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Supporting Information

Ionic-Liquid-Based Acidic Aqueous Biphasic Systems for Simultaneous Leaching and Extraction of Metallic Ions

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SUPPORTING INFORMATION

EXPERIMENTAL DETAILS

Chemicals

Tributyltetradecylphosphonium chloride [P_{44414}][Cl] was gratefully provided by Cytec. Concentrated HCl solution (37 %) and NaOH (99.0 % purity) were purchased from Sigma. $NiCl_2.6H_2O$ (99.5 % purity), $FeCl_3.4H_2O$ (99.5 % purity), $CoCl_2.6H_2O$ (99.5 % purity) and H_2PtCl_6 (99.9% purity) were purchased from AlfaAesar. All chemicals were used as received. Ultrapure water (18.2 M□.cm) was used.

Instrumentation

UV-vis spectra were recorded using a Cary 50 (Varian) spectrometer with a 1 cm wide quartz cell. The concentrations of metal ions before and after extraction were determined with the help of an Atomic Absorption Spectrophotometer (AAS) PinAAcle 900F (Perkin Elmer). Stirring was performed with a Stuart rotator drive STR4 apparatus. A Titroline 7500 KF Trace (SI Analytics Karl Fischer) was used to determine the water content of the upper phases.

Cloud-point titration

[P_{44414}][Cl] is a hydrophilic ionic liquid, has the appearance of a white waxy solid at room temperature. Its melting point is 38.5 °C, as determined by differential scanning calorimetry (DSC). This ionic liquid is soluble in any proportion in pure water. However, upon mixing [P_{44414}][Cl] with a 37 % HCl solution at room temperature, two liquid immiscible phases are formed.

The phase diagram was thus obtained using a cloud point titration method. Typically, 1 g of an aqueous solution containing 50 wt % [P_{44414}][Cl] is prepared in a 10 mL vial. The vial is then thermostated at a given temperature using a water bath. Drops of a concentrated HCl solution are then added until the solution becomes cloudy, which is characteristic of the apparition of a biphasic system. Drops of ultrapure water are then added to the vial until the solution becomes clear again. These steps are repeated in order to obtain a series of cloud points, corresponding to the binodal curve that is the is border line between the monophasic and biphasic state. In line with previous works, the binodal curve is presented by plotting the wt % of ionic liquid as a function of the wt % of HCl. Experimental errors on the cloud points are in the order of 0.1 wt%, corresponding to the mass of a drop, of about 20 mg.

Phase diagrams raw data for [p_{44414}][cl]-hcl-h2o

Table TS1. Raw data for phase diagrams of the aqueous biphasic system [P_{44414}][Cl]/HCl/H_2O at 24, 36, 45, 50 and 56°C.

24°C					
wt % HCl	wt % IL	wt % HCl	wt % IL	wt % HCl	wt % IL
17.93354029	27.97375476	22.07719617	6.547225892	24.22865673	0.986315348
18.48668804	25.93707071	22.07681689	6.439301665	24.31471111	0.924564489
18.45852535	24.69174243	22.09119386	6.336902669	24.36659891	0.863209108
18.6954956	23.40752111	22.21171266	6.119491218	24.45179507	0.808531617
18.94064899	22.22159951	22.33186989	5.797756057	24.4481076	0.783863821
19.15446723	21.0612982	22.42257517	5.505956636	26.19023585	0.37687044
19.43353732	19.88864366	22.55232707	5.257007432	28.77073495	0.145148501
19.62236096	18.89624934	22.55423668	5.0097051	27.77600646	0.289468215
19.6909727	18.01372041	22.65858954	4.894578696	26.72347824	0.372887023

19.91095563	17.23088957	22.91182262	4.43953571	25.8570685	0.54135115
19.91230284	16.67718191	22.93227228	4.21170984	25.16161806	0.706440468
20.10846996	15.89369463	22.95249013	3.96994602	-	-
20.11225569	15.53013983	22.90745225	3.878617444	-	-
20.208841	15.09671033	23.03987686	3.742026766	-	-
20.38015016	14.52114997	23.05028708	3.629310442	-	-
20.48395123	14.09376888	23.09412234	3.521768237	-	-
20.52371733	13.7083391	23.12180285	3.412776909	-	-
20.61004664	13.30492265	23.11490789	3.308167845	-	-
20.68283412	12.88090442	23.23322594	3.234368228	-	-
20.80350422	12.53992852	23.27033455	3.123550082	-	-
20.8707658	12.2880962	23.25214721	3.086397984	-	-
20.91081999	11.91370452	23.28900811	2.995920171	-	-
20.93589293	11.61190183	23.33886304	2.914296612	-	-
21.08183362	11.21958121	23.38680372	2.825760889	-	-
21.12184619	10.9451775	23.32715763	2.744009326	-	-
21.14855649	10.68819581	23.40201246	2.69756807	-	-
21.17540818	10.25952855	23.35672053	2.636400233	-	-
21.28700815	9.975344671	23.37411395	2.615556407	-	-
21.3296154	9.762643423	23.40638875	2.579671854	-	-
21.35491061	9.605601047	23.50290414	2.506332871	-	-
21.55177029	9.309259955	23.43341879	2.470571026	-	-
21.5515727	9.116619148	23.47125151	2.424649978	-	-
21.58077398	8.895120583	23.47377064	2.402683458	-	-
21.70068368	8.633077861	23.44719222	2.337972688	-	-
21.69578873	8.471679166	23.52490557	2.262902919	-	-
21.66293569	8.295326164	23.49966825	2.210222538	-	-
21.67865842	8.254741532	23.53302697	2.156987074	-	-
21.74684676	8.053214177	23.61403885	2.108192981	-	-
21.77875931	7.853351291	23.58877784	2.073144733	-	-
21.74622098	7.723624747	23.57601482	2.001051763	-	-
21.76799908	7.594185133	23.59386069	1.931980325	-	-
21.79484389	7.439582708	23.63186665	1.895015324	-	-
21.827774	7.294905525	23.67679336	1.810617701	-	-
21.88506949	7.147106008	23.72829572	1.775062829	-	-
21.90892309	7.038003444	23.83307274	1.708529515	-	-
21.9323879	6.95053115	23.86696667	1.689638045	-	-
22.0109116	6.845649171	24.10930275	1.165006952	-	-
22.01905767	6.746754241	24.13865036	1.067641706	-	-
22.03468256	6.640095122	24.19430628	1.05544513	-	-

36°C		45°C		50°C		56°C	
wt % HCl	wt % IL	wt % HCl	wt % IL	wt % HCl	wt % IL	wt % HCl	wt % IL
16.01086346	27.26296123	12.52401747	27.25991024	12.57380423	0.923816962	6.174175569	4.54276953
16.26222718	23.1889358	12.04950115	21.55896969	10.3883594	5.154408361	7.43287286	3.534085925
16.37483743	19.92702444	13.33593587	15.66613454	9.872473004	8.407419011	7.164733179	2.621437362
17.23930269	15.37844163	13.19219397	11.0748423	9.643857594	14.31805511	8.419226812	2.089421662
17.83521579	11.53703087	14.90647275	8.090240478	9.172079823	27.15888103	8.315918723	1.617427286
19.12923265	8.490503689	15.07446579	6.929502636	9.255195058	26.04657191	5.847230321	24.35655474
21.28809391	3.982022582	16.74418605	5.211929784	9.033883614	23.7539892	5.604989605	21.71075435
21.1803086	3.48951183	17.59113573	2.731570956	8.740406404	22.39682009	5.74346578	14.19940408
21.72087458	2.583066246	18.6254508	1.693452027	8.804927536	21.8442029	-	-
22.17427757	1.990900006	19.69185164	1.06944232	8.943851416	19.92465052	-	-
22.74776931	1.55034568	20.34558114	0.771453137	8.846837852	18.81064553	-	-
-	-	-	-	9.040571089	17.93277811	-	-
-	-	-	-	9.411822083	16.80229642	-	-
-	-	-	-	9.014464802	15.71320597	-	-
-	-	-	-	8.934342171	15.08004002	-	-

| | | | | 9.866846448 | 13.89618771 | - | - |
| - | - | - | - | 9.958921208 | 13.43809205 | - | - |

Extraction of metallic ions

Five different mixtures of [P$_{44414}$][Cl], HCl and water, denoted as A to E, were prepared. Details on their preparation and composition are given in Table 1. All mixtures were prepared adding various amounts of ionic liquid to 1 ml of aqueous phase containing concentrations of HCl ranging from 6.0 to 10 mol.L^{-1} HCl. Mixtures A, B and C all contain around 18 wt % of ionic liquid and variable concentration of HCl. Mixtures A and B were prepared in order to form two immiscible phases at 24 °C, while mixture C was monophasic at 24 °C. Mixtures D and E contain the same concentration of HCl but different concentration of ionic liquid. In addition, the compositions of the mixtures D and E were chosen to be close to the binodal curve at 24 °C, mixture D being biphasic while mixture E is monophasic.

These five mixtures were used to study the partitioning of Co(II), Ni(II), Fe(III) and Pt(IV) metal ions. Typically, 1 mL of an initial aqueous solution containing a concentration of HCl ranging from 6 to 12 mol.L^{-1} and 0.01 mol.L^{-1} of FeCl$_3$.4H$_2$O, H$_2$PtCl$_6$, NiCl$_2$.6H$_2$O or CoCl$_2$.6H$_2$O was mixed in a 2 mL tube, with [P$_{44414}$][Cl]. The tube was then stirred in a rotator during two hours until complete dissolution of the IL and placed in a heating bath for 6 hours. The separation of Co(II) from Ni(II) was studied in an additional set of experiments using a solution containing both metal ions at a concentration of 0.01 mol.L^{-1}.

Table S1. Composition of mixtures A to E and volumes of each phases of the corresponding AcABS formed.

	Mixture preparation			Amounts of each compound			Phase volumes at 24 °C		Phase volumes at 50 °C (mL)	
Mixture	1 ml [HCl] (mol.L^{-1})	[P$_{44414}$][Cl] (g)	Total mass (g)	[P$_{44414}$][Cl] (wt %)	HCl (wt %)	H$_2$O (wt %)	Upper (mL)	Lower (mL)	Upper (mL)	Lower (mL)
A	10	0.25	1.40	17.8	25.9	56.3	0.45	0.85	0.35	0.95
B	8.0	0.25	1.36	18.1	20.8	61.1	0.40	0.88	0.35	0.93
C	6.0	0.25	1.35	18.6	15.7	65.7	-	-	0.60	0.68
D	8.0	0.375	1.48	25.0	19.0	56.0	0.70	0.68	0.63	0.75
E	6.6	0.125	1.25	10.2	19.0	70.8	-	-	0.23	0.98

Table S2 – Water contents and HCl concentration of the immiscible phases formed upon preparing mixtures A to E

| Mixture | Water-content in the upper phase | | HCl-content in the lower phase | | | |
| | 24 °C | 50 °C | 24 °C | | 50 °C | |
	wt %	wt %	wt %	mol.L^{-1}	wt %	mol.L^{-1}
A	17.5	15.3	29.4	9.2	28.7	9
B	23.3	13.3	25.3	7.8	25.2	7.8
C	-	43	-	-	17.1	5.1
D	26.1	20.3	25.1	7.7	24.8	7.6
E	-	31.0	-	-	21.6	6.5

Aliquots of the upper and lower phases were then taken and the concentration of metals determined with the help of an AAS apparatus. Please note that unlike the analysis reported previously in the case of the extraction of metal ions using ionic liquid, the concentrations of metal ions were measured in both phases. The mass conservation law was confirmed (± 5 %). All concentrations were determined after cooling down aliquots at 24 °C when necessary.

Measurements

Concentrations of metal ions were measured by atomic absorption spectrophotometry. To that end, calibration solutions ranging from 5.10^{-5} to 10^{-3} mol.L^{-1} Ni(II) or Fe(III), from 2.10^{-5} to 10^{-3} mol.L^{-1} Co(II) and from 5.10^{-5} to 3.10^{-4} mol.L^{-1} Pt(IV) were prepared in 1 mol.L^{-1} HCl. After dilution of the samples ranging from 10 to 100 in water, the influence of the initial concentration of hydrochloric acid and of the ionic liquid was found to be negligible on the measurements.

The distribution coefficient (D) and the extraction yield (%E) were calculated as follows:

$$D = \frac{\frac{[M]_0 V_{initial}}{V_{low}} - [M]_{low}}{[M]_f} \times \frac{V_{low}}{V_{up}}$$ (1)

$$\%E = \frac{\frac{[M]_0 V_{initial}}{V_{low}} - [M]_{low}}{[M]_0}$$ (2)

$[M]_0$ is the concentration in mol.L^{-1} of metal in mixtures A to E before extraction (i.e before addition of the IL). $V_{initial}$ is the volume in ml of the mixture before extraction and addition of IL. $[M]_{low}$ is the concentration in mol.L^{-1} of the metal ion in the lower phase after extraction.

V_{low} and V_{up} are respectively the volumes, expressed in mL, of the lower and upper phase after extraction. The volume of each phase of the AcABS was measured by preparing a mixture containing

the same proportions of ionic liquids and HCl solution as those used for the extraction experiments but starting from a larger amount of ionic liquid, typically 1 g to minimise experimental errors. However using lower amounts of solutions during metal extractions does not affect the accuracy of the experiment and is justifiable to minimize the cost of the ionic liquid.

The volume of each phase was carefully determined by separating the two phases with a small volume separating funnel immersed in a heating bath for 6 hours. The values of each volume were taken after cooling the phases in a 10 mL measuring cylinder at room temperature and are given in Table 1. Once separated, minimal exchange between the two phases occurs: when a monophasic solution at 24 °C is heated at 50 °C and forms a biphasic solution, the two phases stay immiscible for several days.

After measuring the volumes of each phase, the water content of the upper phase was analysed by Karl Fischer titration and the hydrochloric concentration of the lower phase was measured by titration with a solution of sodium hydroxide 3.0 mol.L^{-1}.

In the case of Fe(III) extraction, the amount of metal ion in the lower phase was too low to be measured. Therefore, and because this type of extracting system allows it, the distribution coefficients and extraction yields were measured analysing the upper phase. D and %E were then measured as follows:

$$D = \frac{[M]_{up}}{[M]_0 - [M]_{up}} \times \frac{V_{low}}{V_{up}} \tag{3}$$

$$\%E = \frac{[M]_{up}}{[M]_o} \tag{4}$$

with *up* subscript referring to the upper phase.

According to our experimental protocol, and to the uncertainty related to the measurement of the AcABS phase volumes, we assume that the maximum calculable values for %E are 99.6 and 97.9 for Fe(III) and Co(II), respectively. For Ni(II), the minimum calculable values for %E are 3.7. For platinum, which was found to precipitate in presence of [P$_{44414}$][Cl] in water, the maximal values for %E that can be obtained according to our protocol is 97.6. For each extraction experiment, the maximal value for D varies according to the volumes of the phases forming the AcABS.

The separation factor of cobalt(II) from nickel(II) was calculated as described by the following equation:

$$\beta_{Co}^{Up} = \frac{D_{Co}}{D_{Ni}} \tag{5}$$

In addition, the proportion of each metal ion in the upper (x_{Co}^{Up}) and lower (x_{Ni}^{Low}) phases were calculated as following:

$$x_{Co}^{Up} = \frac{[Co]^{up}}{[Ni]^{up} + [Co]^{up}} \tag{6}$$

$$x_{Ni}^{Low} = \frac{[Ni]^{low}}{[Ni]^{low} + [Co]^{low}} \tag{7}$$

With superscripts up and low standing for the upper and lower phases, respectively.
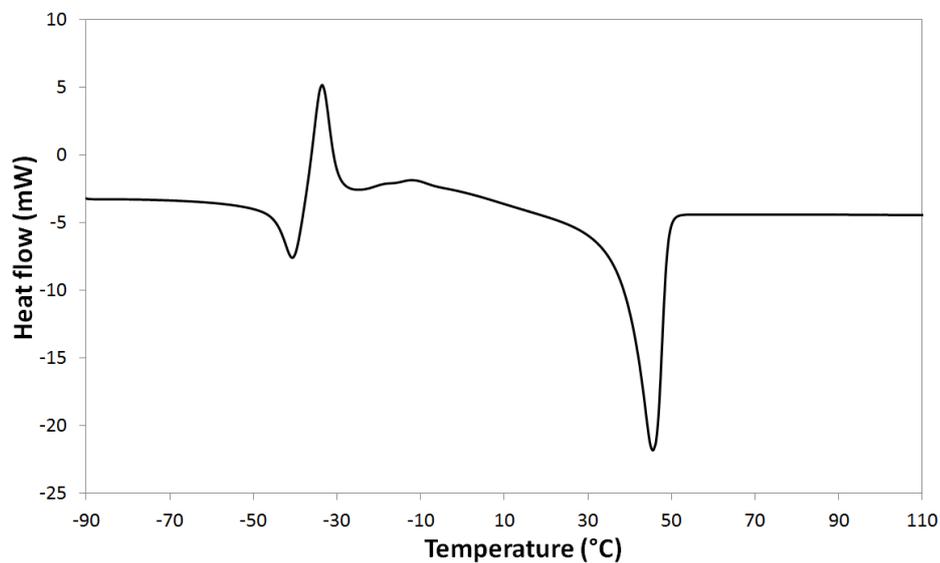
THERMAL BEHAVIOR OF [P$_{44414}$][Cl]

Figure FS1. Differential scanning calorimetry curve after three scans of [P$_{44414}$][Cl] from -90 °C to 110 °C with a speed of 10°C.min^{-1}. The melting point corresponds to the onset of the peak (38.5°C).

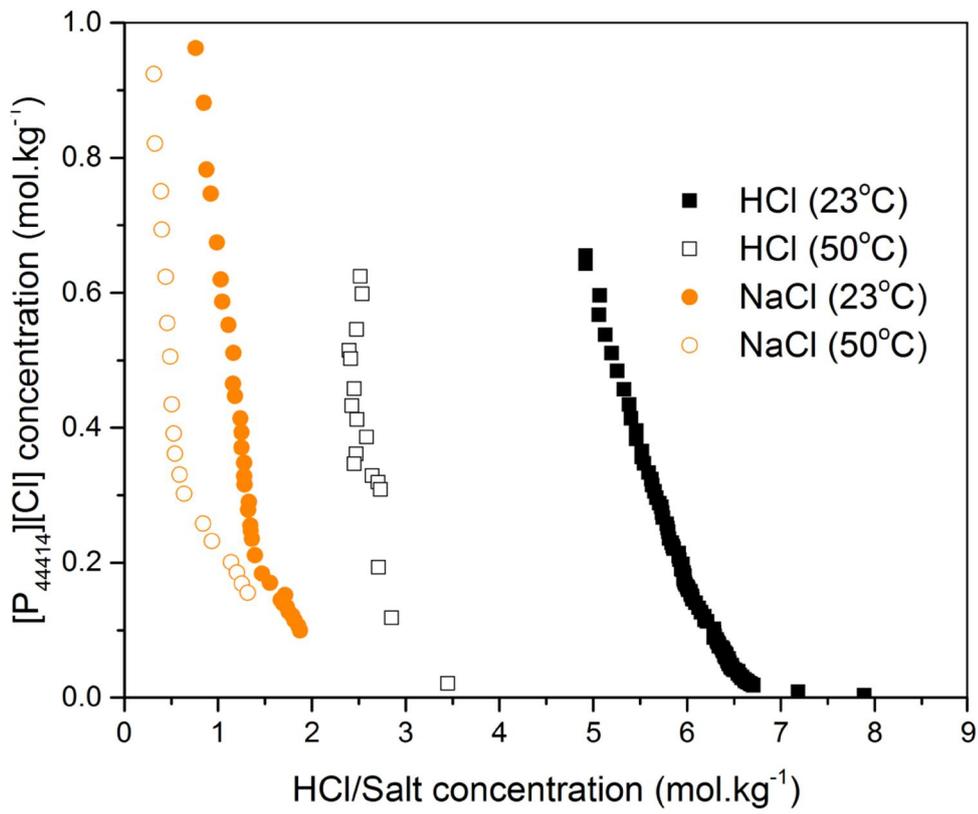# COMPARAISON OF THE [P$_{44414}$][Cl]-H$_2$O SYSTEM WITH HCl AND NaCl

Figure FS2. Phase diagrams of $[P_{44414}][Cl]$-H_2O with NaCl and HCl, evidence of the LCST behavior.

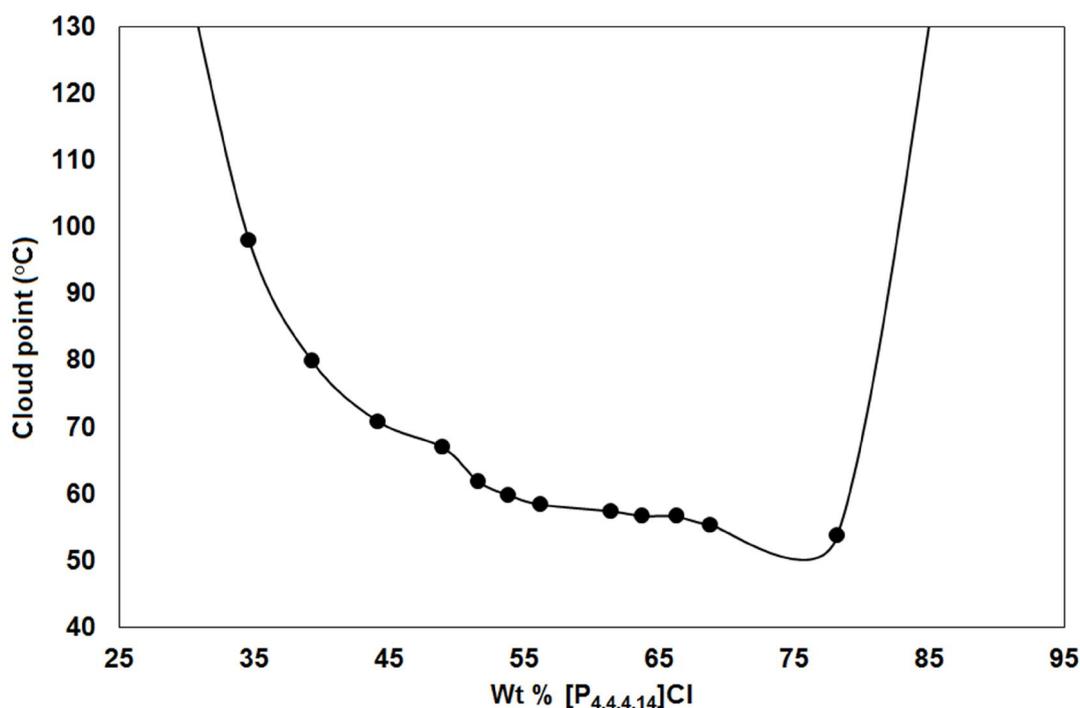# LCST TYPE BEHAVIOR OF [P$_{44414}$][Cl]-H$_2$O SYSTEM

Figure FS3. Cloud point temperature of the [P$_{44414}$][Cl]-H$_2$O system at various concentrations of ionic liquid showing a clear LCST type behaviour.

DATA FOR THE EXTRACTION OF Fe(III), Pt(IV), Co(II) and Ni(II)

The extraction yeilds and the distribution coefficients for the single extraction of Fe(III), Pt(IV), Co(II) and Ni(II) using mixtures A and E at 24 and 50 °C are collected in Table S3. Competitive extraction and separation of Co(II) from Ni(II) is presented in Table S3.

Table 3. Extraction yields for various metal ions in mixtures A to E at 24 and 50 °C.

		Fe(III)[a]		Co(II)		Ni(II)		Pt(IV)	
	Mixture	% E	D	% E	D	% E	D	% E	D
24 °C	A	>99.6	>500	86.67	12.3	5.40	0.107	93.62	27.7
	B	94.2	29.4	88.72	17.2	4.35	0.099	-[b]	-[b]
	D	95.9	22.3	94.19	15.6	11.10	0.121	> 97.60	>39.3
50 °C	A	96.7	80.8	87.50	19.0	<3.70	<0.01	93.52	39.2
	B	97.4	84.1	88.64	20.6	4.29	0.119	-[b]	-[b]
	C	97.0	36.5	97.92	>53	12.20	0.156	> 97.60	>45.8
	D	97.2	42.4	94.55	20.8	6.50	0.084	>97.34	>43.8
	E	95.2	72.6	75.09	11.7	3.28	0.261	-[b]	-[b]

a: values for D and %E calculated using equations 3 and 4. b: not measured.

Table S4. Extraction yields (%E), distribution coefficients (D), separation factors (β_{Co}^{Up}) and mole fractions of cobalt in the upper phase (x_{Co}^{Low}) and of nickel in the lower phase (x_{Ni}^{Low}) for the separation of Co(II) from Ni(II) using [P$_{44414}$][Cl]-HCl-H$_2$O at 24 and 50 °C. Initial concentrations for all metals were 10 mmol L^{-1}.

	Mixture	Co(II)		Ni(II)				
		% E	D	% E	D	β_{Co}^{Up}	x_{Co}^{Up}	x_{Ni}^{Low}
24 °C	A	87.08	12.7	2.39	0.05	254	0.970	0.888
	B	88.45	16.8	2.75	0.06	280	0.960	0.899
	D	93.71	14.4	11.38	0.13	111	0.900	0.937
50 °C	A	87.98	19.9	<2.00	<0.05	>400	0.974	0.901
	B	87.68	18.8	<2.00	<0.05	>376	0.960	0.897
	C	95.84	25.9	11.27	0.14	181	0.872	0.957
	D	97.70	21.4	9.18	0.12	178	0.917	0.948
	E	71.75	9.88	5.57	0.23	43	0.961	0.779

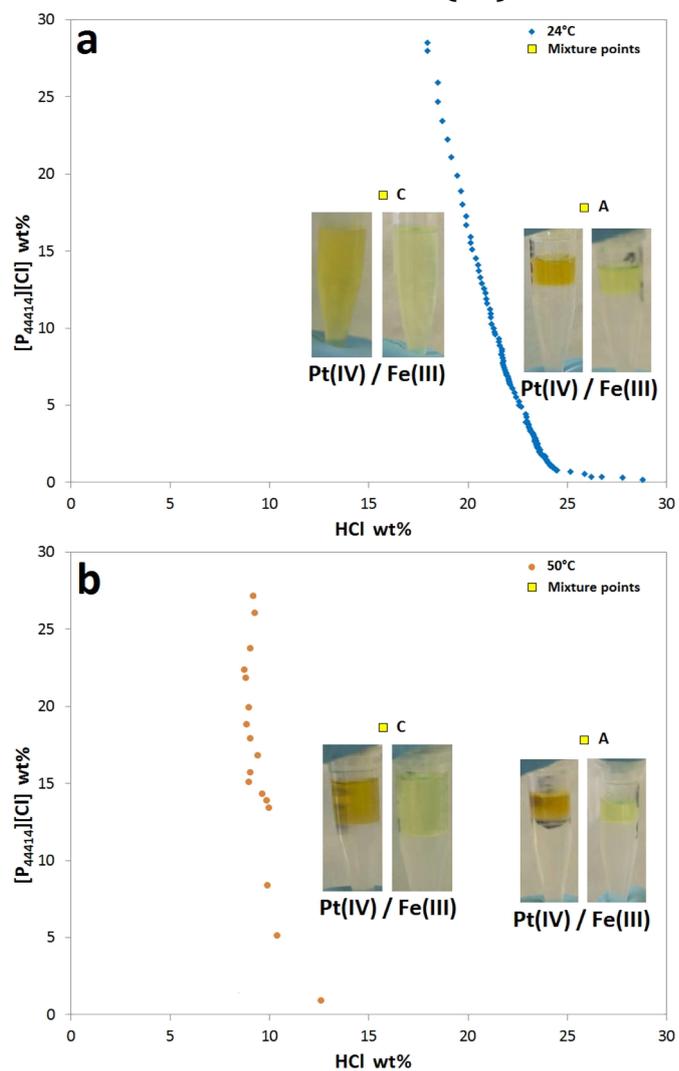# SNAPSHOTS AFTER IRON(III) AND PLATINUM(IV) EXTRACTIONS

Figure FS4. Phase diagrams at 24 and 50 °C and related snapshots taken after extraction of Pt(IV) and Fe(III) using [P$_{44414}$][Cl]-HCl-H$_2$O. Upper diagram a: binodal curve obtained at 24 °C. Snapshots were obtained when preparing mixtures A, C, D and E. Mixtures C and E are monophasic. Lower diagram b: binodal curve measured at 50 °C. All mixtures are biphasic at this temperature.
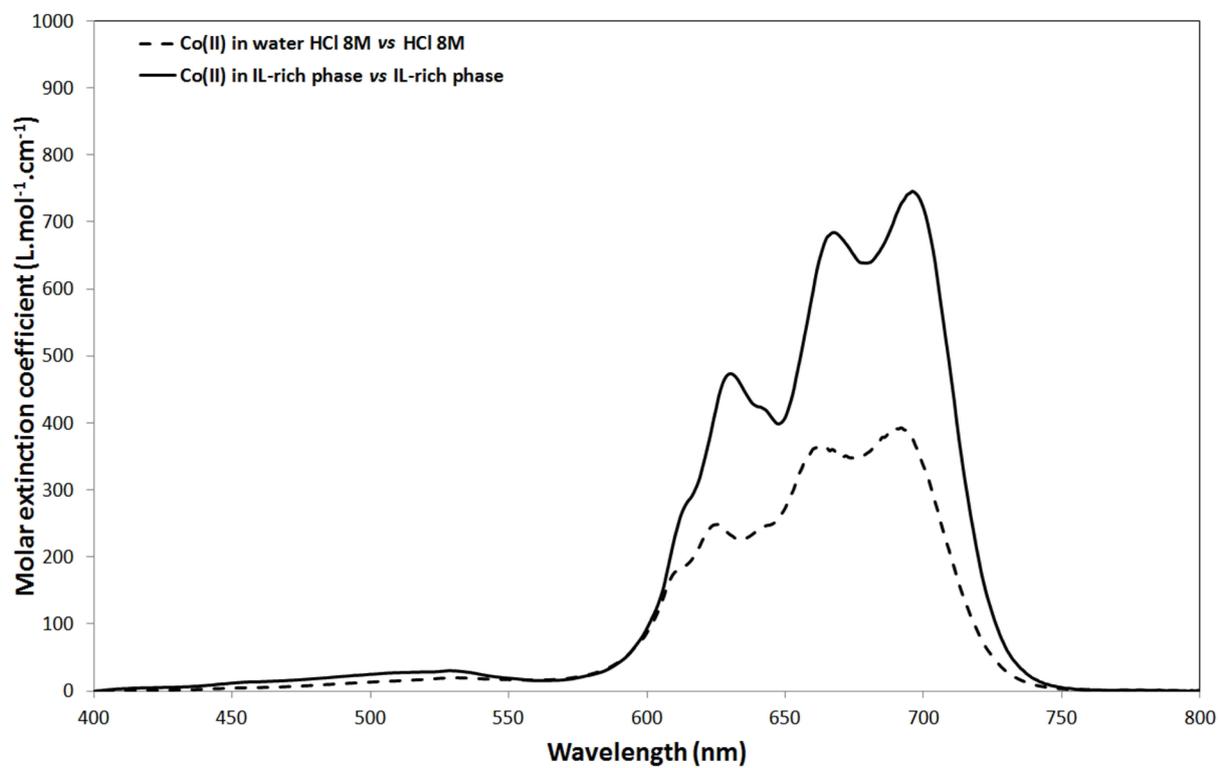
COBALT CHLORIDE COMPLEXES

Figure FS5. UV-vis measurements of cobalt(II) in an aqueous phase containing 8 mol.L^{-1} of HCl and in the IL-rich phase after extraction.