Supplementary Information

Metal extraction from a deep eutectic solvent, an insight into activities

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Section A

1. Reagents and chemicals

Aliquat 336 was supplied by Sigma-Aldrich and was diluted to required concentration with ethylbenzene. Aliquat 336 is a mixture of quaternary ammonium salts in which the nitrogen bears one methyl group and three other alkyl groups. The longer alkyl groups are a mixture of octyl and hexyl groups.

Cyanex 923 is a mixture of trialkyl phosphine oxides and was supplied by Cytec. Cytec used to trade under the name "American Cyanamid Company". Cyanex 923 is currently marketed by Solvay. The major compounds in Cyanex 923 are trihexyl phosphine oxide (8.5 %), octyl dihexyl phosphine oxide (30.4 %), dioctyl hexyl phosphine oxide (37.4 %) and trioctyl phosphine oxide (16.1 %).[i]

Solvent 70 is an aliphatic kerosene which was purchased from Statol, which is a Norwegian petrochemical company.

Super pure hydrochloric acid was purchased from Sigma-Aldrich and was diluted to 1 M with ultrapure water. The ultrapure water was made by a Milli-Q machine from Millipore Corporation. The deep eutectic solvent used in this work was prepared by combining choline chloride and ethylene glycol. All other reagents were purchased from Sigma Aldrich and used as received without further treatment.

2. Solvent extraction method

Solvent extraction experiments were performed in triplicate by shaking an equal volume (0.5 mL) of the aqueous phase and organic phase in a glass vial (3.5 mL) using a shaker (IKA VXR Basic Vibrax) equipped with a heated circulating water bath (Grant TC120) to control the temperature precisely. According to preliminary experiments, all samples were shaken at 30^{o}C for 120 minutes to reach equilibrium. After shaking the samples were centrifuged (Thermo Scientific Heraeus Labofuge 200) at 3000 revolutions per minute (rpm) for 15 minutes. Then the contents of elements in aqueous phases and initial concentrations were measured using ICP-OES (Inductively coupled plasma optical emission spectrometry, Thermo Scientific iCAP6500) or ICP-MS (Inductively coupled plasma mass spectroscopy, Thermo Scientific iCAP Q) analyses. Thus the distribution ratio (D) can be obtained according to following equation:

$$D = (C_o - C_e)/C_e$$

where C_o and C_e are concentrations of metals in starting and equilibrated aqueous phase respectively. Besides, the phase ratio was modified by measuring the mass of the shaking vial with and without samples.

3. Initial solvent extraction of metals

In the following tables a distribution ratio equal to 1000 or more is regarded as being infinite. Any distribution ratio below 0.001 is treated as being zero

The extractant code is

M	30 % Malonamide in solvent 70
C	30 % Cyanex 923 in solvent 70
A	10 % Aliquat 336 in ethyl benzene

Sodium chloride / DES system.

	^{106}Pd	^{106}Pd	^{115}In	^{115}In	^{115}In	^{187}Re	^{187}Re	^{197}Au	^{197}Au
Extractant	M	C	M	C	A	M	C	C	A
DES % (v/v)									
0	∞	0.53	0.925	799	37.4	6.24	188	753	504
0	∞	0.55	0.848	947	37.6	5.59	190	850	426
0	∞	0.53	0.950	316	38.1	5.75	132	314	946
10	∞	0.30	0.608	416	24.5	4.49	112	451	125
10	∞	0.31	0.790	173	28.4	4.63	95.3	182	320
10	∞	0.32	0.780	215	28.1	4.49	112	231	372
20	∞	0.16	0.576	675	23.1	3.59	77.2	747	488
20	∞	0.16	0.601	927	22.3	3.66	83.2	∞	525
20	∞	0.15	0.609	586	23.5	3.58	79.2	651	∞
30	∞	0.02	0.255	113	16.8	1.92	59.9	150	787
30	997	0.05	0.287	648	17.3	1.90	52.0	831	938
30	∞	0.00	0.259	203	16.7	1.75	46.9	241	∞
40	698	0	0.364	254	13.7	1.71	39.8	399	∞
40	621	0	0.345	211	13.8	1.62	39.9	276	∞
40	677	0	0.345	166	13.6	1.59	43.2	207	574
50	149	0	0.308	123	9.82	0.969	42.6	186	442
50	158	0	0.304	207	9.55	0.945	22.3	309	∞
50	113	0	0.284	150	9.61	0.938	31.2	214	671
60	9.90	0	0.157	162	5.83	0.577	13.8	305	210
60	16.6	0	0.194	114	5.87	0.564	25.5	195	337
60	17.4	0	0.172	121	5.92	0.533	21.0	218	515
70	1.75	0	0.116	74.5	2.80	0.267	15.6	174	321
70	1.78	0	0.118	13.3	2.76	0.251	1.51	32.4	448
70	1.73	0	0.120	99.8	2.72	0.255	7.80	238	830
80	0.318	0	0.020	55.0	1.21	0.079	3.22	203	534
80	0.362	0	0.014	55.6	1.19	0.058	3.05	224	325
80	1.01	0	0.058	62.8	1.20	0.090	2.21	323	471
90	0.176	0	0.030	24.9	0.467	0.004	3.23	136	181
90	0.237	0	0.019	26.3	0.452	0	0.965	173	181
90	0.198	0	0.018	25.7	0.476	0	0.814	155	126

Choline chloride / DES

	^{106}Pd	^{106}Pd	^{115}In	^{115}In	^{115}In	^{187}Re	^{187}Re	^{197}Au	^{197}Au
Extractant	M	C	M	C	A	M	C	C	A
DES % (v/v)									
0	4.13	0.041	0.045	99.37	2.521	1.189	26.6	233	∞
0	6.65	0.025	0.096	170.31	2.471	1.221	26.8	617	∞
0	8.84	0.032	0.105	113.18	2.157	1.244	38.2	396	62
10	0.802	0.009	0	101.18	2.425	0.418	16.7	519	∞
10	3.76	0	0.280	81.55	2.421	1.116	38.2	785	∞
10	5.60	0.001	0.133	79.74	2.348	0.851	28.4	392	218
20	2.11	0	0.070	80.24	1.897	0.601	22.0	807	∞
20	3.00	0.005	0.071	77.84	1.988	0.549	24.1	827	∞
20	2.85	0	0.074	92.81	1.951	0.609	16.9	683	929
30	0.819	0.009	0.070	76.42	1.754	0.397	12.2	829	∞
30	1.263	0.001	0.109	75.86	1.783	0.409	12.5	914	∞
30	0.877	0.019	0.094	71.58	1.798	0.401	17.4	∞	∞
40	0.444	0.002	0.048	63.07	1.435	0.247	4.493	298	∞
40	0.604	0	0.073	62.07	1.436	0.277	9.181	876	414
40	0.517	0	0.113	67.11	1.470	0.312	6.922	700	∞
50	0.332	0.003	0.068	45.64	1.060	0.160	4.148	516	594
50	0.329	0	0.065	53.20	1.093	0.152	3.443	673	629
50	0.451	0	0.052	48.40	1.115	0.141	3.610	838	416
60	0.141	0	0.029	37.44	0.804	0.113	2.244	612	620
60	0.102	0	0.026	36.57	0.760	0.122	2.480	708	506
60	0.182	0	0.074	36.86	0.766	0.120	2.572	618	501
70	0.207	0	0.057	26.72	0.519	0.058	2.414	435	389
70	0.228	0	0.023	27.42	0.572	0.019	1.611	377	338
70	0.217	0	0.039	29.18	0.565	0.037	1.000	302	535
80	0.094	0	0.056	21.91	0.397	0.062	0.844	213	234
80	0.086	0	0.023	19.86	0.423	0.040	0.852	181	255
80	0.077	0	0.027	20.78	0.375	0.046	1.478	243	307
90	0.065	0	0.003	13.48	0.201	0	0.868	186	131
90	0.083	0	0.019	13.56	0.236	0	1.066	230	127
90	0.050	0	0	14.37	0.238	0	1.996	537	132

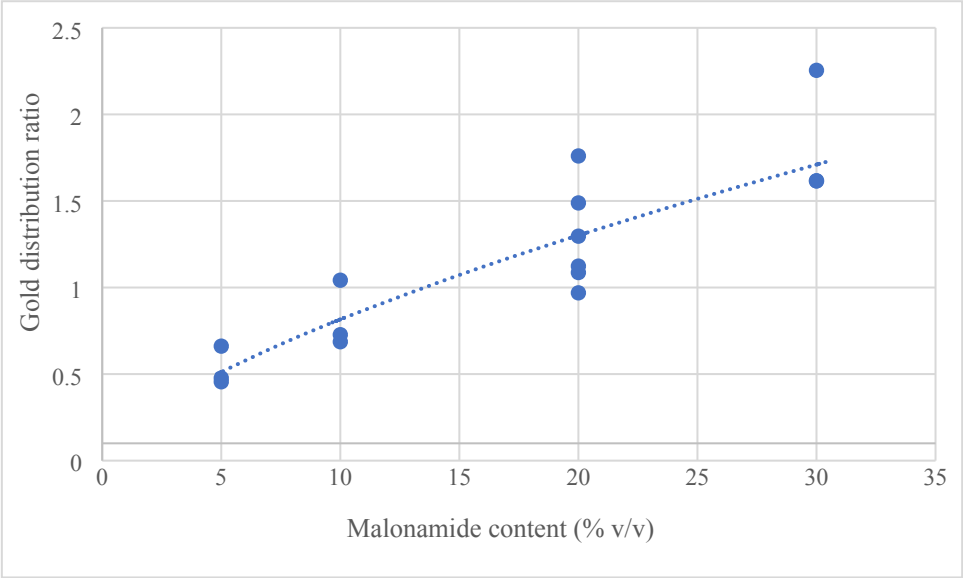
Sodium chloride / Choline chloride

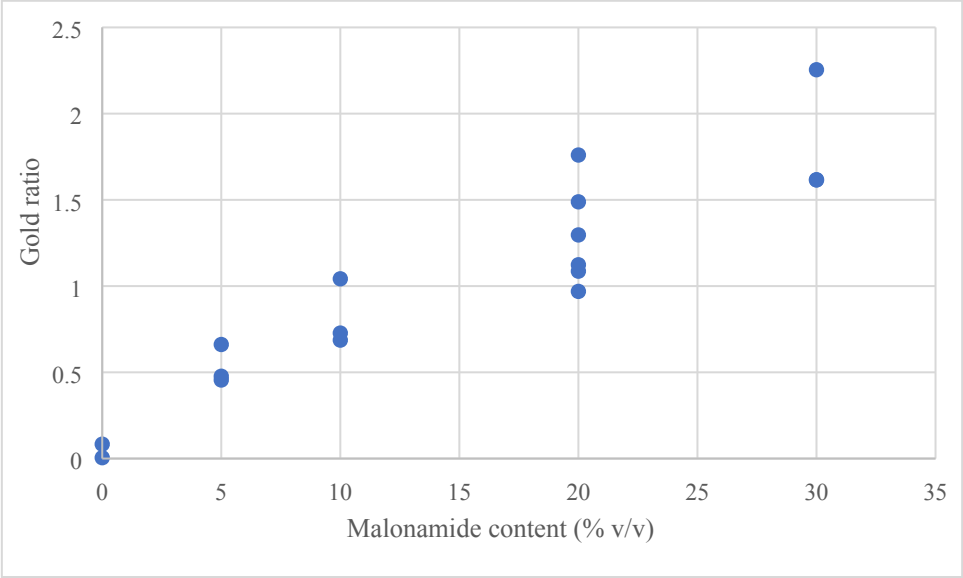
	^{106}Pd	^{106}Pd	^{115}In	^{115}In	^{115}In	^{187}Re	^{187}Re	^{197}Au	^{197}Au
Extractant	M	C	M	C	A	M	C	C	A
NaCl %									
0	9.93	0.009	0.102	83.9	2.83	1.25	50.6	283	∞
0	20.03	0.005	0.065	121	2.81	1.12	38.9	393	412
0	13.2	0.016	0.084	209	2.84	1.19	35.9	809	916
10	44.4	0.005	0.122	225	3.28	1.60	45.6	831	∞
10	105	-0.006	0.096	123	3.39	1.43	42.6	271	989
10	94.1	-0.001	0.133	139	3.28	1.51	57.5	649	∞
20	338	0.025	0.144	242	4.39	1.89	46.4	858	∞
20	284	0.034	0.127	250	4.30	1.92	47.0	675	∞
20	190	0.035	0.153	116	4.22	1.90	45.4	211	∞
30	682	0.003	0.121	482	5.80	2.09	61.6	∞	∞
30	304	0.013	0.120	180	5.92	2.00	56.0	350	∞
30	262	0.009	0.132	98.7	5.90	1.99	63.8	193	∞
40	∞	0.065	0.178	513	8.08	2.38	75.9	∞	∞
40	∞	0.050	0.211	493	8.14	2.34	74.0	∞	∞
40	∞	0.038	0.236	505	8.04	2.35	74.0	∞	∞
50	∞	0.078	0.284	349	10.62	3.01	75.3	690	∞
50	∞	0.082	0.288	147	10.63	2.80	66.4	215	∞
50	∞	0.087	0.276	170	10.64	2.72	142	443	∞
60	∞	0.105	0.339	124	13.72	3.72	83.0	210	∞
60	∞	0.112	0.372	125	13.93	3.61	98.6	233	∞
60	∞	0.099	0.366	129	13.35	3.42	96.1	236	∞
70	∞	0.155	0.449	947	16.61	4.53	125	∞	∞
70	∞	0.325	0.478	124	16.06	4.29	104	200	∞
70	∞	0.327	0.470	151	15.96	4.36	114	266	680
80	∞	0.377	0.496	469	22.05	5.02	106	∞	∞
80	∞	0.363	0.496	893	22.23	5.13	120	∞	∞
80	∞	0.383	0.523	790	20.34	5.10	119	∞	352
90	∞	0.392	0.769	125	28.83	6.68	112	195	448
90	∞	0.387	0.588	138	30.78	6.10	106	202	∞
90	∞	0.404	0.794	169	9.31	6.31	119	228	31

Using a mixture of DES (80 % v/v) and sodium chloride solution containing gold, platinum, palladium and perrhenate (all metals at 10 ppm) a shaking experiment was done to test the

hypothesis that 2 hours (120 minutes) of shaking time was sufficient to reach equilibrium and that the extraction of the gold was due to the malonamide rather than an impurity in the diluent.

Malonamide concentration (% v/v)	Shaking time (hours)	Distribution ratio			
		Palladium	Rhenium	Platinum	Gold
0	4	0,027	0,0829	0,0343	0,0833
0	4	0,0248	0,0629	0,0625	0,00495
0	4	0,0345	0,0751	0,0363	-0,0524
5	4	0,0318	0,0666	0,0232	0,661
5	4	0,011	0,0316	0,0129	0,477
5	4	0,0278	0,0603	0,0319	0,455
10	4	0,0184	0,0587	0,0438	1,04
10	4	0,00222	0,00646	-0,0153	0,687
10	4	0,0156	0,0576	0,0422	0,728
20	4	0,248	0,245	0,179	1,76
20	4	0,0337	0,0515	0,0116	0,969
20	4	0,0748	0,0674	-0,0366	1,09
20	2	0,038	0,045	-0,00932	1,49
20	2	0,066	0,156	0,0511	1,3
20	2	0,0661	0,0551	-0,038	1,12
30	4	0,154	0,099	0,0216	2,25
30	4	0,154	0,133	0,0523	1,62
30	4	0,117	0,0728	-0,00678	1,62


Gold distribution ratio
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25
30
35
Malonamide content (% v/v)


Gold ratio
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25
30
35
Malonamide content (% v/v)

4. Solvent Extraction of gold

The chloride content of the DES was 3.871 mol/L. Sodium chloride (56.56 g) was dissolved in water in a volumetric flask (250 mL) to make a NaCl solution of 3.871 mol/L. Choline chloride (ChCl, 136.8 g) was dissolved in water in a flask (200 mL). The chloride content, measured with silver precipitation method, was 4.8996 mol/L. Then to another flask (250 mL) 4.8996 M choline chloride solution and water were added to form a 3.871 mol/L ChCl solution.

Gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 0.0411g) was dissolved with 1mol/L hydrochloric acid in a vial (20mL) to make a gold stock solution of circa 1.03 g/L. The palladium solution mentioned above (0.4 mL) was mixed with 1 mol/L hydrochloric acid in a vial (20mL) to make a new Pd stock solution of *circa* 1.3 g/L. Ammonium perrhenate (0.032 g) was dissolved in 20 mL water to form the Re stock solution of about 1.10 g/L. The existing indium solution (1 mL) in the lab was mixed with 19 mL water to obtain a new In stock solution of approximately 1.15 g/L. These solutions were used to make a series of aqueous phase solutions according to the following three tables. 0.05 mL of each stock was added to each empty vial.

Table S7 Initial aqueous solutions (NaCl vs. DES)

DES (v/v %)	Mass (g)						
	Empty vial	With Pd stock	With In stock	With Re stock	With Au stock	With NaCl solution	With DES
0	6.7160	6.7642	6.8113	6.8564	6.9050	18.2200	18.2200
10	6.7165	6.7647	6.8114	6.8578	6.9054	17.0383	18.1493
20	6.7498	6.7976	6.8455	6.8915	6.9367	15.9294	18.1368
30	6.7062	6.7542	6.8020	6.8484	6.8961	14.7471	18.0488
40	6.7109	6.7590	6.8039	6.8499	6.8973	13.6177	18.0160
50	6.7136	6.7609	6.8067	6.8526	6.8982	12.4950	17.9866
60	6.7594	6.8077	6.8551	6.9014	6.9482	11.4178	17.9858
70	6.7067	6.7547	6.8022	6.8447	6.8906	10.2255	17.9057
80	6.7095	6.7573	6.8035	6.8479	6.8951	9.1158	17.8862
90	6.6988	6.7464	6.7906	6.8345	6.8788	8.0119	17.8595

Table S8 Initial aqueous solution (ChCl vs. DES)

DES (v/v %)	Mass (g)						
	Empty vial	With Pd stock	With In stock	With Re stock	With Au stock	With ChCl solution	With DES
0	6.6881	6.7377	6.7855	6.8318	6.8803	17.3847	17.3847
10	6.6985	6.7478	6.7930	6.8373	6.8842	16.2922	17.4028
20	6.6918	6.7411	6.7858	6.8292	6.8750	15.2408	17.4329
30	6.7017	6.7500	6.7961	6.8396	6.8848	14.1896	17.4637
40	6.7245	6.7738	6.8192	6.8648	6.9112	13.1292	17.5020
50	6.6931	6.7422	6.7873	6.8299	6.8778	12.0754	17.5503
60	6.7239	6.7721	6.8190	6.8608	6.9086	11.0668	17.6383
70	6.7158	6.7642	6.8081	6.8501	6.8930	10.0105	17.6696
80	6.7239	6.7721	6.8196	6.8620	6.9117	8.9781	17.7456
90	6.7082	6.7540	6.7971	6.8697	6.8890	7.9428	17.8066

Table S9 Initial aqueous solution (ChCl vs. NaCl)

NaCl (v/v %)	Mass (g)						
	Empty vial	With Pd stock	With In stock	With Re stock	With Au stock	With ChCl solution	With NaCl solution
0	6.6798	6.7294	6.7777	6.8228	6.8715	17.3601	17.3601
10	6.6502	6.6981	6.7450	6.7893	6.8360	16.2421	17.3711
20	6.6481	6.6959	6.7430	6.7880	6.8359	15.1650	17.3795
30	6.6438	6.6911	6.7394	6.7859	6.8323	14.1065	17.4426
40	6.6873	6.7351	6.7830	6.8270	6.8749	13.1333	17.6105
50	6.7349	6.7805	6.8282	6.8744	6.9217	12.1352	17.7402
60	6.6956	6.7411	6.7874	6.8336	6.8818	11.0443	17.7583
70	6.6638	6.7102	6.7581	6.8040	6.8523	9.9758	17.7989
80	6.6835	6.7311	6.7783	6.8229	6.8714	8.9261	17.8944
90	6.6823	6.7369	6.7831	6.8263	6.8775	7.9252	18.0259

N,N,N'N'-tetrakis(2-ethylhexyl)malonamide was made by the reaction of diethyl malonate with *bis*-(2-ethylhexyl) amine in a similar manner to the reaction of dibutyl amine with diethyl malonate. *N,N,N'N'-tetrakis*(2-ethylhexyl)malonamide (75ml) was mixed with kerosene in a flask (250 mL) to form a 30% (v/v) malonamide, which was used as the organic phase in solvent extraction experiments. 5% and 10% malonamide were also made by diluting the 30% extractant. All the samples for ICP-MS measurement were diluted with superpure hydrochloric acid (1 mol/L) with spiked with Rhodium (40 ppb) as internal standard. DL-Methionine (1 wt%) was present in the acid to eliminate the memory effect of gold in ICP-MS.

The second blank always gave at least a 4000 times lower response for gold than the starting solution (50 ppb). The measured values of the distribution ratio are listed as following tables.

Table S10 Distribution ratio of Au (NaCl vs. DES)

DES (v/v %)	D_{Au} (30 v/v% malonamide)	D_{Au} (10 v/v% malonamide)	D_{Au} (5 v/v% malonamide)
0	179	113	—
0	384	73.3	—
0	135	66.0	—
10	110	45.3	22.1
10	191	41.6	22.1
10	187	41.2	21.9
20	164	36.1	11.8
20	195	33.3	12.2
20	163	33.6	11.5
30	91.9	15.5	7.41
30	79.4	15.9	7.66
30	90.6	15.1	7.32
40	52.5	7.44	3.62
40	65.5	7.46	3.60
40	53.3	7.47	3.49
50	22.9	4.15	2.36
50	23.2	3.86	2.27
50	23.5	3.78	2.30
60	8.70	2.04	1.11
60	8.99	2.02	1.34
60	8.59	2.00	1.13
70	2.82	1.14	1.17
70	2.79	1.13	1.16
70	2.80	1.08	1.18
80	0.740	0.721	0.645
80	0.730	0.731	0.624
80	0.771	0.692	0.654
90	0.225	0.341	0.207
90	0.203	0.353	0.226
90	0.193	0.355	0.210

Table S11 Distribution ratio of Au (ChCl vs. DES)

DES (v/v %)	D_{Au} (30 v/v% malonamide)
0	38.1
0	44.8
0	49.2
10	5.81
10	21.0
10	21.4
20	10.6
20	9.84
20	10.3
30	5.17
30	5.01
30	5.11
40	2.93
40	2.76
40	2.73
50	1.34
50	1.32
50	1.33
60	0.745
60	0.704
60	0.739
70	0.429
70	0.410
70	0.413
80	0.246
80	0.211
80	0.216
90	0.0834
90	0.0889
90	0.0850

Table S12 Distribution ratio of Au (ChCl vs. NaCl)

NaCl (v/v %)	(30 v/v% malonamide)	(10 v/v% malonamide)	(5 v/v% malonamide)
	D_{Au}	D_{Au}	D_{Au}
0	27.8	2.43	0.675
0	36.2	2.47	0.766
0	35.3	2.44	0.769
10	46.6	5.54	2.23
10	76.1	5.66	2.05
10	84.8	5.85	1.96
20	153	8.3	2.84
20	171	8.16	2.79
20	107	8.23	2.86
30	147	11.3	3.23
30	119	11	3.24
30	109	11.7	3.4
40	263	16.2	4.64
40	224	15.9	4.59
40	225	15.9	4.78
50	558	21.8	6.66
50	251	26	6.45
50	444	23.4	6.74
60	460	28.9	8.34
60	477	27.2	9.17
60	829	26.7	8.69
70	675	44	13.7
70	944	43.2	13.1
70	777	43	12.3
80	881	47.2	17.7
80	880	62.9	17.5
80	1920	51.1	17.5
90	1920	70.9	25.4
90	1240	53.3	23.1
90	1710	70.3	25.7

3. Solvent extraction of palladium and rhenium

The chloride content of the DES was 3.871 mol/L. Sodium chloride (56.5512 g) was dissolved in water in a volumetric flask (250 mL) to make a NaCl solution of 3.871 mol/L. Choline chloride (ChCl, 130.3 g) was dissolved in water in a flask (200 mL). The chloride content, measured with silver precipitation method, was 4.65 mol/L. Then to another flask (200 mL) 4.65 M choline chloride solution and water were added to form a 3.871 mol/L solution.

Palladium (II) chloride (2.2987 g) and 20 mL NaCl solution were mixed in an empty vial. The mixture was then heated in an oven (100^{o}C) for about 30 minutes. After three days, the mixture was filtered to form a Pd stock solution (Na_2PdCl_4). Ammonium perrhenate (0.5597 g) was dissolved in 20 mL water to form the Re stock solution. These stock solutions were used to make a series of aqueous phase solutions according to the following three tables. 0.25 mL of Re stock and 0.075 mL Pd stock were added to each empty vial.[1]

Table S1 Initial aqueous solution (NaCl vs. DES)

DES (v/v %)	Mass (g)				
	Empty vial	With Re stock	With Pd stock	With NaCl solution	With DES
0	6.6821	6.9484	7.0306	18.1325	18.1325
10	6.7028	6.9675	7.0518	16.9965	18.0946
20	6.7076	6.9719	7.0548	15.8812	18.0245
30	6.7212	6.9872	7.0711	14.7561	18.0122
40	6.7521	7.0170	7.1012	13.7012	18.0150
50	6.6795	6.9442	7.0279	12.5153	17.8992
60	6.6669	6.9315	7.0158	11.3948	17.8529
70	6.6687	6.9332	7.0181	10.3102	17.8464
80	6.7127	6.9751	7.0607	9.3087	17.9998
90	6.6679	6.9322	7.0191	8.1405	17.9758

[1] All significant figures displayed by the balance were recorded to reduce rounding errors and to preserve the original data, it was reasoned that rounding up in the lab would increase the likelihood of a mistake. To test the balance a rubber cone with a mass of *circa* 19.82 grams was examined 12 times with the balance. The mean mass recorded by the balance was 19.82926 grams and the estimated standard deviation was 0.000156 grams.

Table S2 Initial aqueous solution (ChCl vs. DES)

DES (v/v %)	Mass (g)				
	Empty vial	With Re stock	With Pd stock	With ChCl solution	With DES
0	6.6942	6.9586	7.0562	17.3489	17.3489
10	6.7361	6.9998	7.0975	16.2898	17.3805
20	6.7157	6.9794	7.0744	15.1557	17.3040
30	6.6698	6.9343	7.0282	14.1646	17.4046
40	6.6874	6.9516	7.0488	13.1733	17.4678
50	6.6990	6.9617	7.0605	12.1664	17.5279
60	6.7025	6.9665	7.0631	11.1504	17.5476
70	6.7041	6.9690	7.0644	10.1452	17.6100
80	6.6997	6.9641	7.0572	9.0954	17.6141
90	6.6960	6.9604	7.0588	8.0932	17.6729

Table S3 Constitution of initial aqueous solution (ChCl vs. NaCl)

NaCl (v/v %)	Mass (g)					
	Empty vial	With Re stock	With Pd stock	With DES	With NaCl solution	With ChCl solution
0	6.7091	6.9733	7.0580	12.5181	12.5181	17.6499
5	6.7233	6.9882	7.0693	12.5038	13.0690	17.6864
10	6.7127	6.9770	7.0619	12.4903	13.6111	17.7204
15	6.7712	7.0346	7.1192	12.5443	14.2198	17.8061
20	6.7515	7.0162	7.0986	12.5218	14.7499	17.8340
25	6.7138	6.9796	7.0608	12.5081	15.2629	17.8337
30	6.7169	6.9816	7.0620	12.4966	15.8155	17.8949
35	6.7681	7.0322	7.1131	12.5336	16.3549	17.9189
40	6.7624	7.0270	7.1088	12.5359	16.9296	17.9742
45	6.6963	6.9619	7.0428	12.4540	17.3512	17.8792
50	6.6834	6.9467	7,0288	12.4505	17.9604	17.9604

Aliquat 336 (25 mL) was mixed with ethylbenzene in a flask (250 mL) to form a 10% (v/v) aliquat 336, which was used as the organic phase in solvent extraction experiments. All the samples for ICP-OES measurement were diluted with super pure hydrochloric acid (1 mol/L) spiked with ruthenium (1 ppm) as internal standard. The measured values of the distribution ratio are listed as follows.

Table S4 Distribution ratios of Pd and Re (NaCl vs. DES) and sodium and chloride concentrations.

DES (v/v %)	D_{Re}	D_{Pd}	$[Cl^-]$	$[Na^+]$
50	145.6	52.2	3,91	2,00
50	151.5	53.3	3,91	2,00
50	155.9	48.5	3,91	2,00
60	79.7	22.7	3.90	1.61
60	84.6	22.1	3.90	1.61
60	85.5	22.7	3.90	1.61
70	44.0	9.20	3.87	1.20
70	43.8	8.70	3.87	1.20
70	44.3	8.47	3.87	1.20
80	19.9	2.65	3.85	0.814

80	20.2	2.79	3.85	0.814
80	19.8	2.70	3.85	0.814
90	9.23	1.13	3.85	0.391
90	7.73	0.704	3.85	0.391
90	7.70	0.706	3.85	0.391

Table S5 Distribution ratio of Pd and Re (ChCl vs. DES). No sodium could be detected in the starting solutions

DES (v/v %)	D_{Re}	D_{Pd}	[Cl^-]
0	235.4	34.4	3.99
0	228.5	34.5	3.99
0	220.4	34.5	3.99
10	173.1	25.5	3.96
10	178.9	25.5	3.96
10	174.4	25.7	3.96
20	122.8	18.2	3.92
20	127.8	18.0	3.92
20	122.9	18.1	3.92
30	84.8	12.2	3.89
30	85.1	12.1	3.89
30	86.2	12.2	3.89
40	58.0	7.46	3.87
40	57.2	7.56	3.87
40	58.0	7.57	3.87
50	36.9	4.44	3.85
50	36.9	4.46	3.85
50	37.2	4.42	3.85
60	22.5	2.37	3.82
60	23.8	2.59	3.82
60	22.8	2.44	3.82
70	14.1	1.32	3.80
70	14.2	1.32	3.80
70	14.0	1.30	3.80
80	8.72	0.704	3.77

80	8.52	0.671	3.77
80	8.72	0.722	3.77
90	5.27	0.351	3.75
90	5.22	0.364	3.75
90	5.25	0.380	3.75

Table S6 Distribution ratio of Pd and Re (ChCl vs. NaCl in 50 v/v% DES)

NaCl (v/v %)	D_{Re}	D_{Pd}	[Cl^-]	[Na^+]
0	32.2	3.53	4.02	0.00
0	32.4	3.64	4.02	0.00
0	32.3	3.51	4.02	0.00
5	39.5	5.00	4.01	0.188
5	39.7	4.79	4.01	0.188
5	39.7	4.99	4.01	0.188
10	47.6	6.62	4.00	0.391
10	47.5	6.81	4.00	0.391
10	47.9	6.69	4.00	0.391
15	53.6	8.59	4.00	0.595
15	54.6	8.53	4.00	0.595
15	54.5	8.75	4.00	0.595
20	61.9	11.4	3.98	0.810
20	62.7	11.3	3.98	0.810
20	64.9	11.3	3.98	0.810
25	71.0	14.1	3.96	1.00
25	83.5	14.1	3.96	1.00
25	72.8	14.6	3.96	1.00
30	80.0	17.9	3.96	1.18
30	79.9	18.1	3.96	1.18
30	81.3	17.6	3.96	1.18
35	87.0	22.5	3.92	1.42
35	90.9	22.6	3.92	1.42
35	92.9	22.5	3,92	1.42
40	102.5	28.7	3.94	1.58
40	101.3	28.5	3.94	1.58
40	101.2	28.8	3.94	1.58
45	108.2	34.7	3.92	1.81
45	104.9	35.3	3.92	1.81

45	105.8	35.1	3.92	1.81
50	115.8	44.9	3.91	1.38
50	121.7	44.2	3.91	1.38
50	124.0	44. 4	3.91	1.38

Section B

1. Procedure for measurement of distribution ratios with technetium

WARNING : The metastable excited state of technetium-99 emits gamma photons at 140 keV. Before attempting to work with radioactivity you must ensure that you are in compliance with all national laws and local rules. Also note that a technetium generator (technetium cow) is likely to contain large amounts of molybedum-99.

In Europe it is common to obtain ^{99m}Tc by elution from a ^{99}Mo bearing alumina column with saline in a device known as a technetium cow. Molybdeum-99 is a beta emitting radionuclide with a 66 hour half life which also emits gamma rays (main emissions are photons at 181, 366, 740 and 778 keV. In North America ^{99m}Tc is often supplied as an aqueous solution from a centralized radiopharmacy facility.

Both ^{99m}Tc and the ^{99}Mo containing technetium cows should only be handled by suitably trained radiation workers, all work with open containers of ^{99m}Tc (open sources) should occur either within a suitable fume hood or while using other engineering controls to prevent the spread of contamination (such as a glovebox or ventilated hot cell). You need to work in a radiochemical lab with open sources of radioactivity. if in doubt do not attempt this type of work.

All open source radioactivity work should be done by either a classified radiation worker with experience of radiochemical work or a person working under the direct supervision of a classified worker with radiochemical experience. No object with the potential to be contaminated should be allowed out of the fume hood or sealed enclosure without being first sealed within an externally uncontaminated plastic bag or other container which is able to prevent the uncontrolled spread of radioactivity.

To reduce or eliminate the need to dispose of radioactive waste all unwanted ^{99m}Tc radioactivity should be allowed to decay for one week before disposal.

Do not attempt this work while pregnant or while breast feeding unless you have obtained special clearance from your radiation protection officer to work while either pregnant or while nursing a child.

Method

To a polyethene vial was added either the deep eutectic solvent or a sodium chloride (M) solution. To this was added a small volume of a pertectinate solution (^{99m}Tc as $NaTcO_4^-$) obtained by eluting an alumina column bearing molybdenum (^{99}Mo) with a saline solution.

In the interests of radiation safety the organic phase (900 microliters of 10 % aliquat 336 in ethyl benzene) was added to the shaking vials first. This is done to reduce the number of operations which need to be made with radioactivity in the vials.

The denser phase (900 microliters) was added by pipette to each vial. To a vial was either added an aqueous phase or the DES phase. The shaking vials were sealed with plastic caps. They were further sealed with parafilm and then placed within a screw top 100 ml plastic beaker. The tubes were shaken by hand for five minutes at room temperature

After allowing the vials to stand for 25 minutes they were wrapped in plastic bags. the method is similar to that used to pick up dog excrement with a plastic bag. Place your hand inside the bag. reach out and take hold of the vial through the bag. Now turn the bag inside out and tie it shut. The vials were centrifuged to fully separate the two liquid layers.

The vials were returned to the radiochemical fume hood. they were unsealed one at a time. From the upper layer was withdrawn a sample (600 microliters) and this was placed in a 7 ml screw top polythene

tube. With a new pipette tip a sample (600 microliters) was taken of the lower phase. this was transferred to another 7 ml polyethene vial.

The vials were sealed inside plastic bags and transferred out of the fume hood. they were both measured using a cryogenically cooled (liquid nitrogen) high purity germanium gamma detector to determine the gamma activity in them.

2. Health and Safety case for the use of radioactivity

The use of radioactivity in green chemistry research might be surprising. but we wished to check if the behavior of the perrhenate was abnormal in some way. By using pertechtinate we reasoned that we could compare the stable rhenium with another element. We were also able to work at a very low chemical concentration of technetium to make sure that the addition of the metal was not causing the DES to behave differently to how it would without the metal.

We wished to consider if the system would behave in a similar way with a zero chemical concentration of the metal. We have made an analysis of the worst case of what could happen if a worker at Chalmers was to suddenly choose to harm themselves or someone else with radioactivity. All of the authors except Cen Peng are radiation workers who are or (were during their time at Chalmers. MST is now living in Russia) under special medical supervision (UK term is Classified Workers) and many of them have been vetted for security purposes as workers in the nuclear sector.

We have calculated that when we took possession of the technetium cow that it contained 2.84 GBq of ^{99}Mo. If we assume that it contains an equal amount of ^{99m}Tc. Then this would be 2.84 GBq.

As the activity to effective dose coefficient for the inhalation of M type ^{99m}Tc in the form of 5 micrometer particles is 2.9×10^{-11} Sv Bq^{-1}. I have calculated that if one was to have inhaled the whole of the technetium that was in the radionuclide generator then one of us would be able to commit themselves to a radiation dose of 82.3 mSv. This is slightly more than 4 times the annual limit for a radiation worker and represents an extreme exposure scenario. To do this I would have to a deliberate choice to adsorb the radioactivity.

As the ^{99}Mo is sealed within a metal container which includes both steel and lead we have discounted the possibility that a person gains access to the ^{99}Mo inside the technetium cow. To do so would require a prolonged and determined effort. We cannot imagine a credible accident which would disperse ^{99}Mo into the lab or allow a person to gain access to it.

The smallest amount of ^{99m}Tc which can cause a fatal or life changing injury has been estimated by the United Nations (IAEA) to be 700 GBq. this amount of radioactivity could cause either an injury if carried in the hand for one hour. kept in a pocket for ten hours or if a person was to remain for 100 hours at a distance of 1 meter.

The UN have also estimated that if 70000 GBq of ^{99m}Tc was dispersed then a person doing one of the following could get a fatal or life changing injury.

1. Inhale 0.01 % of the spilled radioactivity
2. Swallow a fraction equal to 10^{-5} of the spill
3. Smear 1 % of the spill onto a 1 m^2 area of skin and make no attempt to decontaminate for five hours.

So based on these estimates I reason you would have to inhale 7 GBq of ^{99m}Tc. swallow 700 MBq or smear 700 GBq on your skin to be likely to cause death or serious injury. I reason that accidently swallowing a quarter of a stock solution which is being handed inside a fume hood is not possible.

It is difficult to know which of the three dispersed material events is the one which most concerns the IAEA. it is not in the public interest to work out which one most concerns the IAEA.

After the experiment if we were to place all the ^{99}Tc in a single waste carton and a member of the public was to gain access to it then the member of the public would have gained access to can be estimated. If we reason that the technetium cow had been loaded at the factory with 40 GBq and that for some reason the hospital who owned it before us had made no effort to use it then if we were to release all the Tc-99

from the cow and place it in a single waste container then we would have 1430 Bq. This amount of radioactivity is far too small to cause injury or death.

If a person was to inhale this amount of ^{99}Tc then the largest dose they could get would be 5.57 microSv. this would be less than one day's worth of natural background radiation in many parts of Cornwall. Aberdeen or Göteborg.

The worst misadventures which I imagine the world's worst radioactivity worker could have with the amount of ^{99m}Tc are relatively harmless compared with a careless X-ray crystallographer who keeps their hand in a working beam for several seconds. This act is one which I would expect to cause a very painful injury to the soft tissues of the hand.

3 Radiochemical results for the extraction of technetium.

All count rates are expressed in counts per second. All count rates were decay corrected to midnight of the night before the experiment started.

Extractions from sodium chloride solution (3.8 M)

Tube number	1	2	3
Count rate organic layer	71744	67818	68178
Count rate aqueous layer	100	111	100
Distribution ratio	717	611	683

Six hundred microliters of the aqueous starting solution gave 70145 counts per second

Extractions from deep eutectic solvent

Tube number	4	5	6
Count rate organic layer	40567	40388	41146
Count rate aqueous layer	14365	14792	15219
Distribution ratio	2.82	2.73	2.70

Six hundred microliters of the aqueous starting solution gave 54067 counts per second

Section C

6. Chloride contents in starting aqueous phases

Chloride contents in starting aqueous solutions are designed to be constant. Due to the low solubility of silver chloride in water, silver precipitation method was applied to measure chloride contents in all the aqueous phase solutions. Silver nitrate ($AgNO_3$, 19.68 g) and yttrium nitrate ($Y(NO_3)_3$, 16.97 g) were dissolved with water in an empty flask (250 mL) resulting in a silver stock solution (25 g/L). Yttrium was regarded as a standard element because it does not precipitate with chloride.

Aqueous phase samples (0.1 mL) were mixed with super pure nitric acid (1 mol/L, 2 mL) and Ag stock (2 mL) in empty centrifuge tubes. Then all the tubes were wrapped with a piece of aluminum foil to protect the silver chloride precipitation from light and were left to stand for a week. After centrifuged at 5000 rpm for 10 minutes, the supernatant liquids were sampled (0.2 mL) and diluted with 0.1 mol/L super nitric acid (4.8 mL) containing magnesium (1 ppm) as internal standard. Silver concentrations were obtained by ICP-OES measurement and chloride contents were accordingly calculated and displayed in Fig. S1.

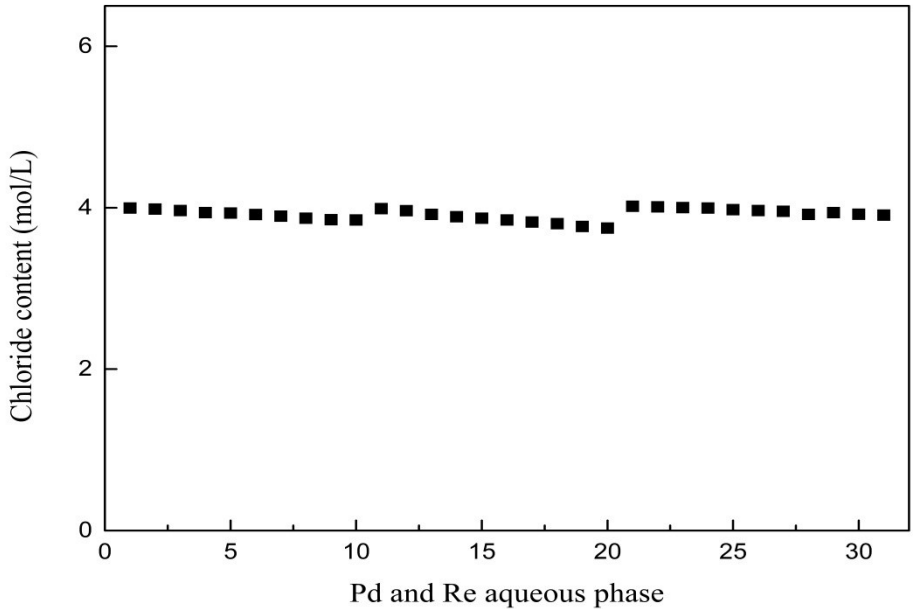


Fig. S1 Chloride content in Pd and Re aqueous phase

The chloride and sodium concentrations are shown in tables S4, S5 and S6.

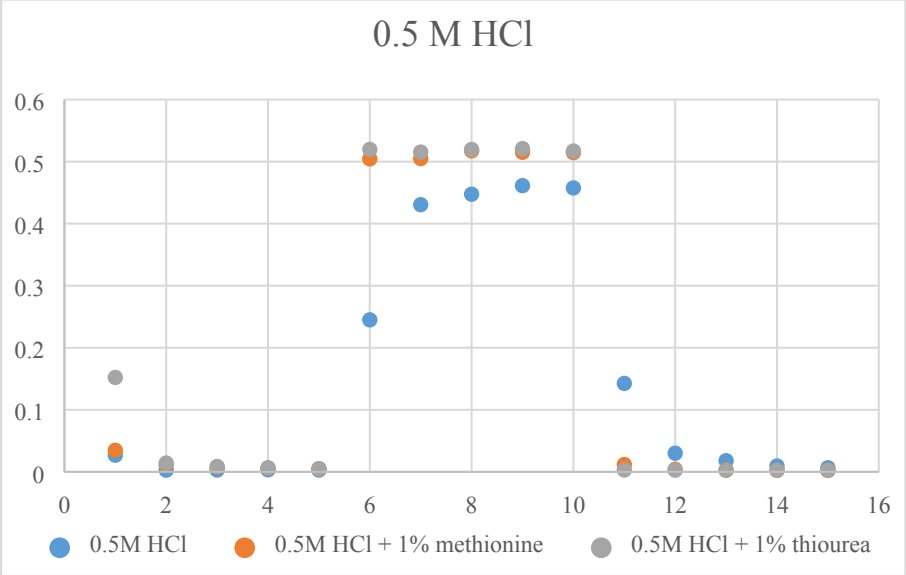
Section D

Method development experiments for ICPMS with gold.

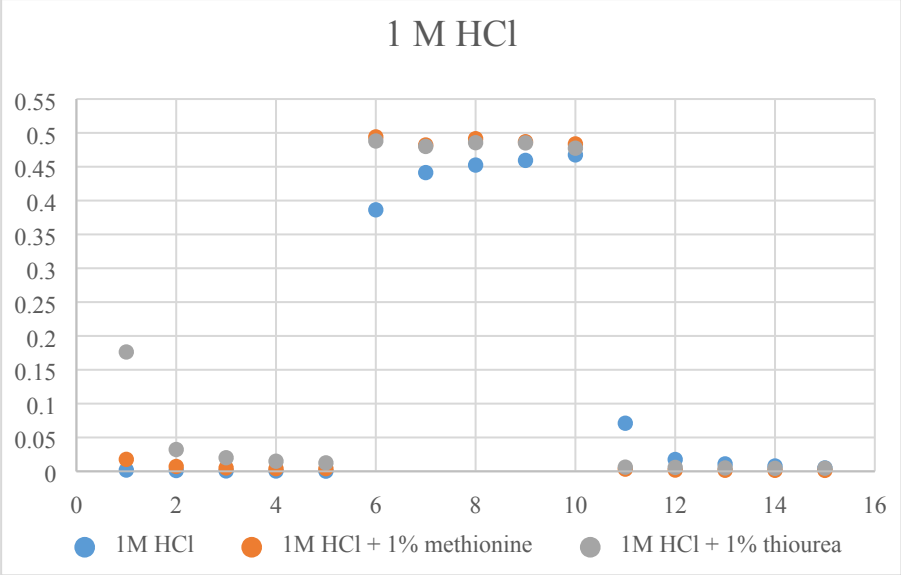
To samples of hydrochloric acid was added either 1 % thiourea or 1 % methionine. The ICMPS machine was laoded with five samples of either pure acid or acid with the matrix modifier. Then with five samples of the same acid with 10 ppb gold added followed by five samples of the same acid.

If A. B and C represent 0.5 M hydrochloric acid. 0.5 M hydrochloric acid with methionine. 0.5 M hydrochloric acid with thiourea. While A'. B' and C' represent 0.5 M hydrochloric acid with 10 ppb gold. 0.5 M hydrochloric acid with both methionine and gold and 0.5 M hydrochloric acid with thiourea and gold. Then the order of the tubes for the experiment were

A. A. A. A. A. A'. A'. A'. A'. A'. A. A. A. A. A. B. B. B. B. B. B'. B'. B'. B'. B'. B. B. B. B. B. C. C. C. C. C. C'. C'. C'. C'. C'. C. C. C. C. C



The experiment was repeated with 1M hydrochloric acid.



It was found that when no sulfur additive was present that a strong memory effect existed for gold.

Section E

The theory of solvent extraction equilibria in greater depth

In solvent extraction (liquid-liquid extraction) it is normal to have two immiscible liquid phases, by means of shaking or another form of agitation a large surface area between the two liquids can be obtained. After the agitation ceases if the phases have different densities, then the two liquids can be separated either by gravity or centrifugation.

It is important to understand that two things are able to exert control on the distribution ratio. These two things are the physical portioning of chemical species between the two liquid layers and the chemical reactions which occur in either one phase or both phases.

The most simple system is one in which the solute is unable to undergo a chemical change in either liquid layer. For example if a solution of xenon or a neutral pharmaceutical was to be shaken with an organic solvent then the solute will distribute between the two layers. Here we can describe the distribution of the solute using the following mathematical expression.

$$K_D = \frac{a_{Xe_{org}}}{a_{Xe_{aq}}}$$

If we assume all activity coefficients are equal to one we can then write the following expression where the values in the square brackets are the concentrations in the different liquid layers.

$$K_D = \frac{[Xe_{org}]}{[Xe_{aq}]}$$

If an element (or organic substance) is able to exist in more than one chemical form then we need to consider the distribution ratio. The distribution ratio is the sum of the concentrations of all forms present in the organic layer divided by the sum of all the forms present in the aqueous layer. It is important to never accidently substitute the distribution ratio for the partitioning coefficient (K_D) or *vice a versa*. The distribution ratio of a metal is given by the following equation.

$$D_M = \frac{\left[M^{total}_{org}\right]}{\left[M^{total}_{aq}\right]}$$

In the case of a radioactive metal the distribution ratio can be found by dividing the radioactivity of the organic layer (expressed in Bq dm^{-3}) by that of the aqueous layer. The ideas from the solvent extraction of xenon can be applied to other systems.

For example, if we were to place a drop of mercury on the floor of a room and seal the room then the mercury concentration in the air will reach an equilibrium level. This is dictated by the vapor pressure of the mercury. Equally the pressure in the headspace in a sealed tube is dictated by the vapor pressure of water at the temperature of the water (assume that we seal the water in the tube without any air present in the tube). Static headspace gas chromatography using liquid samples sealed in headspace vials also involves an equilibrium between the gas phase and the solution (liquid) layer present in the vials.

If the partitioning coefficient is a coefficient which is expressed in terms of activities, then we can write.

$$K_D = D_{Xe}\frac{f_{Xe_{org}}}{f_{Xe_{aq}}}$$

Thus we can write after rearrangement

$$D_M = K_D \frac{f_{Xe_{aq}}}{f_{Xe_{org}}}$$

Within our paper we originally assumed that the activity function and coefficients of neutral species are 1, this is because there is no ion-ion interactions between the neutral species and their surroundings. Also without this assumption it would be impossible for us to make further progress.

We will not discuss in great detail the equilibrium between chloride and metals such as gold, we assume that the average chemist should have a good understanding of the chemistry and mathematics of the equilibria. If we assume that the lower phase has a given chloride or nitrate activity and that the ratio of the different metal complexes with either the chloride or nitrate is fixed. We will also assume that only one of these complexes formed between the metal cation and the chlorides (or nitrates) can be extracted.

For clarity we have chosen in the next section to assume that all activity functions are equal to one.

If we start by assuming that the reaction occurs in the aqueous phase then we can write the following equations for the concentration of the organic ligand (L) in the aqueous phase. This is if we assume that the concentration of L in neither phase is limited by its solubility in the liquids.

$$K_{D_L} = \frac{[L_{org}]}{[L_{aq}]}$$

$$[L_{aq}] = \frac{[L_{org}]}{K_{D_L}}$$

If we now have a series of equilibria between the hydrated metal (M) and the ligand L then we can write.

$ML_{(n-1)} + L \leftrightarrow ML_n$

The reaction equilibria can be described using the following type of equation.

$$\beta_n = \frac{[ML_n]}{[M]\,[L]^n}$$

We can now write a series of equations which describe the fraction of the metal in the aqueous phase which is in the form of each of the complexes. If we assume for example that our metal is able to form two complexes with a 1:1 and 1:2 ratio of metal to ligand then we can write a series of equations like this where L is the concentration of the ligand in the aqueous phase.

$$\frac{[ML_{n_{aq}}]}{[M^{total}_{aq}]} = \frac{\beta_n[L]^n}{1 + K_1[L] + \beta_2[L]^2}$$

As the concentration of each of the forms of the metal is given by a series of equations like this.

$$[ML_{n_{org}}] = \frac{K_{D_{ML_n}}[M^{total}_{aq}]\beta_n[L]^n}{1 + K_1[L] + \beta_2[L]^2}$$

We can create an equation for the distribution ratio of our hypothetical system.

$$D_M = \frac{\left\{\frac{K_{D_M}[M^{total}_{aq}]}{1 + K_1[L] + \beta_2[L]^2} + \frac{K_{D_{ML}}[M^{total}_{aq}]K_1[L]}{1 + K_1[L] + \beta_2[L]^2} + \frac{K_{D_{ML_2}}[M^{total}_{aq}]\beta_2[L]^2}{1 + K_1[L] + \beta_2[L]^2}\right\}}{[M^{total}_{aq}]}$$

This equation can be simplified a little to provide

$$D_M = \frac{K_{D_M}}{1 + K_1[L] + \beta_2[L]^2} + \frac{K_{D_{ML}} K_1[L]}{1 + K_1[L] + \beta_2[L]^2} + \frac{K_{D_{ML_2}} \beta_2[L]^2}{1 + K_1[L] + \beta_2[L]^2}$$

A fuller equation could be created which would be

$$D_M = \frac{K_{D_M}}{1 + K_1\left\{\frac{[L_{org}]}{K_{D_L}}\right\} + \beta_2\left\{\frac{[L_{org}]}{K_{D_L}}\right\}^2} + \frac{K_{D_{ML}} K_1\left\{\frac{[L_{org}]}{K_{D_L}}\right\}}{1 + K_1\left\{\frac{[L_{org}]}{K_{D_L}}\right\} + \beta_2\left\{\frac{[L_{org}]}{K_{D_L}}\right\}^2} + \frac{K_{D_{ML_2}} \beta_2\left\{\frac{[L_{org}]}{K_{D_L}}\right\}^2}{1 + K_1\left\{\frac{[L_{org}]}{K_{D_L}}\right\} + \beta_2\left\{\frac{[L_{org}]}{K_{D_L}}\right\}^2}$$

If K_D for ML_2 is much larger than the values for M and ML then it is possible often to neglect some of the terms in the equation to give.

$$D_M = \frac{K_{D_{ML_2}} \beta_2\left\{\frac{[L_{org}]}{K_{D_L}}\right\}^2}{1 + K_1\left\{\frac{[L_{org}]}{K_{D_L}}\right\} + \beta_2\left\{\frac{[L_{org}]}{K_{D_L}}\right\}^2}$$

If the majority of the metal in the aqueous phase is in the form of M, then the equation for the special case can be simplified to

$$D_M = K_{D_{ML_2}} \beta_2\left\{\frac{[L_{org}]}{K_{D_L}}\right\}^2$$

It is then possible to write an even more simple expression for the special case equation.

$$D_M = \frac{K_{D_{ML_2}} \beta_2}{K_{D_L}^2}[L_{org}]^2$$

This equation can be rewritten with a new constant k'

$$D_M = k' [L_{org}]^2$$

Where k' is given by the following equation

$$k' = \frac{K_{D_{ML_2}} \beta_2}{K_{D_L}^2}$$

Derivation of equations for the gold extraction with the malonamides (for the aqueous system).

Gold(III) is known to form chloride complexes, these include the neutral complex $AuCl_3$. This neutral complex can react with a lewis base such as a malonamides or phosphine oxide to form a lipophilic gold complex. The lipophilic gold complex can be transferred into a hydrocarbon solvent.

However gold can form an anionic complex $AuCl_4^-$ by the reaction of the neutral complex with a chloride anion. According to the following equation.

$AuCl_3 + Cl^- \rightarrow AuCl_4^-$

The equilibrium for this reaction can be expressed in the following equation in which the activities of the species are shown.

$$K_4 = \frac{a_{AuCl_4^-}}{a_{Cl^-}\, a_{AuCl_3}}$$

Next if we rewrite the equation to include activity functions we have.

$$K_4 = \frac{f_{AuCl_4^-}\left[AuCl_4^-\right]}{f_{Cl^-}\left[Cl^-\right] f_{AuCl_3}\left[AuCl_3\right]}$$

This equation deals with the equilibrium between the two forms of gold found in the lower phase. A second equilibrium operates in the system, this is the equilibrium between the neutral gold complex in the lower phase and the malonamides complex ($AuCl_3MA_n$) in the organic phase. The chemical equation for the forward reaction in this equilibrium is

$AuCl_{3(aq)} + nMA_{(org)} \rightarrow AuCl_3Ma_{n(org)}$

If we assume that n is equal to two, but regardless of the value of n we can write

$$K_{ex} = \frac{f_{AuCl_3MA_n{}_{org}}\left[AuCl_3MA_n\right]_{org}}{f_{AuCl_3{}_{aq}}\left[AuCl_3\right]_{aq}\; f_{MA}^{\,n}{}_{org}\left[MA\right]_{org}^{n}}$$

As the concentrations of the malonamide and the activity functions in the organic phase are constant in an experimental series, the fact that they are unknown does not matter. They can be adsorbed into a new constant C. Thus we can now write.

$$K_{ex} = \frac{C\left[AuCl_3MA_n\right]_{org}}{f_{AuCl_3{}_{aq}}\left[AuCl_3\right]_{aq}}$$

We can also make the equation a little more simple, if we assume that the activity function (and activity coefficient) of a neutral species in the aqueous phase is one then the equation reduces in complexity to.

$$K_{ex} = \frac{C\left[AuCl_3MA_n\right]_{org}}{\left[AuCl_3\right]_{aq}}$$

Returning to the equation for the equilibrium between the different forms of gold in the aqueous phase, we can now write.

$$\frac{\left[AuCl_4^-\right]}{\left[AuCl_4^-\right]+\left[AuCl_3\right]}=\frac{\left(\frac{K_4[Cl^-][AuCl_3]f_{Cl^-}f_{AuCl_3}}{f_{AuCl_4^-}}\right)}{\left[AuCl_3\right]+\left(\frac{K_4[Cl^-][AuCl_3]f_{Cl^-}f_{AuCl_3}}{f_{AuCl_4^-}}\right)}$$

And

$$\frac{\left[AuCl_3\right]}{\left[AuCl_4^-\right]+\left[AuCl_3\right]}=\frac{\left[AuCl_3\right]}{\left[AuCl_3\right]+\left(\frac{K_4[Cl^-][AuCl_3]f_{Cl^-}f_{AuCl_3}}{f_{AuCl_4^-}}\right)}$$

If we divide the right hand side of the equation by the concentration of the neutral trichloro complex of gold we get.

$$\frac{\left[AuCl_3\right]}{\left[AuCl_4^-\right]+\left[AuCl_3\right]}=\frac{1}{1+\left(\frac{K_4[Cl^-]f_{Cl^-}f_{AuCl_3}}{f_{AuCl_4^-}}\right)}$$

As we can safely assume that the only forms of gold in the denser phase are the two chloride complexes then we can write the following equation which gives us the fraction of the gold in the lower phase which exists as the neutral trichloride complex.

$$\frac{\left[AuCl_3\right]}{[Au]_{total}}=\frac{1}{1+\left(\frac{K_4[Cl^-]f_{Cl^-}f_{AuCl_3}}{f_{AuCl_4^-}}\right)}$$

Next if we combine this last equation with

$$\frac{K_{ex}[AuCl_3]_{aq}}{C}=\left[AuCl_3MA_n\right]_{org}$$

We can get

$$\frac{[AuCl_3MA_n]_{org}}{[Au]_{total}}=\frac{\left(K_{ex}/C\right)}{1+\left(\frac{K_4[Cl^-]f_{Cl^-}f_{AuCl_3}}{f_{AuCl_4^-}}\right)}$$

As the distribution ratio is the total organic concentration of gold divided by the total aqueous concentration of gold we can now write.

$$D_{Au} = \frac{\left(K_{ex}/_{C}\right)}{1 + \left(\frac{K_4[Cl^-]f_{Cl^-}f_{AuCl_3}}{f_{AuCl_4^-}}\right)}$$

As already stated we can remove the activity function for the neutral gold trichloride complex in the aqueous phase. This now gives us.

$$D_{Au} = \frac{\left(K_{ex}/_{C}\right)}{1 + \left(\frac{K_4[Cl^-]f_{Cl^-}}{f_{AuCl_4^-}}\right)}$$

Now consider the activity function of an ion. We can write for a simple salt solution an equation which describes how the activity function changes as a function of the ionic strength and the concentration of the counter ion j.

$$log_{10} f_i = \left(\frac{-z^2 A\sqrt{I}}{1 + (1.5\sqrt{I})}\right) + \epsilon_{i,j}[j]$$

For chloride in a mixture of sodium and choline chlorides we can write

$$log_{10} f_{Cl^-} = \left(\frac{-z^2 A\sqrt{I}}{1 + (1.5\sqrt{I})}\right) + \epsilon_{Na,Cl}[Na^+] + \epsilon_{Na,Cl}[Ch^+]$$

While for the tetrachloroaurate anion we write

$$log_{10} f_{AuCl_4^-} = \left(\frac{-z^2 A\sqrt{I}}{1 + (1.5\sqrt{I})}\right) + \epsilon_{Na,AuCl_4}[Na^+] + \epsilon_{Ch,AuCl_4}[Ch^+]$$

Now when

$X = Y \,.\, Z$

Then

$$log_{10} X = (log_{10} Y) + (log_{10} Z)$$

So

$$\frac{f_{Cl^-}}{f_{AuCl_4^-}} = 10^{\left(\frac{\left(\frac{-z^2A\sqrt{I}}{1+(1.5\sqrt{I})}\right)+\epsilon_{Na,Cl}[Na^+]+\epsilon_{Na,Cl}[Ch^+]}{\left(\frac{-z^2A\sqrt{I}}{1+(1.5\sqrt{I})}\right)+\epsilon_{Na,AuCl_4}[Na^+]+\epsilon_{Ch,AuCl_4}[Ch^+]}\right)}$$

We can rearrange this to give

$$\frac{f_{Cl^-}}{f_{AuCl_4^-}} = 10^{\left(\frac{\left(\frac{-z^2A\sqrt{I}}{1+(1.5\sqrt{I})}\right)-\left(\frac{-z^2A\sqrt{I}}{1+(1.5\sqrt{I})}\right)+\epsilon_{Na,Cl}[Na^+]+\epsilon_{Na,Cl}[Ch^+]}{\epsilon_{Na,AuCl_4}[Na^+]+\epsilon_{Ch,AuCl_4}[Ch^+]}\right)}$$

The two terms with the square root of the ionic strength inside them cancel out. We now have

$$\frac{f_{Cl^-}}{f_{AuCl_4^-}} = 10^{\left(\frac{\epsilon_{Na,Cl}[Na^+]+\epsilon_{Na,Cl}[Ch^+]}{\epsilon_{Na,AuCl_4}[Na^+]+\epsilon_{Ch,AuCl_4}[Ch^+]}\right)}$$

This can be rearranged a little further to give

$$\frac{f_{Cl^-}}{f_{AuCl_4^-}} = 10^{\left((\epsilon_{Na,Cl}[Na^+]+\epsilon_{Na,Cl}[Ch^+])-(\epsilon_{Na,AuCl_4}[Na^+]+\epsilon_{Ch,AuCl_4}[Ch^+])\right)}$$

As
$[Na^+] = I - [Ch^+]$

We can go further with our maths

$$\log\frac{f_{Cl^-}}{f_{AuCl_4^-}} = \Delta\varepsilon_1[Na^+] + \Delta\varepsilon_2([Na^+]+[Ch^+])$$

then

$$\log\frac{f_{Cl^-}}{f_{AuCl_4^-}} = \Delta\varepsilon_1[Na^+] + \Delta\varepsilon_2 I$$

Where

$$\Delta\varepsilon_1 = \varepsilon(Na^+,Cl^-) + \varepsilon(Ch^+,AuCl_4^-) - \varepsilon(Ch^+,Cl^-) - \varepsilon(Na^+,AuCl_4^-)$$

and

$$\Delta\varepsilon_2 = \varepsilon(Ch^+,Cl^-) - \varepsilon(Ch^+,AuCl_4^-)$$

If we were to deal with a less halophilic element which exists as M^+ and MCl in aqueous media then we can write.

$$K_1 = \frac{a_{MCl}}{a_{Cl^-}\, a_{M^+}}$$

Then we can write

$$\frac{K_1 [Cl^-] f_{M^+} f_{Cl^-}}{f_{MCl}} = \frac{[MCl]}{[M^+]}$$

From this we can move to

$$\frac{K_1 [Cl^-] [M^+] f_{M^+} f_{Cl^-}}{f_{MCl}} = [MCl]$$

So

$$\frac{[MCl]}{[M^+] + [MCl]} = \frac{\left(\frac{K_1 [Cl^-] [M^+] f_{M^+} f_{Cl^-}}{f_{MCl}}\right)}{[M^+] + \left(\frac{K_1 [Cl^-] [M^+] f_{M^+} f_{Cl^-}}{f_{MCl}}\right)}$$

We can now make this a bit more simple

$$\frac{[MCl]}{[M]_{total_{aq}}} = \frac{\left(\frac{K_1 [Cl^-]\, f_{M^+} f_{Cl^-}}{f_{MCl}}\right)}{1 + \left(\frac{K_1 [Cl^-] f_{M^+} f_{Cl^-}}{f_{MCl}}\right)}$$

If the equation immediately above this text is combined with the following equation (where the metal chloride is extracted by n ligands named L).

$$ZK_{ex}[MCl]_{aq} = [MClL_n]_{org}$$

Then we can have the following equation

$$\frac{[MClL_n]_{org}}{[M]_{total_{aq}}} = \frac{ZK_{ex}\left(\frac{K_1 [Cl^-]\, f_{M^+} f_{Cl^-}}{f_{MCl}}\right)}{1 + \left(\frac{K_1 [Cl^-] f_{M^+} f_{Cl^-}}{f_{MCl}}\right)}$$

Which can be expressed as the following way if only one form of the metal can be found in the organic phase.

$$D_M = \frac{ZK_{ex}\left(\frac{K_1\left[Cl^-\right] f_{M^+} f_{Cl^-}}{f_{MCl}}\right)}{1 + \left(\frac{K_1\left[Cl^-\right] f_{M^+} f_{Cl^-}}{f_{MCl}}\right)}$$

It is possible to have situations where an increase in a species in the aqueous phase causes the distribution ratio to first increase and then decrease. One example would be the extraction of lanthanides using acetylacetone.

Here we start with the following four equations. Imagine we were to repeat the work with gold using an exceptionally wide range of chloride concentrations (and activities)

$$K_4 = \frac{f_{AuCl_4^-}\left[AuCl_4^-\right]}{f_{Cl^-}[Cl^-]f_{AuCl_3}[AuCl_3]}$$

$$K_3 = \frac{f_{AuCl_3}\left[AuCl_3\right]}{f_{Cl^-}[Cl^-]f_{AuCl_2^+}\left[AuCl_2^+\right]}$$

$$K_2 = \frac{f_{AuCl_2^+}\left[AuCl_2^+\right]}{f_{Cl^-}[Cl^-]f_{AuCl^{2+}}\left[AuCl^{2+}\right]}$$

$$K_1 = \frac{f_{AuCl^{2+}}\left[AuCl^{2+}\right]}{f_{Cl^-}[Cl^-]f_{Au^{3+}}\left[Au^{3+}\right]}$$

We can combine these equations to create the following

$$\beta_2 = K_1K_2 = \frac{f_{AuCl^{2+}}\left[AuCl^{2+}\right]}{f_{Cl^-}[Cl^-]f_{Au^{3+}}\left[Au^{3+}\right]} \frac{f_{AuCl_2^+}\left[AuCl_2^+\right]}{f_{Cl^-}[Cl^-]f_{AuCl^{2+}}\left[AuCl^{2+}\right]}$$

We can make this a little more simple by cancelling terms on the right hand side.

$$\beta_2 = \frac{1}{f_{Cl^-}[Cl^-]f_{Au^{3+}}\left[Au^{3+}\right]} \frac{f_{AuCl_2^+}\left[AuCl_2^+\right]}{f_{Cl^-}[Cl^-]}$$

We can rewrite it in a neater way

$$\beta_2 = \frac{f_{AuCl_2^+}\left[AuCl_2^+\right]}{f^2_{Cl^-}[Cl^-]^2f_{Au^{3+}}\left[Au^{3+}\right]}$$

We can repeat the process and then create

$$\beta_3 = \frac{f_{AuCl_3}\left[AuCl_3\right]}{f^3_{Cl^-}[Cl^-]^3f_{Au^{3+}}\left[Au^{3+}\right]}$$

$$\beta_4 = \frac{f_{AuCl_4^-}\left[AuCl_4^-\right]}{f^4_{Cl^-}\left[Cl^-\right]^4 f_{Au^{3+}}\left[Au^{3+}\right]}$$

If we wish to know the fraction of the gold in the aqueous phase which is present in the form of the neutral trichloro complex then we can do the following.

$$\frac{K_1 f_{Cl^-}\left[Cl^-\right] f_{Au^{3+}}}{f_{AuCl^{2+}}} = \frac{\left[AuCl^{2+}\right]}{\left[Au^{3+}\right]}$$

$$\frac{\beta_2 f^2_{Cl^-}\left[Cl^-\right]^2 f_{Au^{3+}}}{f_{AuCl_2^+}} = \frac{\left[AuCl_2^+\right]}{\left[Au^{3+}\right]}$$

$$\frac{\beta_3 f^3_{Cl^-}\left[Cl^-\right]^3 f_{Au^{3+}}}{f_{AuCl_3}} = \frac{\left[AuCl_3\right]}{\left[Au^{3+}\right]}$$

$$\frac{\beta_4 f^4_{Cl^-}\left[Cl^-\right]^4 f_{Au^{3+}}}{f_{AuCl_4^-}} = \frac{\left[AuCl_4^-\right]}{\left[Au^{3+}\right]}$$

If we combine the equations we can get

$$\frac{\left[AuCl_3\right]}{[Au]_{total}} = \frac{\left(\frac{\beta_3 f^3_{Cl^-}\left[Cl^-\right]^3\left[Au^{3+}\right] f_{Au^{3+}}}{f_{AuCl_3}}\right)}{\left[Au^{3+}\right] + \left(\frac{K_1 f_{Cl^-}\left[Cl^-\right]\left[Au^{3+}\right] f_{Au^{3+}}}{f_{AuCl^{2+}}}\right) + \left(\frac{\beta_2 f^2_{Cl^-}\left[Cl^-\right]^2\left[Au^{3+}\right] f_{Au^{3+}}}{f_{AuCl_2^+}}\right) + \left(\frac{\beta_3 f^3_{Cl^-}\left[Cl^-\right]^3\left[Au^{3+}\right] f_{Au^{3+}}}{f_{AuCl_3}}\right) + \left(\frac{\beta_4 f^4_{Cl^-}\left[Cl^-\right]^4\left[Au^{3+}\right] f_{Au^{3+}}}{f_{AuCl_4^-}}\right)}$$

We can make this a little more simple

$$\frac{\left[AuCl_3\right]}{[Au]_{total}} = \frac{\left(\frac{\beta_3 f^3_{Cl^-}\left[Cl^-\right]^3 f_{Au^{3+}}}{f_{AuCl_3}}\right)}{1 + \left(\frac{K_1 f_{Cl^-}\left[Cl^-\right] f_{Au^{3+}}}{f_{AuCl^{2+}}}\right) + \left(\frac{\beta_2 f^2_{Cl^-}\left[Cl^-\right]^2 f_{Au^{3+}}}{f_{AuCl_2^+}}\right) + \left(\frac{\beta_3 f^3_{Cl^-}\left[Cl^-\right]^3 f_{Au^{3+}}}{f_{AuCl_3}}\right) + \left(\frac{\beta_4 f^4_{Cl^-}\left[Cl^-\right]^4 f_{Au^{3+}}}{f_{AuCl_4^-}}\right)}$$

For a given organic phase made from a malonamides in an inert diluent at a given temperature, the amount of gold extracted will be proportional to the amount of the neutral gold trichloride complexes present in the aqueous phase.

Derivation of equations for the indium extraction with aliquat 336 (for the aqueous system).

Two equilibria exist. there is the chemical equilibrium in the denser phase and the exchange of anions between the two liquid phases. First start with the chemical equilibrium in the denser phase.

If activity functions are ignored then we can write.

$$K_4 = \frac{\left[InCl_4^-\right]}{\left[InCl_3\right]\left[Cl^-\right]}$$

If we add the activity functions then we now have

$$K_4 = \frac{f_{InCl_4^-}\left[InCl_4^-\right]}{f_{InCl_3}\left[InCl_3\right]f_{Cl^-}\left[Cl^-\right]}$$

We can rearrange this to give

$$\left[InCl_4^-\right] = \frac{K_4\left[Cl^-\right]\left[InCl_3\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}$$

Next we create an equation which gives us the fraction of the indium in the denser phase which exists as the tetrachloro anion.

$$\frac{\left[InCl_4^-\right]}{\left[InCl_4^-\right]+\left[InCl_3\right]} = \frac{\left(\frac{K_4\left[Cl^-\right]\left[InCl_3\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}{\left[InCl_3\right] + \left(\frac{K_4\left[Cl^-\right]\left[InCl_3\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}$$

Next we can remove the [$InCl_3$] terms from the right hand side of the equation.

$$\frac{\left[InCl_4^-\right]}{\left[InCl_4^-\right]+\left[InCl_3\right]} = \frac{\left(\frac{K_4\left[Cl^-\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}{1 + \left(\frac{K_4\left[Cl^-\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}$$

If we assume that all of the indium in the lower phase is in the form of either the neutral InCl3 or the anionic InCl4- complex then we can write.

$$\frac{\left[InCl_4^-\right]}{\Sigma\left[In\right]_{aq}} = \frac{\left(\frac{K_4\left[Cl^-\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}{1 + \left(\frac{K_4\left[Cl^-\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}$$

Next we can rearrange the equation slightly

$$\left[InCl_4^-\right] = \left\{\frac{\left(\frac{K_4\left[Cl^-\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}{1 + \left(\frac{K_4\left[Cl^-\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}\right\}\Sigma\,[In]_{aq}$$

Now we consider the exchange of anions between the two layers. we can write the following equation

$$K_{ex} = \frac{\left[InCl_4^-\right]_{org}f_{InCl_{4\,org}^-}\left[Cl^-\right]f_{Cl^-}}{\left[InCl_4^-\right]f_{InCl_4^-}\left[Cl^-\right]_{org}f_{Cl_{org}^-}}$$

We can now write a more simple version of this equation for a system where we keep the chloride concentration and activity function in the organic phase constant.

$$K_{ex} = \frac{\left[InCl_4^-\right]_{org}k\left[Cl^-\right]f_{Cl^-}}{\left[InCl_4^-\right]f_{InCl_4^-}}$$

Now we rearrange this equation to give us the concentration of the anionic indium complex in the organic phase.

$$\frac{1}{\left[InCl_4^-\right]_{org}} = \frac{K_{ex}k\left[Cl^-\right]f_{Cl^-}}{\left[InCl_4^-\right]f_{InCl_4^-}}$$

Next turn the equation upside down to give us

$$\left[InCl_4^-\right]_{org} = \frac{\left[InCl_4^-\right]f_{InCl_4^-}}{K_{ex}k\left[Cl^-\right]f_{Cl^-}}$$

The next step is to combine the two equations to form the following expression

$$\left[InCl_4^-\right]_{org} = \frac{f_{InCl_4^-}}{K_{ex}k\left[Cl^-\right]f_{Cl^-}}\left\{\frac{\left(\frac{K_4\left[Cl^-\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}{1 + \left(\frac{K_4\left[Cl^-\right]f_{Cl^-}f_{InCl_3}}{f_{InCl_4^-}}\right)}\right\}\Sigma\,[In]_{aq}$$

We can express ourselves in terms of the distribution ratio using the following equation.

$$D_{In} = \frac{f_{InCl_4^-}}{K_{ex} k [Cl^-] f_{Cl^-}} \left\{ \frac{\left(\frac{K_4 [Cl^-] f_{Cl^-} f_{InCl_3}}{f_{InCl_4^-}} \right)}{1 + \left(\frac{K_4 [Cl^-] f_{Cl^-} f_{InCl_3}}{f_{InCl_4^-}} \right)} \right\}$$

Now we can reduce the complexity of the equation a little. if we assume that the activity function of the neutral indium trichloride complex is equal to one. then the equation becomes.

$$D_{In} = \frac{f_{InCl_4^-}}{K_{ex} k [Cl^-] f_{Cl^-}} \left\{ \frac{\left(\frac{K_4 [Cl^-] f_{Cl^-}}{f_{InCl_4^-}} \right)}{1 + \left(\frac{K_4 [Cl^-] f_{Cl^-}}{f_{InCl_4^-}} \right)} \right\}$$

Section Fs.

1 Explanation of method used in excel to calculate $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$

To solve the problem we need to determine K_{ex}/C, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$. These three items will be varied by the solver routine in excel.

We set up a set of three cells with guessed values for these three items. In the following way

Column	Row	What it is	Contents
D	1	$\Delta\varepsilon_1$	=(B14+B16)-(B15+B17)
D	2	$\Delta\varepsilon_2$	=B15-B16
D	3	K_{ex}/C	=B30
D	4	Ionic strength	3.873
D	5	K_4	Value of the binding constant

To generate the values in D1 and D2 we have a set of cells in column B

Column	Row	What it is	Contents
B	14	ε Na,Cl	0,0406
B	15	ε Ch, Cl	0,0074
B	16	ε Na,$AuCl_4$	=B28-2
B	17	ε Ch, $AuCl_4$	=B29-2
B	28	Guess for $(2+\Delta\varepsilon_1)$	
B	29	Guess for $(2+\Delta\varepsilon_2)$	
B	30	Guess for K_{ex}/C	

We use the values generated in cells D1, D2, D3 in the following way

We create a column of cells with the sodium ion concentrations for the denser phase. Put these in column D starting at row 8. Next in column F we have a set of cells. These cells calculate the fraction created by dividing one activity function by the other. Each cell contains

=(10^(D{X}*D$1))*(10^(D$4*D$2))

Where {X} is the row number of the cell.

Next in the same row in column G we have the following equation which should predict the distribution ratio.

=D$3/(1+(F{X}*D$5*D$4))

In row H we put the real distribution data in cells lines up with the cells in columnD which have the correct sodium ion concentrations.

In column I we have the following equations in cells

=ABS(LOG10(H{X}/G{X}))

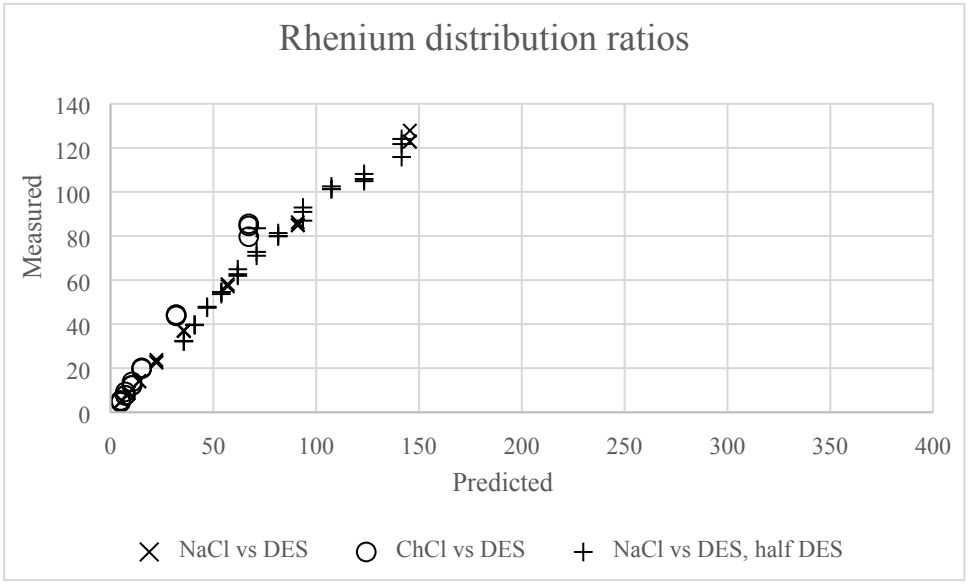
The sum of the error values in column I are then sent to B26 by placing in B26 the following =SUM(I8:I{bottom row in use})

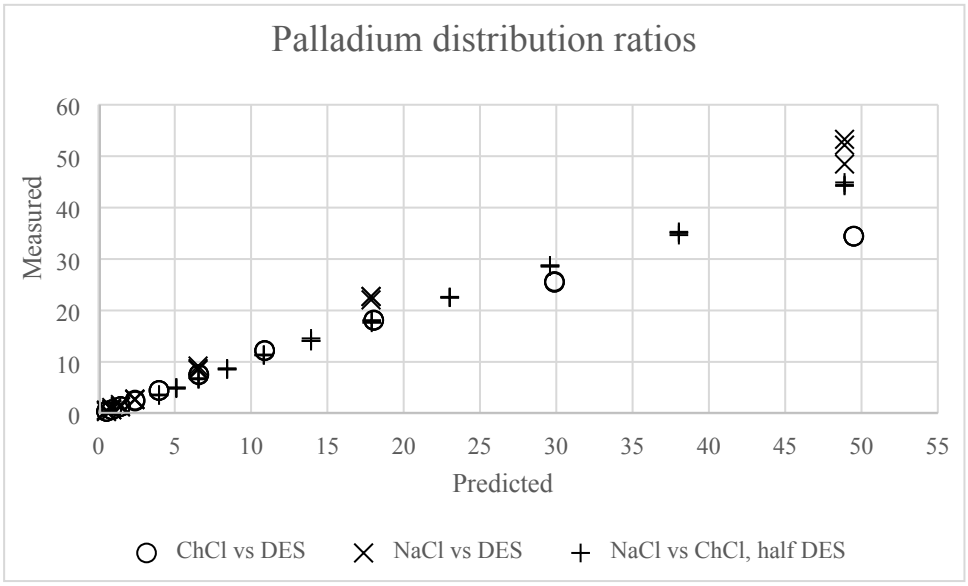
Then using the GRG non linear engine we search for a solution where B26 is as small as possible by changing B28, B29 and B30.

2 Modelling of rhenium and palladium extraction using the assumption that the chloride concentration was perfectly constant in all the starting solutions.

For the rhenium system $\Delta\psi$ obtained from the experiments with the mixtures of aqueous choline chloride and ethaline has a value of 2.04, during a fitting exercise using distribution ratios which were no higher than 110 a value of 1.95 was obtained when data obtained with mixtures containing sodium chloride were included. By fitting the data against our model we determined that the value of $\varepsilon_{Ch^+,ReO_4^-}$ to be -0.427. For palladium extraction in the model $\psi_{PdCl_4^{2-}}$ - $2\psi_{Cl^-}$, ε Na^+,$PdCl_4^{2-}$, ε Ch^+,$PdCl_4^{2-}$and C''K_{ex} are -2.19, 0.00, -0.611 and 2.01 x 10^{-6} respectively. In these experiments the concentration of the chloride solution is assumed to always be 3.873 M.

The graphs of predicted distribution ratios against real distribution ratios for this constant chloride model are shown below.





3 Activity coefficients / functions in the organic phase

As the metal loading of the organic phase is very low and as for the majority of experiments the concentration of the extraction agent is kept constant in the main body of the paper we have chosen to make the assumption that all the activity coefficients in the organic phase remain constant.

For the gold extraction.

However, rather than just expressing the opinion we have chosen to consider how valid an assumption it is here. If the organic phase is considered to consist of three substances (1) diluent, (2) extractant and (3) metal extractant complex then we can have mole fractions for each x_1, x_2 and x_3.

If we use the Bonham equations for this system.

$$\ln \gamma_1 = \frac{\left(x_2\sqrt{B_{12}} + x_3 A_{32}\sqrt{B_{13}}\right)^2}{T\left(x_1 A_{12} + x_2 + x_3 A_{32}\right)^2}$$

$$\ln \gamma_2 = \frac{\left(x_1 A_{12}\sqrt{B_{21}} + x_3 A_{32}\sqrt{B_{23}}\right)^2}{T\left(x_1 A_{12} + x_2 + x_3 A_{32}\right)^2}$$

$$\ln \gamma_3 = \frac{\left(x_1 A_{12}\sqrt{B_{31}} + x_2\sqrt{B_{32}}\right)^2}{T\left(x_1 A_{12} + x_2 + x_3 A_{32}\right)^2}$$

Here the parameters are related according to the following two sub equations.

$$A_{ij} = \frac{1}{A_{ji}}$$

and

$$B_{ij} = \frac{B_{ji}}{A_{ji}}$$

Then if $x_3 = 0$ then the equations will simplify to

$$\ln \gamma_1 = \frac{\left(x_2\sqrt{B_{12}}\right)^2}{T\left(x_1 A_{12} + x_2\right)^2}$$

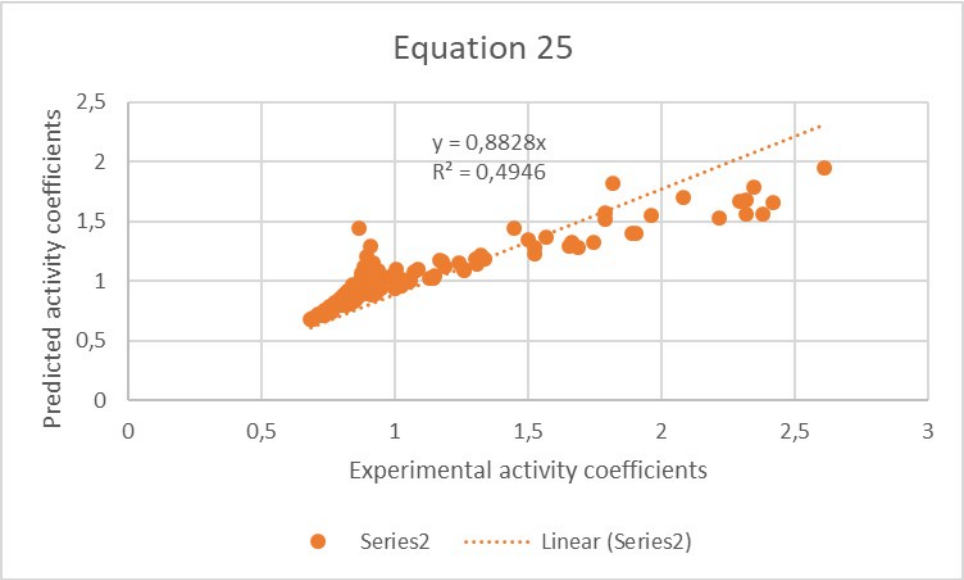
$$\ln \gamma_2 = \frac{\left(x_1 A_{12}\sqrt{B_{21}}\right)^2}{T\left(x_1 A_{12} + x_2\right)^2}$$

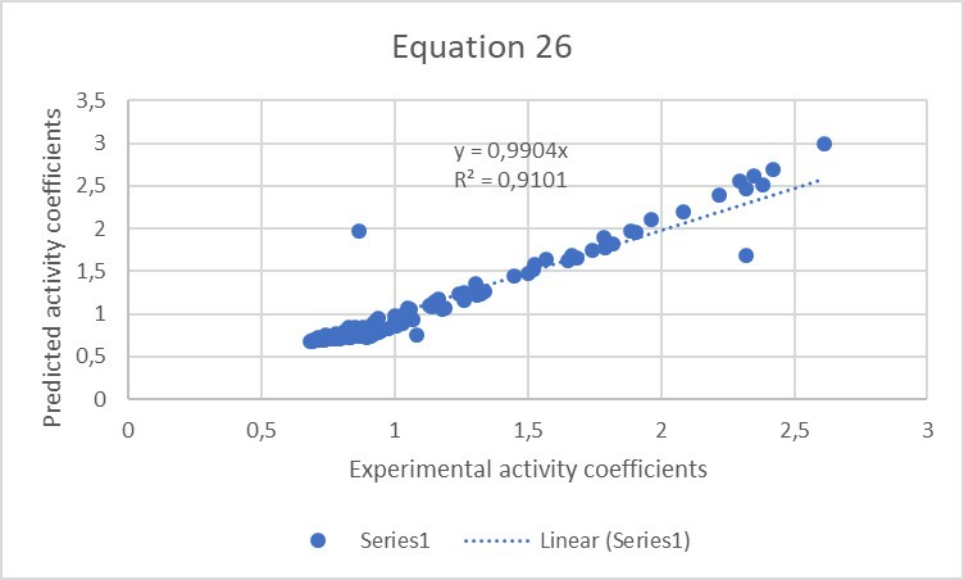
$$\ln \gamma_3 = \frac{\left(x_1 A_{12}\sqrt{B_{31}} + x_2\sqrt{B_{32}}\right)^2}{T\left(x_1 A_{12} + x_2\right)^2}$$

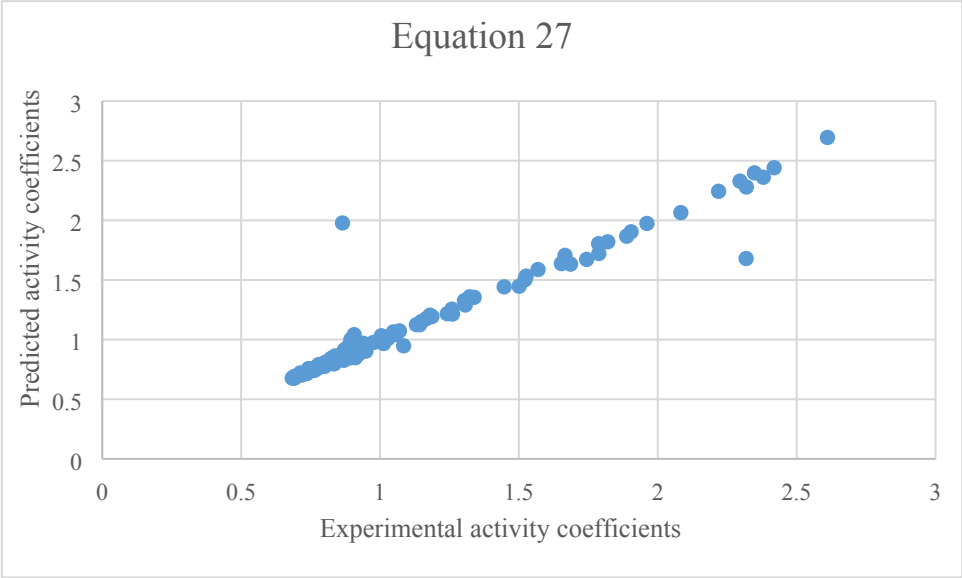
Hence while we can still in principle decide on an activity coefficient for substance 3, in our experiment this will be fixed by the ratio between x_1 and x_2.

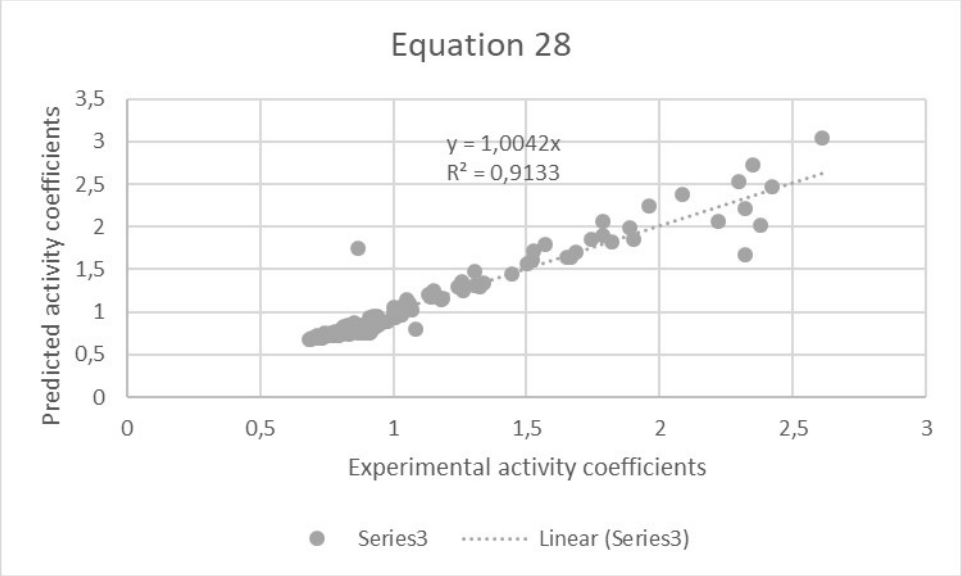
An alternative would be to use the Wilson equations again when $x_3 = 0$ then the equations will simplfy so that the activity coefficients of all three components in the organic phase will depend only on a series of constants which are fixed and the ratio of x_1 to x_2. So as the metal loading of the organic phase is very low we can assume that the activity functions of the things in it will remain constant.

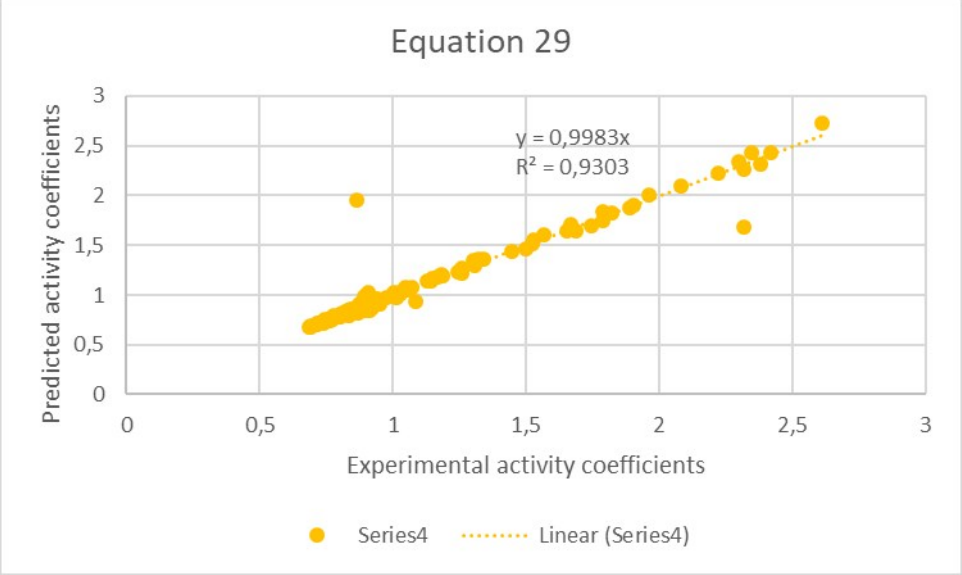
Section G. Graphs comparing the predictions of our models to experimental data obtained by others






Equation 27
Predicted activity coefficients
Experimental activity coefficients
0
0.5
1
1.5
2
2.5
3


Equation 28
y = 1,0042x
R² = 0,9133
Predicted activity coefficients
Experimental activity coefficients
Series3
Linear (Series3)


Equation 29
y = 0,9983x
R² = 0,9303
Predicted activity coefficients
Experimental activity coefficients
Series4
Linear (Series4)

[i] E. Dziwinski and J. Szymanowski, *Solvent Extraction and Ion Exchange*, 1998, **16**, 1515.