Studies on the Extraction of Metal Complexes

XXIII. On the Complex Formation of Thorium with Salicylic Acid, Methoxybenzoic Acid, and Cinnamic Acid

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The extraction of thorium with salicylic acid H_2A , methoxybenzoic acid HA , and cinnamic acid HA has been studied at $25^\circ C$ in the solvent systems: methyl isobutyl ketone-aqueous solution and chloroform-aqueous solution at a constant ionic strength of 0.1 M.

The complex formation in the aqueous phase between thorium and the acids is described by two parameters a and b^* which are given in Table 7. The thorium complex extracted into the hexone solution of salicylic acid has been found to have an associated salicylic acid molecule. By comparison with methoxybenzoic acid it seems plausible to write the formula as $Th(HA)_4 \cdot H_2A$.

In our studies of the metal extraction with some phenylcarboxylic acids (Part XXIV¹) a considerable number of data are reported for thorium.

In the present paper the data for thorium with salicylic acid, methoxybenzoic acid and cinnamic acid are given. Calculations of the data are made in order to draw some conclusions about the complexes formed and if possible to estimate the relevant equilibrium constants.

The distribution of thorium between the organic and aqueous phase was measured radiometrically, using $^{234}Th(UX_1)$ as a tracer for thorium. The distribution was measured after a shaking time of 18 hours at $25^\circ C$. The organic solvent was methyl isobutyl ketone (hexone) or chloroform and the aqueous phase was made 0.1 M by addition of $NaClO_4$. The hydrogen ion concentration of the aqueous phase was determined with a glass electrode after equilibration. The anion concentration was then calculated by means of the constants given in Part XV². In the experiments the thorium concentration was kept $\sim 10^{-5}$ M by addition of inactive thorium perchlorate. Only mononuclear complex formation was assumed to take place at this low metal concentration.

Table 1. Distribution of $^{234}\text{Th} - \text{UX}_1$ between hexone and water. $\text{H}_2\text{A} = \text{Salicylic acid}$.

$[\text{H}_2\text{A}]_{\text{M}}^{\text{tot}}$	$[\text{H}_2\text{A}]_{\text{aq}}^{\text{M}}$	$[\text{Th}]_{\text{M}}$	I'_{org}	I'_{aq}	$\log q = \frac{\log I'_{\text{org}} - \log I'_{\text{aq}}}{-0.01}$	$\frac{\log q}{[\text{H}_2\text{A}]_{\text{aq}}}$	$-\log [\text{H}^+]$	$-\log [\text{HA}^-]$
1.5	$10^{-2.35}$	10^{-5}	13 706		4		3.83	1.33
»	$10^{-2.34}$	»	13 620	7	+3.28	5.62	3.45	1.71
»	»	»	13 787	44	+2.48	4.82	2.87	2.29
»	»	»	11 687	170	+1.83	4.17	2.47	2.59
»	»	»	11 218	722	+1.18	3.52	2.11	2.94
»	»	»	9 716	2 595	+0.56	2.90	1.86	3.29
»	»	»	4 320	8 113	-0.28	2.06	1.55	3.60
»	»	»	577	11 639	-1.30	1.04	1.28	3.87
1.0	$10^{-2.54}$	»	19 026	29	+2.81	5.35	4.08	1.25
»	»	»	18 653	22	+2.92	5.46	4.06	1.27
»	$10^{-2.53}$	»	19 142	28	+2.82	5.35	3.80	1.53
»	$10^{-2.51}$	»	19 013	119	+2.19	4.70	3.06	2.27
»	»	»	16 029	578	+1.43	3.94	2.61	2.72
»	»	»	14 097	2 833	+0.69	3.20	2.17	3.16
»	»	»	11 542	7 581	+0.17	2.68	1.96	3.38
»	»	$10^{-5.17}$	3 351	3 429	-0.02	2.49	1.90	3.43
»	»	»	2 885	3 882	-0.14	2.37	1.81	3.52
»	»	10^{-5}	519	14 645	-1.44	1.07	1.51	3.83
»	»	»	193	15 409	-1.91	0.60	1.20	4.13
0.50	$10^{-2.87}$	$10^{-5.17}$	4 937	26 ± 5	+2.27	5.14	4.42	1.25
»	$10^{-2.85}$	»	5 431	13 ± 4	+2.60	5.45	4.30	1.36
»	»	»	5 550	30 ± 5	+2.25	5.10	4.18	1.47
»	$10^{-2.83}$	»	5 388	18 ± 4	+2.47	5.30	3.90	1.74
»	$10^{-2.82}$	10^{-5}	8 722	46 ± 4	+2.27	5.09	3.64	1.98
»	»	»	8 196	92 ± 5	+1.94	4.76	3.43	2.20
0.50	$10^{-2.82}$	10^{-5}	9 653	440	+1.33	4.15	3.10	2.53
»	»	»	6 372	2 038	+0.49	3.31	2.64	2.98
»	$10^{-2.81}$	»	3 397	4 847	-0.16	2.65	2.27	3.35
»	»	»	1 884	6 441	-0.54	2.27	2.07	3.56
»	»	»	898	7 375	-0.92	1.89	1.98	3.65
»	»	»	125 ± 9	7 482	-1.79	1.02	1.64	3.99
»	»	»	29 ± 3	7 663	-2.43	0.38	1.48	4.15
0.1	$10^{-3.75}$	10^{-5}	11 292	157	+1.85	5.60	5.19	1.37
»	$10^{-3.61}$	»	9 361	160	+1.76	5.37	4.71	1.70
»	$10^{-3.57}$	»	11 725	232	+1.69	5.26	4.45	1.93
»	»	$10^{-5.17}$	6 261	185	+1.52	5.03	4.35	2.02
»	$10^{-3.55}$	»	6 364	319	+1.29	4.84	4.28	2.09
»	»	10^{-5}	8 941	315	+1.44	4.99	4.23	2.13
»	$10^{-3.54}$	$10^{-5.17}$	5 658	245	+1.35	4.89	4.18	2.18
»	»	»	5 714	308	+1.26	4.80	4.06	2.29
»	$10^{-3.53}$	»	5 651	604	+0.96	4.49	3.85	2.48
»	$10^{-3.52}$	10^{-5}	6 481	1 080	+0.77	4.29	3.72	2.62
»	»	»	7 488	7 336	+0.00	3.52	3.33	3.01
»	$10^{-3.51}$	»	162	14 386	-1.96	1.55	2.51	3.83
»	»	»	34 ± 4	7 184	-2.33	1.18	2.43	3.90

Fig. 1. Plot of $\log q$ against $-\log [HA^-]$ for the distribution of $^{232}\text{Th}-\text{UX}_1$ between hexone and H_2O with salicylic acid as the organic reagent (H_2A).

Fig. 2. Plot of $\log(q/[H_2A]_{aq})$ against $-\log [HA^-]$ for the system Th -salicylic acid (H_2A) —hexone — H_2O .

Salicylic acid

In a previous work the distribution of UO_2^{2+} in the system salicylic acid-hexone- 0.1 M NaClO_4 was studied (Part XVI³). If salicylic acid

is denoted H_2A , it was shown that the complexes formed in appreciable amount in the organic phase are $\text{UO}_2(\text{H}_2\text{A})_2(\text{H}^+)_{-2}$ and $\text{UO}_2(\text{H}_2\text{A})_3(\text{H}^+)_{-2}$, which we presumed to correspond to the formulae $\text{UO}_2(\text{HA})_2$ and $\text{UO}_2(\text{HA})_2 \cdot \text{H}_2\text{A}$. In the present study we started to assume that the ligand combining with thorium was HA^- .

The experimental data for the hexone system are given in Table 1. I'_{org} and I'_{aq} represent the radiometric counts obtained from equal aliquots of the organic and aqueous phases. The distribution ratio q involves a correction factor taken from Part X⁴ for the density of the sample solution. In Fig. 1 the data are represented by plotting $\log q$ against $-\log [HA^-]$. For a given concentration of HA^- the values of q are found to increase when the H_2A concentration is raised. Thus q is a function not only of $[HA^-]$ but also of $[H_2A]_{\text{aq}}$.

When $\log (q/[H_2A]_{aq})$ is now plotted against $-\log[HA^-]$ for thorium, as in Fig. 2, the curves for varying initial reagent concentrations are found to coincide. The experimental data can therefore be explained by the very simple assumption that the predominant complex in the organic phase is $Th(HA)_4 \cdot H_2A$.

The slope of the curve in Fig. 2 is seen to decrease from 4 to 0; thus at one end Th^{4+} , and at the other $Th(HA)_4$ predominates in the aqueous phase. The curve deviates from the calculated curve (*cf.* Fig. 2, dotted line), where the only thorium species are assumed to be Th^{4+} and $Th(HA)_4$. This clearly shows that intermediate complexes $Th(HA)_n^{4-n+}$ are also formed. For the equilibria in the aqueous phase we shall use an approximation, which has been successfully applied to many of the systems studied in this series⁵. Approximate values of the complexity constants k_n of the successive complexes are obtained from the formulae (1)–(4)

$$k_1 k_2 k_3 k_4 = 10^{4a} = \kappa_4, \quad (1)$$

$$k_1/k_2 = k_2/k_3 = k_3/k_4 = 10^{2b} \quad (2)$$

$$k_n = \frac{[Th(HA)_n]}{[Th(HA)_{n-1}][HA]} \quad (n = 1, 2, 3, 4) \quad (3)$$

$$\kappa_n = \frac{[Th(HA)_n]}{[Th][HA]^n} \quad (n = 1, 2, 3, 4) \quad (4)$$

In the organic phase only the species $Th(HA)_4 \cdot H_2A$ need be considered. Presumably the distribution coefficient of $Th(HA)_4$ between the two phases is very low and that of $Th(HA)_4 \cdot H_2A$ very large. Thus $Th(HA)_4$ is not detected in the organic phase, and $Th(HA)_4 \cdot H_2A$ is not detected in the aqueous phase.

In the present case we need only consider the reaction

with the equilibrium constant

$$K = \frac{[Th(HA)_4 \cdot H_2A]_{org}}{[Th(HA)_4]_{aq} [H_2A]_{aq}} \quad (6)$$

The equation for q then follows eqn. (7)

$$q = \frac{[Th]_{tot \ org}}{[Th]_{tot \ aq}} = \frac{[Th(HA)_4 \cdot H_2A]_{org}}{[Th]_{tot \ aq}} = \frac{K \kappa_4 [HA^-]^4 [H_2A]_{aq}}{\sum_{j=0}^4 \kappa_n [HA^-]^n} \quad (7)$$

where κ_n is defined by eqn. (4) ($\kappa_0 = 1$).

By introducing the parameters a and b in eqn. (7) the curve in Fig. 2 may be described by

$$\begin{aligned} \log(q/[H_2A]_{aq}) &= \log K + 4a + 4 \log [HA^-] - \\ &-\log (1 + [HA^-] \times 10^{a+3b} + [HA^-]^2 \times 10^{2a+4b} + [HA^-]^3 \times 10^{3a+3b} + \\ &+ [HA^-]^4 \times 10^{4a}) \end{aligned} \quad (8)$$

Using a similar method as in Part V⁵ one can now compare the experimental curve in Fig. 2 with curves calculated for different values of b , i. e. $\log Z (\log y)^b$, where

$$\log Z = 4 \log y - \log (1 + y \times 10^{3b} + y^2 \times 10^{4b} + y^3 \times 10^{3b} + y^4) \quad (9)$$

The two asymptotes to this family of curves are

$$y \rightarrow 0 \quad \log Z = 4 \log y \quad (10)$$

$$y \rightarrow \infty \quad \log Z = 0 \quad (11)$$

The curve in Fig. 2 is now moved parallel with the $\log Z$ - and $\log y$ -axes until a position is found, where the experimental curve coincides with one of the curves in the family; then from eqn. (8) and (9)

$$\log Z = \log (q/[H_2A]_{aq}) - \log K \quad (12)$$

$$\log y = a + \log [HA^-] \quad (13)$$

The experimental data in Fig. 2 were found to fall between the calculated curves for $b = 0.40$ and $b = 0.50$ (shown in Fig. 2 by broken lines). One finds from eqn. (12) and Fig. 2 for $\log Z = 0$

$$\log K = \log (q/[H_2A]_{aq}) = 5.7 \quad (14)$$

For $\log y = 0$, one gets from eqn. (13) and Fig. 2

$$a = -\log [HA^-] = 2.9 \quad (15)$$

The full lines in Fig. 1 are calculated according to eqn. (8) with the values of the constants found above ($a = 2.9$, $b = 0.45$ and $\log K = 5.7$).

Table 2. Distribution of $^{234}\text{Th}-\text{UX}_1$ between CHCl_3 and water. $H_2A = \text{Salicylic acid}$.

$[H_2A]_{\text{tot}}$ M	$[Th]$ M	I'_{org}	I'_{aq}	$\log q =$ $\log I'_{\text{tot}} - \log I'_{\text{aq}} + 0.02$	$-\log [H^+]$	$-\log [HA^-]$
0.15	10^{-5}	5 954	946	+0.82	3.33	1.49
»	»	4 901	2 478	+0.32	3.03	1.74
0.10	»	2 248	616	+0.58	3.52	1.46
»	»	1 251	709	+0.27	3.46	1.50
»	»	3 840	1 231	+0.51	3.26	1.65
»	»	5 201	2 083	+0.42	3.10	1.80
»	»	3 667	3 825	0.00	2.93	1.95
0.07	»	87	325	-0.54	3.71	1.45
»	»	610	1 571	-0.39	3.19	1.83
»	»	4 180	2 872	+0.18	3.10	1.91
»	»	3 072	4 080	-0.10	2.93	2.06
»	»	1 940	5 454	-0.63	2.77	2.20
»	»	931	8 761	-0.95	2.58	2.37
»	»	58	8 724	-2.16	2.16	2.78

Fig. 3. Plot of $\log q$ against $-\log [HA^-]$ for the distribution of $^{234}\text{Th}-\text{UX}_3$ between CHCl_3 and H_2O with salicylic acid as the organic reagent (H_2A).

The results obtained with chloroform as organic solvent are given in Table 2 and recorded in Fig. 3 by a plot of $\log q$ against $-\log [HA^-]$. Because of the low solubility of salicylic acid in chloroform, the highest reagent concentration which could be used in the distribution experiments was $[\text{H}_2\text{A}]_{\text{tot}} = 0.15 \text{ M}$. If the complex formation in the aqueous phase is assumed to be independent of the organic solvent, the distribution curve in Figs. 2 and 3 ought to have the same shape⁶ (broken line in Fig. 3). However, the irregular results obtained with chloroform were not sufficient to confirm the results previously obtained with hexone.

Methoxybenzoic acid

For comparison the distribution of thorium was studied with *o*-methoxybenzoic acid, the methyl ether of salicylic acid, in the same solvent systems. The anion concentration was calculated on the basis of the following constants ($\log k_d - \log k_a$ was obtained from two-phase titrations)

solvent system	$\log k_d - \log k_a$	$-\log k_a$	$\log k_d$
hexone-0.1 M NaClO_4	5.43 ± 0.01	3.89 ± 0.01	1.54 ± 0.02
chloroform-0.1 M NaClO_4	5.49 ± 0.01	3.89 ± 0.01	1.60 ± 0.02

The distribution data are given in Tables 3—4 and plots of $\log q$ against $-\log [A^-]$ are recorded in Figs. 4—5. Since a variation of $[\text{HA}]_{\text{tot}}$ does not affect the distribution curve in the present system, it is concluded that the organic solvent dissolves the uncharged complex ThA_4 , while the aqueous phase contains the complexes ThA^{3+} , ThA_2^{2+} , ThA_3^+ and ThA_4 . Let us assume as before that the complex formation in the aqueous phase is described by the parameters a and b (eqns. (1) and (2)) and let λ_4 denote the distribution coefficient of ThA_4 between the two phases. To find the constants λ_4 , a and b the experimental curves are compared with the family of curves $\log Z(\log y)_b$. The parameter b is thus easily determined from the best fitting curve, whereas, in this case, $\log \lambda_4 = \log q$ for $\log Z = 0$ and $a = -\log [A^-]$ for $\log y = 0$. If the

Table 3. Distribution of $^{234}\text{Th}-\text{UX}_1$ between hexone and water. HA = Methoxybenzoic acid.

$[\text{HA}]_{\text{tot}}$ M	$[\text{Th}]$ M	I'_{org}	I'_{aq}	$\log q =$ $\log I'_{\text{org}} - \log I'_{\text{aq}} - 0.01$	$-\log [\text{H}^+]$	$-\log [\text{A}^-]$
0.72	$10^{-5.57}$	24 567	1 154	+1.32	4.31	1.29
»	»	24 184	2 037	+1.06	3.81	1.67
»	»	23 391	4 239	+0.73	3.40	2.17
»	»	20 745	6 924	+0.47	3.09	2.49
»	»	12 686	14 393	-0.07	2.73	2.84
»	»	6 094	19 997	-0.53	2.40	3.17
0.5	$10^{-5.57}$	11 408	908	+1.09	4.59	1.21
»	»	14 485	4 374	+0.51	3.41	2.33
»	»	11 017	7 853	+0.14	3.12	2.62
»	»	4 939	12 822	-0.43	2.66	3.08
»	»	1 281	16 744	-1.13	2.35	3.39
»	»	491	16 640	-1.54	2.18	3.55
0.2	$10^{-5.48}$	4 261	456	+0.96	4.99	1.31
»	»	7 780	736	+1.01	4.53	1.69
»	»	11 798	554	+1.32	4.21	1.98
»	»	10 417	1 030	+1.01	4.11	2.08
»	»	9 650	1 816	+0.72	3.91	2.26
»	$10^{-5.57}$	16 460	2 366	+0.69	3.85	2.33
»	$10^{-5.48}$	8 323	3 623	+0.35	3.63	2.54
»	»	1 177	9 193	-0.90	3.06	3.11
»	»	108	10 180	-1.98	2.56	3.61
»	»	17	11 134	-2.83	2.23	3.94

accuracy admits it and the experimental data approach the two asymptotes (eqns. (10) and (11)), one may determine the unknown λ_4 , a and b from the curve $\log Z (\log y)_b = -\infty$ (recorded in Figs. 4—7 by a broken line). b is then determined by measuring the vertical distance at $\log y = 0$ between this curve and the experimental one.

The following results were obtained for methoxybenzoic acid

$$\begin{aligned}
 a &= 2.8 & b &= 0.3 \\
 \log \lambda_4 &= 1.2 \text{ for the hexone system} \\
 \log \lambda_4 &\sim 1.6 \text{ for the chloroform system}
 \end{aligned}$$

In the chloroform system especially some points fall outside the distribution curves at the lower HA concentrations (Fig. 5). These points correspond to a loss of radioactivity (*cf.* Table 4). After equilibration of the solutions particles are occasionally seen at the boundary between the phases. In such cases the irregularities may be explained by losses of thorium due to adsorption.

Cinnamic acid

The experimental results obtained for thorium with cinnamic acid are given in Tables 5—6 for the two solvent systems studied. The data are plotted in

Table 4. Distribution of $^{234}\text{Th}-\text{UX}_1$ between CHCl_3 and water. $\text{HA} = \text{Methoxybenzoic acid}$.

$[\text{HA}]_{\text{tot}}$ M	$[\text{Th}]$ M	I'_{org}	I'_{aq}	$\log q =$ $\log I'_{\text{org}} - \log I'_{\text{aq}} + 0.02$	$-\log [\text{H}^+]$	$-\log [\text{A}^-]$
0.8	$10^{-5.18}$	15 818	314	+1.72	4.61	0.95
»	»	15 567	323	+1.70	4.46	1.08
»	»	15 739	402	+1.61	4.23	1.30
»	»	16 699	419	+1.62	4.02	1.50
»	»	16 431	1 122	+1.17	3.53	1.99
»	$10^{-5.57}$	14 465	3 187	+0.67	2.99	2.52
»	»	3 036	15 318	-0.68	2.67	2.84
»	»	1 286	17 628	-1.12	2.37	3.14
0.5	$10^{-5.18}$	13 653	956	+1.17	3.64	2.15
»	»	2 191	12 356	+0.77	3.35	2.44
»	»	2 527	13 445	-0.71	2.82	2.97
»	»	469	16 724	-1.53	2.35	3.43
»	»	132	18 107	-2.12	2.14	3.64
0.2	$10^{-5.57}$	14 612	760	+1.30	3.75	2.45
»	»	12 172	4 200	+0.48	3.40	2.80
»	»	423	17 360	-1.59	2.99	3.21
»	»	366	19 017	-1.70	2.63	3.57
0.1	$10^{-5.18}$	2 278	71	+1.53	4.95	1.66
»	»	7 991	187	+1.65	4.33	2.18
»	»	11 839	400	+1.49	3.85	2.65
»	»	7 371	4 246	+0.26	3.67	2.83
»	»	736	13 907	-1.26	3.11	3.38
»	»	41	16 174	-2.58	2.42	4.09

Fig. 4. Plot of $\log q$ against $-\log [\text{A}^-]$ for the distribution of $^{234}\text{Th}-\text{UX}_1$ between hexone and H_2O with methoxybenzoic acid as the organic reagent (HA). Fig. 5. Plot of $\log q$ against $-\log [\text{A}^-]$ for the distribution of $^{234}\text{Th}-\text{UX}_1$ between CHCl_3 and H_2O with methoxybenzoic acid as the organic reagent (HA).

Table 5. Distribution of $^{234}\text{Th}-\text{UX}_1$ between hexone and water. HA = Cinnamic acid.

$[\text{HA}]_{\text{tot}}$ M	$[\text{Th}]$ M	I'_{org}	I'_{aq}	$\log q =$ $\log I'_{\text{org}} - \log I'_{\text{aq}} - 0.01$	$-\log [\text{H}^+]$	$-\log [\text{A}^-]$
0.2	10^{-5}	11 538	20 ± 8	+2.75	5.24	2.08
»	»	12 729	2 ± 8	+3.81	5.16	2.16
»	»	12 258	13 ± 8	+2.97	4.88	2.43
»	»	9 218	12 ± 9	+2.88	4.19	3.11
»	»	1 275	7 542	-0.78	2.95	4.35
»	»	822	10 332	-1.11 ± 0.01	2.68	4.62
»	»	864	10 242	-1.08	2.53	4.77
0.05	»	12 468	8 ± 7	+3.18	5.50	2.44
»	»	11 076	196 ± 12	+1.74	5.24	2.68
»	»	11 374	3 ± 8	+3.41	5.07	2.84
»	»	11 408	10 ± 8	+3.05	4.82	3.09
»	»	11 353	36 ± 8	+2.49	4.34	3.56
»	»	8 251	2 328	+0.54	3.69	4.21
»	»	1 909	7 910	-0.63	3.20	4.70
»	»	347	9 709	-1.46	2.81	5.09

Table 6. Distribution of $^{234}\text{Th}-\text{UX}_1$ between CHCl_3 and water. HA = Cinnamic acid.

$[\text{HA}]_{\text{tot}}$	$[\text{Th}]$ M	I'_{org}	I'_{aq}	$\log q =$ $\log I'_{\text{org}} - \log I'_{\text{aq}} + 0.02$	$-\log [\text{H}^+]$	$-\log [\text{A}^-]$
0.1	10^{-5}	7 069	3.2 ± 4	+3.36	4.60	2.69
»	»	5 616	5.2 ± 4	+3.05	4.44	2.84
»	»	9 105	30 ± 4	+2.50	4.05	3.23
»	»	8 469	32 ± 4	+2.44	3.87	3.40
»	»	5 676	264	+1.35	3.86	3.41
»	»	8 859	70 ± 5	+2.12	3.90	3.38
»	»	8 633	136 ± 6	+1.82	3.64	3.64
»	»	7 465	921	+0.93	3.38	3.90
»	»	4 756	611	+0.91	3.33	3.95
»	»	2 358	6 443	-0.42	3.04	4.23
»	»	1 583	6 560	-0.60	2.88	4.39
»	»	911	4 488	-0.67	2.64	4.63
»	»	703	8 072	-1.04	2.58	4.69
»	»	162	5 821	-1.53	2.52	4.75
0.05	»	7 839	7 ± 4	+3.07	4.68	2.77
»	»	8 787	38 ± 9	+2.38	3.80	3.65
»	»	8 059	144 ± 6	+1.77	3.74	3.70
»	»	6 679	1 889	+0.57	3.25	4.19
»	»	6 568	2 764	+0.40	3.23	4.21
»	»	1 024	8 676	-0.91	2.79	4.65
»	»	736	8 641	-1.05	2.86	4.58
»	»	388	8 919	-1.34	2.62	4.82
0.01	»	4 241	41 ± 4	+2.04	4.40	3.48
»	»	2 603	2 092	+0.11	3.77	4.09
»	»	732	3 756	-0.69	3.63	4.24
»	»	178	5 327	-1.46	3.25	4.62
»	»	13 ± 4	8 790	-2.81	2.46	5.40

Fig. 6. Plot of $\log q$ against $-\log [A^-]$ for the distribution of $^{232}\text{Th}-\text{UX}_1$ between hexone and H_2O with cinnamic acid as the organic reagent (HA).

Fig. 7. Plot of $\log q$ against $-\log [A^-]$ for the distribution of $^{232}\text{Th}-\text{UX}_1$ between CHCl_3 and H_2O with cinnamic acid as the organic reagent (HA).

Figs. 6—7. The constants, a , b and λ_4 , were determined in the same way as before. For cinnamic acid one then obtains

$$\begin{aligned} a &= 3.6 & b &= 0.2 \\ \log \lambda_4 &\sim 3.7 \text{ for the hexone system} \\ \log \lambda_4 &\sim 3.2 \text{ for the chloroform system} \end{aligned}$$

A certain spreading of the data is to be seen in Fig. 6. As will be discussed below the effects are probably due to the hydrolysis of thorium.

DISCUSSION

A summary of the constants obtained is given in Table 7, together with the dissociation constants and distribution coefficients of the acids. In the methoxy-compound thorium is only bound to the carboxyl group, while for salicylic acid one also has the possibility that the phenolic hydrogen participates in the reaction. However, the slope in Fig. 2 approaches 4, which suggests, that the salicylic acid ligand is HA^- . It is seen in Table 7 that the parameter a calculated for salicylic acid with the ligand HA^- is about the same as for methoxybenzoic acid.

The salicylate complexes of Cu^{2+} , Be^{2+} and Fe^{3+} have been reported⁸⁻¹⁰ as chelate compounds, with the dissociation of the phenolic hydrogen. In the

Table 7.

Organic reagent	$-\log k_a$	$\log k_d$ hexone- H ₂ O	$\log k_d$ CHCl ₃ - H ₂ O	$\log k_s$ CHCl ₃	Metal	$\log \lambda_4$ hexone- H ₂ O	$\log \lambda_4$ CHCl ₃ - H ₂ O	$\log \kappa_4$	a	b	$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$
Salicylic acid H ₂ A	2.82	2.51	0.5	1.6	Th ⁴⁺	$\log K^* = 5.7$		11.6	2.9	0.45	4.25	3.35	2.45	1.55
Methoxybenzoic acid HA	3.89	1.54	1.6		Th ⁴⁺	1.2	~ 1.6	11.2	2.8	0.3	3.7	3.1	2.5	1.9
Cinnamic acid (<i>trans</i> form) HA	4.27	2.33	1.2	2.2	Th ⁴⁺	~ 3.7	~ 3.2	14.4	3.6	0.2	4.2	3.8	3.4	3.0

* K is defined by eqn. (6).

last work ¹⁰ the first complex between Fe³⁺ and salicylic acid H₂A is written as FeA and the complexity constant κ_1 is defined

$$\kappa_1 = \frac{[\text{H}^+][\text{FeA}]}{[\text{HA}][\text{Fe}]}$$

The actual complex could equally well be of the isomeric form Fe(OH)(HA) with the following equilibrium constant

$$K = \frac{[\text{Fe(OH)(HA)}]}{[\text{Fe}][\text{HA}][\text{OH}]}$$

The weak complex formation between Fe³⁺ and methyl salicylate ¹¹, however, gives evidence for displacement of the phenolic hydrogen in this case. X-ray measurements of salicylates of K, Rb, NH₄ ¹² and of Zn ¹³ have been made. The composition of the latter compound seemed to be Zn(HA)₂ · 3H₂O. It might be pointed out in this connection that the parameter a for thorium (*cf.* Table 7) when complexed with the acids studied in this work is much smaller than for typical inner complex formers, such as oxine ($a = 9.8$ ¹⁴), cupferron ($a = 6.8$ ¹⁴) and acetylacetone ($a = 6.7$ ⁴; *cf.* also ⁵).

The present results give evidence for the association of a salicylic acid molecule to the uncharged complex both for thorium and UO₂²⁺, *i. e.* the complexes found are written as Th(HA)₄ · H₂A and UO₂(HA)₂ · H₂A. When a methyl group replaces the phenolic hydrogen the data indicated no such association of an extra acid molecule, which may be explained by the more limited space available around the central group in this case.

Chloroform is found to be a poor solvent for the salicylate complex. The solubility of the complex is markedly improved when the phenolic group is replaced by a methoxy group (*cf.* Figs. 3 and 5 and Table 7). The distribution of the metal complexes and of the actual acids are roughly parallel (*cf.* Table 7).

Because of the strength of the acids a high anion concentration is attainable at relatively low pH values. Thereby it was thought possible to avoid hydrolysis effects. In a recent publication by Hietanen¹⁵ the hydrolysis of thorium has been discussed. The concentration of total thorium ranged from 2×10^{-2} M down to 10^{-3} M and the data were explained by the formation of successive polynuclear complexes. Under the experimental conditions of the present study the total thorium concentration in the aqueous phase was always $<10^{-5}$ M. Although the hydrolysis process may be chiefly mononuclear at these low metal concentrations one may nevertheless estimate a maximum value of the hydrolysis from Hietanen's data. If the function $X = \log [\text{Th}]_{\text{aq tot}} - 3 \log [\text{H}^+]$ is <7 (cf. Fig. 3, Ref.¹⁵) one can state that the experiments will be very little affected by hydrolysis. Since $[\text{Th}]_{\text{aq tot}}$ is obtained from $[\text{Th}]_{\text{tot}}/(q+1)$ and the hydrogen ion concentration has been measured in each case, it is easy to calculate X . It was found that difficulties due to hydrolysis could be expected for salicylic acid and cinnamic acid at the lowest concentrations studied in the hexone system. A spread of the data was also noticed here with occasional losses of thorium. With methoxybenzoic acid extraction was carried out on the border, where the thorium hydrolysis might start to become appreciable.

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