Electronic Supplementary Material (ESI) for Green Chemistry.

Solvent extraction in extended hydrogen bonded fluids – separation of Pt(IV) from Pd(II) using TOPO-based Type V DES

Silvia J.R. Vargas,[1] Germán Pérez-Sánchez,[1] Nicolas Schaeffer,[1*] João A.P. Coutinho[1]

[1] CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

* Corresponding author: nicolas.schaeffer@ua.pt

Number of pages – 10

Number of Figures – 9

Number of Tables – 3

FIGURES

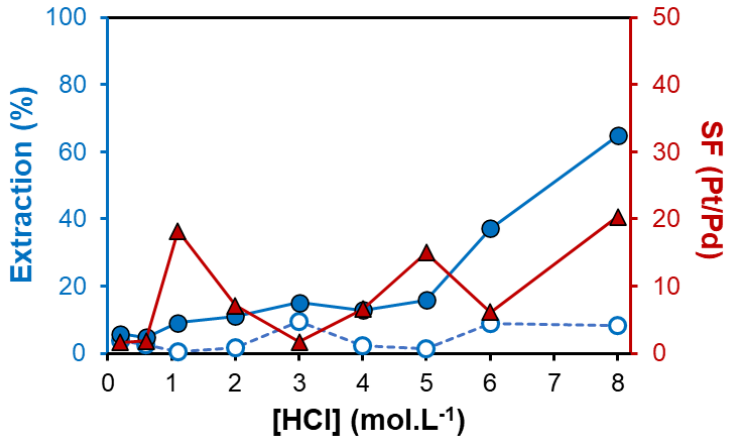

Figure S1. Pt(IV) (filled symbols) and Pd(II) (empty symbols) extraction efficiencies and Pt/Pd selectivity in the TOPO + $C_{10}H_{19}OOH$ eutectic for x_{TOPO} of 0.2 as a function of the initial aqueous phase HCl concentration.

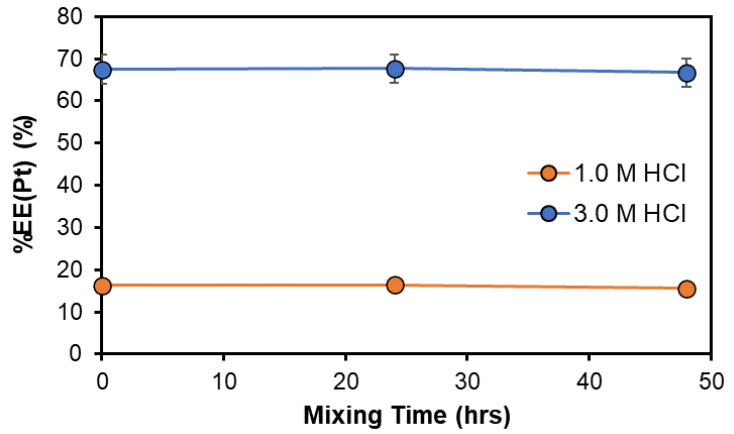

Figure S2. Platinum(IV) extraction efficiency in the TOPO + $C_{10}H_{19}OOH$ eutectic for x_{TOPO} of 0.3 as a function of the initial aqueous phase HCl concentration and mixing time.

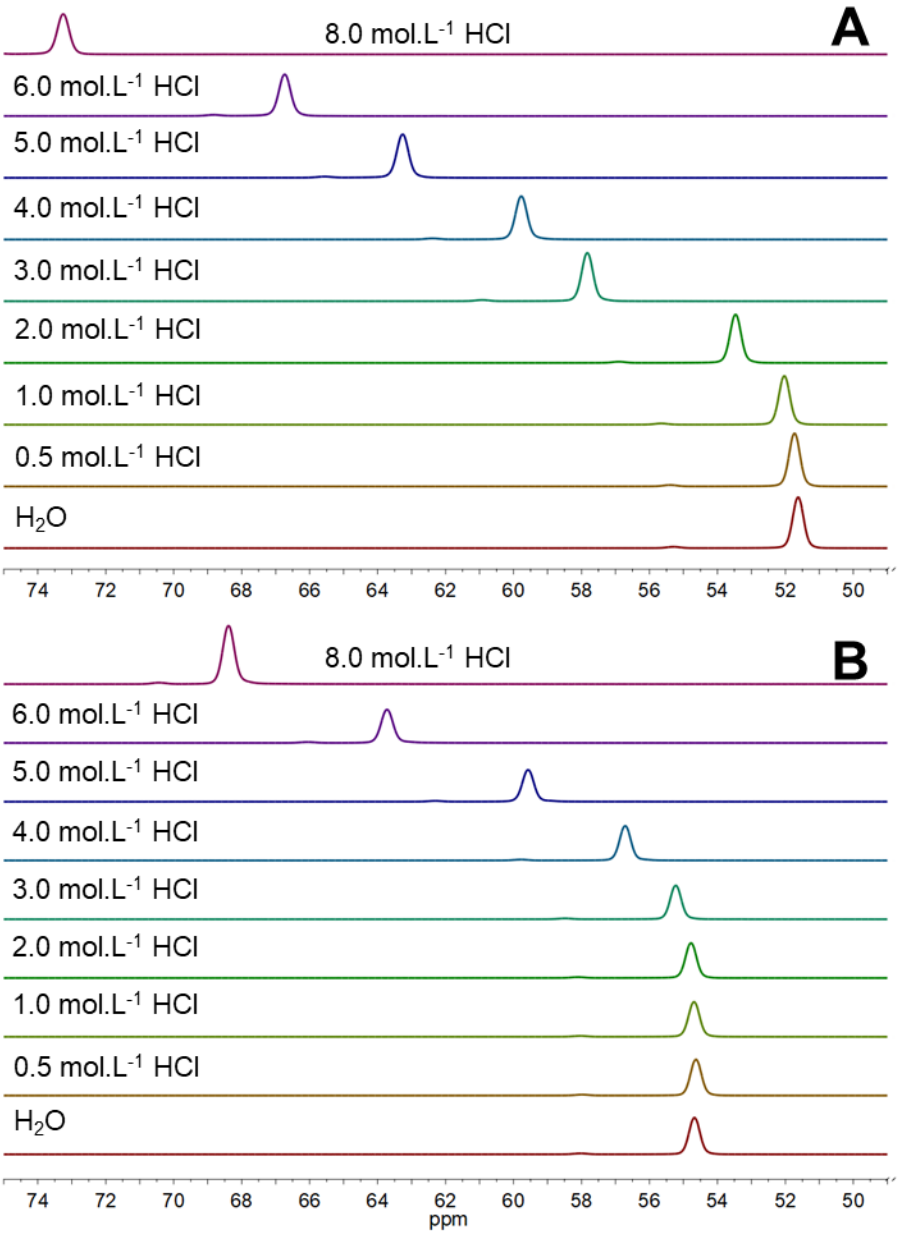

Figure S3. ^{31}P-NMR spectra of the TOPO + $C_{10}H_{19}OOH$ eutectic phase after equilibration with various HCl solutions for A) x_{TOPO} = 0.5 and B) x_{TOPO} = 0.3. D_2O in a co-axial insert was used as solvent.

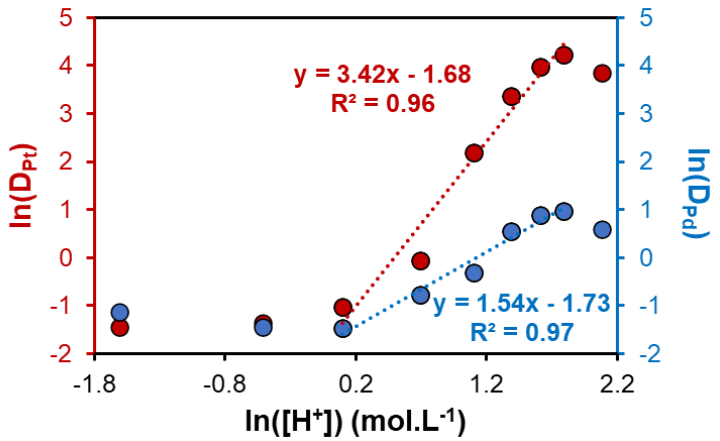

Figure S4. Pt(IV) and Pd(II) distribution coefficients to the TOPO + $C_{10}H_{19}OOH$ eutectic phase as a function of the initial aqueous phase HCl concentration for x_{TOPO} = 0.4.

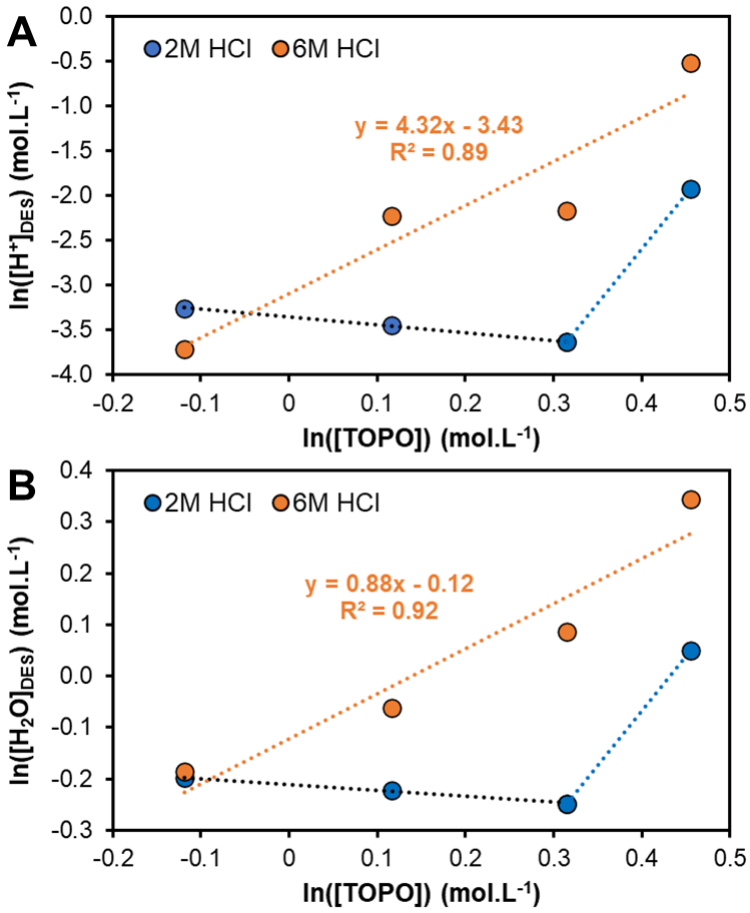

Figure S5. Pt(IV) and Pd(II) distribution coefficients to the TOPO + $C_{10}H_{19}OOH$ eutectic phase as a function of the initial aqueous phase HCl concentration for x_{TOPO} = 0.4.

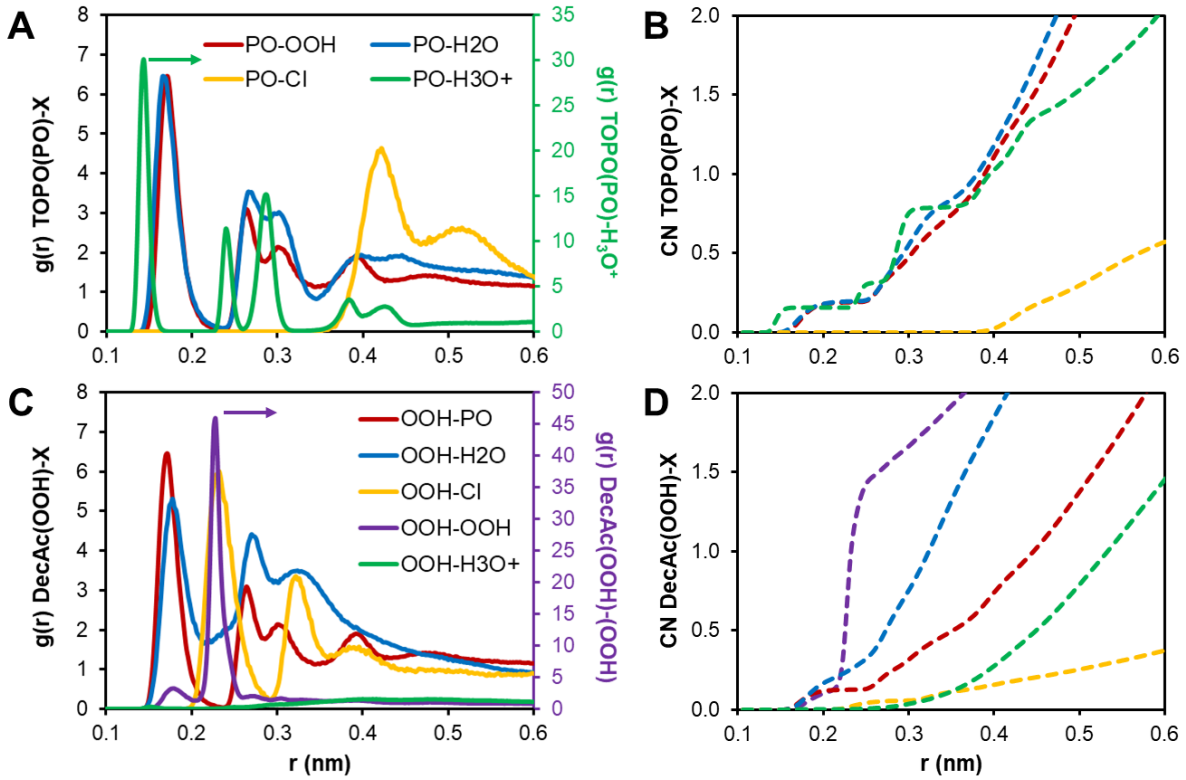

Figure S6. Radial distribution function (A and C) and corresponding coordination numbers (B and D) for TOPO reference (top panels) and $C_{10}H_{19}OOH$ reference (bottom panels) in the TOPO + $C_{10}H_{19}OOH$ eutectic for x_{TOPO} = 0.5 (composition – system (8) in **Table S2**). The P=O group was selected for TOPO and the OOH group for $C_{10}H_{19}OOH$.

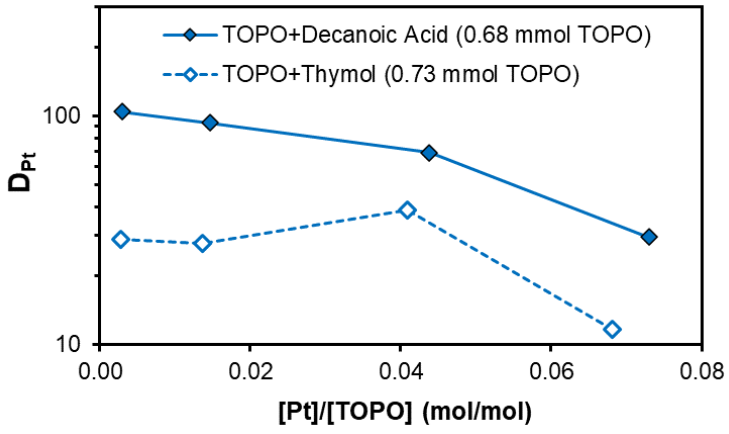

Figure S7. Pt(IV) distribution coefficient in the TOPO + $C_{10}H_{19}OOH$ (filled symbol) and TOPO + thymol (empty symbols) eutectics for x_{TOPO} = 0.4 and 8.0 mol.L^{-1} HCl as a function of initial metal concentration of 2.0 x 10^{-3}, 0.01, 0.03 and 0.05 mol.L^{-1}.

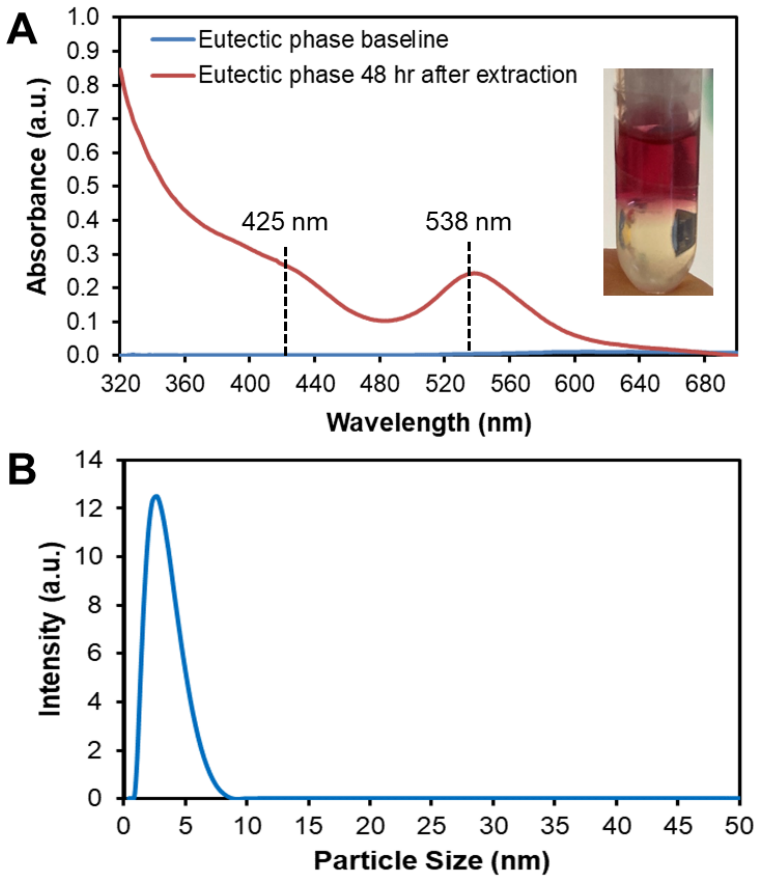

Figure S8. A) UV-vis spectra of the TOPO + thymol eutectic phase (x_{TOPO} = 0.4) 48 hr after extraction of 2.0 x 10^{-3} mol.L^{-1} Pt(IV) from 8.0 mol.L^{-1} HCl. Inset photo shows the appearance of the red DES phase after 48 hrs. B) Particle size distribution of the eutectic phase shown in A) diluted in ethanol.

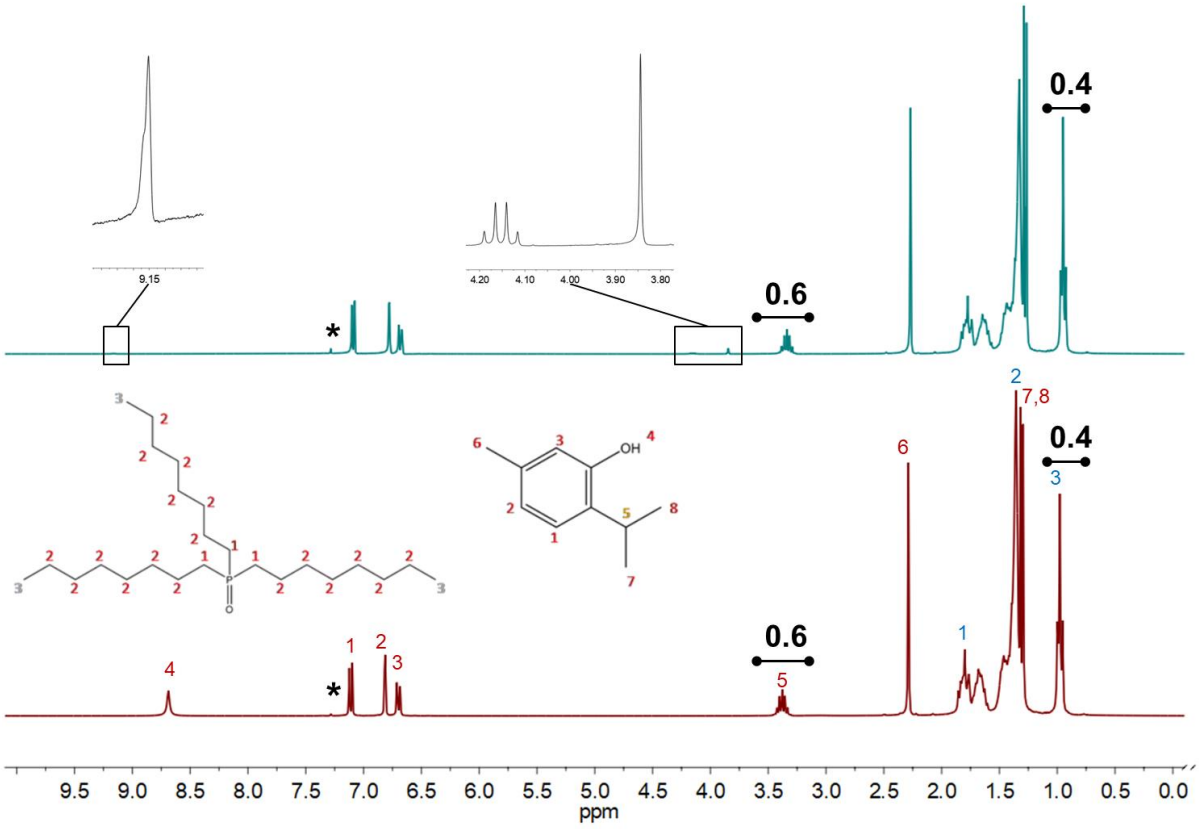

Figure S9. ^{1}H-NMR spectra and identified peaks of the TOPO + Thymol (x_{TOPO} = 0.4) eutectic phase after preparation (bottom) and after five extraction and stripping cycles using 0.1 mol.L^{-1} in 0.5 mol.L^{-1} HCl as stripping solution (x_{TOPO} = 0.4, O/A = 1, [M] = 2.0 mmol.L^{-1}, [HCl] = 2.0 mol.L^{-1}). Chloroform solvent is identified by the asterix. Shift of acidified thiourea is highlighted at δ= 9.15 ppm.

TABLES

Table S1. Experimentally determined platinum(IV) and palladium(II) extraction efficiencies ($\%EE_M$), distribution coefficients (D_M) and separation factors (SF) in the TOPO + $C_{10}H_{19}OOH$ system as a function of the initial aqueous phase HCl concentration and TOPO molar fraction (x_{TOPO}). An organic to aqueous phase volumetric ratio of 0.5 was used throughout.

HCl (mol L^{-1})	TOPO + $C_{10}H_{19}OOH$ (x_{TOPO} = 0.3)					TOPO + $C_{10}H_{19}OOH$ (x_{TOPO} = 0.4)					TOPO + $C_{10}H_{19}OOH$ (x_{TOPO} = 0.5)				
	$\%EE_{Pd}$	$\%EE_{Pt}$	D_{Pd}	D_{Pt}	SF_{Pt-Pd}	$\%EE_{Pd}$	$\%EE_{Pt}$	D_{Pd}	D_{Pt}	SF_{Pt-Pd}	$\%EE_{Pd}$	$\%EE_{Pt}$	D_{Pd}	D_{Pt}	SF_{Pt-Pd}
0.25	3.86	3.86	0.04	0.04	1.00	24.29	19.03	0.32	0.24	0.73	76.95	77.90	3.34	3.53	1.06
0.60	2.33	4.33	0.02	0.05	1.90	19.14	20.56	0.24	0.26	1.09	77.33	94.94	3.41	18.76	5.50
1.10	3.48	3.48	0.04	0.04	1.00	18.86	26.38	0.23	0.36	1.54	82.76	98.12	4.80	52.14	10.86
2.00	3.38	4.20	0.03	0.04	1.25	31.50	48.59	0.46	0.95	2.06	87.62	99.15	7.08	116.38	16.44
3.00	12.67	27.42	0.15	0.38	2.60	42.55	90.02	0.74	9.02	12.18	90.76	99.67	9.82	306.34	31.18
4.00	19.05	53.43	0.24	1.15	4.88	63.33	96.65	1.73	28.87	16.71	92.95	99.69	13.19	320.39	24.29
5.00	27.43	77.09	0.38	3.36	8.90	70.95	98.17	2.44	53.70	21.98	90.38	99.69	9.40	316.99	33.74
6.00	41.14	88.60	0.70	7.77	11.11	72.76	98.57	2.67	68.74	25.73	89.90	99.63	8.91	270.23	30.34
8.00	37.24	92.22	0.59	11.85	19.97	64.57	97.92	1.82	47.11	25.85	82.10	99.51	4.59	202.21	44.10

Table S2. System composition for all-atom molecular dynamic simulations at 298 K based on experimentally measure DES phase composition. All systems contain a total of 400 TOPO and $C_9H_{19}COOH$ atoms with 120 TOPO molecules for $x_{TOPO,ini}$ = 0.3 and 200 for $x_{TOPO,ini}$ = 0.5. $x_{(HCl+H2O),f}$ represents the experimentally determined molar fraction of HCl and H_2O in the DES phase based on $[HCl]_{DES,f}$ and $[H_2O]_{DES,f}$. The suffixes *DES* and *aq* denote the DES and aqueous phase respectively whilst *f* and *in* indicate the sampling timeframe, final and initial respectively. HCl was considered as fully dissociated and simulated as the H_3O^+ and Cl^{-1} ions.

System	$[HCl]_{aq,ini}$ ($mol.L^{-1}$)	$x_{TOPO,ini}$	$[HCl]_{DES,f}$ ($mol.L^{-1}$)	$[H_2O]_{DES,f}$ ($mol.L^{-1}$)	$x_{(HCl+H2O),f}$	$n(H_2O)$	n(HCl)
1	0.0	0.30	0.000	0.000	0.00	0	0
2	0.0	0.30	0.000	0.735	0.17	80	0
3	2.0	0.30	0.032	0.802	0.19	88	4
4	6.0	0.30	0.108	0.936	0.22	103	12
5	0.0	0.50	0.000	0.000	0.00	0	0
6	0.0	0.50	0.000	0.988	0.24	128	0
7	2.0	0.50	0.145	1.050	0.28	137	19
8	6.0	0.50	0.593	1.409	0.40	189	79

Table S3. Experimentally determined platinum(IV) and palladium(II) extraction efficiencies ($\%EE_M$), distribution coefficients (D_M) and separation factors (SF) in the TOPO + Thymol (x_{TOPO} = 0.4) system as a function of the initial aqueous phase HCl concentration. An organic to aqueous phase volumetric ratio of 0.5 was used throughout.

HCl (mol L^{-1})	**TOPO + Thymol (x_{TOPO} = 0.4)**				
	$\%EE_{Pd}$	**$\%EE_{Pt}$**	**D_{Pd}**	**D_{Pt}**	**$\Sigma\Phi_{Pt-Pd}$**
0.25	0.28	11.90	0.00	0.14	47.64
0.60	1.18	14.33	0.01	0.17	13.97
1.10	1.64	23.21	0.02	0.30	18.07
2.00	4.26	63.10	0.04	1.71	38.41
3.00	16.52	84.97	0.20	5.65	28.56
4.00	26.15	87.58	0.35	7.05	19.90
5.00	27.62	90.53	0.38	9.55	25.04
6.00	25.00	91.26	0.33	10.44	31.32
8.00	19.19	89.39	0.24	8.42	35.48