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Studies on the Extraction of Metal Complexes

XXII. The Complex Formation of Thorium with 1-Nitroso-2-naphthol and 2-Nitroso-1-naphthol

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The extraction of thorium with chloroform or hexone using 1-nitroso-2-naphthol and 2-nitroso-1-naphthol as complexing agents has been studied at 25° C. The perchlorate ion concentration in the aqueous phase was kept constant at 0.1 M.

The mean complexity constants are found to be $10^{8.50}$ for 1-nitroso-2-naphthol and $10^{8.30}$ for 2-nitroso-1-naphthol. These values are lower than for oxine, but higher than for acetylacetone.

It was shown by Fischer [1] in 1940 that the nitroso-naphtholates of transition metal cations like Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} may be extracted into chloroform. It has also been reported by Harvey *et al.*[2] that plutonium(IV) gives a complex with 1-nitroso-2-naphthol, which is extractable with hexone (methyl *iso*butyl ketone) at pH 2, and we therefore expected that thorium could be extracted from aqueous solutions into chloroform or hexone using either of the two nitroso-naphthols as complexing agents. A study was carried out to confirm whether thorium was extracted in these systems and whether the data for the two-phase distribution of thorium as a function of the nitroso-naphtholate ion concentration would enable us to determine the complex formation between Th^{4+} and the nitroso-naphtholate ions. A summary of our data for thorium with other chelating agents was given in Part XXI [3] of this series.

EXPERIMENTAL

Only a few experimental details will be given here as the general experimental technique has been described in several previous papers of this series, *e. g.* Part VI [4]. In making our solutions we sometimes added 1 ml of 0.1 M sodium acetate per 15 ml to buffer our solutions. This small amount of acetate ion seemed to have no effect on the extraction of thorium. We are not entirely satisfied with our results on these systems as the mass balance ^{234}Th was not always very good (50—100 %; see Table 1, column 2). A possible

Table 1. Distribution of Th-^{234}Th between chloroform and hexone and 0.1 M perchlorate solutions as a function of the nitroso-naphtholate concentration in the aqueous phase at 25° C.
1A. The 1-nitroso-2-naphthol-$CHCl_3$ system.

$[HA]_{org}$	Mass balance %	I_{org} cpm	I_{aq} cpm	log q	$-\log[H^+]$	$-\log[A^-]$
1	2	3	4	5	6	7
0.1	102	412	5 490	−1.11	1.21	10.39
0.1	98	1 140	4 495	−0.58	1.46	10.14
0.1	85	2 416	2 856	−0.06	1.66	9.94
0.1	89	3 861	1 115	+0.56	1.88	9.72
0.1	51	2 830	257	+1.06	2.04	9.56
0.1	54	3 250	57.0	+1.77	2.31	9.29
0.1	73	3 509	3.6	+3.01	2.69	8.91
0.1	75	3 630	0.8	+3.67	3.12	8.48
0.05	90	26.5	8 694	−2.50	1.25	10.65
0.05	88	86.9	8 466	−1.97	1.35	10.55
0.05	94	42.7	11 361	−2.41	1.37	10.53
0.05	79	736	8 824	−1.06	1.67	10.23
0.05	62	2 684	4 803	−0.24	2.04	9.86
0.05	68	3 430	2 987	+0.08	2.31	9.59
0.05	51	5 839	180	+1.53	2.72	9.18

1B. The 1-nitroso-2-naphthol-hexone system.

1	2	3	4	5	6	7
0.1	95	26.8	7 689	−2.47	2.09	9.09
0.1	91	164	7 254	−1.66	2.37	8.81
0.1	87	1 774	5 363	−0.49	2.92	8.26
0.1	94	6 697	722	+0.95	3.95	7.23
0.1	60	4 680	92.9	+1.69	4.75	6.43
0.05	90	0.7	9 007	−4.12	1.82	9.66
0.05	94	7.0	9 336	−3.14	2.02	9.46
0.05	88	356	8 418	−1.39	2.77	8.71
0.05	90	7 894	378	+1.31	4.50	6.98
0.05	99	8 841	195	+1.64	5.20	6.28
0.05	91	8 237	65.0	+2.09	6.37	5.11
0.05	89	8 116	60.1	+2.12	7.38	4.10

1C. The 2-nitroso-1-naphthol-$CHCl_3$ system.

1	2	3	4	5	6	7
0.05	97	256	9 158	−1.54	1.04	9.61
0.05	100	667	9 014	−1.11	1.21	9.44
0.05	94	1 476	8 665	−0.75	1.35	9.30
0.05	81	3 154	4 592	−0.15	1.73	8.92
0.05	71	6 071	553	+1.06	2.22	8.43
0.05	63	6 488	70.7	+1.98	2.83	7.82
0.05	61	6 348	7.4	+2.95	3.20	7.45
0.02	100	7.8	9 169	−3.05	1.04	10.01
0.02	98	27.0	8 926	−2.50	1.19	9.86
0.02	92	259	8 141	−1.48	1.70	9.35
0.02	72	1 145	5 410	−0.66	2.24	8.81

1D. The 2-nitroso-1-naphthol-hexone system.

1	2	3	4	5	6	7
0.1	90	3.6	5 808	−3.22	1.28	9.19
0.1	101	10.8	5 799	−2.74	1.45	9.02
0.1	91	51.7	4 921	−1.99	1.56	8.91
0.1	74	211	4 640	−1.36	1.97	8.50
0.1	103	995	4 963	−0.71	2.25	8.22
0.1	70	2 527	2 066	+0.07	2.68	7.79
0.1	72	3 347	705	+0.66	3.10	7.37
0.1	103	5 341	126	+1.61	4.06	6.41
0.1	104	6 037	33.2	+2.25	5.44	5.03
0.1	94	5 092	79.2	+1.80	5.84	4.63
0.1	97	5 106	34.4	+2.16	6.21	4.26

explanation is that even recrystallized analytical reagents might still contain some solid particles capable of adsorbing radioactivity. However, by centrifuging our solutions after shaking, we assumed that these particles did not interfere with the measurements of the distribution equilibria.

DATA AND EQUILIBRIUM CONSTANTS

The data are given in Table 1, and are plotted in Fig. 1. When the two-parameter method of Dyrssen and Sillén [5] was applied to the data it was found that a templet with a value of $b = 0.70$ fitted the experimental data very well for all of the nitroso-naphthol systems if it was moved parallel to the log q and $-\log[A^-]$ axes. In a plot of log q $-\log \lambda_4$ against $\log[A^-] + a$ (*cf.* Fig. 2 in Part V [5]) all data would consequently fall on the same curve.

Using this templet it was thus possible to determine the second parameter a for the complex-formation, as well as the distribution constants between chloroform and the aqueous phase, λ_4, of the uncharged, extractable thorium nitroso-naphtholate complexes. It is however assumed that complex formation in the aqueous phase is not greatly influenced by the presence of small amounts of the organic solvents.

The complexity constants are defined by

$$k_n = [MA_n]/[MA_{n-1}][A] \text{ or } \varkappa_n = [MA_n]/[M][A]^n$$

and the parameters a and b were so chosen that a defines the mean complexity constant

$$\sqrt{\varkappa_4} = 10^a$$

and $2b$ defines the mean spreading factor

$$k_n/k_{n+1} = 10^{2b}$$

Thus the approximate values of log k_n may be obtained from

$$\log k_n = a + b(5-2n)$$

The following sets of constants determine the distribution curves in Fig. 1:

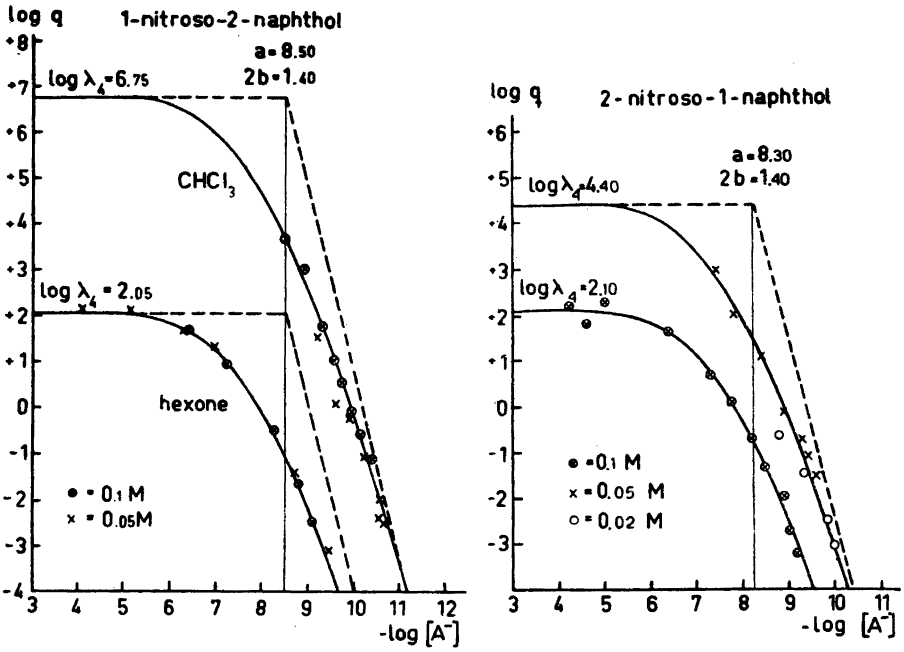


Fig. 1. The distribution ratio of Th-^{234}Th as a function of the nitroso-naphtholate ion concentration in the aqueous phase. The fulldrawn curves are determined by the parameters λ_4, a *and* b, *and the broken lines by the equations* $\log q = \log \lambda_4 + 4 \log[A^-]$ *and* $\log q = \log \lambda_4$, *(equations 7 and 8 in Part V*[5]*).*

For 1-nitroso-2-naphthol

$$a = 8.50;\ 2b = 1.40$$
$$\log \lambda_4 = 6.75 \text{ for chloroform}$$
$$\log \lambda_4 = 2.05 \text{ for hexone}$$

For 2-nitroso-1-naphthol

$$a = 8.30;\ 2b = 1.40$$
$$\log \lambda_4 = 4.40 \text{ for chloroform}$$
$$\log \lambda_4 = 2.10 \text{ for hexone}$$

STRENGTH OF COMPLEXES WITH 1-NITROSO-2-NAPHTHOL AND 2-NITROSO-1-NAPHTHOL

It was shown in Part XX[6] of this series that 2-nitroso-1-naphthol ($pk_a = 7.24$) is a stronger acid than 1-nitroso-2-naphthol ($pk_a = 7.63$) and consequently one would expect a lower value of the parameter a for the complex formation of Th with the former derivative. This seems to be the case, although the difference is not definitely outside the experimental error ($\pm$ 0.05 or 0.10).

Jonassen and DeMonsabert [7] studied the zirconyl complexes of the two nitroso-naphthols in 50 % alcohol at pH 3.5 by a spectrophotometric method and concluded: "The decrease in stability in the 1-nitroso-2-naphthol complex as compared to the 2-nitroso-1-naphthol is to be expected from a comparison of the reactions of α- and β-naphthols". The relation between the "instability constant", K, of these authors and the complexity constant k_1 defined above is

$$K = [ZrO^{2+}]\ [HA]/[ZrOA^{+}] = [H^{+}]/k_1 k_a$$

From Jonassen and DeMonsabert's values of K and $[H^{+}]$ we obtain

$$k_1 k_a = 10^{0.1 \pm 0.05} \text{ for 1-nitroso-2-naphthol}$$
$$k_1 k_a = 10^{0.6 \pm 0.05} \text{ for 2-nitroso-1-naphthol}$$

The values of k_a are approximately $10^{-7.6-\delta}$ and $10^{-7.2-\delta}$ for the two nitroso-naphthols, respectively, where a value of $\delta \sim 0.5$ may be estimated from a value of $k_a = 10^{-8.7}$ for 1-nitroso-2-naphthol in 96 % alcohol [8]. We then arrive at $k_1 = 10^{8.2 \pm 0.05}$ for the complex formation of ZrO^{2+} with 1-nitroso-2-naphthol and $k_1 = 10^{8.3 \pm 0.05}$ for the 2,1 derivative, *i. e.* again in this case there is no significant difference between the two constants.

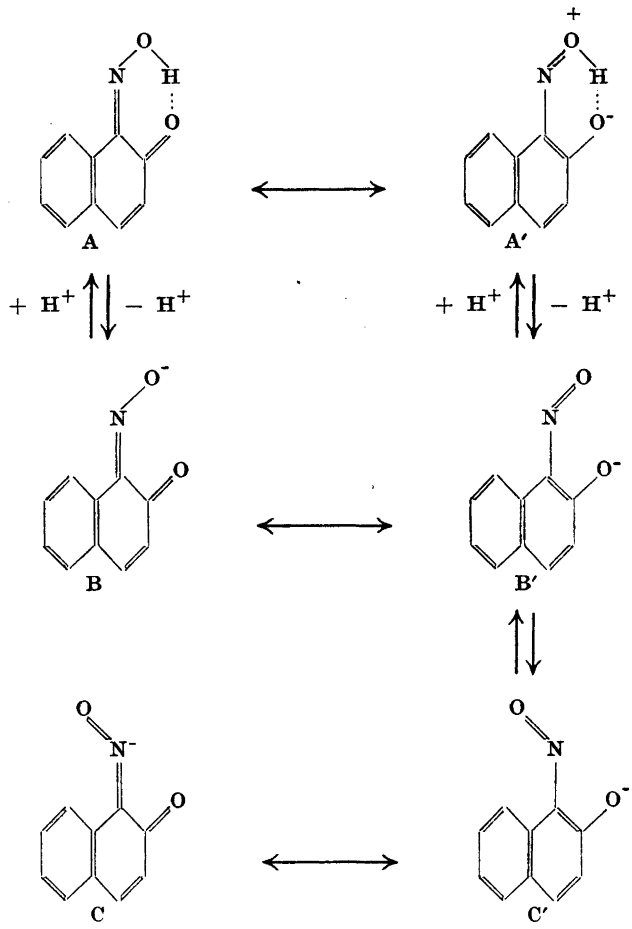
FORM OF THE CHELATE RING

In Part XX [6] we concluded that the two nitroso-naphthols should be regarded as quinone oximes having the structure A. It was also concluded that a structure A′ might contribute to a mesomeric state. Even if it seems to be well established that the proton forms a six-membered chelate ring with the nitroso-naphtholate ion, this does not necessarily have to be the case with metal cations, *i. e.* the nitroso-naphtholate ligand may have the form C↔C′ in these complexes. Feigl [9] has critically reviewed various opinions on this topic, and he accepted the form C on the basis of Pfeiffer's studies on nickel with dimethylglyoxime and similar compounds. Godycki *et al.*[10] have proved the existence of a five-membered ring in nickel dimethylglyoxime and have shown that it is stabilized by two short hydrogen bonds. However, such bonds cannot be formed in the case with the nitroso-naphthols. On the basis of the stability of the cobalt(III)complexes with 1-nitroso-2-naphthol and its 3,6-disulfonate in acid Feigl [9] also postulates a pH-dependent tautometric equilibrium. Studies by West [11] indicate, however, that this stability is due to a very slow exchange between cobalt and the proton.

No deductions about the size of the chelate ring can be made from the value of a as it lies between the value for oxine ($a = 9.70$), which forms a five-membered chelate ring (*cf.* Part XXI [3]), and the value for acetylacetone ($a = 6.70$), which forms a six-membered ring. X-ray measurements may settle this question.

CHOICE OF SYSTEM FOR EXTRACTION

The choice of a system for the extraction of thorium is somewhat arbitrary. If the price of the reagent is considered important one would choose 1-nitroso-



2-naphthol, and if one wants an organic solvent that is lighter than water one would choose hexone.

It is probably unimportant which of the nitroso-naphthols one chooses for the separation of metal cations. A few experiments were carried out with 1-nitroso-2-naphthol in order to see if Th^{4+} could be separated from UO_2^{2+} and trivalent ions such as La^{3+} and Sm^{3+}. These experiments revealed that the UO_2^{2+} ion was extractable, but that the trivalent ions were not. Fifty percent of the uranium was extracted at $-\log[H^+] = 3.07$ with an 0.1 M solution of 1-nitroso-2-naphthol in chloroform; the corresponding value for thorium was 1.66. Thus it is possible to separate Th^{4+} and UO_2^{2+} at pH 2, and it is also possible to separate these two ions from the trivalent ions at pH 4. Other metals that have been extracted with either of these nitroso-naphthols [1,2,13] are: Mn(II), Fe(II), Co, Ni, Cu(II), Pd(II), Ag, Cd, Hg(II) and Pu(IV).

In many cases it is important to extract in a low pH-range. This range is approximately defined by

$$\tfrac{1}{4}\log K = \log[H^+] - \log[HA]_{org} = \tfrac{1}{4}\log \lambda_4 + a - pk_a - \log k_d$$

The above equation was discussed in Part VIII[12]. The following values of $\frac{1}{4}\log K$ may be calculated for the four systems:

1-nitroso-2-naphthol and chloroform:	—0.41
1-nitroso-2-naphthol and hexone:	—1.17
2-nitroso-1-naphthol and chloroform:	+0.05
2-nitroso-1-naphthol and hexone:	—0.64

For a given value of $[HA]_{org}$ extraction occurs in the lowest pH range for the third system. It is also apparent that chloroform is the better solvent in this respect.

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