	23.48
15.27	20.57	4.45	23.49
14.57	20.78	4.24	23.55
13.47	20.94	4.10	23.59
13.07	20.98	3.91	23.56
12.41	21.30	3.76	23.59
11.95	21.40	3.60	23.74
11.68	21.40	3.49	23.72
11.14	21.54	3.38	23.76
10.72	21.67	3.26	23.74
10.43	21.64	10.11	21.76
[P_{44414}][HSO_4] + H_2SO_4 + H_2O			
[P_{44414}][HSO_4] (wt %)	H_2SO_4 (wt %)	[P_{44414}][HSO_4] (wt %)	H_2SO_4 (wt %)
44.87	13.63	12.70	16.98
43.09	13.82	12.17	17.09
41.01	13.94	11.82	17.13
39.58	14.08	11.35	17.20
37.90	14.04	10.96	17.25
36.83	14.15	10.43	17.39
35.55	14.27	10.06	17.42
34.38	14.27	9.67	17.43
33.20	14.38	9.24	17.59
31.73	14.70	8.85	17.63
30.63	14.86	8.42	17.72
29.64	14.90	7.98	17.82
28.05	14.94	7.69	17.87

24.73	15.34	7.39	17.94
24.20	15.45	7.16	17.99
23.66	15.51	6.93	18.01
23.16	15.52	6.69	18.06
22.65	15.54	6.48	18.10
21.93	15.69	6.25	18.17
21.43	15.69	6.08	18.35
20.74	15.86	5.80	18.38
20.33	15.94	5.47	18.42
19.90	15.86	5.20	18.56
19.11	16.07	5.01	18.53
18.51	16.11	4.75	18.67
17.96	16.13	4.53	18.69
17.44	16.33	4.33	18.74
16.86	16.35	4.10	18.85
16.34	16.36	3.94	18.82
16.03	16.40	3.78	18.88
15.65	16.57	3.68	18.84
14.57	16.60	3.56	18.94
14.09	16.72	3.43	19.05
13.65	16.78	3.30	19.00
13.07	16.86		

Table S2. Experimental weight fraction data obtained for the developed AcABS at (323.0 ± 0.1) K and atmospheric pressure (0.10 ± 0.01) MPa.

$[P_{44414}][HSO_4]$ + HCl + H_2O			
$[P_{44414}][HSO_4]$ (wt %)	HCl (wt %)	$[P_{44414}][HSO_4]$ (wt %)	HCl (wt %)
38.68	6.39	15.05	7.43
37.93	6.29	14.65	7.65
36.06	6.41	13.83	7.71
35.36	6.48	13.54	7.56
33.60	6.65	13.26	7.56
30.10	6.29	13.05	7.60
29.30	6.33	12.74	7.60
28.17	6.34	12.60	7.59
27.21	6.47	12.32	7.66
25.87	6.64	12.06	7.73
23.98	6.71	11.80	7.74
22.90	6.69	11.48	7.70
22.61	6.68	11.26	7.78
22.08	6.75	10.98	7.87
21.54	6.69	10.61	7.76
21.29	6.87	10.45	7.82
20.42	6.87	10.23	7.79

20.26	6.88	10.04	7.86
20.00	6.96	9.81	7.82
19.48	7.00	9.70	7.89
18.70	6.96	9.51	7.92
18.39	7.03	9.31	7.89
17.97	7.18	9.10	7.90
17.80	7.27	8.98	7.97
17.38	7.23	8.85	8.02
16.88	7.36	8.70	8.05
16.48	7.36	8.53	8.09
16.09	7.36	8.37	8.12
15.86	7.36	8.16	8.10
15.41	7.39	8.01	8.11
[P_{44414}]Cl + H_2SO_4 + H_2O			
[P_{44414}]Cl (wt %)	H_2SO_4 (wt %)	[P_{44414}]Cl (wt %)	H_2SO_4 (wt %)
47.98	11.63	22.91	8.46
37.94	9.43	22.08	8.88
35.31	8.99	20.22	8.69
33.42	8.92	19.48	8.46
31.33	8.72	18.66	8.56
30.14	8.90	17.79	8.66
28.29	8.93	11.98	8.91
26.86	8.64	11.59	9.10
25.81	8.44	11.12	9.00
24.90	8.63	10.74	9.22
23.49	8.49	10.36	9.19
[P_{44414}][HSO_4] + H_2SO_4 + H_2O			
[P_{44414}][HSO_4] (wt %)	H_2SO_4 (wt %)	[P_{44414}][HSO_4] (wt %)	H_2SO_4 (wt %)
62.45	6.43	19.21	6.83
53.50	6.27	18.37	6.88
46.85	6.47	17.22	6.90
41.52	6.36	16.87	6.99
37.91	6.43	16.08	6.84
35.00	6.41	15.36	7.04
32.74	6.39	14.73	6.90
31.12	6.50	14.40	6.93
29.31	6.45	14.00	6.94
28.08	6.60	13.67	6.94
24.79	6.69	13.44	7.03
23.87	6.74	12.97	7.14
23.02	6.80	12.46	7.06
22.01	6.88	12.22	7.12
21.00	6.88	11.83	7.28
20.28	6.95		

The mixture points were selected considering the phase diagrams in molarity (mol·kg^{-1}) to correctly compare the performance of different acids and ILs in metals extraction. IL concentration was maintained constant at 0.85 mol·kg^{-1} for all systems to facilitate the understanding of the IL anion influence on metal extraction. Two different acid concentrations were selected based on the following criteria: $[Acid]_1$ = [binodal curve] at [IL] = 0.85 mol·kg^{-1} + 0.5 mol·kg^{-1}, $[Acid]_2$ = [binodal curve] at [IL] = 0.85 mol·kg^{-1} + 2 mol·kg^{-1}. In the AcABS based on H_2SO_4 it was not possible to maintain the acid criteria due to the different binodal curves of the $[P_{44414}]Cl$ + H_2SO_4 and $[P_{44414}][HSO_4]$ + H_2SO_4 systems, with the $[P_{44414}]Cl$ + H_2SO_4 system having a larger monophasic area than $[P_{44414}][HSO_4]$ + H_2SO_4. Due to the vicinity of the HNO_3 systems to the origin, the acid criteria were not applied to these systems. Instead, HNO_3 systems were studied in the same mixture point applied to the $[P_{44414}][HSO_4]$ + H_2SO_4 system.

Table S3. Distribution coefficient (*D*) and extraction efficiency percentage (*EE* %) of the HCl-based AcABS at (298 ± 1) K, 6.5 mol·kg^{-1} of acid and different metal concentrations in the systems (0.005 vs 0.01 mol·kg^{-1}).

		D				***EE* (%)**			
IL	[Metal] (M)	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ
$[P_{44414}]Cl$	0.005	21 ± 1	5.4 ± 0.4	1.2 ± 0.1	0.06 ± 0.01	95.0 ± 0.2	86 ± 1	51 ± 3	5.2 ± 0.8
	0.01	18.0 ± 0.9	6.9 ± 0.5	0.89 ± 0.05	0.084 ± 0.004	94.4 ± 0.6	87 ± 1	46 ± 3	7.3 ± 0.7

Table S4. Total mol percentage of $[P_{44414}]^+$, H^+ and Cl^- in the top and bottom phase of the $[P_{44414}][HSO_4]$-HCl-H_2O system at 6.5 and 8.0 mol·kg^{-1} of HCl at (298 ± 1) K.

Mixture point (IL, HCl) (wt %)	Phase	$[P_{44414}]^+$ %	H^+ %	Cl^- %
(30, 19)	Bottom	n.d.	58.2 ± 0.2	54.5 ± 0.1
	Top	100 ± 2	41.8 ± 0.1	45.5 ± 0.2
(30, 23)	Bottom	n.d.	72.7 ± 0.4	69 ± 2
	Top	100 ± 2	27.3 ± 0.3	31 ± 2

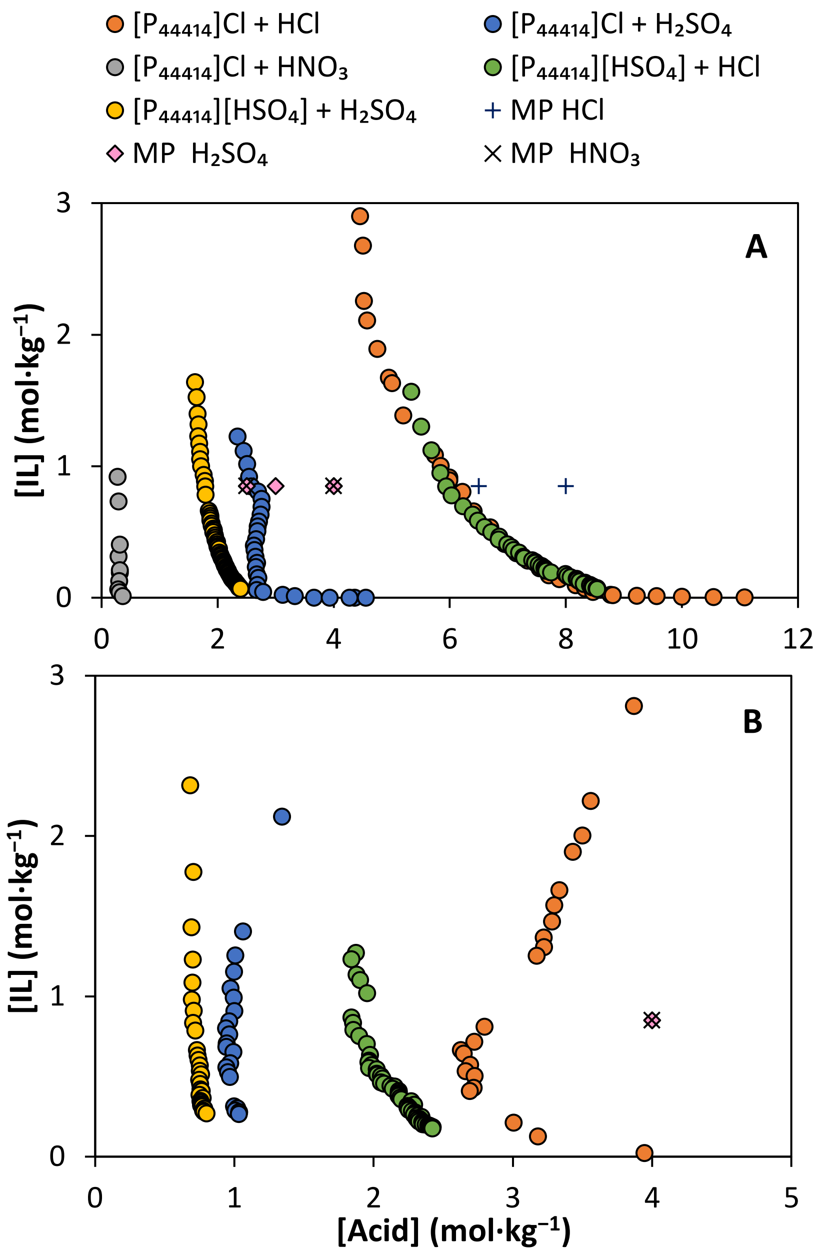

Figure S1. Binodal curves determined in this work and by Mogilireddy *et al.*[1] at (298 ± 1) K (A) and (323 ± 1) K (B). The mixture points (MP) used to study the extraction of metals on the HCl (+), H_2SO_4 (◊) and HNO_3 (×) systems are also represented. The MP of H_2SO_4 and HNO_3 are overlapping at acid concentrations of 2.5 and 4.0 mol·kg^{-1}.

Table S5. Distribution coefficient (*D*) of the HCl-based AcABS at 298 and 323 K (± 1 K) and at different HCl concentrations. Co(II), Cu(II), Mn(II) and Ni(II) were studied in multi-elemental assays while Ce(IV) was studied in single-elemental assays.

			D				
IL	T (K)	[HCl] (mol·kg^{-1})	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ	Ce ± σ
[P_{44414}]Cl	298	6.5	18.0 ± 0.9	6.9 ± 0.5	0.89 ± 0.05	0.084 ± 0.004	0.225 ± 0.005
		8	20 ± 2	4.4 ± 0.3	1.21 ± 0.07	0.0332 ± 0.0001	0.15 ± 0.03
	323	8	26 ± 2	6.1 ± 0.5	2.2 ± 0.2	0.013 ± 0.004	0.15 ± 0.02
[P_{44414}][HSO_4]	298	6.5	15.6 ± 0.1	7.4 ± 0.2	0.84 ± 0.01	0.100 ± 0.003	–
		8	24.7 ± 0.3	5.1 ± 0.3	1.27 ± 0.09	0.05 ± 0.02	–
	323	8	26.7 ± 0.4	6.1 ± 0.1	2.08 ± 0.06	0.0115 ± 0.0004	–

Table S6. Extraction efficiency (*EE* %) of the HCl-based AcABS at (298 and 323) K ± 1 K and at different HCl concentrations. Co(II), Cu(II), Mn(II) and Ni(II) were studied in multi-elemental assays while Ce(IV) was studied in single-elemental assays.

			***EE* (%)**				
IL	T (K)	[HCl] (mol·kg^{-1})	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ	Ce ± σ
[P_{44414}]Cl	298	6.5	94.4 ± 0.6	87 ± 1	46 ± 3	7.3 ± 0.7	10.2 ± 0.9
		8	94.1 ± 0.6	78 ± 2	49 ± 2	2.56 ± 0.05	9.4 ± 0.9
	323	8	94.5 ± 0.6	80 ± 1	59 ± 3	0.9 ± 0.2	8.5 ± 0.8
[P_{44414}][HSO_4]	298	6.5	94.2 ± 0.2	88.518 ± 0.004	46.7 ± 0.9	9.5 ± 0.5	–
		8	95.34 ± 0.06	81 ± 1	51 ± 2	4 ± 1	–
	323	8	94.6 ± 0.3	80.0 ± 0.8	58 ± 2	0.75 ± 0.08	–

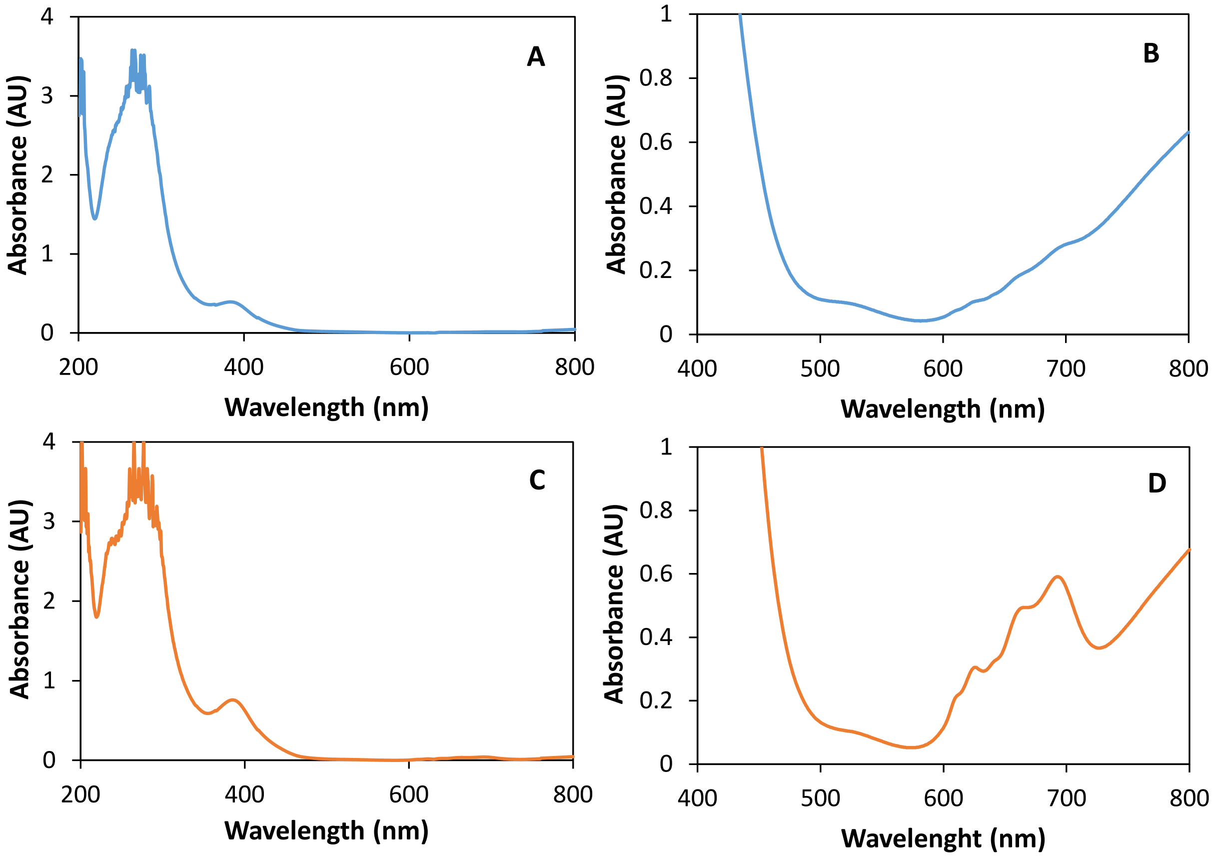

Figure S2. UV-Vis spectrum of the HCl-H_2O mixture at 6.5 mol·kg^{-1} (A and B) and 8.0 mol·kg^{-1} (C and D) of HCl at 298 K with Co(II), Cu(II), Mn(II) and Ni(II) in solution. B and D are a zoom-in of spectra A and C, respectively.

Table S7. Water and acid content on the IL-rich phase of the [P_{44414}]Cl-HCl-H_2O system at (298, 313 and 323) K ± 1 K.

Temperature (K)	HCl (mol)	H_2O (mol)
298	2.6E-03 ± 1.4E-04	1.0E-02 ± 2.0E-3
313	2.5E-03 ± 4.3E-05	7.3E-03 ± 1.7E-03
323	2.3E-03 ± 1.2E-05	6.1E-03 ± 1.7E-3

Table S8. Total mol percentage of $[P_{44414}]^+$ and Cl^- in the top and bottom phase of the $[P_{44414}]Cl$-H_2SO_4-H_2O system at 3.0 and 4.0 mol·kg^{-1} of H_2SO_4 at (298 ± 1) K.

Mixture point (IL, H_2SO_4) wt%	Phase	$[P_{44414}]^+$ %	Cl^- %
(27, 22)	Bottom	n.d.	52.8 ± 0.2
	Top	100 ± 2	47.2 ± 0.2
(27, 28)	Bottom	n.d.	57.2 ± 0.1
	Top	100 ± 3	42.8 ± 0.2

Table S9. Distribution coefficient (*D*) of the H_2SO_4-based AcABS at 298 and 323 K (± 1 K) and at different H_2SO_4 concentrations. Co(II), Cu(II), Mn(II) and Ni(II) were studied in multi-elemental assays.

			D			
IL	T (K)	$[H_2SO_4]$ (mol·kg^{-1})	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ
$[P_{44414}]Cl$	298	3	0.49 ± 0.03	0.70 ± 0.01	0.45 ± 0.03	0.50 ± 0.02
		4	1.4 ± 0.1	2.7 ± 0.2	1.6 ± 0.2	1.18 ± 0.04
	323	4	1.3 ± 0.1	4.0 ± 0.4	1.11 ± 0.08	1.06 ± 0.03
$[P_{44414}][HSO_4]$	298	2.5	1.01 ± 0.05	0.87 ± 0.04	1.30 ± 0.06	1.00 ± 0.04
		4	1.1 ± 0.1	0.89 ± 0.05	1.5 ± 0.2	1.05 ± 0.08
	323	4	0.98 ± 0.03	0.91 ± 0.03	1.01 ± 0.01	0.96 ± 0.03

Table S10. Extraction efficiency percentage (*EE* %) of the H_2SO_4-based AcABS at (298 and 323) K ± 1 K and at different H_2SO_4 concentrations. Co(II), Cu(II), Mn(II) and Ni(II) were studied in multi-elemental assays.

			***EE* (%)**			
IL	T (K)	$[H_2SO_4]$ (mol·kg^{-1})	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ
$[P_{44414}]Cl$	298	3	31 ± 1	39.32 ± 0.09	29 ± 1	31.8 ± 0.6
		4	54 ± 3	73 ± 2	59 ± 5	50 ± 4
	323	4	49 ± 2	75 ± 2	45 ± 2	43.8 ± 0.1
$[P_{44414}][HSO_4]$	298	2.5	48.9 ± 0.3	45.2 ± 0.4	55.3 ± 0.3	48.7 ± 0.4
		4	48 ± 3	43 ± 1	56 ± 3	47 ± 2
	323	4	42 ± 1	40 ± 1	43 ± 1	42 ± 1

Table S11. Phase volumes (mL) of the systems depending on the temperature, type of acid and IL. The presented phase volumes are from the multi-elemental assays at the highest acid content.

IL	Acid	T (K)	Phase	Volume (mL)
$[P_{44414}]Cl$	HCl	298	Bottom	0.85
			Top	0.98
		323	Bottom	0.92
			Top	0.73
	H_2SO_4	298	Bottom	0.73
			Top	0.80
		323	Bottom	0.80
			Top	0.73
	HNO_3	298	Bottom	1.25
			Top	0.69
		323	Bottom	1.21
			Top	0.65
$[P_{44414}][HSO_4]$	HCl	298	Bottom	0.82
			Top	0.95
		323	Bottom	0.94
			Top	0.82
	H_2SO_4	298	Bottom	0.81
			Top	0.82
		323	Bottom	0.89
			Top	0.71
$[P_{44414}][NO_3]$	HNO_3	298	Bottom	1.22
			Top	0.64
		323	Bottom	1.18
			Top	0.66

Table S12. Distribution coefficient (*D*) of the HNO_3-based biphasic systems at (298 and 323) K ± 1 K and at different HNO_3 concentrations. Co(II), Cu(II), Mn(II) and Ni(II) were studied in multi-elemental assays whereas Ce was studied isolated in single-elemental assays.

			D				
IL	T (K)	[HNO_3] (mol·kg^{-1})	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ	Ce ± σ
[P_{44414}]Cl	298	1.0	–	–	–	–	1.02 ± 0.05
		2.5	0.01 ± 0.01	0.020 ± 0.001	0.03 ± 0.01	0.01 ± 0.01	0.27 ± 0.3
		4.0	0.03 ± 0.01	0.001 ± 0.001	0.03 ± 0.01	0.05 ± 0.02	0.00 ± 0.00
	323	4.0	0.70 ± 0.01	0.33 ± 0.05	0.93 ± 0.04	0.67 ± 0.03	0.57 ± 0.06
[P_{44414}][NO_3]	298	1.0	–	–	–	–	4.4 ± 0.5
		2.5	0.20 ± 0.02	0.010 ± 0.001	0.02 ± 0.03	0.05 ± 0.03	1.6 ± 0.1
		4.0	0.05 ± 0.02	0.000 ± 0.001	0.05 ± 0.02	0.08 ± 0.02	0.9 ± 0.1
	323	4.0	0.30 ± 0.04	0.05 ±0.03	0.4 ± 0.1	0.29 ± 0.07	1.53 ± 0.02

Table S13. Extraction efficiency percentage (*EE* %) of the HNO_3-based biphasic systems at (298 and 323) K ± 1 K and at different HNO_3 concentrations. Co(II), Cu(II), Mn(II) and Ni(II) were studied in multi-elemental assays whereas Ce(IV) was studied in single-elemental assays.

			***EE* (%)**				
IL	T (K)	$[HNO_3]$ (mol·kg^{-1})	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ	Ce ± σ
$[P_{44414}]Cl$	298	1.0	–	–	–	–	30 ± 2
		2.5	0.3 ± 0.4	0.84 ± 0.03	1.2 ± 0.5	0.6 ± 0.3	11 ± 2
		4.0	1.4 ± 0.3	0.72 ± 0.09	1.3 ± 0.5	2.5 ± 0.4	0.00 ± 0.00
	323	4.0	24 ± 1	13 ± 3	30 ± 3	23.4 ± 0.9	20.6 ± 0.2
$[P_{44414}][NO_3]$	298	1.0	–	–	–	–	64 ± 2
		2.5	9 ± 1	0.43 ± 0.01	1 ± 1	2 ± 2	42 ± 2
		4.0	2.3 ± 0.7	0.13 ± 0.06	2.3 ± 0.9	3.6 ± 0.7	31 ± 3
	323	4.0	11 ± 1	2 ± 1	14 ± 3	10 ± 2	39 ± 1

Table S14. Distribution coefficient (*D*) of the H_2SO_4-based AcABS at (298 ± 1) K at 4 mol·kg^{-1} of H_2SO_4 spiked with different HCl weight fractions.

		D			
IL	HCl (wt %)	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ
$[P_{44414}]Cl$	0	1.4 ± 0.1	2.7 ± 0.2	1.6 ± 0.2	1.18 ± 0.04
	1	0.58 ± 0.01	2.22 ± 0.09	0.534 ± 0.003	0.51 ± 0.02
	5	1.09 ± 0.06	7.0 ± 0.3	0.58 ± 0.01	0.53 ± 0.01
	10	5.5 ± 0.3	16.3 ± 0.8	1.00 ± 0.04	0.70 ± 0.03

Table S15. Extraction efficiency percentage (*EE* %) of the H_2SO_4-based AcABS at (298 ± 1) K at 4 mol·kg^{-1} of H_2SO_4 spiked with different HCl weight fractions.

		***EE* (%)**			
IL	HCl (wt%)	Co ± σ	Cu ± σ	Mn ± σ	Ni ± σ
$[P_{44414}]Cl$	0	54 ± 3	73 ± 2	58 ± 5	49.7 ± 4
	1	38 ± 1	70.0 ± 0.2	35.9 ± 0.6	35 ± 2
	5	52.2 ± 0.7	87.5 ± 0.3	36.8 ± 0.1	34.81 ± 0.06
	10	83.7 ± 0.6	93.83	48.1 ± 0.8	39.4 ± 0.6

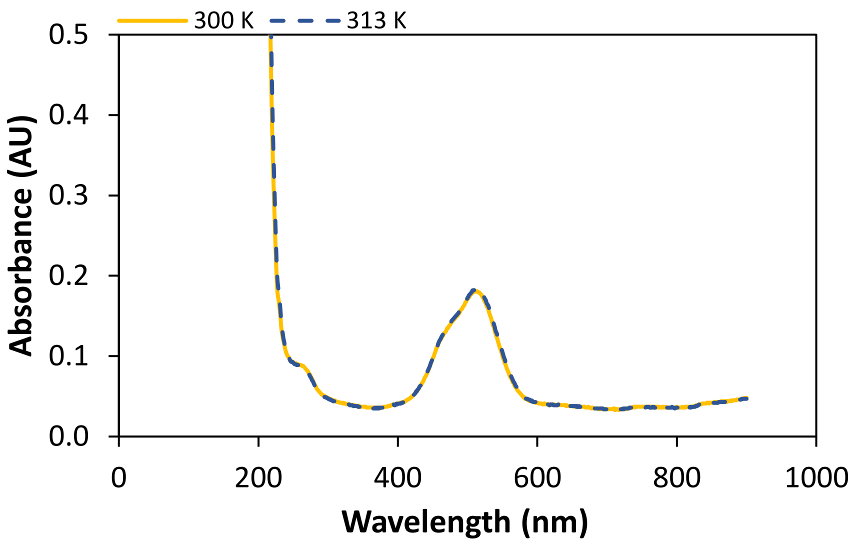

Figure S3. UV-Vis spectrum of the H_2SO_4-H_2O mixture at 1.0 mol·kg^{-1} of H_2SO_4, spiked with 5 wt % of HCl and Co(II) as a metal source at (300.0 and 313.0) K ± 0.1 K.

References

[1] V. Mogilireddy, M. Gras, N. Schaeffer, H. Passos, L. Svecova, N. Papaiconomou, J.A.P. Coutinho, I. Billard, Understanding the fundamentals of acid-induced ionic liquid-based aqueous biphasic system, Phys. Chem. Chem. Phys. 20 (2018) 16477–16484. https://doi.org/10.1039/c8cp02862a.