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 %).

    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°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:

    \[
    D = \frac{(C_o - C_e)}{C_e}
    \]
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

| Code | Description                  |
|------|------------------------------|
| M    | 30 % Malonamide in solvent 70|
| C    | 30 % Cyanex 923 in solvent 70|
| A    | 10 % Aliquat 336 in ethyl benzene |
Sodium chloride / DES system.

| DES % (v/v) | 106Pd | 106Pd | 115In | 115In | 115In | 187Re | 187Re | 197Au | 197Au |
|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 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

| DES % (v/v) | Extractant | 106Pd | 106Pd | 115In | 115In | 115In | 187Re | 187Re | 197Au | 197Au |
|-------------|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|             | M C M C A M C C A |
| 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 |
## 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
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              |
| 10                               | 4                    | 0.0184             |
|                                  |                      | 0.0587             |
|                                  |                      | 0.0438             |
|                                  |                      | 1.04               |
| 10                               | 4                    | 0.00222            |
|                                  |                      | 0.00646            |
|                                  |                      | -0.0153            |
|                                  |                      | 0.687              |
| 20                               | 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               |
Malonamide content (% v/v) vs. Gold distribution ratio

Malonamide content (% v/v) vs. Gold ratio
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 (HAuCl₄ • 3H₂O, 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 %) | 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           | 17.1493 |
| 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 %) | 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%) | 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.
| 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                         |
| 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°C) for about 30 minutes. After three days, the mixture was filtered to form a Pd stock solution (Na₂PdCl₄). 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.

| DES (v/v %) | 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.
| DES (v/v %) | Mass (g) | Mass (g) | Mass (g) | Mass (g) | 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   | 11.1542  | 17.6141  |
| 70         | 6.7041    | 6.9641   | 7.0572   | 10.1452  | 17.6141  |
| 80         | 6.6997    | 6.9641   | 7.0572   | 9.0954   | 17.6141  |
| 90         | 6.6960    | 6.9604   | 7.0588   | 8.0932   | 17.6729  |

| NaCl (v/v %) | Mass (g) | Mass (g) | Mass (g) | Mass (g) | 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    |
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     |
| 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 molybdenum-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 pertechnetate 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 polyethylene 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 pertechnetinate 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 $2.9 \times 10^{-11}$ 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 $^{99}\text{Tc}$ 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 $^{99m}\text{Tc}$ 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.
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.

Extractations 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

Extractations 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.

![](image)

**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 ICPMS machine was loaded 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, 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,

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.

\[ D_M = \frac{[M_{total}^{org}]}{[M_{total}^{aq}]} \]

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.

\[ K_D = \frac{f_{Xe_{org}}}{f_{Xe_{aq}}} \]
Thus we can write after rearrangement

\[ D_M = \frac{K_D f_{\text{Xe}_a}}{f_{\text{Xe}_o}} \]

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.

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

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

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

\[ \text{ML}_{(\text{n-1})} + L \leftrightarrow \text{ML}_n \]

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

\[ \beta_n = \frac{[\text{ML}_n]}{[\text{M}][\text{L}]^n} \]

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.

\[ [\text{ML}_{n_{\text{aq}}}] = \beta_n[L]^n \]

\[ [\text{M}_{\text{total}}_{\text{aq}}] = \frac{1 + K_1[L] + \beta_2[L]^2}{1 + K_1[L] + \beta_2[L]^2} \]

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

\[ [\text{ML}_{n_{\text{org}}}] = \frac{K_{\text{DML}_n}[\text{M}_{\text{total}}_{\text{aq}}]\beta_n[L]^n}{1 + K_1[L] + \beta_2[L]^2} \]

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

\[ D_M = \frac{K_{\text{DML}}[\text{M}_{\text{total}}_{\text{aq}}]}{1 + K_1[L] + \beta_2[L]^2} + \frac{K_{\text{DML}}[\text{M}_{\text{total}}_{\text{aq}}]K_1[L]}{1 + K_1[L] + \beta_2[L]^2} + \frac{K_{\text{DML}}[\text{M}_{\text{total}}_{\text{aq}}]\beta_2[L]^2}{1 + K_1[L] + \beta_2[L]^2} \]

\[ [\text{M}_{\text{total}}_{\text{aq}}] \]
This equation can be simplified a little to provide

\[
D_M = \frac{K_{DM}}{1 + K_1[L] + \beta_2[L]^2} + \frac{K_{DM} K_1[L]}{1 + K_1[L] + \beta_2[L]^2} + \frac{K_{DM} \beta_2[L]^2}{1 + K_1[L] + \beta_2[L]^2}
\]

A fuller equation could be created which would be

\[
D_M = \frac{K_{DM}}{1 + K_1 \left( \frac{[L_{org}]}{K_{DL}} \right) + \beta_2 \left( \frac{[L_{org}]}{K_{DL}} \right)^2} + \frac{K_{DM} K_1 \left( \frac{[L_{org}]}{K_{DL}} \right)}{1 + K_1 \left( \frac{[L_{org}]}{K_{DL}} \right) + \beta_2 \left( \frac{[L_{org}]}{K_{DL}} \right)^2} + \frac{K_{DM} \beta_2 \left( \frac{[L_{org}]}{K_{DL}} \right)^2}{1 + K_1 \left( \frac{[L_{org}]}{K_{DL}} \right) + \beta_2 \left( \frac{[L_{org}]}{K_{DL}} \right)^2}
\]

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.

\[
D_M = \frac{K_{DM} \beta_2 \left( \frac{[L_{org}]}{K_{DL}} \right)^2}{1 + K_1 \left( \frac{[L_{org}]}{K_{DL}} \right) + \beta_2 \left( \frac{[L_{org}]}{K_{DL}} \right)^2}
\]

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

\[
D_M = K_{DM} \beta_2 \left( \frac{[L_{org}]}{K_{DL}} \right)^2
\]

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

\[
D_M = \frac{K_{DM} \beta_2 \left( \frac{[L_{org}]}{K_{DL}} \right)^2}{K_{DL}^2}
\]

This equation can be rewritten with a new constant \( k' \)

\[
D_M = k' \left[ [L_{org}] \right]^2
\]

Where \( k' \) is given by the following equation

\[
k' = \frac{K_{DM} \beta_2}{K_{DL}^2}
\]
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.

\[ \text{AuCl}_3 + \text{Cl}^- \rightarrow \text{AuCl}_4^- \]

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

\[ K_4 = \frac{a_{\text{AuCl}_4^-}}{a_{\text{Cl}^-} a_{\text{AuCl}_3}} \]

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

\[ K_4 = \frac{f_{\text{AuCl}_4^-}[\text{AuCl}_4^-]}{f_{\text{Cl}^-}[\text{Cl}^-] f_{\text{AuCl}_3}[\text{AuCl}_3]} \]

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$_3$MA$_n$) in the organic phase. The chemical equation for the forward reaction in this equilibrium is

\[ \text{AuCl}_3(\text{aq}) + n\text{MA}_{\text{org}} \rightarrow \text{AuCl}_3\text{Ma}_{\text{org}}(\text{org}) \]

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

\[ K_{ex} = \frac{f_{\text{AuCl}_3\text{MA}_n_{\text{org}}}[\text{AuCl}_3\text{MA}_n_{\text{org}}]}{f_{\text{AuCl}_3_{\text{aq}}}[\text{AuCl}_3_{\text{aq}}] f_{\text{MA}_{\text{org}}}[\text{MA}_{\text{org}}]^n} \]

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.

\[ K_{ex} = \frac{C[\text{AuCl}_3\text{MA}_n_{\text{org}}]}{f_{\text{AuCl}_3_{\text{aq}}}[\text{AuCl}_3_{\text{aq}}]} \]

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.

\[ K_{ex} = \frac{C[\text{AuCl}_3\text{MA}_n_{\text{org}}]}{[\text{AuCl}_3_{\text{aq}}]} \]
Returning to the equation for the equilibrium between the different forms of gold in the aqueous phase, we can now write.

\[
\frac{[\text{AuCl}_3]}{[\text{AuCl}_4] + [\text{AuCl}_3]} = \frac{K_4[\text{Cl}^-][\text{AuCl}_3]f_{\text{Cl}^-}\text{f}_{\text{AuCl}_3}}{f_{\text{AuCl}_4} + K_4[\text{Cl}^-][\text{AuCl}_3]f_{\text{Cl}^-}\text{f}_{\text{AuCl}_3}}
\]

And

\[
\frac{[\text{AuCl}_3]}{[\text{AuCl}_4] + [\text{AuCl}_3]} = \frac{[\text{AuCl}_3]}{[\text{AuCl}_3] + \left(\frac{K_4[\text{Cl}^-][\text{AuCl}_3]f_{\text{Cl}^-}\text{f}_{\text{AuCl}_3}}{f_{\text{AuCl}_4}}\right)}
\]

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

\[
\frac{[\text{AuCl}_3]}{[\text{AuCl}_4] + [\text{AuCl}_3]} = \frac{1}{1 + \left(\frac{K_4[\text{Cl}^-]f_{\text{Cl}^-}\text{f}_{\text{AuCl}_3}}{f_{\text{AuCl}_4}}\right)}
\]

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.

\[
\frac{[\text{AuCl}_3]}{[\text{Au}]_{\text{total}}} = \frac{1}{1 + \left(\frac{K_4[\text{Cl}^-]f_{\text{Cl}^-}\text{f}_{\text{AuCl}_3}}{f_{\text{AuCl}_4}}\right)}
\]

Next if we combine this last equation with

\[
\frac{K_{\text{ex}}[\text{AuCl}_3]_{\text{aq}}}{C} = [\text{AuCl}_3\text{MA}_n]_{\text{org}}
\]

We can get

\[
\frac{[\text{AuCl}_3\text{MA}_n]_{\text{org}}}{[\text{Au}]_{\text{total}}} = \frac{K_{\text{ex}}}{C} \left(\frac{[\text{AuCl}_3]}{[\text{Au}]_{\text{total}}}\right)
\]
As the distribution ratio is the total organic concentration of gold divided by the total aqueous concentration of gold we can now write.

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

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

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

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.

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

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

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

While for the tetrachloroaurate anion we write

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

Now when

\[ X = Y \cdot Z \]

Then

\[ \log_{10}X = (\log_{10}Y) + (\log_{10}Z) \]

So
We can rearrange this to give

\[
\frac{f_{Cl}^-}{f_{AuCl}_4^-} = 10 \left( \frac{-z_2^2 A_{Cl} + \epsilon_{Na,Cl} [Na^+] + \epsilon_{Na,Cl} [Na^+] + \epsilon_{Na,AuCl}_4 [Na^+] + \epsilon_{Ch,AuCl}_4 [Ch^+]}{1 + (1.5\sqrt{j})} \right)
\]

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

\[
\frac{f_{Cl}^-}{f_{AuCl}_4^-} = 10 \left( \frac{-z_2^2 A_{Cl} - (-z_2^2 A_{Cl}) + \epsilon_{Na,Cl} [Na^+] + \epsilon_{Na,Cl} [Na^+] + \epsilon_{Na,AuCl}_4 [Na^+] + \epsilon_{Ch,AuCl}_4 [Ch^+]}{1 + (1.5\sqrt{j})} \right)
\]

This can be rearranged a little further to give

\[
\frac{f_{Cl}^-}{f_{AuCl}_4^-} = 10 \left( \frac{\epsilon_{Na,Cl} [Na^+] + \epsilon_{Na,Cl} [Na^+] + \epsilon_{Na,AuCl}_4 [Na^+] + \epsilon_{Ch,AuCl}_4 [Ch^+]}{\epsilon_{Na,AuCl}_4 [Na^+] + \epsilon_{Ch,AuCl}_4 [Ch^+]} \right)
\]

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

\[
\log \frac{f_{Cl}^-}{f_{AuCl}_4^-} = \Delta \varepsilon_1 [Na^+] + \Delta \varepsilon_2 [Na^-]
\]

Where

\[
\Delta \varepsilon_1 = \varepsilon (Na^{+},Cl^-) + \varepsilon (Ch^+,AuCl^-_4) - \varepsilon (Ch^+,Cl^-) - \varepsilon (Na^+,AuCl^-)
\]

and

\[
\Delta \varepsilon_2 = \varepsilon (Ch^+,Cl^-) - \varepsilon (Ch^+,AuCl^-)
\]
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

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

From this we can move to

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

So

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

We can now make this a bit more simple

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

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

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

Which can be expressed as the following way if only one form of the metal can be found in the organic phase.
\[ D_M = \frac{Z K_{ex} \left( \frac{K_1 [Cl^-] f_M + f_{Cl^-}}{f_{MCl}} \right)}{1 + \left( \frac{K_1 [Cl^-] f_M + f_{Cl^-}}{f_{MCl}} \right)} \]
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)

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

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

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

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

We can combine these equations to create the following

\[
\beta_2 = K_1 K_2 = \frac{f_{AuCl^2+} [AuCl^2+]}{f_{Cl^-} [Cl^-] f_{Au} [Au^3+] f_{AuCl} [AuCl^2+]} \frac{f_{AuCl^+} [AuCl^+]}{f_{Cl^-} [Cl^-] f_{AuCl^2} [AuCl^2+]}
\]

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

\[
\beta_2 = \frac{1}{f_{Cl^-} [Cl^-] f_{Au} [Au^3+] f_{Cl^-} [Cl^-] f_{AuCl} [AuCl^2+]} \frac{f_{AuCl^+} [AuCl^+]}{f_{Cl^-} [Cl^-] f_{Au} [Au^3+] f_{Cl^-} [Cl^-]}
\]

We can rewrite it in a neater way

\[
\beta_2 = \frac{f_{AuCl^+} [AuCl^+]}{f_{Cl^-} [Cl^-] f_{Au} [Au^3+] f_{Cl^-} [Cl^-]}
\]

We can repeat the process and then create

\[
\beta_3 = \frac{f_{AuCl_3} [AuCl_3]}{f_{Cl^-} [Cl^-] f_{Au} [Au^3+] f_{Cl^-} [Cl^-]}
\]

\[
\beta_3 = \frac{f_{AuCl_3} [AuCl_3]}{f_{Cl^-} [Cl^-] f_{Au} [Au^3+] f_{Cl^-} [Cl^-]}
\]
\[
\beta_4 = \frac{f_{AuCl_4^4} [AuCl_4^-]}{f_{AuCl_4^4}^4 \left[ [Cl^-]^4 f_{Au^{3+}} + [Au^{3+}] \right]}
\]

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.

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

\[
\frac{\beta f_{Cl^-}^2 [Cl^-]^2 f_{Au^{3+}}}{f_{AuCl_2^+}} = \left[ AuCl_2^- \right] \quad [Au^{3+}]
\]

\[
\frac{\beta f_{Cl^-}^3 [Cl^-]^3 f_{Au^{3+}}}{f_{AuCl_3^-}} = \left[ AuCl_3^- \right] \quad [Au^{3+}]
\]

\[
\frac{\beta f_{Cl^-}^4 [Cl^-]^4 f_{Au^{3+}}}{f_{AuCl_4^-}} = \left[ AuCl_4^- \right] \quad [Au^{3+}]
\]

If we combine the equations we can get

\[
\frac{[AuCl_3]}{[Au_{total}]} = \frac{\frac{\beta f_{Cl^-}^3 [Cl^-]^3 f_{Au^{3+}}}{f_{AuCl_3^-}}}{1 + \frac{f_{AuCl^{2+}}}{f_{Au^{3+}}}} + \frac{\frac{\beta f_{Cl^-}^2 [Cl^-]^2 f_{Au^{3+}}}{f_{AuCl_2^+}}}{f_{AuCl_3^-}} + \frac{\frac{\beta f_{Cl^-} [Cl^-] f_{Au^{3+}}}{f_{AuCl^{2+}}}}{f_{AuCl_3^-}} + \frac{\frac{f_{AuCl^{2+}}}{f_{Au^{3+}}}}{f_{AuCl_4^-}}
\]

We can make this a little more simple

\[
\frac{[AuCl_3]}{[Au_{total}]} = \frac{\frac{\beta f_{Cl^-}^3 [Cl^-]^3 f_{Au^{3+}}}{f_{AuCl_3^-}}}{1 + \frac{f_{AuCl^{2+}}}{f_{Au^{3+}}}}
\]

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.

$$K_4 = \frac{[\text{InCl}_4^-]}{[\text{InCl}_3][\text{Cl}^-]}$$

If we add the activity functions then we now have

$$K_4 = \frac{f_{\text{InCl}_4^-}[\text{InCl}_4^-]}{f_{\text{InCl}_3}[\text{InCl}_3]f_{\text{Cl}^-}[\text{Cl}^-]}$$

We can rearrange this to give

$$[\text{InCl}_4^-] = \frac{K_4[\text{Cl}^-][\text{InCl}_3]f_{\text{Cl}^-}f_{\text{InCl}_3}}{f_{\text{InCl}_4^-}}$$

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

$$\frac{[\text{InCl}_4^-]}{[\text{InCl}_4^-] + [\text{InCl}_3]} = \frac{K_4[\text{Cl}^-][\text{InCl}_3]f_{\text{Cl}^-}f_{\text{InCl}_3}}{f_{\text{InCl}_4^-} ([\text{InCl}_4^-] + \frac{[\text{InCl}_3][\text{Cl}^-]f_{\text{Cl}^-}f_{\text{InCl}_3}}{f_{\text{InCl}_4^-}})}$$

Next we can remove the $[\text{InCl}_3]$ terms from the right hand side of the equation.

$$\frac{[\text{InCl}_4^-]}{[\text{InCl}_4^-] + [\text{InCl}_3]} = \frac{K_4[\text{Cl}^-]f_{\text{Cl}^-}f_{\text{InCl}_3}}{f_{\text{InCl}_4^-} (1 + \frac{K_4[\text{Cl}^-]f_{\text{Cl}^-}f_{\text{InCl}_3}}{f_{\text{InCl}_4^-}})}$$

If we assume that all of the indium in the lower phase is in the form of either the neutral InCl$_3$ or the anionic InCl$_4$- complex then we can write.

$$\frac{[\text{InCl}_4^-]}{\Sigma[\text{In}]_{aq}} = \frac{K_4[\text{Cl}^-]f_{\text{Cl}^-}f_{\text{InCl}_3}}{f_{\text{InCl}_4^-} (1 + \frac{K_4[\text{Cl}^-]f_{\text{Cl}^-}f_{\text{InCl}_3}}{f_{\text{InCl}_4^-}})}$$
Next we can rearrange the equation slightly

$$[\text{InCl}_4^-] = \left( \frac{K_4[\text{Cl}^-]f_{\text{Cl}^-}f_{\text{InCl}_3}}{f_{\text{InCl}_4^-}} \right) \Sigma [\text{In}]_{aq}$$

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

$$K_{ex} = \frac{[\text{InCl}_4^-]_{org}f_{\text{InCl}_4^-}[\text{Cl}^-]_{org}f_{\text{Cl}^-}}{[\text{InCl}_4^-]_{org}[\text{Cl}^-]_{org}f_{\text{Cl}^-}}$$

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.

$$K_{ex} = \frac{[\text{InCl}_4^-]_{org}k[\text{Cl}^-]f_{\text{Cl}^-}}{[\text{InCl}_4^-]f_{\text{InCl}_4^-}}$$

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

$$1 \left[ \frac{K_{ex}k[\text{Cl}^-]f_{\text{Cl}^-}}{[\text{InCl}_4^-]_{org}[\text{InCl}_4^-]f_{\text{InCl}_4^-}} \right]$$

Next turn the equation upside down to give us

$$[\text{InCl}_4^-]_{org} = \frac{[\text{InCl}_4^-]f_{\text{InCl}_4^-}}{K_{ex}k[\text{Cl}^-]f_{\text{Cl}^-}}$$

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

$$[\text{InCl}_4^-]_{org} = \frac{f_{\text{InCl}_4^-}}{K_{ex}k[\text{Cl}^-]f_{\text{Cl}^-}} \left( \frac{K_4[\text{Cl}^-]f_{\text{Cl}^-}f_{\text{InCl}_3}}{f_{\text{InCl}_4^-}} \right) \Sigma [\text{In}]_{aq}$$

We can express ourselves in terms of the distribution ratio using the following equation.
\[ D_{In} = \frac{f_{InCl}^{-}}{K_{ex}k[Cl^-]f_{Cl}^-} \left( \frac{\left( \frac{K_4[Cl^-]}{f_{Cl}^-} \right) f_{Cl}^- f_{InCl}}{f_{InCl}^-} \right) \left( \frac{1}{1 + \left( \frac{K_4[Cl^-]}{f_{Cl}^-} \right) f_{Cl}^- f_{InCl}} \right) \]

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.

\[ D_{In} = \frac{f_{InCl}^{-}}{K_{ex}k[Cl^-]f_{Cl}^-} \left( \frac{\left( \frac{K_4[Cl^-]}{f_{Cl}^-} \right) f_{Cl}^- f_{InCl}}{f_{InCl}^-} \right) \left( \frac{1}{1 + \left( \frac{K_4[Cl^-]}{f_{Cl}^-} \right) f_{Cl}^- f_{InCl}} \right) \]
Section Fs.

1 Explanation of method used in excel to calculate Δε₁ and Δε₂

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  | $\varepsilon_{Na,Cl}$ | 0.0406   |
| B      | 15  | $\varepsilon_{Ch, Cl}$ | 0.0074   |
| B      | 16  | $\varepsilon_{Na,AuCl_4}$ | $B28-2$ |
| B      | 17  | $\varepsilon_{Ch, AuCl_4}$ | $B29-2$ |
| 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 column D which have the correct sodium ion concentrations.

In column I we have the following equations in cells
=ABS(LOG10(I{X}/G{X}))

The sum of the error values in column I are then sent to B26 by placing in B26 the following
=SUM(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 $\chi_{\text{CH}^+,\text{ReO}_4^-}$ to be -0.427. For palladium extraction in the model $\psi_{\text{PdCl}_2^2-,\text{Cl}^-}$, $\varepsilon_{\text{Na}^+,\text{PdCl}_2^2}$, $\varepsilon_{\text{Ch}^+,\text{PdCl}_2^2}$ and $C''K_{ex}$ are -2.19, 0.00, -0.611 and $2.01 \times 10^{-6}$ 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.

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

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

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

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

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

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

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

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 simplify 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

Equation 28

Equation 29
E. Dziwinski and J. Szymanowski, *Solvent Extraction and Ion Exchange*, 1998, 16, 1515.