

Studies on the Extraction of Metal Complexes

VIII. The Extraction of La, Sm, Hf, Th, and U(VI) with Oxine and Cupferron

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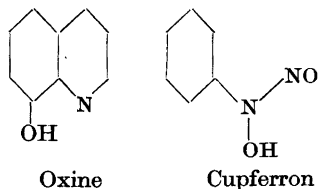
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Solvent extraction has proved to be an important method for the separation and determination of metals in analytical chemistry. The procedures worked out in that field should be applicable to chemical industry as well as in preparative laboratory work since extraction is a very practical unit operation. With a multistage countercurrent extraction process a practically complete fractionation of materials which are closely related may be obtained.

The importance of solvent extraction led our group to study the extraction of lanthanide and actinide complexes with organic solvents. For this purpose, the following metal ions were chosen: La^{+3} (radius* = 1.15 Å), Sm^{3+} ($r = 1.07$ Å), Th^{4+} ($r = 1.02$ Å), Hf^{4+} ($r = 0.86$ Å) and UO_2^{2+} . As the behavior of these elements to some extent is determined by the ion charges and sizes it might be feasible to predict the behavior of other rare earth metals as of the transuranium elements, *e.g.* Am^{3+} ($r = 1.11$ Å) or Pu^{4+} ($r = 0.92$ Å).

It was further considered as favorable if the distribution of the metals between the two phases could be measured radiometrically; suitable radioisotopes were available for La (La^{140}), Sm (Sm^{153}), Hf (Hf^{181}), and Th (Th^{234} , UX_1). Two organic solvents were used, chloroform and hexone (methyl isobutyl ketone). Chloroform is known as a very good solvent for metal chelates and hexone was chosen as representative for oxygen-containing solvents.

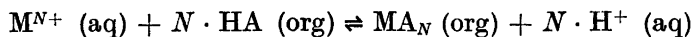
The ionic strength in the aqueous phase was kept constant at 0.1 *M* using HClO_4 , NaClO_4 and NaOH , and all experiments were carried out at 25° C. In the following part the extraction of the oxinates and cupferrates are reported.



* The radii are approximately given in the Pauling scale by comparison with data by Zachariasen¹.

INTERPRETATION OF DATA

Data on metal extraction with complex forming agents (HA) such as dithizone and oxine are usually given in diagrams plotting the per cent metal extracted against the pH for a given reagent concentration. The theoretical understanding of these curves have been based on the following reaction



with the equilibrium constant

$$K = \frac{[\text{MA}_N]_{\text{org}} \cdot [\text{H}^+]^N}{[\text{M}^{N+}] \cdot [\text{HA}]_{\text{org}}^N}$$

This equation is however only valid when the water-soluble M—A complexes may be neglected.

From the very beginning of our work we looked upon this problem of metal extraction as a stepwise complex formation of M^{N+} with a ligand A^- giving among other complexes MA_n , an uncharged extractable complex MA_N . With the use of radioactive tracers we extended the measurable range of the net distribution ratio of M,

$$q = \frac{[\text{M}]_{\text{total, org}}}{[\text{M}]_{\text{total, aq}}}$$

from about 100—0.01 to about 1 000—0.001. In doing so we found in most cases that q approached a maximum value (see Fig. 1). This could be explained by assuming the presence of MA_N in the aqueous phase. The distribution constant of this complex is

$$\lambda_N = \frac{[\text{MA}_N]_{\text{org}}}{[\text{MA}_N]_{\text{aq}}}$$

Furthermore the data could only be explained if all the complexes MA , MA_2 , MA_N were considered. In the mathematical treatment^{2,3} of our data we have found it most useful to plot $\log q$ against $\log [A^-]$. Calculations on these curves have enabled the more or less independent determination of λ_N and the various complexity products κ_n .

$$\kappa_n = \frac{[\text{MA}_n]}{[\text{M}][\text{A}]^n} = k_1 \cdot k_2 \cdot \dots \cdot k_n$$

Most of the experimental data in this work is therefore found in other articles^{4,5}, where the complex formation constants and distribution constants are calculated. The $\log q$ curves in those papers are here transformed to curves where the ordinate is $100 \cdot q/1 + q$, *i.e.* per cent metal extracted. Figure 1 shows an evenly spaced family of $\log q$ curves with different values of λ_N and how it spreads out around $q = 1$ in the $100 \cdot q/1 + q$ interpretation. The characteristic type of curves in Figure 6 are obtained when $\log \lambda_N \geq 2$.

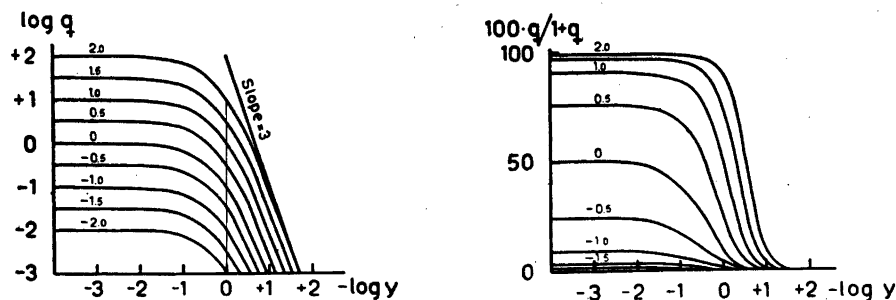


Fig. 1. Variation of the net distribution ratio q in two different graphical representations for various values for the logarithm of the partition coefficient λ_0 of the uncharged complex MA_3 . Abscissa: $-\log y = -\log [A^-] - a$ (cf. part V³, the parameter b is 0.25, $N = S = 3$).

As stated above the abscissa chosen is generally pH while we prefer to use $-\log [A^-]$. With this representation the points for different values of the initial reagent concentration in one phase, C_A , will usually coincide. In Figures 2 and 3 the relations between pH ($-\log [H^+]$) and $-\log [A^-]$ for the oxine-chloroform and cupferron-hexone, cupferron-chloroform systems are shown.

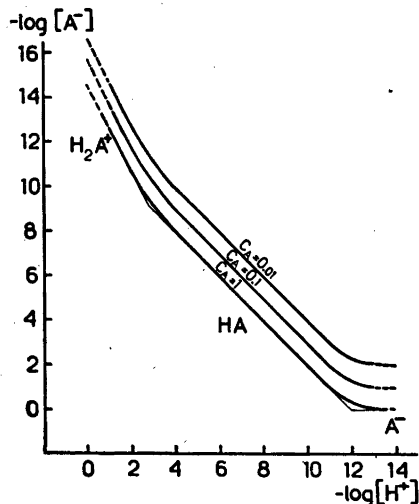


Fig. 2. The oxinate ion concentration ($-\log [A^-]$) as a function of the hydrogen ion concentration for different values of the initial oxine concentration in the chloroform phase C_A (in moles/lit.). The volume of the aqueous phase is equal to the volume of the organic phase.

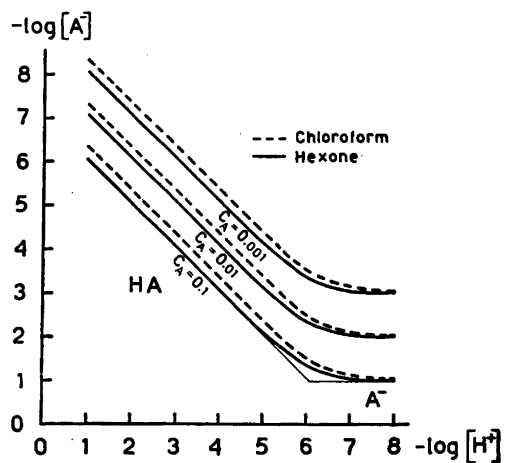


Fig. 3. The cupferrate ion concentration ($-\log [A^-]$) as a function of the hydrogen ion concentration for different values of the initial Na-cupferrate concentration in the aqueous phase C_A (in moles/lit.). The volume of the aqueous phase is equal to the volume of the organic phase.

Table 1. Distribution of UO_2^{2+} . The oxine-chloroform system.

| Initial conc. of oxine in the CHCl_3 phase M | Initial conc. of U in the aq. phase M | $\frac{100 \cdot q}{1 + q}$ | $\log q$ | $-\log [\text{H}^+]$ | $-\log [\text{A}^-]$ |
|--|--|-----------------------------|----------|----------------------|----------------------|
| 0.100 | 0.001 | 0.1 | (-3.00) | 1.91 | 11.95 |
| 0.100 | 0.001 | 0.5 | (-2.30) | 2.05 | 11.70 |
| 0.100 | 0.001 | 2.8 | (-1.54) | 2.21 | 11.42 |
| 0.100 | 0.001 | 9.4 | -0.98 | 2.34 | 11.21 |
| 0.100 | 0.001 | 32.1 | -0.32 | 2.46 | 11.03 |
| 0.100 | 0.001 | 36.2 | -0.24 | 2.48 | 11.00 |
| 0.100 | 0.001 | 55.5 | +0.11 | 2.57 | 10.87 |
| 0.100 | 0.001 | 57.6 | +0.13 | 2.59 | 10.84 |
| 0.100 | 0.001 | 55.5 | +0.11 | 2.68 | 10.71 |
| 0.100 | 0.001 | 79.2 | +0.59 | 2.71 | 10.67 |
| 0.100 | 0.001 | 85.2 | +0.77 | 2.73 | 10.64 |
| 0.100 | 0.0001 | 4.6 | (-1.32) | 2.23 | 11.39 |
| 0.100 | 0.0001 | 16.2 | -0.70 | 2.32 | 11.25 |
| 0.100 | 0.0001 | 40.4 | -0.16 | 2.46 | 11.03 |
| 0.100 | 0.0001 | 56.6 | +0.11 | 2.58 | 10.85 |
| 0.100 | 0.0001 | 69.2 | +0.35 | 2.59 | 10.84 |
| 0.100 | 0.0001 | 77.4 | +0.54 | 2.63 | 10.78 |
| 0.100 | 0.0001 | 81.6 | +0.65 | 2.67 | 10.72 |
| 0.100 | 0.0001 | 90.5 | +0.97 | 2.72 | 10.66 |
| 0.100 | 0.0001 | 94.0 | (+1.20) | 2.79 | 10.56 |
| 0.100 | 0.0001 | 94.5 | (+1.24) | 2.85 | 10.49 |
| 0.100 | 0.0001 | 99.0 | (+1.99) | 3.53 | 9.69 |
| 0.100 | 0.0001 | 84.4 | +0.73 | 10.38 | 2.57 |
| 0.100 | 0.0001 | 77.5 | +0.54 | 10.55 | 2.41 |
| 0.100 | 0.0001 | 68.2 | +0.33 | 10.77 | 2.20 |
| 0.100 | 0.0001 | 58.2 | +0.14 | 10.90 | 2.08 |
| 0.100 | 0.0001 | 47.5 | -0.05 | 11.17 | 1.84 |
| 0.050 | 0.0001 | 12.1 | -0.86 | 2.40 | 11.42 |
| 0.050 | 0.0001 | 18.8 | -0.64 | 2.45 | 11.34 |
| 0.050 | 0.0001 | 22.3 | -0.54 | 2.49 | 11.29 |
| 0.050 | 0.0001 | 29.1 | -0.39 | 2.53 | 11.23 |
| 0.050 | 0.0001 | 39.3 | -0.19 | 2.59 | 11.14 |
| 0.050 | 0.0001 | 46.6 | -0.06 | 2.71 | 10.97 |
| 0.050 | 0.0001 | 67.9 | +0.40 | 2.85 | 10.79 |
| 0.050 | 0.0001 | 72.5 | +0.42 | 2.88 | 10.75 |
| 0.050 | 0.0001 | 79.7 | +0.59 | 2.98 | 10.61 |
| 0.050 | 0.0001 | 83.8 | +0.71 | 3.04 | 10.54 |
| 0.020 | 0.0001 | 6.7 | (-1.14) | 2.69 | 11.40 |
| 0.020 | 0.0001 | 6.7 | (-1.14) | 2.75 | 11.31 |
| 0.020 | 0.0001 | 10.8 | -0.87 | 2.79 | 11.26 |
| 0.020 | 0.0001 | 15.9 | -0.72 | 2.78 | 11.27 |
| 0.020 | 0.0001 | 19.1 | -0.63 | 2.86 | 11.17 |
| 0.020 | 0.0001 | 35.3 | -0.26 | 3.04 | 10.95 |
| 0.020 | 0.0001 | 53.1 | +0.05 | 3.19 | 10.77 |
| 0.020 | 0.0001 | 76.1 | +0.51 | 3.43 | 10.49 |
| 0.020 | 0.0001 | 86.5 | +0.81 | 3.54 | 10.38 |
| 0.020 | 0.0001 | 86.5 | +0.81 | 3.70 | 10.22 |

Table 2. Distribution of UO_2^{2+} . The oxine-hexone system.

| Initial conc. of oxine in the CHCl_3 phase M | Initial conc. of U in the aq. phase M | $\frac{100 \cdot q}{1 + q}$ | $\log q$ | $-\log [\text{H}^+]$ | $-\log [\text{A}^-]$ |
|--|--|-----------------------------|----------|----------------------|----------------------|
| 0.100 | 0.001 | 4.7 | (-1.31) | 2.32 | 11.17 |
| 0.100 | 0.001 | 12.7 | -0.83 | 2.44 | 10.97 |
| 0.100 | 0.001 | 20.2 | -0.59 | 2.53 | 10.81 |
| 0.100 | 0.001 | 27.5 | -0.41 | 2.57 | 10.75 |
| 0.100 | 0.001 | 37.5 | -0.21 | 2.63 | 10.65 |
| 0.100 | 0.001 | 48.8 | -0.02 | 2.65 | 10.61 |
| 0.100 | 0.001 | 59.0 | +0.16 | 2.74 | 10.47 |
| 0.100 | 0.001 | 66.0 | +0.29 | 2.78 | 10.40 |
| 0.100 | 0.001 | 72.5 | +0.43 | 2.82 | 10.35 |
| 0.100 | 0.001 | 80.5 | +0.62 | 2.91 | 10.21 |
| 0.100 | 0.001 | 83.3 | +0.70 | 2.93 | 10.17 |

These curves are calculated from data given in Part IV of this series⁶. It is seen from the curves that the same $-\log [\text{A}^-]$ value may be obtained for different C_A values simply by changing $-\log [\text{H}^+]$ in the aqueous phase. The figures also show that the oxine-chloroform systems has two buffer points at $-\log [\text{H}^+]$ 2.72 ($\text{pk}_1 - \log p$) and 11.94 ($\text{pk}_2 + \log p$) and that the cupferron-hexone system has one point at $-\log [\text{H}^+]$ 6.09 ($\text{pk}_a + \log p$).

Table 3. Distribution of UO_2^{2+} . The cupferron-chloroform system.

| Initial conc. of Na-cupferrate in the aq. phase M | Initial conc. of U in the aq. phase M | $\frac{100 \cdot q}{1 + q}$ | q^* | $-\log [\text{H}^+]$ | $-\log [\text{A}^-]$ |
|--|--|-----------------------------|-------|----------------------|----------------------|
| 0.01 | 0.0001 | 7.3 | | 2.42 | 5.92 |
| 0.01 | 0.0001 | 14.3 | | 2.86 | 5.48 |
| 0.01 | 0.0001 | 24.8 | | 3.22 | 5.12 |
| 0.01 | 0.0001 | 36.1 | 0.57 | 3.58 | 4.76 |
| 0.01 | 0.0001 | 38.0 | 0.61 | 3.63 | 4.71 |
| 0.01 | 0.0001 | 35.3 | 0.55 | 3.78 | 4.56 |
| 0.01 | 0.0001 | 35.3 | 0.55 | 4.01 | 4.33 |
| 0.01 | 0.0001 | 28.2 | 0.39 | 4.35 | 3.99 |
| 0.01 | 0.0001 | 27.2 | 0.37 | 4.70 | 3.65 |
| 0.01 | 0.0001 | 27.5 | 0.38 | 5.14 | 3.22 |
| 0.01 | 0.0001 | 25.6 | 0.34 | 5.26 | 3.12 |
| 0.01 | 0.0001 | 30.6 | 0.44 | 5.69 | 2.76 |
| 0.01 | 0.0001 | 23.4 | 0.31 | 5.88 | 2.60 |

* 10 q -values chosen for the determination of $q_{\text{max}} = \lambda_2 = 0.45$

Table 4. Distribution of UO_2^{2+} . The cupferron-hexone system.

| Initial conc. of Na-cupferrate in the aq. phase M | Initial conc. of U in the aq. phase M | $\frac{100 \cdot q}{1 + q}$ | q^* | $-\log [\text{H}^+]$ | $-\log [\text{A}^-]$ |
|---|---------------------------------------|-----------------------------|-------|----------------------|----------------------|
| 0.01 | 0.0001 | 17.5 | | 1.30 | 6.75 |
| 0.01 | 0.0001 | 15.9 | | 1.43 | 6.62 |
| 0.01 | 0.0001 | 42.3 | | 1.84 | 6.21 |
| 0.01 | 0.0001 | 50.9 | | 1.96 | 6.09 |
| 0.01 | 0.0001 | 67.3 | 2.97 | 2.12 | 5.93 |
| 0.01 | 0.0001 | 82.2 | 4.62 | 2.36 | 5.69 |
| 0.01 | 0.0001 | 69.0 | 3.29 | 2.42 | 5.63 |
| 0.01 | 0.0001 | 65.2 | 2.63 | 2.59 | 5.46 |
| 0.01 | 0.0001 | 50.7 | 1.03 | 2.61 | 5.44 |
| 0.01 | 0.0001 | 76.8 | 3.31 | 2.99 | 5.06 |
| 0.01 | 0.0001 | 42.5 | 0.74 | 3.57 | 4.48 |
| 0.01 | 0.0001 | 71.1 | 2.46 | 5.30 | 2.82 |

* 8 q -values chosen for the determination of $q_{\max} = \lambda_2 = 2.63$

EXPERIMENTAL

All experiments were carried out as described earlier⁴. The volume of the two phases were equal. Only small amounts of the metals were used and the distribution between the organic and aqueous phases was measured radiometrically in the case of La, Sm, Hf, and Th and spectrophotometrically in the case of U (VI)⁷. The radioisotopes of La, Sm, and Hf were obtained by neutron irradiation of the corresponding oxides at AERE, Harwell; Th^{234} (UX_1) was used as a tracer for Th. It might be pointed out that the metals were not mixed, the experiments being run separately for each metal. The La and Sm data are given in Part XVII⁵, the Th data have been given in Part VI⁴ and the data on the uranyl ion are given in Tables 1–4 and in Figures 4 and 5. With Hf very few experiments were carried out and the results are only approximate.

It should be noted that we used no buffers such as phosphate and the pH in the 0.1 M NaClO_4 aqueous phase was adjusted with HClO_4 and NaOH . The reason for this is apparent as perchlorate ions are considered not to form metal complexes. Of course it was then somewhat difficult to obtain the right pH between 5 and 9 with the oxine system.

RESULTS

The uranyl-oxine system: Within the small $\log q$ range investigated it is not possible to calculate κ_1 , κ_2 and λ_2 as the points fall on a straight line with a slope equal to 2. From Fig. 4 we may obtain at $\log q = 0$ $\lambda_2 \cdot \kappa_2 = 10^{2 \cdot 10.94}$ for the chloroform system and $\lambda_2 \cdot \kappa_2 = 10^{2 \cdot 10.54}$ for hexone (equation 7 in Part V³). Figure 5 gives likewise $\lambda_2 \cdot \kappa_2 \cdot \kappa_3^{-1} = 10^{-1.88}$ for chloroform (equation 8 in Part V³). In this way

$$\kappa_3 = \frac{[\text{UO}_2\text{A}_3^-]}{[\text{UO}_2^{2+}][\text{A}]^3} = 10^{23.76}$$

is obtained.

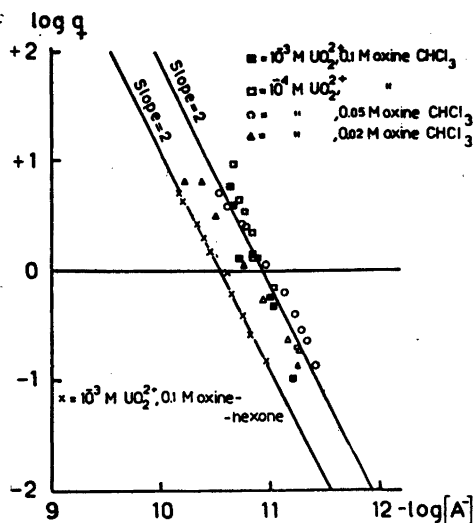


Fig. 4. The distribution of the uranyl ion between chloroform or hexone and acid perchlorate solutions as a function of the oxinate ion concentration ($-\log [A^-]$).

The oxine-system: The difference between chloroform and hexone as a solvent extraction liquid for oxine or the metal oxinates is very small, chloroform having a slightly better solving capacity. Fig. 6 shows the results with the chloroform-oxine system. It is seen that all of these metals can be extracted at different $-\log [A^-]$ values, thus it is possible to separate them by means of controlled pH. The sequence between Hf^{4+} , Th^{4+} , Sm^{3+} , and La^{3+} is the one expected from the charges and sizes of the ions, the uranyl ion, however, seems to hold a unique position. It should also be noted that Th and U are re-extracted at high concentration of A^- (low $-\log [A^-]$ values) probably because negative complexes are formed.

The cupferron system: For the metal cupferrates investigated here hexone is a better solvent, even though cupferron (HA) itself is more soluble in chloroform than hexone (*cf.* Part IV⁶). The extraction of Hf^{4+} and Th^{4+} is very good and takes place at low values of $-\log [A^-]$ as seen from Fig. 7. The extraction of La^{3+} and especially UO_2^{2+} is poor, the solubility in the organic

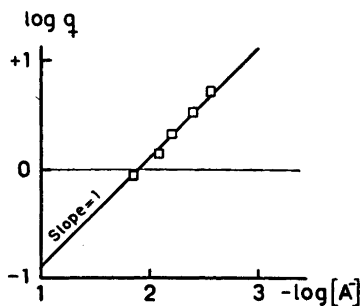
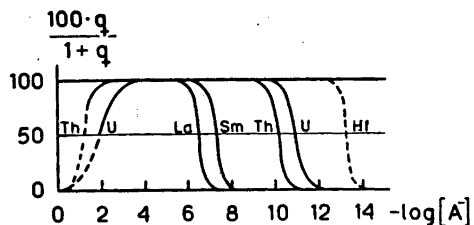


Fig. 5. The distribution of the uranyl ion between chloroform and alkaline perchlorate solutions as a function of the oxinate ion concentration ($-\log [A^-]$).

Fig. 6. The distribution of La (III), Sm (III), Hf (IV), Th (IV), and U (VI) between chloroform and perchlorate solutions as a function of the oxinate ion concentration ($-\log [A^-]$).



phase being only slightly greater than in the aqueous phase. The sequence between Hf, Th, Sm and La is the same as for oxine, but it may be noted that the position of U in relation to Th has changed. Also in this case it is possible to separate the metals at a controlled pH. However, it should be remembered that cupferron decomposes quite readily.

DISCUSSION

Although oxine and cupferron show excellent possibilities for separating the metals investigated by us, it should be pointed out that the total metal concentration always was low ($< 10^{-3} > 10^{-8} M$). If we had used higher metal concentrations the metal oxinates and cupferrates would have precipitated at certain pH values. Some data on the solubilities that we have obtained are given in Table 5 together with Lacroix's⁸ values of the Al, Ga and In oxinates.

Feigl⁹ connects the solubility of the oxinates with their content of bound water or oxine (HA). We are of the same opinion as Pokras, Kilpatrick, and Bernay¹⁰ that H_2O or HA in many cases is bound only by weak lattice for-

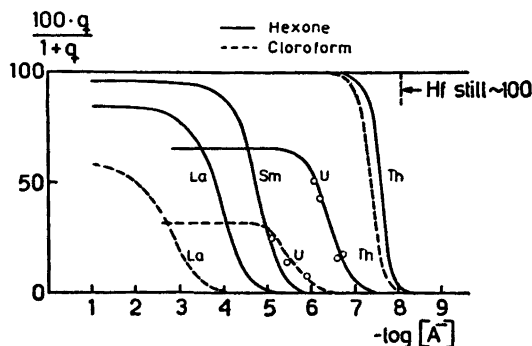


Fig. 7. The distribution of La (III), Sm (III), Hf (IV), Th (IV), and U (VI) between hexone or chloroform and perchlorate solutions as a function of the cupferrate ion concentration ($-\log [A^-]$). The plateaus for the uranyl curves are calculated from data in Tables 3 and 4.

Table 5. Solubilities of some metal oxinates and cupferrates.

| Solvent / reagent | Metal ion | Temp. °C | Solubility moles / lit |
|----------------------------------|-------------------------------|----------|-------------------------------|
| Chloroform (aq.sat.) / oxine | Th ⁴⁺ | 25 | $(6.4 \pm 1.7) \cdot 10^{-4}$ |
| Hexone (») / » | Th ⁴⁺ | 25 | $(5.4 \pm 1.0) \cdot 10^{-4}$ |
| Chloroform (») / » | UO ₂ ²⁺ | 25 | $7.76 \cdot 10^{-4}$ |
| » (») / » | Sr ²⁺ | 25 | $0.94 \cdot 10^{-4}$ |
| Chloroform / oxine | Al ³⁺ | 18 | 0.045 |
| » / » | Ga ³⁺ | 18 | 0.092 |
| » / » | In ³⁺ | 18 | 0.24 |
| Chloroform (aq.sat.) / cupferron | La ³⁺ | 25 | $(5.6 \pm 0.6) \cdot 10^{-4}$ |
| Hexone (») / » | La ³⁺ | 25 | $(4 \pm 4) \cdot 10^{-4}$ |

ces. It is therefore questionable if this binding should be connected with the extraction of the metal oxinates. How irregular the H₂O or HA appears is shown by a few examples^{9,11}:

Precipitates with HA: Sc³⁺, Th⁴⁺, UO₂²⁺
 » with 2 H₂O: Mg²⁺, Mn²⁺, Ni²⁺, Cd²⁺, Ce⁴⁺
 » without HA or H₂O: Al³⁺, Fe³⁺, Cu²⁺, La³⁺, WO₂²⁺

As pointed out by Moeller¹² the pH of the extraction is closely related to the pH of the precipitation of the metal oxinates. This case may however not be taken as a rule, it should rather be taken as a coincidence of the factors that determine extraction and precipitation.

The pH at which the extraction begins depends on the reagent concentration, C_A , as seen from Figures 2, 3, 6 and 7. If the reagent concentration is too low the metal ions will be hydrolyzed before the complex formation and extraction with A⁻ takes place. With oxine a rather high concentration (0.1–0.5 M) is generally needed and with cupferron much lower concentrations can be used (0.005–0.010 M).

The lanthanides and actinides are of course not the only metals that are extractable as oxinates and cupferrates. Table 6 summarizes data found on oxine-chloroform extraction of different metals. The extraction of cupferrates has been extensively treated by Furman, Mason and Pekola¹⁵ and qualitative data on the extraction of many metal oxinates and cupferrates with chloroform are given by Gorbach and Pohl¹⁶.

SUMMARY

Extraction data on the oxinates and cupferrates of La(III), Sm(III), Hf(IV), Th(IV) and U(VI) are given. Two organic solvents have been used, chloroform and hexone. The ionic strength of the aqueous phase has been kept constant at 0.1 M using HClO₄, NaClO₄ and NaOH, and all experiments were carried out at 25° C. Curves are given showing the partition of the metals.

Table 6. The pH for 50 % extraction of metal oxinates with chloroform.

| Metal ion | pH | Procedure | Reference |
|--|---|---|-----------|
| Ga ³⁺ In ³⁺ Al ³⁺ | 1.0 2.1 3.4 | $V_{aq} = V_{org}$, 0.1 M total oxine. Anions in aq. sol.: chloride | 8 |
| Fe ³⁺ Cu ²⁺ In ³⁺ Bi ³⁺ Al ³⁺ Ni ²⁺ Co ²⁺ | 1.6 2.0 2.2 3.0 4.2 6.1 6.5 | 4 successive extractions with 0.01 M solution of oxine in chloroform. Anions in aq. sol.: sulfate, acetate, nitrate, chloride | 12, 13 |
| Sn ⁴⁺ Mo Fe ³⁺ Cu Ni Al Mn ²⁺ | 0.0 1.0 2.0 2.1 3.7 3.8 6.4 | $V_{aq} = 5 \cdot V_{org}$, 0.07 M oxine. Anions in aq. sol.: acetate, chloride, tartrate | 14 |
| Hf ⁴⁺ UO ₂ ²⁺ Th ⁴⁺ Sm ³⁺ La ³⁺ | 1.3 * 2.6 3.1 5.7 6.5 | $V_{aq} = V_{org}$, 0.1 M total oxine. Anions in aq. sol.: perchlorate | this work |

$$* \text{pH} = -\log [\text{H}^+] + 0.1$$

between the organic phase and the aqueous phase as a function of the oxinate or cupferrate ion concentration.

From these curves it is evident that the metals can be separated by extraction with these systems.

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REFERENCES

- Zachariasen, W. H. *Phys. Rev.* **73** (1948) 1104.
- Rydberg, J. *Acta Chem. Scand.* **4** (1950) 1503 (= Part II).
- Dyrssen, D., and Sillén, L. G. *Acta Chem. Scand.* **7** (1953) 663 (= Part V).
- Dyrssen, D. *Svensk Kem. Tidskr.* **65** (1953) 43 (= Part VI).
- Dyrssen, D. *To be published* (= Part XVII).
- Dyrssen, D. *Svensk Kem. Tidskr.* **64** (1952) 213 (= Part IV).
- Hök, Brita *Svensk Kem. Tidskr.* **65** (1953) 105 (= Part VII).
- Lacroix, S. *Anal. Chim. Acta* **1** (1947) 260.

9. Feigl, F. *The Chemistry of Specific, Selective and Sensitive Reactions*, New York, 1949.
10. Pokras, L., Kilpatrick, M., and Bernays, P. M. *J. Am. Chem. Soc.* **75** (1953) 1254.
11. Welcher, F. J. *Organic Analytical Reagents I*, New York 1947, p. 263 ff.
12. Moeller, T. *Ind. Eng. Chem., Anal. Ed.* **15** (1943) 346.
13. Moeller, T. *Ind. Eng. Chem., Anal. Ed.* **15** (1943) 270.
14. Gentry, C. H. R., Sherrington, L. G. *Analyst* **75** (1950) 17.
15. Furman, N. H., Mason, W. B., and Pekola, J. S. *Anal. Chem.* **21** (1949) 1325.
16. Gorbach, G., and Pohl, F. *Mikrochemie ver. Mikrochim. Acta* **38** (1951) 258.

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