Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2020

Separation of precious metals by split-anion extraction using water-saturated ionic liquids

Viet Tu Nguyen, Sofía Riaño and Koen Binnemans*

Electronic supplementary information (ESI)

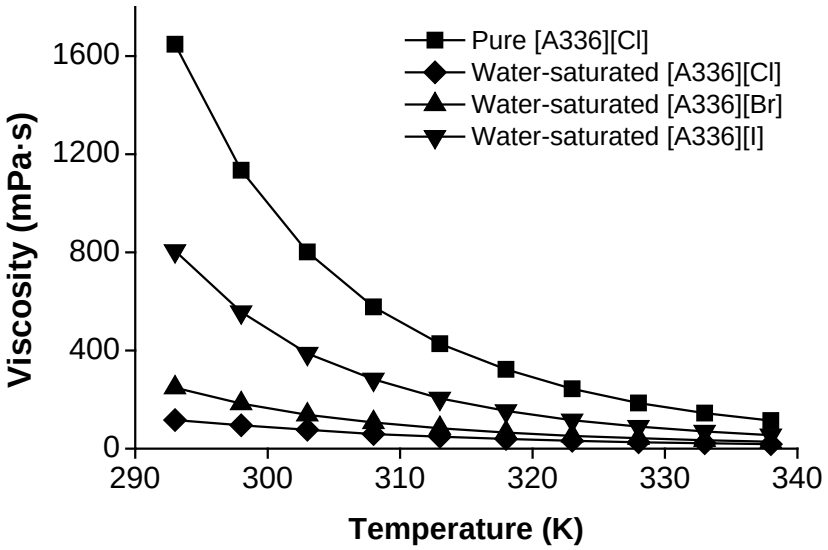

Fig. S1 Viscosity of ionic liquids as a function of temperature. Water contents in the ionic liquids are 4.25 wt% (pure [A336][Cl]), 18.4 wt% (water-saturated [A336][Cl]), 9.28 wt% (water-saturated [A336][Br]), and 8.46 wt% (water-saturated [A336][I]).

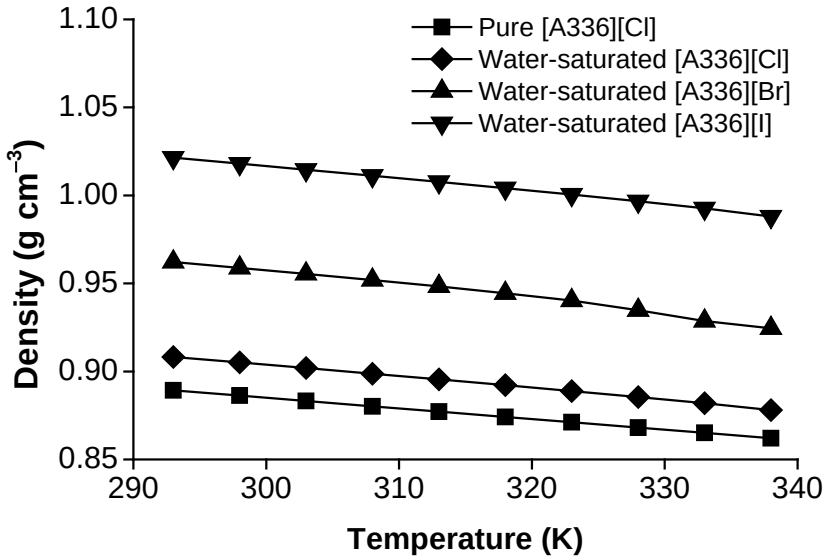

Fig. S2 Density of ionic liquids as a function of temperature. Water contents in the ionic liquids are 4.25 wt% (pure [A336][Cl]), 18.4 wt% (water-saturated [A336][Cl]), 9.28 wt% (water-saturated [A336][Br]), and 8.46 wt% (water-saturated [A336][I]).

Fresh [A336][Cl]: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.88 (t, 9H, *J* = 4.53 Hz), 1.27-1.38 (m, 32H), 1.66-1.70 (m, 6H), 3.31 (s, 3H), 3.43 (t, 6H, *J* = 6.24 Hz). FTIR (ν cm^{-1}): 3349, 2921, 2853, 1611, 1464, 1379, 1055, 896, 721.

Fresh [A336][Br]: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.88 (t, 9H, *J* = 4.77 Hz), 1.26-1.36 (m, 32H), 1.63-1.67 (m, 6H), 3.33 (s, 3H), 3.46 (t, 6H, *J* = 5.16 Hz). FTIR (ν cm^{-1}): 3417, 2926, 2853, 1618, 1461, 1376, 1052, 891, 720.

Fresh [A336][I]: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.88 (t, 9H, *J* = 4.80 Hz), 1.27-1.38 (m, 32H), 1.66-1.70 (m, 6H), 3.32 (s, 3H), 3.44 (t, 6H, *J* = 6.33 Hz). FTIR (ν cm^{-1}): 3419, 2923, 2854, 1610, 1462, 1378, 1055, 893, 723.

Regenerated [A336][I]: ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.88 (t, 9H, *J* = 4.68 Hz), 1.27-1.38 (m, 32H), 1.66-1.70 (m, 6H), 3.33 (s, 3H), 3.45 (t, 6H, *J* = 6.33 Hz). FTIR (ν cm^{-1}): 3419, 2923, 2854, 1627, 1462, 1378, 1054, 893, 723.

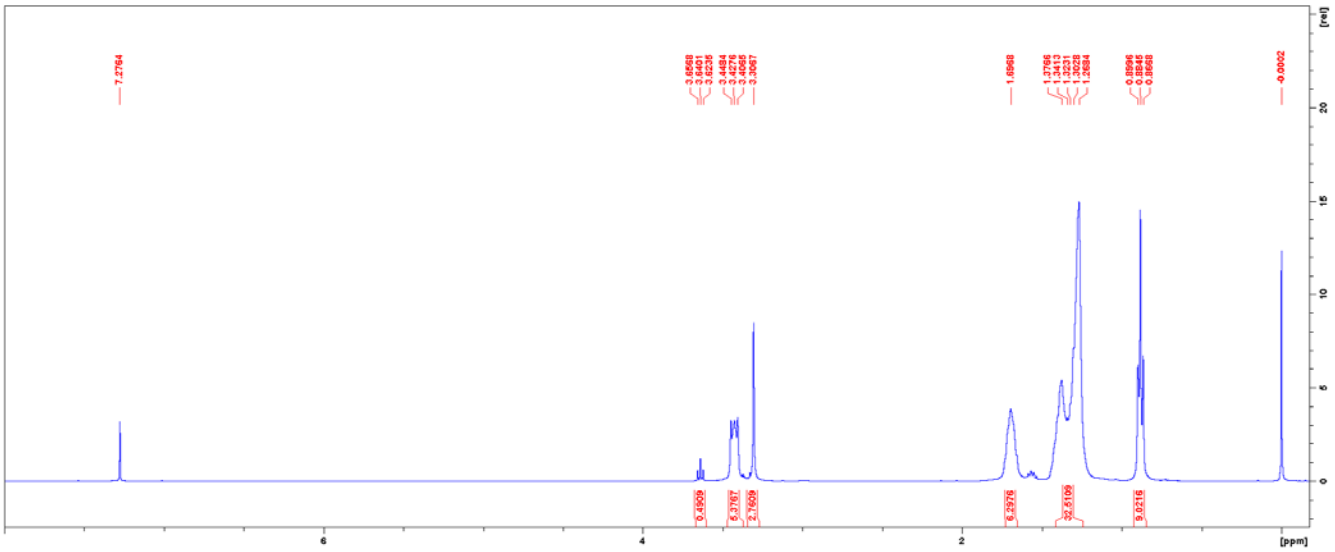

Fig. S3 ^{1}H NMR spectrum of the pure ionic liquid [A336][Cl]

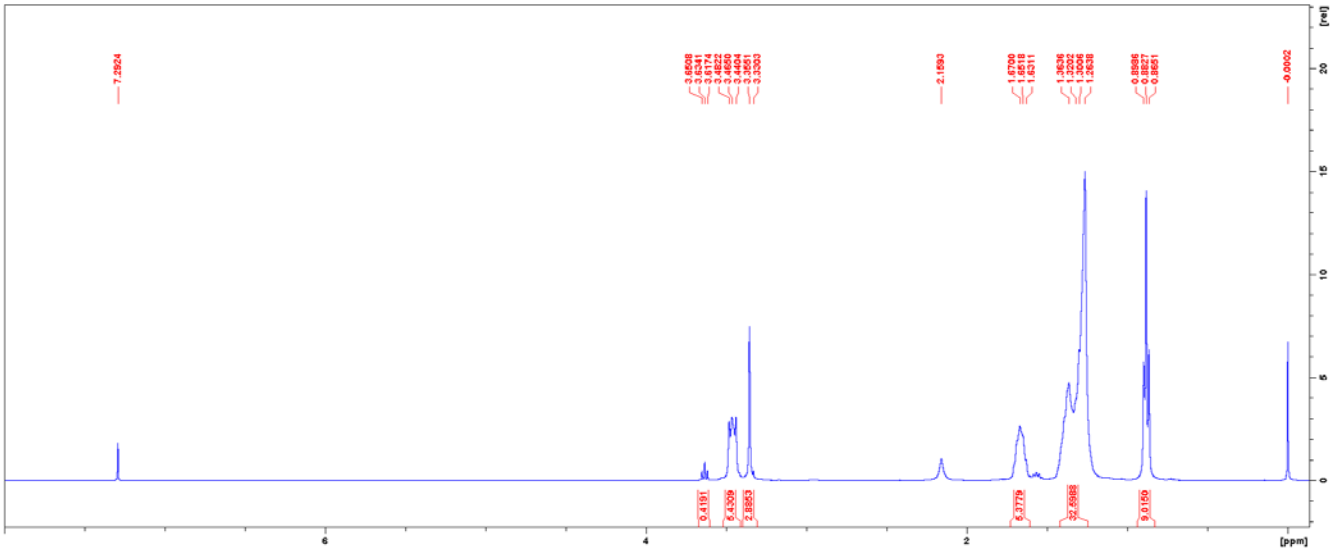

Fig. S4 ^{1}H NMR spectrum of the pure ionic liquid [A336][Br].

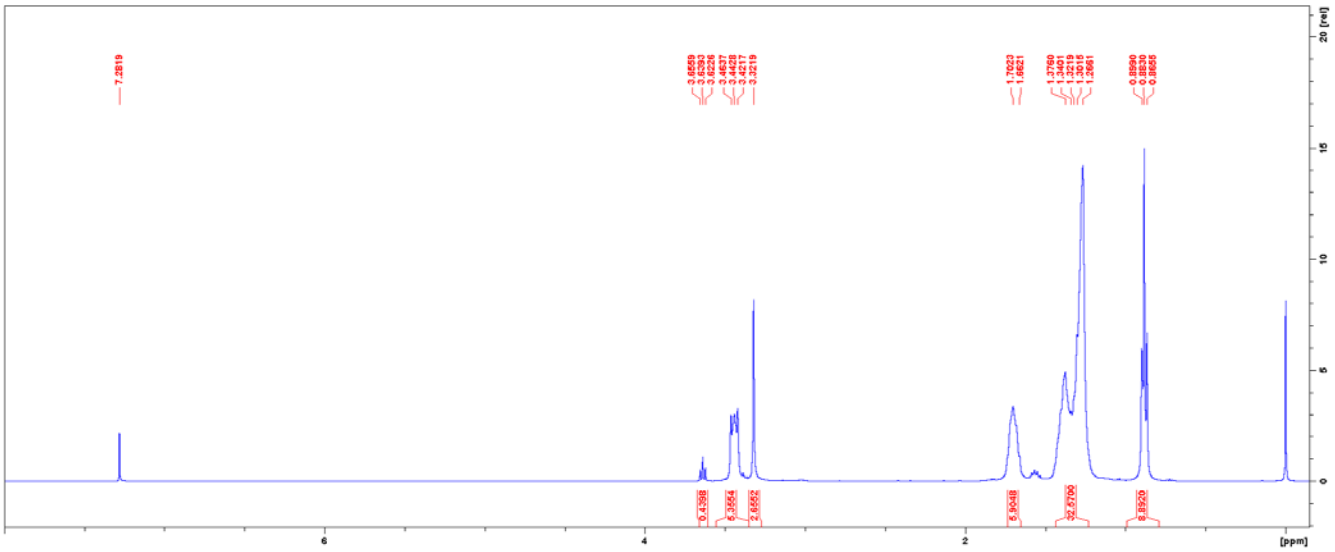

Fig. S5 ^{1}H NMR spectrum of the pure ionic liquid [A336][I].

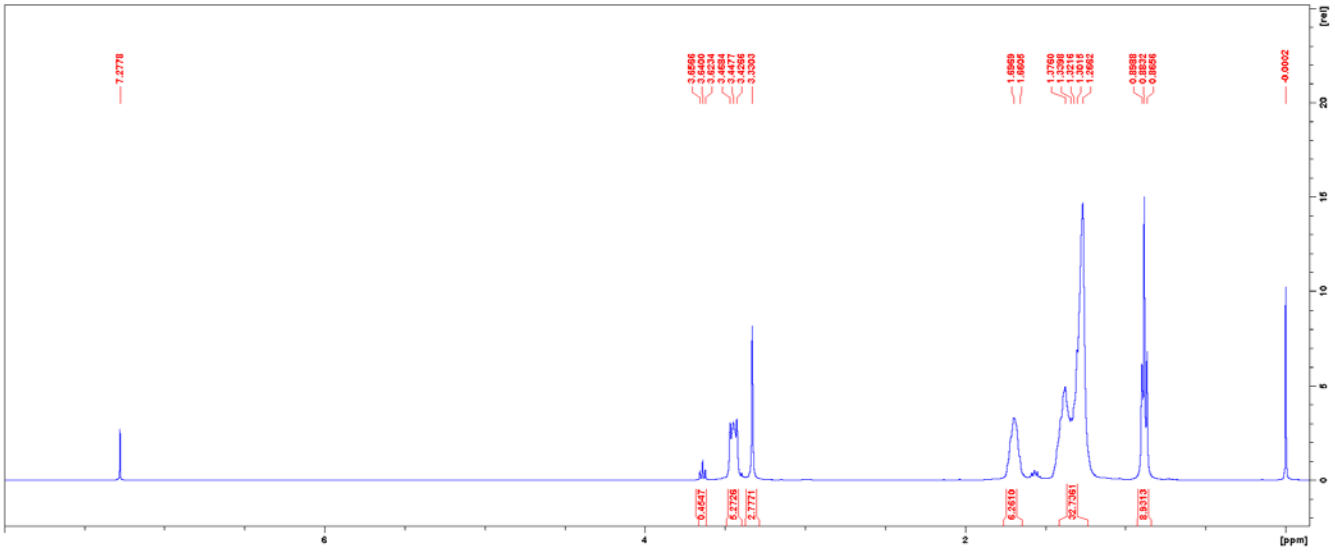

Fig. S6 ^{1}H NMR spectrum of the regenerated ionic liquid [A336][I].

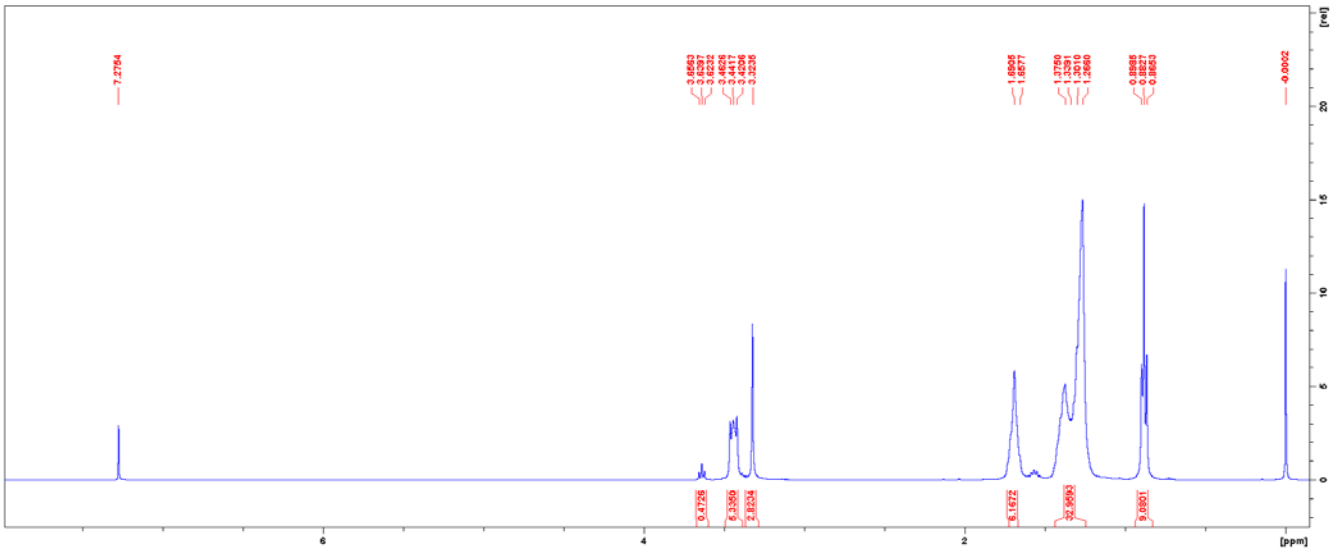

Fig. S7 ^{1}H NMR spectrum of the pure ionic liquid [A336][I] after stripping with NH_4OH.

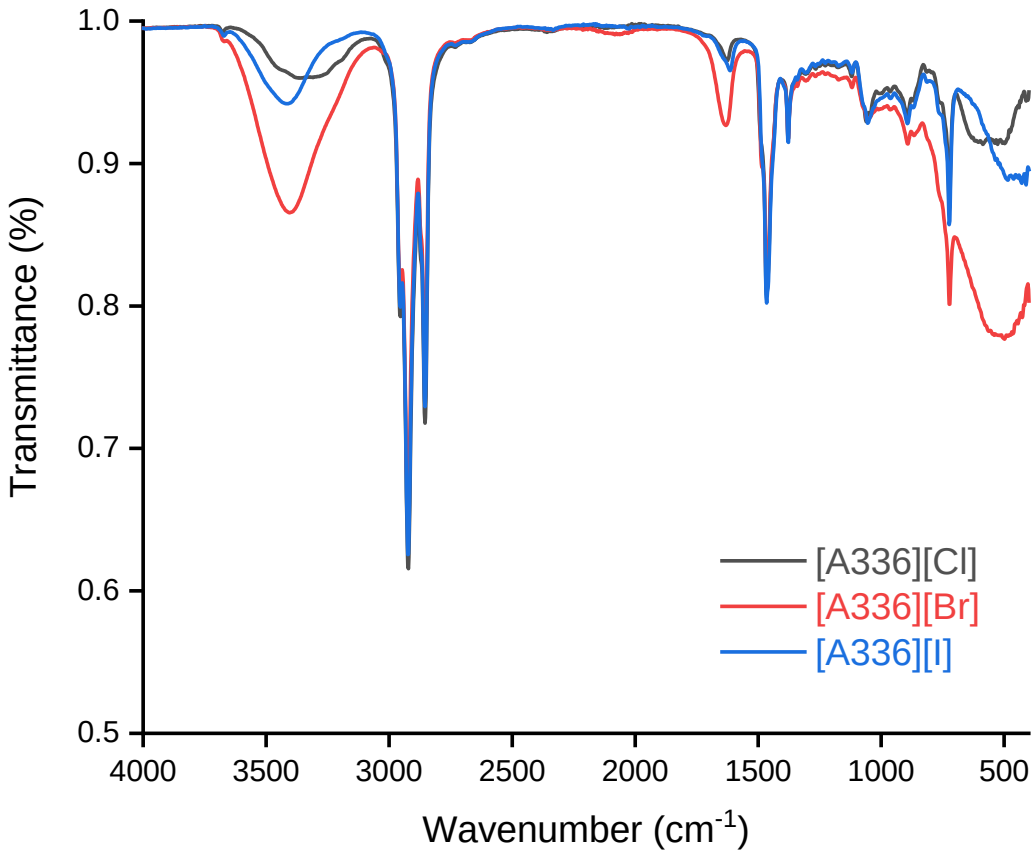

Fig. S8 FTIR spectra of the fresh ionic liquids [A336][Cl], [A336][Br], and [A336][I].

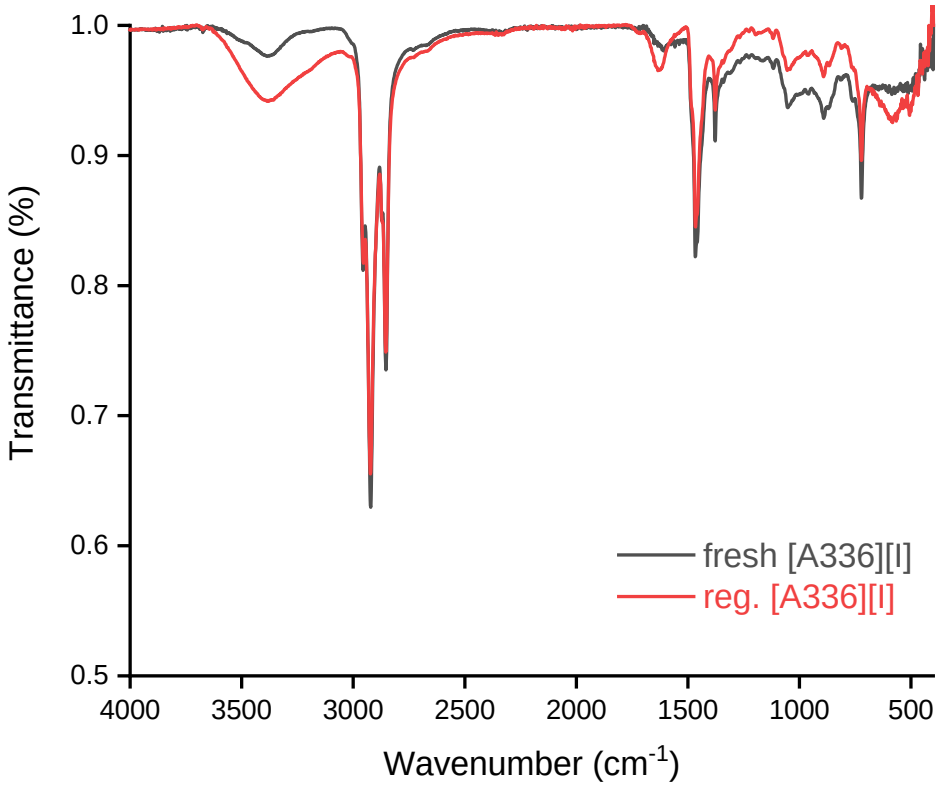

Fig. S9 FTIR spectra of the fresh and the regenerated ionic liquid [A336][I].

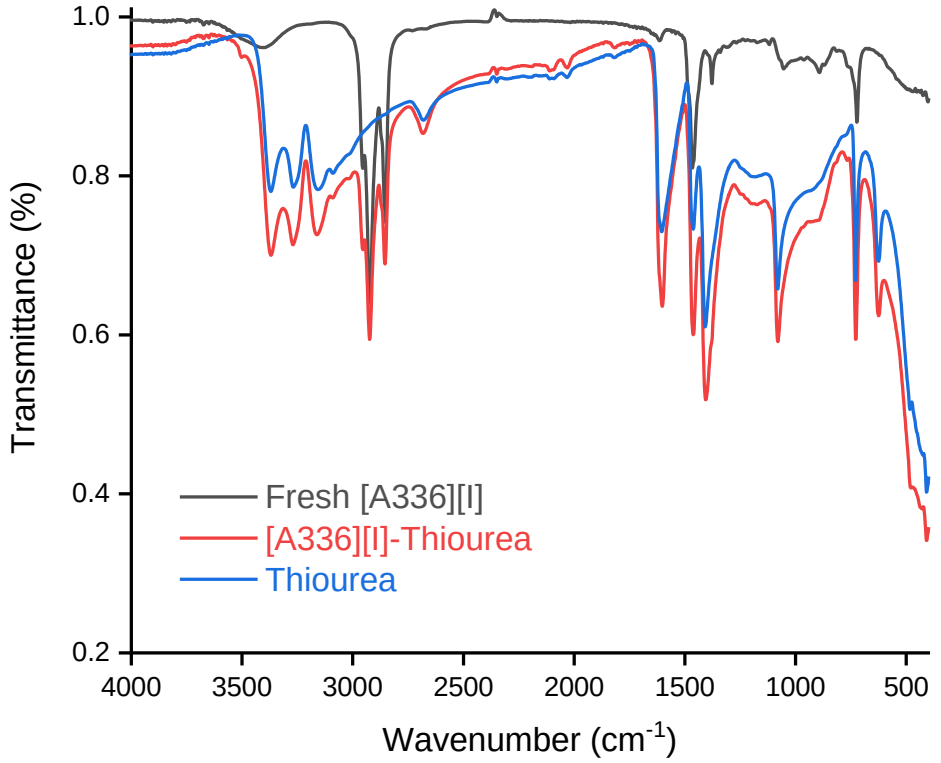

Fig. S10 FTIR spectra of thiourea, fresh [A336][I], and thiourea-loaded [A336][I].

Table S1 Extraction behavior of HCl in the water-saturated ionic liquids phase as a function of the acidity of aqueous feeds.

Extractant	Refractive index		Concentration (mol L^{-1})			Extraction
	$n_{20\ HCl\ feed}$	$n_{20\ HCl\ raf}$	HCl_{feed}	HCl_{raf}	HCl_{org}	$\%E_{HCl}$
[A336][Cl]	1.3337	1.3337	0.09	0.09	0.01	0.00
	1.3371	1.3368	0.50	0.46	0.04	7.41
	1.3409	1.3399	0.97	0.85	0.15	12.8
	1.3484	1.3458	1.91	1.58	0.42	17.2
	1.3632	1.3570	3.84	3.02	0.98	21.3
	1.3773	1.3680	5.77	4.49	1.51	22.3
[A336][Br]	1.3337	1.3337	0.09	0.09	0.01	0.01
	1.3371	1.3371	0.50	0.50	0.00	0.01
	1.3409	1.3409	0.97	0.97	0.03	0.01
	1.3484	1.3481	1.91	1.87	0.13	2.02
	1.3632	1.3609	3.84	3.53	0.47	8.01
	1.3773	1.3731	5.77	5.19	0.81	10.2
[A336][I]	1.3337	1.3337	0.09	0.09	0.01	0.01
	1.3371	1.3371	0.50	0.50	0.00	0.01
	1.3409	1.3409	0.97	0.97	0.03	0.01
	1.3484	1.3484	1.91	1.91	0.09	0.01
	1.3632	1.3627	3.84	3.77	0.23	1.70
	1.3773	1.3752	5.77	5.48	0.52	5.10

Table S2 Stripping behavior of precious metals from loaded organic phase using various striping reagents.[§]

Extractant	Stripping reagent	Concentration	Percentage stripping (%S)							
			Loaded organic from 6 mol L^{-1} HCl feed[a]				Loaded organic from 6 mol L^{-1} NaCl feed[b]			
		(mol L^{-1})	Pt	Pd	Rh	Au	Pt	Pd	Rh	Au
[A336][Cl]	NH_4OH	1.0	0.16	1.95	24.5	0.61	22.9	100	68.8	96.2
	$Na_2S_2O_3$	1.0	0.60	0.20	2.73	2.70	1.51	2.43	82.4	0.60
	$CS(NH_2)_2$/HCl	1.0	25.0	23.0	6.16	20.2	49.5	48.2	21.8	34.3
[A336][Br]	NH_4OH	1.0	0.11	2.30	9.24	0.07	16.2	100	68.6	3.40
	$Na_2S_2O_3$	1.0	8.48	0.28	1.98	9.40	1.24	8.59	31.5	14.1
	$CS(NH_2)_2$/HCl	1.0	19.0	16.1	4.50	14.5	34.9	35.6	14.7	25.0
[A336][I]	NH_4OH	0.1	0.01	0.11	0.31	0.31	0.01	7.16	1.46	0.47
		0.2	0.01	0.03	0.22	0.19	0.11	66.8	1.12	0.14
		0.5	0.03	0.12	0.14	0.10	0.71	90.1	1.23	0.12
		1.0	0.97	89.8	4.25	0.04	1.38	100	2.54	0.07
	$Na_2S_2O_3$	1.0	2.23	0.09	1.63	100	0.65	36.8	12.6	6.34
	$CS(NH_2)_2$/HCl	1.0	67.5	61.2	53.6	18.6	79.4	80.9	36.6	38.6

[§]Aqueous phase: 1.0 mol L^{-1} $Na_2S_2O_3$, NH_4OH, and $CS(NH_2)_2$/HCl. Loaded organic phases: [A336][Cl], 680 mg L^{-1} Pt(IV), 674 mg L^{-1} Pd(II), 25.5 mg L^{-1} Rh(III), and 28.8 mg L^{-1} Au(III); [A336][Br], 676 mg L^{-1} Pt(IV), 675 mg L^{-1} Pd(II), 31.9 mg L^{-1} Rh(III), and 28.9 mg L^{-1} Au(III); and [A336][I], 678 mg L^{-1} Pt(IV), 672 mg L^{-1} Pd(II), 11.8 mg L^{-1} Rh(III), and 27.7 mg L^{-1} Au(III); O/A = 1/1; equilibrium time 60 min; 298 K; 2000 rpm. [a]Loaded organic phase from 6.0 mol L^{-1} HCl feed (Fig. 2). [b]Loaded organic phase from 6.0 mol L^{-1} NaCl feed (Fig. 4)

Table S3 Mass balance of batch simulation extraction and stripping of precious metals from chloride leachate of spent automotive catalysts.

Element	Metal concentration in the aqueous phases (mg L^{-1})				
	Feed	Raffinate	Scrubbing (NaCl)	Pd stripping (NH_4OH)	Pt stripping ($CS(NH_2)_2$/HCl)
Al	1427	1408	7.22	0.78	0.25
As	< 1.0	0.49	0.41	1.36	< 0.01
Ba	0.30	0.27	0.04	0.02	0.04
Bi	< 0.01	0.07	< 0.01	0.28	< 0.01
Ca	46.6	40.4	5.50	1.73	5.37
Ce	60.3	55.2	5.74	0.23	< 0.01
Cr	4.03	3.66	< 0.01	< 0.01	0.25
Cu	0.69	< 0.01	0.21	9.47	0.06
Fe	80.2	78.2	2.80	< 0.01	0.16
K	59.0	71.9	8.26	8.91	< 0.01
La	8.70	8.00	0.57	< 0.01	0.02
Mg	310	300	1.99	< 0.01	0.18
Mn	3.25	3.17	0.05	< 0.01	< 0.01
Mo	2.28	0.89	1.71	1.34	0.04
Na	33591	30703	13885	13577	323
Ni	4.74	4.34	0.23	< 0.01	0.03
P	4.47	2.51	2.66	< 0.01	6.62
Pb	0.96	0.46	< 0.01	0.08	0.18
Pd	**24.0**	< 0.01	< 0.01	**209**	6.09
Pt	**10.5**	< 0.01	< 0.01	0.81	**89.1**
Rh	**6.81**	**5.12**	< 0.01	3.84	0.91
S	18047	17520	349.6	36.9	866
Si	3.28	3.08	0.23	0.21	0.14
Sn	28.7	12.4	< 0.01	1.22	1.96
Sr	9.68	9.02	0.91	0.02	0.01
Ti	4.12	3.93	0.08	0.01	0.01
V	0.45	0.56	< 0.01	< 0.01	< 0.01
Zn	60.4	0.16	0.36	404	0.28
Zr	419	391	2.01	< 0.01	0.06