

Studies on the Extraction of Metal Complexes

XXXI. Investigations with some 5,7-Dihalogen Derivatives of 8-Quinolinol

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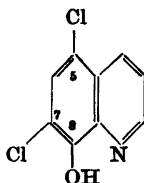
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Some equilibrium constants describing the chloroform extraction of La(III), Th(IV) and U(VI) complexes with the 5,7-dichloro, 5,7-dibromo, 5,7-diiodo and 5-chloro-7-iodo derivatives of 8-quinolinol (oxine) have been investigated at 25 °C. The ionic strength in the aqueous phase was kept constant at 0.1 M. The overall equilibrium constant K (eqn. 8) for the extraction of metal complexes is increased by halogen substitution of the reagent (Table 6). This effect, which is very pronounced for thorium, is discussed in terms of the separate dissociation and distribution equilibria (eqns. 2-6). The dihalogen substituted oxines are stronger acids than oxine, but the mean com-

plexity constant, $\sqrt[N]{\kappa_N} = 10^a$, for the complex formation of thorium ($N = 4$) with dichloro-oxine is about the same ($10^{9.90}$) as with oxine ($10^{9.80}$). The distribution constants of both the reagent, k_d , and of the metal complex, λ_a , are increased by halogen substitution. The molar solubilities of the dihalogen reagents in chloroform are considerably smaller (<0.06 M) than the solubility of oxine (2.63 M), whereas thorium dichloro-oxinate is much more soluble in chloroform (0.0135 M) than is thorium oxinate (0.00088 M). A favorable property of the 5,7-dihalogen derivatives is the fact that they are not extracted as oxinium ions from chloroform by moderately acidic solutions (Fig. 1). Our studies suggest that 5,7-dichloro-oxine may often be preferable to ordinary oxine as a reagent for solvent extraction.

An important aspect of our studies on the extraction of inner complexes of the lanthanides and actinides is to investigate the influence of the structure of the chelating agent. This may be done both by investigating various types of reagents and by studying derivatives of one particular compound. In this paper, the results obtained with some 5,7-dihalogen derivatives of oxine are reported. Moeller and Jackson¹ have previously pointed out that 5,7-dichloro-oxine is preferable to oxine for the extraction of neodymium and er-

bium. Recently Rulfs, De, Lakritz and Elving² state that oxine is a better reagent than its dichloro and dibromo derivatives for the extraction of uranium(VI).



5,7-dichloro-oxine

The effect of structural changes in a reagent on the various factors that govern metal extraction has been discussed by Martell and Calvin³. We shall extend their discussion somewhat, using our own symbols and apply it to the dihalogenated derivatives of oxine.

One may regard the extraction of a metal ion M^{N+} with an organic reagent HA as a stepwise complex formation of M^{N+} with the ligand ion A^- giving among other complexes an uncharged extractable complex MA_N . If the complexes in the aqueous phase are neglected, the distribution ratio is given by

$$q = [MA_N]_{\text{org}}/[M^{N+}] \quad (1)$$

The ligand concentration $[A^-]$ is determined by the reagent concentration and the pH as well as by the two dissociation constants

$$k_1 = [H^+] [HA] / [H_2A^+] \text{ and } k_2 = [H^+] [A^-] / [HA] \quad (2, 3)$$

and the distribution constant

$$k_d = [HA]_{\text{org}} / [HA] \quad (4)$$

The formation of MA_N is determined by the complexity product

$$\kappa_N = \frac{[MA_N]}{[M^{N+}] [A^-]^N} \quad (5)$$

and the distribution of MA_N by the distribution constant

$$\lambda_N = [MA_N]_{\text{org}} / [MA_N] \quad (6)$$

For a given system the main experimental variables governing q are generally the reagent concentration $[HA]_{\text{org}}$ and the hydrogen ion concentration $[H^+]$ (pH). Thus using eqns. (3)—(6) we may transform (1) to

$$q = \frac{[HA]_{\text{org}}^N}{[H^+]^N} \cdot \kappa_N \cdot \lambda_N \cdot \left(\frac{k_2}{k_d}\right)^N \quad (7)$$

The overall equilibrium constant K we then define by

$$K = \kappa_N \cdot \lambda_N \cdot \left(\frac{k_2}{k_d}\right)^N \quad (8)$$

Although halogen substitution would be expected to increase both the dissociation constant k_2 of the reagent, and the distribution constant λ_N of the uncharged metal complex, these changes will probably be offset by an increase in the distribution constant k_d of the reagent (*cf. e. g.* Collander ⁴) and possibly also by a decrease in the complexity constant κ_N . The total effect on the extraction constant K may therefore be rather small.

Eqn. (7) is based on the approximation that the organic phase contains only the uncharged complex MA_N , and the aqueous phase only the uncomplexed metal ion M^{N+} . As has been pointed out by Dyrssen and Sillén ⁵, eqn. (7) corresponds to the asymptote

$$\log q = \log \lambda_N + \log \kappa_N + N \log [A^-] \quad (9)$$

to the distribution curve $\log q$ versus $\log [A^-]$ (see Fig. 2 and 3).

Using eqns. (7) and (8), we may in many cases obtain an approximate value of the pH ($-\log [H^+]$) for 50 % extraction ($q = 1$):

$$\log [H^+] = \frac{1}{N} \log K + \log [HA]_{\text{org}} \quad (10)$$

Since the tendency for the lanthanide and actinide ions to form inner complexes is rather small compared with their tendency to hydrolyze, it is important to extract in a low pH range; *i. e.* a high value of $\frac{1}{N} \log K$ and of the reagent concentration $[HA]_{\text{org}}$ is desirable.

EXPERIMENTAL

Many details in the experimental technique are described in previous parts in this series. As usual, the measurements were carried out at 25 °C, and $-\log [H^+]$ denotes the hydrogen ion concentration. The ionic strength was kept constant at 0.1 M by the addition of Na^+ or ClO_4^- ions.

Reagents. The chloroform was saturated with water and alcohol-free, and the methyl isobutyl carbinol (hexol) was shaken with a 10 % sodium bicarbonate solution. 8-Quinolinols of analytical quality were purchased from Merck-Darmstadt (oxine) and Schuchardt, and were used without further purification. Pure 5,7-dichloro-oxine was however prepared according to Berg ⁶. Other reagents were of analytical grade.

Measurements on the oxines. The solubilities in chloroform were obtained by weighing after careful evaporation of the chloroform at 40–50 °C. The solubility of 5,7-dichloro-oxine was checked by diluting 1 ml of a saturated solution to 250 ml and determining the concentration by spectrophotometric analysis at 330 $m\mu$. This method gave a solubility of 0.0584 M, which agreed well with the value obtained by weighing (see p. 346).

The values of $(pk_2 + \log k_d)$ were obtained by shaking 15 ml of a 0.01–0.05 M chloroform solution of the dihalogen substituted oxine with 15 ml of a 0.1 M sodium borate-perchlorate buffer ($-\log [H^+] = 9.50-9.60$, 0.05 M in boric acid + sodium borate). The oxine concentration in the aqueous phase ($\cong [A^-]$) was determined spectrophotometrically at 350–370 $m\mu$. The values of $(pk_1 - \log k_d)$ were determined in a similar manner by shaking with 0.1 M perchloric acid. The determination of the oxine concentration in the aqueous phase ($\cong [H_2A^+]$) was carried out at 370 $m\mu$.

The distribution constants k_d were determined by shaking 50 ml of a 0.01–0.05 M chloroform solution of the dihalogen substituted oxine with 900 ml of 0.1 M $NaClO_4$ + 100 ml of 0.1 M phthalate buffer (pH = 5) previously saturated with chloroform. The

Table 1. Distribution of U(VI) between 0.05 M solutions of 5,7-dichloro-oxine in chloroform and 0.1 M HClO₄-NaClO₄ solutions at 25 °C. Initial concentration of U in the aqueous phase = 1.33 · 10⁻⁴ M.

A_{330}	$\log q^*$	$-\log [H^+]$	$-\log [A^-]^{**}$
0.104	-1.00	1.48	11.09
0.315	-0.42	1.70	10.87
0.514	-0.09	1.88	10.69
0.690	+0.19	2.03	10.54
0.880	+0.53	2.21	10.36
1.07	+1.18	2.53	10.04

* q was calculated from the measured absorbancy A_{330} as $q = A_{330}/(1.140 - A_{330})$.

** $-\log [A^-] = \log [H^+] + 12.57$ (eqn. 11).

aqueous phase was centrifuged, 250–750 ml were drawn off and shaken with 10 ml of fresh chloroform. The oxine concentration in this chloroform layer was determined spectrophotometrically at 325–340 $m\mu$.

If 25 cm cuvettes are available, an alternative method is quite useful for the determination of k_d . Ten ml of a 0.01–0.05 M solution of the dihalogen substituted oxines in the organic solvent is shaken with 99 ml of 0.1 M NaClO₄ + 1 ml of 0.1 M phthalate buffer (pH = 5). The aqueous phase is centrifuged and acidified to pH = 1 with 1 ml conc. HClO₄. The oxine concentration of this solution is determined spectrophotometrically at 370 $m\mu$. This method was used with hexol.

Extraction of the metals. The use of small amounts of buffering substances such as 1 ml of 0.1 M anilinium perchlorate, sodium acetate, hydrazinium perchlorate, or ammonium perchlorate per 15 ml, does not appear to have any

Table 2. Distribution of La(III) between 0.05 M solutions of 5,7-dichloro-oxine in chloroform and 0.1 M NaClO₄ at 25 °C. Initial concentration of La-¹⁴⁰La in the aqueous phase $\sim 10^{-5}$ M

I_{org} cpm	I_{aq} cpm	$\log q^*$	$-\log [H^+]$	$-\log [A^-]^{**}$
68.0	8 385	-2.01	5.15	7.42
85.4	8 096	-1.90	5.19	7.38
232	7 834	-1.45	5.35	7.22
690	22 075	-1.43	5.16	7.41
1 391	18 679	-1.05	5.42	7.15
872	6 068	-0.76	5.46	7.11
7 821	11 042	-0.07	5.66	6.91
5 865	2 181	+0.51	6.12	6.45
14 521	725	+1.38	6.27	6.30
8 824	389	+1.43	6.51	6.06
5 502	35.5	+2.27	6.94	5.63
8 560	44.4	+2.36	6.61	5.96

* $q = 1.20 \cdot I_{org}/I_{aq}$ (cf. Part XVII¹⁸).

** $-\log [A^-] = \log [H^+] + 12.57$ (eqn. 11).

Table 3. Distribution of Th (IV) between chloroform and perchlorate solutions at 25 °C as a function of the concentration of the 5,7-dichloro-oxinate ion in the aqueous phase. Initial concentration of Th—²³⁴Th in the aqueous phase $\sim 10^{-6}$ M.

[HA] _{org} M	I _{org} cpm	I _{aq} cpm	log q *	—log [H ⁺]	—log [A ⁻] **
0.05	257	21 104	-1.89	1.02	11.55
»	340	5 207	-1.16	1.21	11.36
»	1 249	4 252	-0.50	1.52	11.05
»	10 863	8 036	+0.16	1.71	10.86
»	3 670	900	+0.64	1.80	10.77
»	4 160	252	+1.25	2.08	10.49
»	4 229	51.4	+1.94	2.37	10.20
»	4 397	8.8	+2.73	3.00	9.57
0.02	11.4	18 143	-3.17	1.11	11.86
»	51.4	17 759	-2.51	1.28	11.69
»	205	16 635	-1.88	1.55	11.42
»	2 522	14 700	-0.74	1.88	11.09
»	7 994	7 667	+0.05	2.15	10.82
»	10 408	5 524	+0.30	2.25	10.72
»	11 302	4 112	+0.47	2.43	10.54
»	14 222	599	+1.40	2.89	10.08
»	12 768	166	+1.91	3.26	9.71
0.01	7.2	7 991	-3.02	1.50	11.77
»	61.0	6 306	-1.99	1.82	11.45
»	196	6 731	-1.51	2.12	11.15
»	422	5 308	-1.07	2.20	11.07
»	1 044	4 930	-0.65	2.38	10.89
»	2 428	2 510	+0.01	2.62	10.65
»	4 361	442	+1.02	2.95	10.32
»	4 396	422	+1.05	3.17	10.10

* $q = (1.067 \pm 0.010) \cdot I_{org}/I_{aq}$ (cf. Part XXI¹⁷).

** $-\log[A^-] = \log[H^+] - \log[HA]_{org} + 11.27$ (eqn. 11).

influence on the extraction. The pH and the volume of the solution were adjusted with 0.1 M HClO₄, NaOH and NaClO₄.

The distribution ratios of La and Th were measured radiometrically using ¹⁴⁰La and ²³⁴Th (UX₁) as tracers. The distribution of U(VI), however, was determined spectrophotometrically at 390 mμ with a Beckman DU spectrophotometer with 1 cm cells, using a 0.05 M solution of 5,7-dichloro-oxine of chloroform in the blank cell. With this technique, the following values for the molecular extinction coefficient were obtained:

$\epsilon \cdot 10^{-4} \text{ M}^{-1}$	0.816	0.821	0.855	0.818	0.738	0.646
$\lambda \text{ m}\mu$	370	380	390	400	410	420

The absorbancy of the blank became too high below 370 mμ. Moeller and Ramaniah⁸ have pointed out that the determinations, which are made on steep parts of the absorption curves, will be very sensitive to small errors in

Table 4. Distribution of Th(IV) between 0.01 M solutions of 5,7-dichloro-oxine in hexol and 0.1 M perchlorate solutions at 25°C as a function of the 5,7-dichloro-oxinate ion concentration in the aqueous phase. Initial concentration of Th-²³²Th in the aqueous phase $\sim 5 \cdot 10^{-6}$ M.

I_{org} cpm	I_{aq} cpm	$\log q$ **	$-\log [H^+]$	$-\log [A^-]$ ***
16.6	4 237	-2.46	1.59	11.02
50.4	4 522	-2.00	1.71	10.90
194	4 376	-1.40	1.93	10.68
483	4 758	-1.04	2.12	10.49
1 099	3 124	-0.50	2.22	10.39
2 512	2 659	-0.08	2.37	10.24
4 600	717	+0.77	2.78	9.83
5 693	106	+1.68	3.39	9.22
6 631	16.2	+2.56	4.42	8.19
6 457	14.3	+2.60	4.83	7.78
6 861 *	12.5 *	+2.69	5.44	7.17
6 944 *	16.6 *	+2.57	6.27	6.34
8 619 *	12.3 *	+2.80	7.28	5.33
6 791 *	13.5 *	+2.65	7.32	5.29
8 300 *	11.3 *	+2.82	7.39	5.22
8 436 *	12.1 *	+2.79	7.56	5.05

* Values on the plateau used for the calculation of $\lambda_d = 0.89 \cdot 45\,951/78.3 = 10^{3.72}$.

** $q = 0.89 \cdot I_{org}/I_{aq}$.

*** $-\log[A^-] = \log[H^+] + 12.61$ (eqn. 11).

wave-length setting. This objection is, however, not serious since the wave-length is not altered in shifting from the blank to the sample. The free ligand concentration was calculated from the relationship

$$\log[A^-] = \log[HA]_{org} - \log[H^+] - pk_2 - \log k_d \quad (11)$$

SOME PROPERTIES OF THE OXINES

It is clear from the introductory discussion that a high value of $[HA]_{org}$ favors the extraction of the metal. A limit is of course set by the solubility of the reagent in wet chloroform. The following solubilities were obtained at 25°C:

Oxine	(M.W. 145.15):	2.63 ± 0.08 M
5,7-Dichloro-oxine	(M.W. 214.05):	0.0587 ± 0.0003 M
5,7-Dibromo-oxine	(M.W. 302.97):	0.0302 ± 0.0003 M
5,7-Diiodo-oxine	(M.W. 396.97):	0.0109 ± 0.0003 M
5-Chloro-7-iodo-oxine	(M.W. 305.51):	0.0585 ± 0.0003 M

The solubility of 5,7-dichloro-oxine in hexol is only 0.0119 M.

In this respect the dichloro and chloro-iodo compounds are the best extracting agents of these dihalogen substituted oxines. They are, however, about 45 times less soluble in chloroform than is oxine itself.

Table 5. Stoichiometric acid dissociation constants and chloroform/water distribution constants of oxine and some of its 5,7-dihalogen derivatives at 25°C. Ionic strength in the aqueous phase = 0.1 M.

Constants	5,7-Substituent				
	H, H	Cl, Cl	Br, Br	I, I	Cl, I
$pk_2 + \log k_d$	12.24	<i>11.27^c</i>	<i>11.47</i>	<i>12.15</i>	<i>11.79</i>
$\log k_d$	<i>2.58^a</i>	<i>3.86 ± 0.06^d</i>	<i>4.15 ± 0.1^d</i>	<i>4.15 ± 0.1</i>	<i>3.88 ± 0.1</i>
pk_2	<i>9.66^b</i>	<i>7.4^e</i>	<i>7.3</i>	<i>8.0</i>	<i>7.9</i>
$pk_1 - \log k_d$	+2.42	-0.92	-1.59	-1.43	-1.20
pk_1	<i>5.00^b</i>	<i>2.9^e</i>	<i>2.6</i>	<i>2.7</i>	<i>2.7</i>

Values determined experimentally are given in italics; where not stated they have an error of $\pm 0.01-0.02$ units.

- a) This distribution ratio is shown to be somewhat dependent on $[HA]_{org}$: 2.61 at 0.1 M, 2.64 at 0.2 M and 2.70 at 0.5 M.
 b) Reported in Part IV⁹.
 c) A value of 11.28 was obtained by a two-phase titration (cf. Part IV⁹).
 d) For hexol we obtained 3.14 (dichloro-oxine) and 3.36 ± 0.09 (dibromo-oxine).
 e) From thermodynamic dissociation constants given by Näsänen¹⁰ (2.887 and 7.617 at 25°C) one may calculate $pk_1 = 2.89$ and $pk_2 = 7.47$.

The ligand concentration is also determined by the two-phase dissociation constant k_2/k_d . In the discussion above it is emphasized that an increase in k_2/k_d is desirable, provided the decrease in $\kappa_N \cdot \lambda_N$ is not too large. Table 5 shows that 5,7-dichloro-oxine has the most favorable value ($10^{-11.27}$); the value for oxine being about 10 times less.

A valuable property of the dihalogen compounds is their very low values of $(pk_1 - \log k_d)$ in comparison with unsubstituted oxine (see Table 5). This means that while oxine is extracted out of the chloroform phase into moderately acidic solutions ($pH < 3$) as an oxinium salt, its dihalogen derivatives will show this behavior only in very acidic solutions ($pH < -0.5$; see Fig. 1).

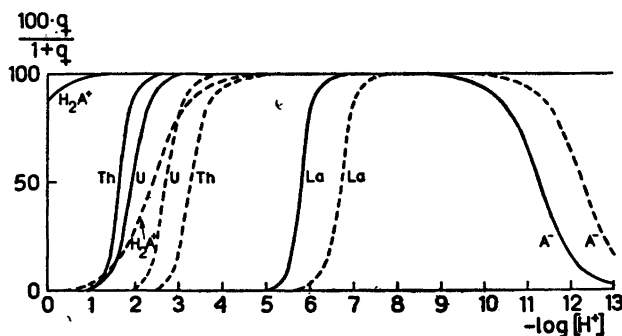


Fig. 1. Comparison of oxine (dashed curves) and 5,7-dichloro-oxine (full curves) as extracting agents. The distribution of La (III), Th (IV) and U (VI) is calculated for the case where a 0.05 M solution of the reagent in chloroform is shaken with an equal volume of an aqueous solution. The H_2A^+ and A^- curves show the extraction of the oxines into the aqueous phase as oxinium and oxinate ions.

The values of the dissociation constants k_1 and k_2 in Table 5 emphasizes the well-known fact (*cf. e. g.* Watson¹¹) that the influence of halogen substituents on aromatic nuclei cannot be expressed completely in terms of their inductive effects. The order of pk_1 , $Br \sim I < Cl$, and of pk_2 , $Br \sim Cl < I$, was also found by Feldman and Powell¹² for the 7-halogen derivatives of 8-quinolinol-5-sulfonic acid. It may be assumed from data reported by Minegishi and Nagakura¹³ and by Judson and Kilpatrick¹⁴ on monochloro phenols that the lowering of pk_2 of oxine by halogen substitution is primarily due to the 7-substituent.

Since the values of k_d are so very large for the dihalogen compounds, it was very difficult to obtain accurate results for these distribution constants. This uncertainty is reflected in the values of pk_1 and pk_2 calculated from the two-phase dissociation constants $k_1 \cdot k_d$ and k_2/k_d . Table 5, however, shows that there is a more than tenfold increase of k_d on substitution.

EXTRACTION OF La(III), Th(IV) AND U(VI)

The results given in the preceding section show that the 5,7-dihalogen substituted oxines are much stronger acids than unsubstituted oxine. We also found larger distribution constants k_d with the dihalogen substituted compounds. In the introductory discussion it was indicated that one might expect analogous changes for the metal chelate, *i. e.* a decrease in κ_N and an increase in λ_N , thus leaving the overall equilibrium constant K unchanged.

The results of an investigation of UO_2^{2+} , La^{3+} and Th^{4+} with 5,7-dichloro-oxine are given in Tables 1, 2 and 3 and summarized in Table 6 and Fig. 1. These results show that for the same initial concentration of reagent in the chloroform phase (*e. g.* 0.05 M), 5,7-dichloro-oxine extracts in a lower pH range than oxine (Fig. 1); *i. e.*, $\frac{1}{N} \log K$ has increased on halogen substitution (Table 6). The effect ($\Delta \frac{1}{N} \log K$) is in fact so large for Th^{4+} that it reverses its position in relation to UO_2^{2+} (Fig. 1).

Eqn. (8) can be written as

$$\frac{1}{N} \log K = \frac{1}{N} \log \kappa_N \cdot \lambda_N - (pk_2 + \log k_d) \quad (12)$$

Table 6. Comparison of some chloroform extraction constants for oxine and 5,7-dichloro-oxine.

Metal	N	$\frac{1}{N} \log \kappa_N \cdot \lambda_N$		$\Delta \frac{1}{N} \log \kappa_N \cdot \lambda_N$	$\frac{1}{N} \log K$		$\Delta \frac{1}{N} \log K$
		H, H	Cl, Cl		H, H	Cl, Cl	
U (VI)	2	11.03	10.64	-0.39	-1.21 *	-0.63	0.58
La (III)	3	7.02	6.79	-0.23	-5.22 **	-4.48	0.74
Th (IV)	4	10.46	11.05	+0.59	-1.78	-0.22	1.56

* Calculated from data on 0.05 M oxine in Part VIII¹⁵.

** Calculated from data in Part XVII¹⁶.

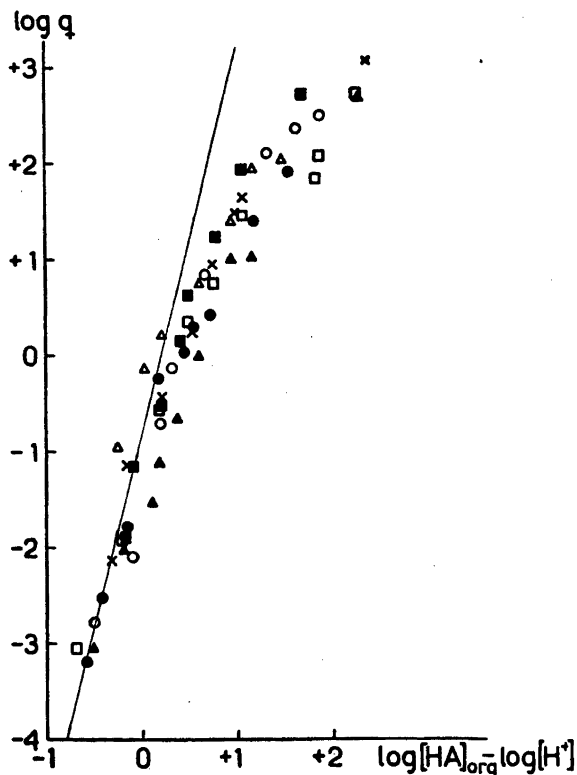


Fig. 2. Comparison of some 5,7-dihalogen substituted oxines as extracting agents for thorium. The distribution ratio of $\text{Th}-^{232}\text{Th}$ between chloroform and 0.1 M perchlorate solutions is given as a function of $\log[\text{HA}]_{\text{org}} - \log[\text{H}^+]$ ($= \log[A^-] + \text{pk}_2 + \log k_d$). Dihalogen derivative and its total concentration in the organic phase ($[\text{HA}]_{\text{org}}$): dichloro: ■ 0.05 M, ● 0.02 M, ▲ 0.01 M; dibromo: □ 0.02 M, ○ 0.01 M; chloro-iodo: Δ 0.05 M, × 0.02 M.

and thus values of $\frac{1}{N} \log \kappa_N \cdot \lambda_N$ may be calculated using the values of $(\text{pk}_2 + \log k_d)$ given previously in Table 5. The values of $\frac{1}{N} \log \kappa_N \cdot \lambda_N$ are given in Table 6. As λ_N probably is larger for the 5,7-dichloro-oxinates, it seems as if the complexity products κ_N of UO_2^{2+} and La^{3+} are smaller with dichloro-oxine than with oxine. In order to evaluate κ_4 and λ_4 for Th^{4+} a separate investigation was carried out using hexol (methyl *iso*-butyl carbinol) as a solvent. The results are reported below.

Fig. 2 shows the results obtained with Th^{4+} and the various 5,7-dihalogen substituted oxines. The distribution ratio q of Th^{4+} between chloroform and the aqueous phase does not obey eqn. (7) with $\frac{1}{4} \log K = -0.22$, but as was pointed out in the introduction this line should be regarded as an asymptote,

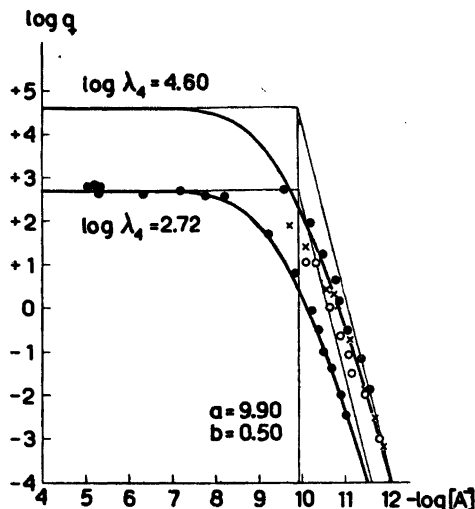


Fig. 3. The distribution ratio of Th as a function of the 5,7-dichloro-oxinate ion concentration in the aqueous phase. Hexol: ● 0.01 M dichloro-oxine; chloroform: ⊗ 0.05 M, × 0.02 M and ○ 0.01 M dichloro-oxine.

and the deviation is undoubtedly due to the presence of Th complexes in the aqueous phase. Values outside $\log q = \pm 3.2$ are not included since they are rather unreliable. Furthermore it seems as if there is no significant difference between the dihalogen substituted compounds in this plot. This means that the values of $\frac{1}{4} \log K$ are about the same and consequently that according to eqn. (12) the values of $\frac{1}{4} \log \kappa_4 \cdot \lambda_4$ are shifted by an amount equal to the changes of their $(pk_2 + \log k_2)$ values. One might then be tempted to think that equal shifts in the constants for the proton complexes, k_2 and k_2 , and in the constants for the thorium complexes, $\sqrt[4]{\kappa_4} = 10^a$ and $\sqrt[4]{\lambda_4}$, compensate each other.

COMPLEX FORMATION OF THORIUM WITH 5,7-DICHLORO-OXINE

In order to evaluate $\frac{1}{4} \log \kappa_4$ and $\frac{1}{4} \log \lambda_4$ separately for thorium, 5,7-dichloro-oxine was studied using hexol (methyl isobutyl carbinol) as a solvent. Hexol was chosen instead of chloroform so that $\log \lambda_4$ would be lower and in a measurable range of $\log q$. However, the solubility of 5,7-dichloro-oxine is much lower in hexol (0.0119 M) than in chloroform (0.0587 M). The solubility of hexol in water is only 1.6 % and should not affect κ_4 very much.

The results with hexol are given in Table 4 and plotted in Fig. 3 together with the chloroform data. The thick curves in Fig. 3 are calculated with the

parameters (*cf.* Part V⁵) $a = 9.90$, $b = 0.50$, $\log \lambda_4 = 2.72$ (hexol) and $\log \lambda_4 = 4.6$ (chloroform) and have consequently the same shape. The thin lines represent the asymptotes to the distribution curves,

$$\begin{aligned} \log q &= \log \lambda_4 & \text{and} & & (13) \\ \log q &= \log \kappa_4 + \log \lambda_4 + 4 \log [A^-] & & & (9a) \end{aligned}$$

A reinvestigation of the thorium-oxine-chloroform system (*cf.* Part VI⁷) gave $a = 9.80$, $b = 0.35$ and $\log \lambda_4 = 2.63$. Within a reasonable limit of error in a (± 0.05 or 0.10) we may say that there is no significant difference between the mean complexity constants ($= 10^a$) for the thorium complexes of oxine and of 5,7-dichloro-oxine. This result was not expected, and cannot alone form a basis for a theoretical discussion. Future investigations may show if it is merely an exception. We may note that the dichloro-oxinate of thorium is much more soluble in chloroform (0.0135 M) than is the oxinate (0.00088 M).

GENERAL CONCLUSIONS

The extraction properties of the dihalogen substituted oxines investigated here are very much alike. The pH range for the extraction of La(III), Th(IV) and U(VI) with chloroform is lower for dichloro-oxine than for oxine itself. The effect is very large for Th⁴⁺ (1.56 pH units), but not so large for La³⁺ (0.74) and UO₂²⁺ (0.58). A very favorable property of the 5,7-dihalogen substituted oxines is that they form oxinium ions (H₂A⁺) only in very acidic solutions (Fig. 1). Furthermore, the solubility of the thorium complex in chloroform is increased many fold on dichloro substitution.

To summarize, we believe that the 5,7-dihalogen substituted oxines have certain advantages over oxine as solvent extraction agents, and would repay more general use in the future. The 5,7-dichloro compound is preferred because it has the largest solubility in chloroform, and because it is very simple to prepare the pure reagent from oxine⁶ with a good yield.

We wish to thank Professor G. Ljunggren and Professor L. G. Sillén for their interest in this work, which has partly been supported by *Atomkommittén*.

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Received January 21, 1956.