Activity coefficents in deep eutectic solvent: Implications for the solvent extraction of metals, Supporting information.

Contents

Experimental

Reagents and materials

All reagents unless otherwise stated were purchased from Aldrich and were used as supplied. Cyanex 923 (A trialkyl phosphine oxide) was purchased from Cytec. Solvent 70 (Aliphatic kerosene) was purchased from Statoil. Suprapure nitric acid (65 %, product number 1.00441.1000) was obtained from Merck and was diluted with ultrapure water to provide 1 and 0.1 M nitric acid. The ultrapure water was obtained from a Milli-Q machine supplied by the Millipore Corperation. The deep eutectic solvent was formed by combining choline chloride and lactic acid.

General conditions

All solvent extraction experiments were performed in triplicate, meaning that three shaking vials were used to gather data for each set of conditions.

All pipetting was done using the forward pipetting method using piston driven air displacement pipettes made by Gilson. Solvent extraction experiments were performed by pipetting equal volumes of an organic phase and either an aqueous phase or a deep eutectic solvent phase into a glass vial (3.5 ml). It was normal to add the aqueous or deep eutectic solvent phase before the addition of the organic phase to the vial. The phase ratio was checked by measuring the mass of the empty shaking vial, then again after the addition of the first liquid and then finally after the addition of the last liquid layer. When viscous liquids such as deep eutectic solvents and ionic liquids were pipetted; additional care was taken as these fluids require a greater time to flow out of the pipette tip. Additionally, filter tips were used to reduce the likelihood of the pipette becoming contaminated with a splash of the liquid. It was found that the moment when the push button of the pipette is released after the liquid had been ejected from the tip was the time when splashing of liquid upward was most likely to occur. After the liquids had been dispensed into the vial, it was sealed with a push on polyethylene cap before being shaken using a IKA Vibrax VXR basic machine equipped with a thermostated sample holder feed with warm water from a Grant TC120 circulating water bath. Unless otherwise stated all samples were shaken at 30°C. After shaking the samples were centrifuged (Heraeus Labofuge 200) at 3000 rotations per minute for at least five minutes to ensure good phase disengagement. Samples (200 µl) of the lower phase were taken using a Gilson pipette in the following manner. A pipette bearing a tip was set to the required volume, the push button depressed to the first stop before the tip was inserted into the lower phase. Through additional pressure on the button one or two bubbles

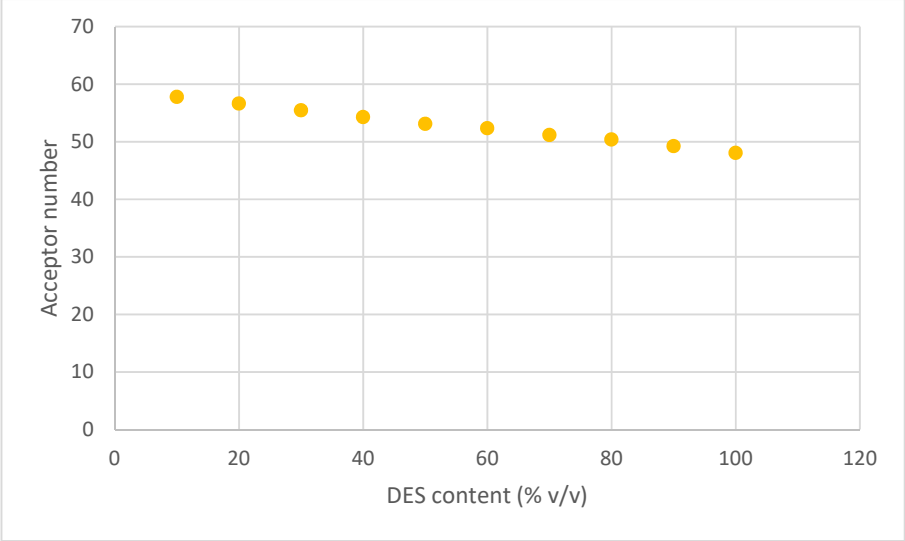
of air were expelled from the nozzle of the tip. The pressure on the push button was slowly relaxed allowing liquid to enter the tip. The pipette and tip were then removed from the shaking vial, using tissue paper the outside of the tip was wiped to remove any trace of the upper phase before the liquid inside the tip was dispensed into a preweighed polyethylene vial (17 ml). To the polyethylene vials was added dilute (0.1 M) nitric acid containing ruthenium (1–2 ppm). All samples and blanks used in an inductively coupled plasma optical emission run were made using a single batch of superpure nitric acid containing the same concentration of ruthenium. The ruthenium was present as an internal standard in case the operation of the ICPOES machine (Thermo Scientific iCAP6500) was subject to some variation. Normally the internal standard was not needed, but was present as a contingency against a pump or nebulizer malfunction. In some cases lower metal concentrations were used and an ICPMS (Inductively Coupled Plasma Mass Spectroscopy) machine (Thermo Scientific iCAP Q) was used in place of the ICPOES machine. The matrix for the ICPMS machine was nitric acid (1M) containing rhodium (25 parts per billion) as an internal standard.

Specific experiments

- ***Acceptor number measurement with the iron dye***

The iron containing dye was dissolved in a series of mixtures of DES and water. These were then examined with the lambda 19 spectrometer using the same settings as were used with the cobalt containing samples. The longest wavelength peak of the iron dye was used to calculate the acceptor number.

The results are shown in the following graph.



The results are shown as numbers in the following table.

% DES	wavelength (nm)	wavelength (cm)	wavenumbers (cm-1)	Aceptor number
100	528	0,000528	1893,939394	48,03662
90	525	0,000525	1904,761905	49,2053
80	522	0,000522	1915,708812	50,37398
70	520	0,00052	1923,076923	51,1531
60	517	0,000517	1934,235977	52,32178
50	515	0,000515	1941,747573	53,1009
40	512	0,000512	1953,125	54,26958
30	509	0,000509	1964,636542	55,43825
20	506	0,000506	1976,284585	56,60693
10	503	0,000503	1988,071571	57,77561

Cobalt extractions by aliquat 336

Starting solutions made 1st August

Tubes 4031 to 4063 started 5th August 2016

A series of cobalt solutions in mixtures of DES and sodium chloride solution were made up according to the following table. The volume of the cobalt stock used as 250 microlitres.

Name	Mass (g)			
	Empty	With Cobalt stock	After adding sodium chloride solution	After adding DES
95	6.6730	6.8927	7.1338	18.1581
92.5	6,6592	6.8778	7.4007	18.1455
90	6.7136	6.9334	7.7405	18.2021
87.5	6.6458	6.8642	7.9521	18.1639
85	6.6977	6.9164	8.2482	18.0946
82.5	6.6829	6.9013	8.5264	18.0993
80	6.6843	6.9026	8.8135	18.1642
77.5	6.6472	6.8654	9.0554	18-0855
75	6.7180	6.9359	9.3729	18.1040
72.5	6.6714	6.8892	9.6094	18-1025
70	6.7038	6.9180	9.9231	18.1405

Using these solutions as the more dense phase and 30 % aliquat 336 in ethyl benzene as the lighter phase a series of shaking experiments were performed.

Cadmium, zinc, palladium extractions by aliquat 336

Made solutions 25th July 2016, started extractions 27th July 2016

Tubes 3917 to 3961

A mixed metal stock was made in the following manner. Palladium(II) chloride (252 mg) was placed in an empty vial (14.9019 g). To this vial was added aqueous sodium chloride (6.4448 g of 3.61 M solution). The resulting mixture was heated in an oven until the palladium chloride dissolved. In a second vial (empty mass 14.8467 g) cadmium(II) oxide (418.2 mg) and zinc(II) oxide (467 mg) were combined with aqueous acetic acid (2 g of 25 % v/v). To this mixture was added sodium chloride solution (20 ml of 3.61 M solution), to the resulting mixture was added more 25 % (v/v) acetic acid (6 ml). At this point the metal oxides had dissolved. To the resulting solution was added nickel(II) chloride hexahydrate (1.335 g). The gross mass of the second vial at this point was 46.5726 g.

To the second vial was added the Na_2PdCl_4 solution formed by dissolving palladium chloride in sodium chloride solution. The gross mass of the second vial was 53.0835 grams. To this vial was added water until the volume was *circa* 50 ml. The final gross mass of the vial was 70.4894 grams.

A series of solutions of cadmium, nickel, palladium and zinc in mixtures of sodium chloride solution and the DES was made up according to the following table.

Name	Mass (g)			
	Empty	With metal stock	After adding DES	After adding sodium chloride solution
95	6.6683	7.1886	18.2523	18.2523
90	6.6782	7.1978	17.6476	18.1686
85	6.7163	7.2355	17.1150	18.2011
80	6.6454	7.1654	16.4400	18.1209
70	6.6683	7.1873	15.3168	18.1322
60	6.7166	7.2380	14.2023	18.1401
50	6.6745	7.1941	13.0269	18.0916
40	6.6827	7.2047	11.8876	18.0781
30	6.6511	7.1733	10.6904	18.0307
20	6.6738	7.1925	9.5299	17.9727
10	6.6693	7.1772	8.3710	17.9309

A 10 % (v/v) solution of aliquat 336 in ethyl benzene was formed by the dilution of the 30 % stock with more ethyl benzene. To an empty 50 ml volumetric flask (41.1845 g) was added two portions of 8.333 ml of the 30 % stock giving a gross mass of 55.8422 g. To this flask was then added ethyl benzene until the volume was 50 %. Thus giving a gross mass of 84.3580 grams.

In a similar manner a 20 % (v/v) solution of aliquat 336 was made in ethyl benzene.

The 10 % v/v solution of aliquat 336 was used with the mixtures containing between 10 and 80 % DES to perform solvent extraction experiments. The phase ratio was 1:1 and each shaking vial contained 600 microlitres of each phase.

The 20 % v/v solution of aliquat 336 was used with the mixture 70 % DES to perform solvent extraction experiments. The phase ratio was 1:1 and each shaking vial contained 600 microlitres of each phase.

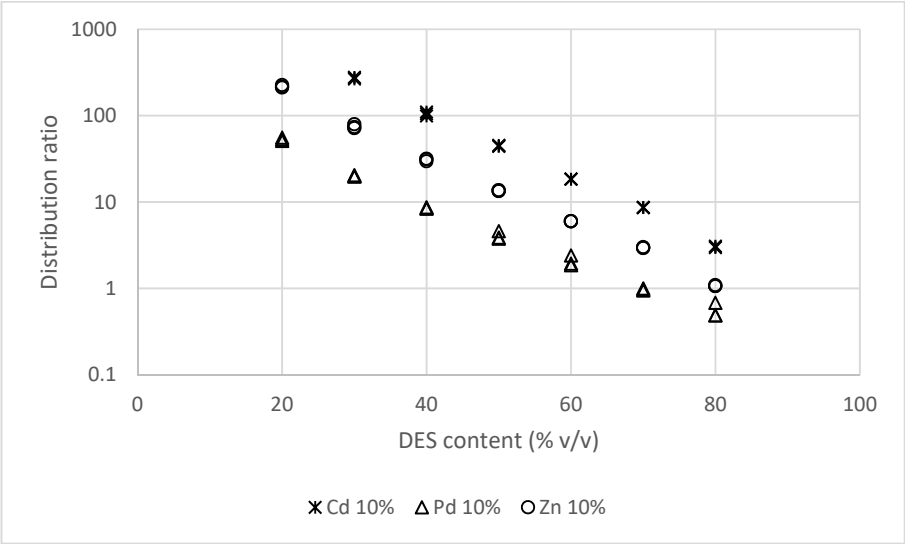
The 30 % v/v solution of aliquat 336 was used with the mixtures containing between 70 and 95 % DES to perform solvent extraction experiments. The phase ratio was 1:1 and each shaking vial contained 600 microlitres of each phase.

With 10 % aliquat 336 in ethyl benzene it is clear that the distribution ratios of cadmium, palladium and zinc decrease exponentially as the DES content of the lower phase increases. The data for these three elements fit well to the following equations where x is the volume percentage of the DES in the lower layer

$$D_{Cd} = 3729.8\, e^{-0.088\, x}$$

$$D_{Zn} = 1054.2\, e^{-0.086\, x}$$

$$D_{Pd} = 200.69\, e^{-0.076\, x}$$

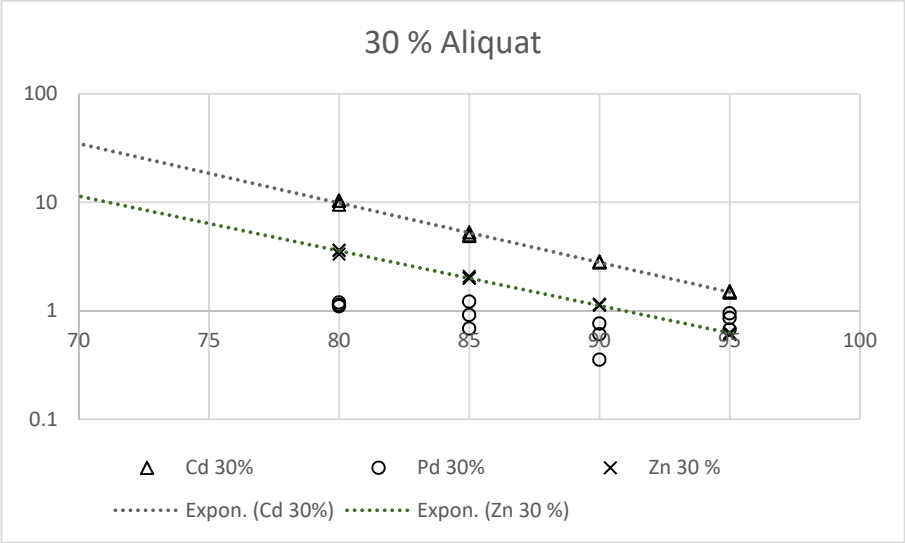


Similar results are obtained with 30 % (v/v) aliquat 336 in ethyl benzene. However for palladium in this system it is not possible to obtain good results, it is suspected that memory effects due to adsorption of palladium prevented the experiment using 30 % aliquat 336 from working well for palladium.

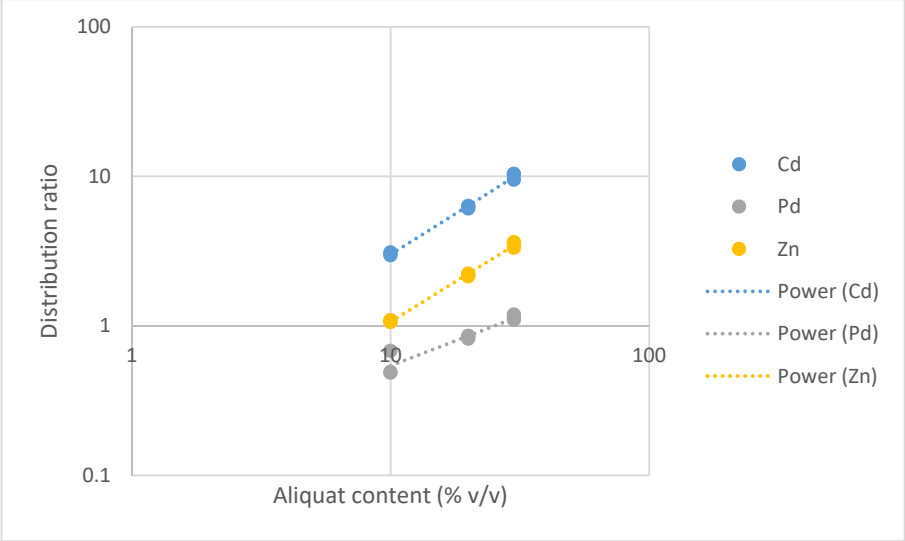
In this experiment with 30 % (v/v) aliquat the cadmium and zinc distribution ratios fitted well to the lines formed by the following equations.

$$D_{Cd} = 238393\, e^{-0.126\, x}$$

$$D_{Zn} = 39064\, e^{-0.116\, x}$$



A variable aliquat experiment indicated that increasing the aliquat content promoted the extraction of cadmium, palladium and zinc. Note that as expected no nickel extraction was observed.



Palladium and rhenium extraction by aliquat 336

Tubes 3980 to 4024 started 3rd August 2016

To an empty vial (14.3938 g) was added palladium(II) chloride (1.0769 g). To this was added aqueous sodium chloride (20 ml of 3.61 M) thus giving a gross mass of 22.9000 grams. This mixture was heated in an oven to cause the palladium chloride to react to form a solution of Na_2PdCl_4. The palladium solution thus obtained was filtered 3 days later through a 0.45 micrometer polypropylene syringe filter into a new vial (empty mass 14.3521 g) to form the palladium stock needed for this experiment.

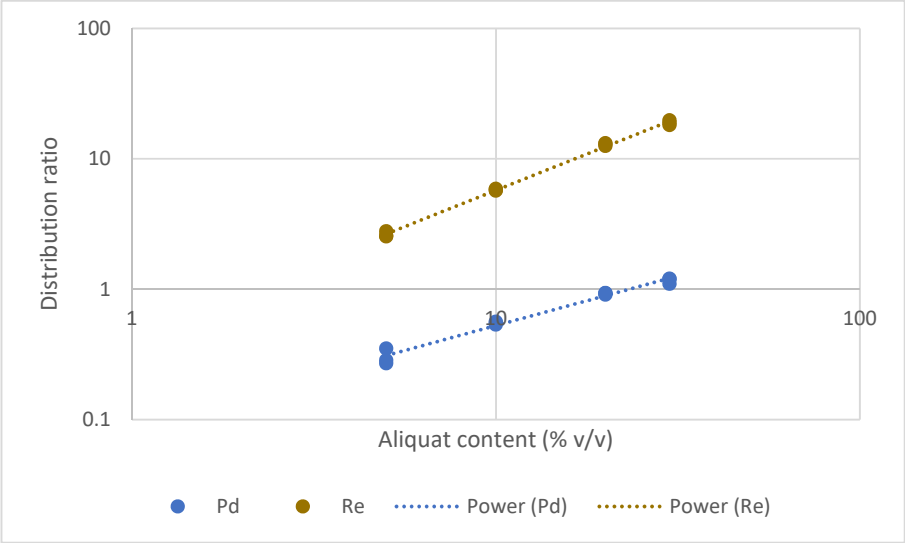
In another vial ammonium perrhenate (557 mg of NH_4ReO_4) was dissolved in water (20 ml) to form the rhenium(VII) stock.

These metal solutions were used to form a series of solutions of palladium and rhenium in mixtures of sodium chloride and DES according to the following table. To each vial 250 microlitres of rhenium stock was used and 125 microlitres of palladium stock were used.

Name	Mass (g)				
	Empty	With Re stock	After Pd stock	After NaCl stock	After adding DES
0	6.6534	6.9162	7.0691	17.9694	17.9694
10	6.6939	6.9565	7.1175	16.9071	18.0794
20	6.7066	6.9693	7.1299	15.7789	18.1363
30	6.6846	9.9520	7.1091	14.6347	18.0949
40	6.6794	6.9454	7.1046	13.4836	18.1232
50	6.6662	6.9300	7.0888	12.3462	18.1515
60	6.6805	6.9460	7.1071	11.2217	18.1786
70	6.6900	6.9523	7.1111	10.1142	18.2338
80	6.7000	6.9636	7.1251	8.9927	18.2663
85	6.6973	6. 9688	7.1321	8.4231	18.2820
90	6.6886	6.9563	7.1197	7.8359	18.2812
95	6.6935	6.9528	7.1122	7.2614	18.2674

Using the 80 % DES mixture a solvent extraction experiment was conducted with 5, 10, 20 and 30 % aliquat 336 in ethyl benzene. The 5 % aliquat solution was obtained by dilution of 30 % (v/v) aliquat 336 (1.6685 g) in ethyl benzene (8.7230 g). The other aliquat solutions were obtained from the preceding experiment.

Using the 10 % (v/v) aliquat 336 in ethyl benzene experiments were conducted with all the mixtures of DES and sodium chloride solutions. To reduce memory effects for palladium in the ICPOES machine the samples were diluted with superpure hydrochloric acid (83 ml of concentrated superpure hydrochloric acid 37 %) diluted to 1 litre with MQ water. Spiked with ruthenium (1 ppm) as an internal standard.



The results of the variable aliquat 336 experiment indicate that increasing the concentration of the aliquat promoted the extraction of both palladium and rhenium. It was interesting that the slope for palladium in the log log graph was only 0.76 while the slope for rhenium was 1.1. It is likely that a change in the activity coefficents in the organic phase as the aliquat concentration changed will have distorted the system away from one in which the solutes in the organic phase are in ideal solutions. It is also possible that the palladium in the organic phase will be in the form of $[Pd_2Cl_6]^{2-}$ complexes or some other similar polynuclear complex. If these polynuclear complexes were to exist then one of the following mechanism would be operating.

$2[PdCl_4]^{2-}_{(aq)} + 2\ R_4NCl_{(org)} \rightarrow (R_4N)_2.[Pd_2Cl_6]_{(org)} + 4Cl^-_{(aq)}$

or

$3[PdCl_4]^{2-}_{(aq)} + 2\ R_4NCl_{(org)} \rightarrow (R_4N)_2.[Pd_3Cl_8]_{(org)} + 6Cl^-_{(aq)}$

Indium and gallium extraction by cyanex 923

A series of solutions of indium, gallium and other metals were made which contain the same analytical concentration of chloride but different ratios of water to DES according to the following table.

Name	Empty	With gallium	After adding Re/Pd/In stock	After adding DES	After adding water	After adding Au stock	After adding NaCl stock
95 % DES	6.6595	6.7574	6.7719	17.7822	18.1311	18.2311	18.2310
90 % DES	6.6846	6,7817	6.7966	17.2419	17.5940	17.6943	18.2380
85 % DES	6.6408	6.7401	6.7548	16.6089	16.9606	17.0618	18.1826
80 % DES	6.6737	6.7496	6.7644	16.0382	16.3876	16.4885	18.1683
75 % DES	6.6737	6.7757	6.7904	15.5215	15.8731	15.9737	18.2258
70 % DES	6.6300	6.7311	6.7456	14.8774	15.2294	15.3303	18.1337
65 % DES	6.6181	6.7210	6.7355	14.2981	14.6498	14.7512	18.1170
60 % DES	6.6166	6.7196	6.7341	13.6852	14.0354	14.1386	18.0752
55 % DES	6.6672	6.7677	6.7825	13.1755	13.5276	13.6284	18.1282
50 % DES	6.6543	6.7574	6.7721	12.5833	12.9359	13.0372	18.0691
45 % DES	6.6694	6.7701	6.7848	12.0241	12.3765	12.4785	18.0945
40 % DES	6.6821	6.7840	6.7987	11.4341	11.7860	11.8880	18.0410
35 % DES	6.6457	6.7478	6.7630	10.8298	11.1818	11.2837	18.0281
30 % DES	6.6945	6.7941	6.8091	10.3019	10.6535	10.7557	18.0430
25 % DES	6.6660	6.7647	6.7797	9.6895	10.0381	10.1402	18.0305
20 % DES	6.6427	6.7424	6.7572	9.0808	9.4321	9.5346	17.9493
15 % DES	6.6691	6.7671	6.7817	8.5324	8.8813	8.9831	17.9525
10 % DES	6.5827	6.6812	6.6958	7.8619	8.2130	8.3150	17.8488
5 % DES	6.6698	6.7658	6.7806	7.3722	7.7206	7.8231	17.9358

The gold solution was 1000 ppm gold in 1 % hydrochloric acid. The gallium solution was 1000 ppm gallium in 1 % nitric acid. The mixed indium, palladium and rhenium stock was made in the following manner. Indium oxide (391 mg In_2O_3) was dissolved in hydrochloric acid (12 M 1.05 g). The resulting solution was diluted to 10 ml with water. This solution was mixed in a 2:1:1 volume ratio with palladium(II) chloride (32 g Pd per litre) dissolved in sodium chloride solution and ammonium perrhenate (16 g Re per litre) dissolved in water. The distribution ratios for rhenium, palladium and gold were either too high or too low to be useful.

Zinc extractions with cyanex301

Variable cyanex 301 concentration, tubes 3818 to 3853, 21 July 2016

To an empty plastic vial (14.9947 g) was added zinc oxide (46 mg) and cadmium(II) carbonate (20 mg). To this vial was added 25 % (v/v) acetic acid (1 ml) and water (9 ml). The resulting mixture was shaken until it became clear. The gross mass of the vial was 25.2223 g. To the vial was added DES (40 ml). The gross mass of the vial was then 72.1745 g. The vial was sealed and shaken before use.

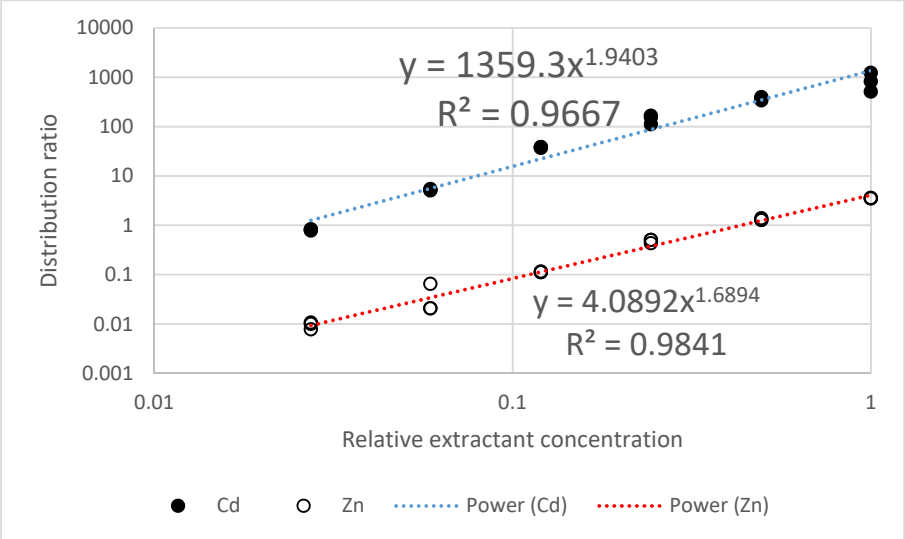
A solution of cyanex 301 (2.5453 g) in a 25 ml volumetric flask was made using solvent 70 as the diluent. The net mass of the reagent and diluent was 20.3716 grams. This stock solution was used for a solvent extraction experiment. The stock was diluted according to the following table

Intended dilution	Volume of stock used (ml)	Volume of solvent 70 used (ml)	Empty mass (g)	With solvent 70 (g)	Total mass (g)
x 2	5.0	5.0	18.3629	22.3582	26.2751
x 4	2.5	7.5	18.6285	24.6220	26.5488
x 8	1.25	8.75	18.4071	25.4157	26.3711
x 16	0.625	9.375	18.3258	25.8332	26.3038
x 32	0.3125	9.688	18.3678	26.1570	26.3760

Using these mixtures of cyanex 301 and solvent 70 together with the solution of cadmium and zinc in wet DES a solvent extraction experiment was conducted. The phase ratio was 1:1 and the volume of each phase was 700 microlitres.

This solution of zinc and cadmium in wet DES was shaken in vials with solutions of cyanex301 in solvent 70. The DES and organic layers had a volume of 700 microlitres.

The results are summarized in the following graph.



The results are shown in the following table.

Tube number	**3818**	**3819**	**3820**	**3839**	**3840**	**3841**
Relative concentration	1	1	1	0,5	0,5	0,5

Cd2144	508,4195	815,2081	1218,156	336,8237	373,8494	392,544
Cd2265	528,9926	864,97	1295,491	349,5137	387,0494	404,4819
Cd2288	508,3981	834,8319	1213,55	338,4254	373,1115	392,0026
Zn2025	3,319673	3,363535	3,426456	1,330436	1,221616	1,228285
Zn2062	3,457348	3,507662	3,559627	1,379753	1,274703	1,271541
Zn2138	3,195276	3,273608	3,378511	1,269465	1,163493	1,195738

Tube number	3842	3843	3844	3845	3846	3847
Relative concentration	0,25	0,25	0,25	0,125	0,125	0,125
Cd2144	110,836	165,3022	153,4598	36,79443	38,19367	37,90364
Cd2265	113,3104	170,1089	156,258	37,52886	38,70365	38,57058
Cd2288	109,8858	165,2319	151,3027	36,48231	37,38414	37,55448
Zn2025	0,415116	0,486619	0,487774	0,114627	0,111628	0,117487
Zn2062	0,430758	0,501613	0,501384	0,112118	0,111171	0,115192
Zn2138	0,398554	0,474914	0,499076	0,129567	0,126375	0,123268

Tube number	3848	3849	3850	3851	3852	3853
Relative concentration	0,0625	0,0625	0,0625	0,03125	0,03125	0,03125
Cd2144	5,377461	5,152775	5,051994	0,77451	0,81432	0,823438
Cd2265	5,467226	5,300322	5,163957	0,78849	0,82724	0,835173
Cd2288	5,457011	5,179519	5,022187	0,768889	0,815592	0,814911
Zn2025	0,13372	0,024784	0,027324	0,012758	0,023086	0,016278
Zn2062	0,06471	0,020533	0,020749	0,007737	0,010632	0,009967
Zn2138	0,260007	0,042691	0,048266	0,027465	0,047781	0,03707

Thermodynamics of stripping of metals from cyanex301 / solvent 70

A series of solutions of metals in sulfuric acid which were originally made for tubes 2045 to 2059 (An experiment on relating to the stripping of metals from DEHPA which has been published in Cogent Chemistry) were used for an experiment with the cyanex301 stock.

Masses (g)					
Empty	6,6533	6,649	6,6465	6,6436	6,6087
With 1M H2SO4	16,6523	11,8506	8,6862	7,6944	7,1305
With metals	16,9208	12,1218	8,9612	7,9661	7,4028
With Cu / Mn / Ni	17,1844	12,3873	9,2268	8,2315	7,6683
With MQ water	17,184	16,7966	16,637	16,6724	16,789
Volumes (ml)					
1M H2SO4	9,433019	4,90717	1,924245	0,991321	0,492264
Metal stock	0,2685	0,2712	0,275	0,2717	0,2723
Cu / Ni / Mn stock	0,2636	0,2655	0,2656	0,2654	0,2655
Water	0	4,4093	7,4102	8,4409	9,1207
Acid content	0,946642	0,49803	0,194859	0,099437	0,048495

When these solutions were shaken with the solution of cyanex301 it was impossible to detect cadmium in the aqueous phases which had been shaken with the organic layer. In all cases the zinc distribution ratio was greater than 200 suggesting that it will be impossible to strip zinc using aqueous sulfuric acid. Tube numbers 3854 to 3868. As a result the data for this experiment was not fully processed.

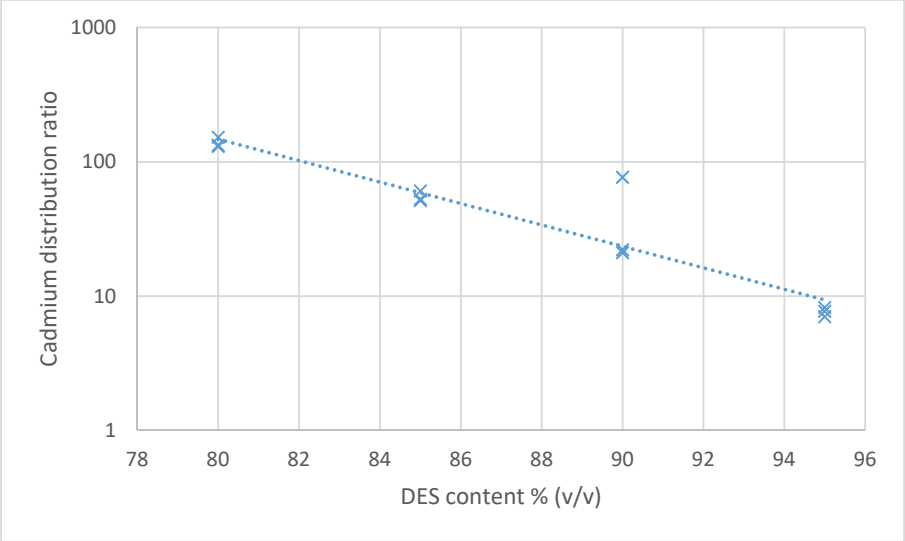
The relationship between water content of the DES layer and the distribution ratio

Tube numbers 3884 to 3916. The mixed Cd/Ni/Pd/Zn DES / sodium chloride mixtures used for the experiment with aliquat 336 in ethyl benzene was used for this experiment. Cyanex301 (5.1209 g) was placed in a 50 ml volumetric flask, the extractant was diluted to 50 ml with solvent 70 to form a solution with a relative density of 0.816.

These solutions of the four metals were shaken with the new solution of cyanex301 in solvent 70 at 30 ^{o}C for at least four hours. Some solid appeared in the tubes at first, this redissolved to form two clear layers. The solid may have been palladium sulfide formed by the trace of H_2S in the extractant. After shaking and centrifugation the contents of the tubes were examined with ICPOES, due to a spray chamber malfunction in the ICPOES the samples for 30 and 70 % needed to be diluted further and reexamined with the ICPMS.

The zinc distribution ratios were too high when the DES content was only 10 or 20 % to be used. Also the nickel and palladium distribution ratios were too high to be of use. When the DES content was below 80 % (v/v) the cadmium distribution ratios were too high to be trustworthy.

The cadmium data can be seen in the following graph.



The distribution ratios are listed in the following tables.

DES contents % (v/v)	10	10	10	20	20	20
D_{Cd}	511,1422	596,8971	1032,64	945,8963	987,1814	799,2422
D_{Zn}	352,0886	379,2415	582,6928	207,5466	205,7144	173,2705

DES contents % (v/v)	30	30	30	40	40	40
D_{Cd}	497	1709	577	1850,327	1313,661	1664,106
D_{Zn}	67,4	76,8	68,1	31,45919	31,08413	29,8018

DES contents % (v/v)	50	50	50	60	60	60
D_{Cd}	365,6545	329,3285	350,3243	692,5019	888,3016	695,1807
D_{Zn}	10,7319	10,88957	10,67251	3,684637	3,631351	3,589869

DES contents % (v/v)	70	70	70	80	80	80
D_{Cd}	283	502	413	133,007	129,9982	152,4495
D_{Zn}	1,24	1,22	1,21	0,300651	0,283954	0,293866

DES contents % (v/v)	85	85	85
D_{Cd}	60,55328	51,38861	52,6929
D_{Zn}	0,13806	0,143423	0,14417

DES contents % (v/v)	90	90	90	95	95	95
D_{Cd}	76,63659	22,07683	21,02534	8,233383	7,709772	7,033098
D_{Zn}	0,072339	0,050002	0,045516	0,026647	0,031808	0,030214

Effect of sodium lactate

Tubes 3869 to 3883, 25 July 2016.

The effect of sodium lactate on the extraction of zinc by cyanex301 from a 8:2 DES / water mixture was examined. Tube numbers 3869 to 3883.

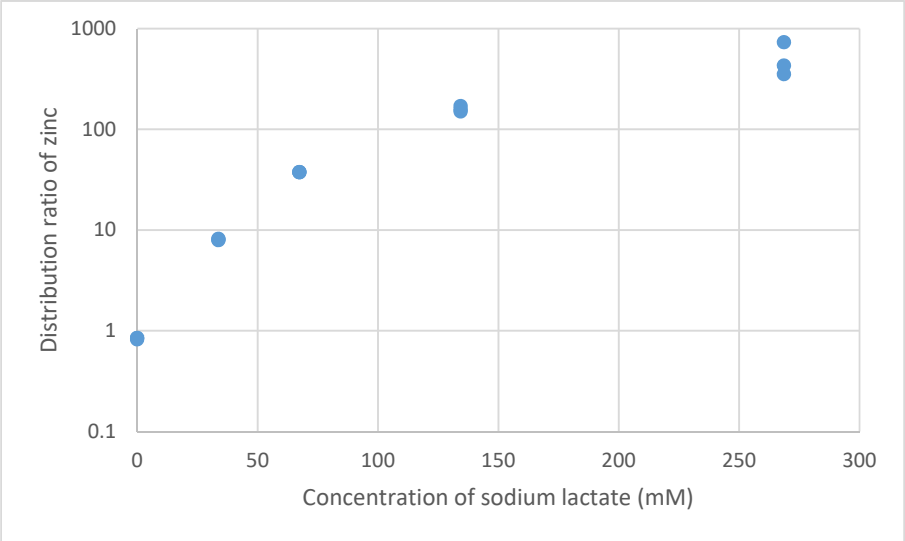
The organic phase was the same cyanex301 solution as was used in the variable water content experiment. The volumes of the two layers were 600 microlitres, overnight shaking at 30 °C was used.

The DES phases were made by combining the Cd/Ni/Pd/Zn metal stock with DES, sodium hydroxide solution and water to maintain the water content and ionic strength at constant values. The sodium hydroxide solution was 6.75 M (density 1.242). The details of the vials are in the following table.

Working name	Lactate concentration	Mass (g)				
		Empty	With metal stock	With DES	With sodium hydroxide solution	With water
No NaOH		6,7081	7,2271	16,5489	16,5484	17,9639
0.05 ml NaOH		6,6699	7,1889	16,5005	16,5624	17,9353
0.1 ml NaOH		6,6451	7,1684	16,4398	16,5629	17,8830
0.2 ml NaOH		6,6827	7,2001	16,5445	16,7912	18,0107
0.4 ml NaOH		6,7194	7,2269	16,5185	17,0093	18,0347

As before the nickel and palladium distribution ratios were too high to be measured. The cadmium distribution ratios are too high.

The results can be seen in the following graph.



The data for zinc is shown in the following tables.

Tube	**3869**	**3870**	**3871**	**3872**	**3873**	**3874**
Sodium lactate conc mM	0	0	0	33,8	33,8	33,8
D_{Zn}	0,820655	0,84636	0,846614	8,181815	8,033602	7,919809

Tube	**3875**	**3876**	**3877**	**3878**	**3879**	**3880**
Sodium lactate conc mM	67,4	67,4	67,4	134	134	134
D_{Zn}	37,56563	37,51572	37,4481	157,0863	170,1744	150,3661

Tube	**3881**	**3882**	**3883**
Sodium lactate conc mM	269	269	269
D_{Zn}	429,1617	353,1155	732,1141

Effect of sulfuric acid on the zinc distribution ratio.

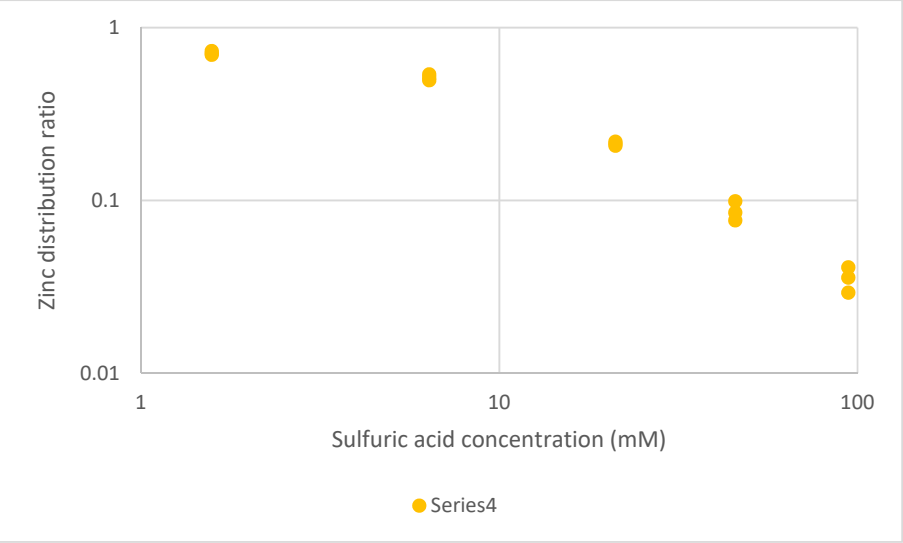
Tubes 3962 to 3979. 1st August 2016.

The effect of sulfuric acid in the 8:2 DES / water mixture was investigated by a similar method as to that used for the effect of sodium lactate.

To 17 ml polyethene vials was added Cd/Ni/Pd/Zn stock solution, sulfuric acid (1 M), water and DES to form a range of mixtures.

Tube numbers 3962 to 3979.

The results for zinc can be summarized in the following graph.



The resulted are also summed up in the following tables.

Concentration of sulfuric acid (mM)	0	0	0
Metal	Distribution ratio		
Cd	339,7993	443,6609456	452,9861924
Ni	1189,842	1287,680943	1280,952821
Pd	1141,727	1407,22963	990,6970837
Zn	0,766473	0,844704061	0,848453393

Concentration of sulfuric acid (mM)	1.58	1.58	1.58
Metal	Distribution ratio		
Cd	319,6806819	363,7765	414,1648
Ni	928,0059061	987,6483	985,8054
Pd	829,4226688	833,2436	952,3474
Zn	0,730791672	0,707798	0,69554

Concentration of sulfuric acid (mM)	6.38	6.38	6.38
Metal	Distribution ratio		
Cd	221,921	500,9513	245,7545

Ni	1029,224	619,0853	1259,192
Pd	741,5857	616,5955	993,5275
Zn	0,535051	0,512674	0,495455

Concentration of sulfuric acid (mM)	21.1	21.1	21.1
Metal	Distribution ratio		
Cd	121,668	157,8989	137,0147
Ni	14,1964	10,76152	10,65136
Pd	16,74736	12,9533	12,75792
Zn	0,2126	0,21842	0,206781

Concentration of sulfuric acid (mM)	45.6	45.6	45.60
Metal	Distribution ratio		
Cd	56,54999	44,91237	40,43027
Ni	2,63703	3,026454	6,325083
Pd	3,316082	3,765395	7,683434
Zn	0,0986	0,084843	0,076495

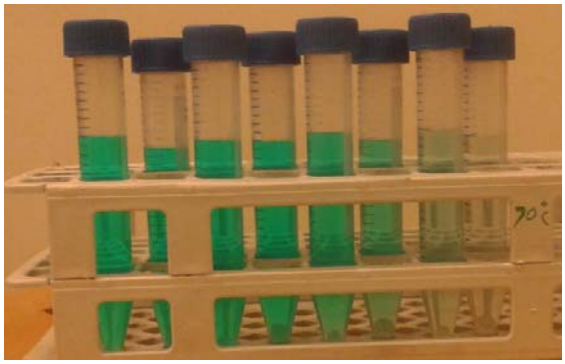
Concentration of sulfuric acid (mM)	94.4	94.4	94.4
Metal	Distribution ratio		
Cd	8,516198	7,858898	12,22166
Ni	1,23289	1,350132	1,674163
Pd	1,639707	1,774989	2,161408
Zn	0,040881	0,035679	0,02922

Thermochromism of the cobalt solutions.

A series of cobalt solutions were made by diluting an aqueous cobalt chloride (8 grams per litre cobalt) in a mixture of water and the DES according to the following table of masses. The solutions were made up in 17 ml ICP vials.

Name	Empty	With DES	After adding cobalt stock	After adding water
95 % DES	6.7019	17.7700	18.2828	18.2828
90 % DES	6.6753	17.1689	17.6797	18.1671
85 % DES	6.7003	16.6183	17.1348	18.1183
80 % DES	6.6892	16.0304	16.5440	18.0292
75 % DES	6.7058	15.4586	15.9721	17.9364
70 % DES	6.6990	14.8803	15.3943	17.8485
65 % DES	6.7144	14.3033	14.8140	17.7640
60 % DES	6.6887	13.7120	14.2289	17.6701

The tubes were violently shaken before being heated in a beaker of water at 70 °C. The tubes were taken out of the beaker and quickly placed in a testtube rack. The tubes were placed (left to right) in order of increasing water content. Before being photographed.



Photograph 1. Photograph of the tubes are 70 °C

The tubes were then placed in a beaker filled with a mixture of ice and water. After several hours in the beaker the tubes were again placed in the same order in the testtube rack. Again the tubes were photographed.

Photograph 2. Photograph of the tubes at 0 °C