

Studies on the Extraction of Metal Complexes

XXXII. N-Phenylbenzohydroxamic Acid

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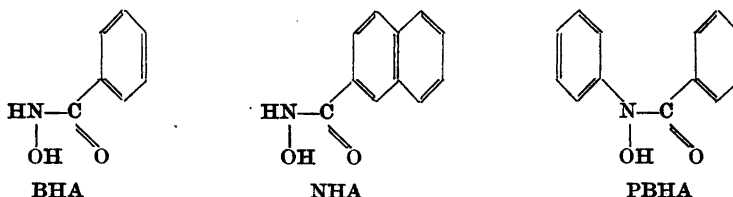
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N-Phenylbenzohydroxamic acid (PBHA) has been investigated at 25 °C as a solvent extraction agent for La(III), Th(IV) and U(VI). Chloroform was used as the organic solvent and the ionic strength in the aqueous phase was kept constant at 0.1 M by addition of HClO₄ and NaClO₄. The values of $\frac{1}{N} \log K$ (eqn. 3) for La, Th and U are -4.80, -0.17 and -1.57, respectively. Fig. 1 shows that Th and U may easily be separated from La by batch extraction, while a good separation of Th and U would require a simple extraction column.

The stoichiometric dissociation constant k_a of PBHA is $10^{-8.15 \pm 0.01}$ and its distribution constant k_d between chloroform and water is $10^{2.33 \pm 0.01}$. The mean complexity constant 10^a for the formation of Th tetra-N-phenylbenzohydroxamate is $10^{9.45}$ and the distribution constant λ_4 of this complex between chloroform and water is $10^{3.45 \pm 0.03}$.

Benzohydroxamic acid (BHA) and α -naphthohydroxamic acid (NHA) have been used¹ for the extraction of trivalent lanthanide and actinide ions. Shome² has pointed out that a stable compound, N-phenylbenzohydroxamic acid (PBHA) was obtained, if the nitroso group in cupferron (N-nitrosophenylhydroxylamine) was substituted with benzoyl, and Lutwick and Ryan³ have prepared several of these hydroxamic acids (or aromatic hydroxylamines). In Part VIII⁴ of this series it was shown that cupferron was a very good reagent for the extraction of the tetravalent ions Hf⁴⁺ and Th⁴⁺.

These were the main facts that led to the investigation of N-phenylbenzohydroxamic acid (or N-benzoylphenylhydroxylamine) as a solvent extraction agent for lanthanide and actinide ions. The complex formation and partition of Th phenylbenzohydroxamate was studied in some detail. The dissociation and distribution constants of PBHA were determined so that the free ligand concentration [A⁻] could be calculated.



EXPERIMENTAL

N-Phenylbenzohydroxamic acid (N-benzoylphenylhydroxylamine) was kindly prepared Mr. Bertil Takman and Mr. Sven Lindström, University of Stockholm. They used Shome's modification² of Bamberger's⁵ method. The product was, however, finally recrystallised from benzene. M. p. 121 °C. (Found: C 73.2; H 5.0; N 6.6. Calc. for C₁₃H₁₁NO₂: C 73.2; H 5.2; N 6.6). Chemicals used were of analytical grade, and the chloroform was saturated with water and alcohol-free.

Values of k_a and k_a/k_d were determined by means of the titration technique described in Part IV⁶. However, saturated KCl was used in the reference electrode instead of 0.1 M NaClO₄/4 M NaCl. The light absorption curve of PBHA in 0.005 M HClO₄ + 0.095 M NaClO₄ has a peak at 253 m μ with an extinction coefficient of 0.765·10⁴ M⁻¹. Alkaline solutions of PBHA are however yellow. The distribution constants k_d between chloroform and 0.005 M HClO₄ + 0.095 M NaClO₄ ($-\log[H^+] = 2.30$) were determined for 0.1–0.02 M solutions of PBHA in chloroform by measuring the hydroxamic acid concentration in the aqueous phase at 250–280 m μ with a Beckman Model DU spectrophotometer (1 cm cells).

The radioisotopes ¹⁴⁰La and ²³⁴Th (UX₁) were employed for the determination of the distribution of La(III) and Th(IV). The distribution of U(VI) was, however, determined in the following way: a 5 ml portion of the 10 ml aqueous phase was removed, and the pH of the solution was adjusted to about 3.3 with 0.1 M sodium acetate. The solution was then shaken with 5 ml of 0.05 M 5,7-dichloro-oxine in chloroform and the absorbancy of the chloroform layer was measured at 390 m μ (cf. Part XXXI⁷).

The ionic strength of the aqueous phase was kept constant at 0.1 M by addition of 0.1 M solutions of HClO₄, NaClO₄ and NaOH. In the distribution measurements of La, Th and U the aqueous phase was sometimes buffered with 1 ml of 0.1 M anilinium perchlorate, sodium acetate or hydrazinium perchlorate per 15 ml. The hydrogen ion concentration, $[H^+]$, was measured with a Radiometer pHM3i potentiometer equipped with glass and calomel electrodes, which were standardized against a 0.01 M HClO₄ + 0.09 M NaClO₄ buffer ($-\log[H^+] = 2.00$).

All experiments were carried out in thermostated rooms at 25.0 ± 0.3 °C.

THE DISSOCIATION AND DISTRIBUTION CONSTANTS OF PBHA

The dissociation constant k_a and distribution constant k_d of PBHA are given in Table 4 together with the solubilities in chloroform and in 0.005 M HClO₄ + 0.095 M NaClO₄. The thermodynamic dissociation constant K_a may be calculated as 10^{-8.30} using activity coefficients given by Conway¹⁰. This value seemed much too low in comparison with the value 10^{-6.7} for benzo-hydroxamic acid, reported by Oliveri-Mandalá¹¹. Recently Wise¹² has shown, however, that the values calculated from electrical conductance measurements of Oliveri-Mandalá were about a hundred times larger than his potentiometric data. Wise reports 10^{-8.88} for the mixed (Brønsted) dissociation constant of benzohydroxamic acid at 20 °C and ionic strength 0.005 M. No values of the dissociation and distribution constants of PBHA have been reported. The value of k_d seemed to increase slightly with the concentration of PBHA in chloroform (0.02–0.1 M). This effect was, however, almost entirely concealed by the experimental error (±0.01) in the determination of $\log k_d$. A two-phase titration (cf. Part IV⁶) of 50 ml of 0.01 M PBHA in chloroform gave $pK_a + \log k_d = 10.46$, in good agreement with the separate determinations of pK_a and $\log k_d$. The value of the solubility of PBHA in water, given in Table 4 is in good agreement with the value, 0.40 g/l (0.0019 M), reported by Lutwick and Ryan³.

Table 1. Distribution of La-¹⁴⁰La between 0.1 M solutions of PBHA in chloroform and 0.1 M sodium perchlorate solutions at 25 °C.

Initial conc. of La in the aq. phase M · 10 ⁵	I _{org} cpm	I _{aq} cpm	log q *	-log[H ⁺]	-log [A ⁻]
14.0	36.3	4 959	-2.06	5.04	6.44
14.0	53.8	4 705	-1.86	5.13	6.35
14.0	201	4 429	-1.26	5.42	6.06
0.15	1 774	5 929	-0.44	5.45	6.03
16.4	2 670	15 591	-0.69	5.53	5.95
16.4	6 783	11 189	-0.14	5.81	5.67
7.0	8 241	1 544	+0.81	6.12	5.36
7.0	9 452	387	+1.47	6.35	5.13
14.0	3 791	67.8	+1.83	6.61	4.87
7.0	10 683	126	+2.01	6.62	4.86

* $q = 1.20 \cdot I_{\text{org}}/I_{\text{aq}}$ (cf. Part XVII⁶).

Table 2. Distribution of U (VI) between chloroform and 0.1 M HClO₄-NaClO₄ solutions at 25 °C as a function of the N-phenylbenzohydroxamate ion concentration in the aqueous phase. Initial concentration of uranium in the aqueous phase 10⁻⁴ M.

Initial conc. of PBHA in the org. phase M	log q	-log[H ⁺]	-log[A ⁻]
0.2	-1.15	1.71	9.47
0.2	-0.53	2.00	9.18
0.2	-0.35	2.08	9.10
0.2	-0.08	2.22	8.96
0.2	+0.25	2.39	8.79
0.2	+0.45	2.51	8.67
0.2	+0.74	2.65	8.53
0.1	-1.20	2.04	9.44
0.1	-0.95	2.10	9.38
0.1	-0.51	2.23	9.25
0.1	-0.32	2.39	9.09
0.1	+0.11	2.68	8.80
0.1	+0.41	2.89	8.59
0.1	+1.17	3.36	8.12

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

The results for the extraction of La³⁺, Th⁴⁺ and UO₂²⁺ are given in Fig. 1 and in Tables 1—3. The ligand concentration [A⁻] is calculated from the equation

$$-\log [A^-] = \log [H^+] - \log [HA]_{\text{org}} + pK_a + \log k_d \quad (1a)$$

Introducing the values of pK_a and $\log k_d$ from Table 4:

$$-\log [A^-] = \log [H^+] - \log [HA]_{\text{org}} + 10.48 \quad (1b)$$

As the distribution constant k_d for PBHA is so large, the initial reagent concentration in chloroform is $\approx [HA]_{\text{org}}$, provided that the pH in the aqueous phase is not too high (<9). Fig. 1 shows that the La, U and Th may be extrac-

Table 3. Distribution of Th-²³⁴Th between chloroform and 0.1 M HClO₄-NaClO₄ solutions at 25 °C as a function of the N-phenylbenzohydroxamate ion concentration in the aqueous phase ($-\log[A^-]$).

Initial conc. of ²³² Th in the aq. phase ^a M · 10 ⁶	Initial conc. of PBHA in the org. phase M	I _{org} ^b cpm	I _{aq} ^b cpm	log q ^c	$-\log[H^+]$	$-\log[A^-]$
1.33	0.1	831	2 311	-0.42	1.20	10.28
1.33	0.1	1 236	1 675	-0.10	1.22	10.26
1.33	0.1	2 255	815	+0.47	1.57	9.91
2.67	0.1	4 946	284	+1.27	1.91	9.57
1.33	0.1	2 838	68.5	+1.64	2.20	9.28
2.67	0.1	5 242	61.9	+1.96	2.70	8.78
2.67	0.1	5 064	9.4	+2.76	3.39	8.09
2.67	0.1	4 964	8.5	+2.79	3.42	8.06
2.67	0.1	4 911	4.5	+3.07 ^d	4.77	6.71
4	0.1	6 667	1.3	+3.74 ^d	5.18	6.30
4	0.1	6 509	-0.2	- ^d	7.46	4.02
4	0.1	6 250	2.3	+3.46 ^d	8.69	2.78
2.67	0.1	4 906	2.2	+3.38 ^d	8.88	2.59
1.33	0.05	359	16 612	-1.64	1.02	10.76
0.67	0.05	318	10 919	-1.51	1.02	10.76
0.67	0.05	795	10 652	-1.10	1.19	10.59
0.67	0.05	2 077	8 999	-0.61	1.48	10.30
0.67	0.05	6 448	4 384	+0.20	1.88	9.90
0.67	0.05	9 834	1 275	+0.92	2.19	9.59
0.67	0.05	11 278	341	+1.55	2.49	9.29
1.33	0.05	20 218	87.0	+2.39	2.89	8.89
1.33	0.05	20 748	28.4	+2.89	3.11	8.67
1.33	0.05	20 788	14.0	+3.20	3.49	8.29
1.33	0.05	20 272	15.3	+3.15	4.01	7.77
1.33	0.05	17 288	16.7	+3.04	4.19	7.59
1.33	0.05	13 805	7.7	+3.28 ^d	6.76	5.02
1.33	0.05	14 306	4.5	+3.53 ^d	7.26	4.52
1.33	0.05	15 361	5.4	+3.48 ^d	7.86	3.92
0.67	0.025	4.5	10 016	-3.32	1.04	11.04
1.33	0.025	36.4	16 793	-2.64	1.13	10.95
1.33	0.025	27.5	9 707	-2.52	1.28	10.80
1.33	0.025	235	16 210	-1.81	1.49	10.59
1.33	0.025	795	15 472	-1.26	1.69	10.39

a) The measured radioactivity from a 10⁻⁶ M Th solution is only 0.026 cpm.

b) The standard deviation of I for values <100 cpm is $\sqrt{I}/\sqrt{10}$ cpm.

c) $q = (1.067 \pm 0.010) \cdot I_{org}/I_{aq}$ (cf. Part XXI⁹).

d) The distribution constant λ_4 was calculated from these eight measurements:

$$\lambda_4 = \frac{72\,715}{27.7 \pm 1.7} \cdot (1.067 \pm 0.010) = 103.45 \pm 0.03$$

Table 4. Properties of N-phenylbenzohydroxamic acid (PBHA).

Stoichiometric dissociation constant pK_a in 0.1 M NaClO ₄	8.15 ± 0.01
Distribution constant log k_d between chloroform and 0.005 M HClO ₄ + 0.095 M NaClO ₄	2.33 ± 0.01
Solubility in chloroform (aq)	0.739 M
Solubility in 0.005 M HClO ₄ + 0.095 M NaClO ₄	0.00195 M

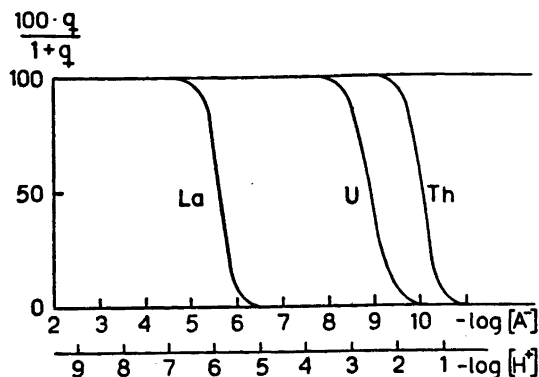


Fig. 1. The distribution of La (III), U (VI) and Th (IV) between chloroform and 0.1 M perchlorate solutions as a function of the *N*-phenylbenzohydroxamate ion concentration in the aqueous phase. The corresponding values of $-\log [H^+]$ are calculated for 0.1 M PBHA in chloroform.

ted very well with chloroform, using PBHA as a complexing agent. As usual lanthanum is extracted in a much higher pH-range (higher range of $\log [A^-]$) than uranium and thorium, and may well be separated from the latter elements by a single extraction at $\text{pH} = 4.5$ with a 0.1 M solution of PBHA in chloroform. A good separation of U and Th would however require some degree of fractionation. Compared with cupferron (*cf.* Part VIII⁴) PBHA is a much more stable compound, and the extraction of La(III) and U(VI) is very much better.

If the distribution data on lanthanum (Table 1) and uranium (Table 2) are plotted against $\log [A^-]$, they will fit rather well to straight lines with slopes

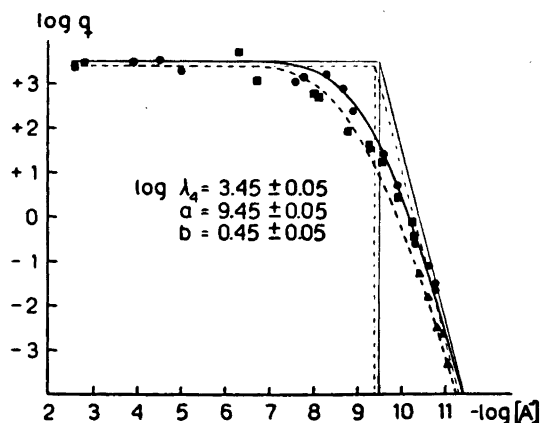


Fig. 2. The distribution ratio of Th (IV) as a function of the *N*-phenylbenzohydroxamate ion concentration in the aqueous phase. The curves are drawn with two sets of parameters (*see text*). Total concentration of PBHA in chloroform: ■ 0.1 M, ● 0.05 M, ▲ 0.025 M.

equal to 3 and 2. The general equation for these lines is (eqn. 9 in Part XXXI⁷ or eqn. 7 in Part V¹³)

$$\log q = \log \kappa_N \lambda_N + N \log [A^-] \quad (2)$$

Thus for La^{3+} ($N = 3$) one obtains

$$\log \kappa_3 \lambda_3 = 17.04$$

and for UO_2^{2+} ($N = 2$)

$$\log \kappa_2 \lambda_2 = 17.82$$

The data for thorium, which are plotted in Fig. 2, cannot be represented by eqn. (2) and this undoubtedly is due to the presence of thorium complexes in the aqueous phase. Using the value of $\log \lambda_4 = 3.45 \pm 0.03$ calculated in Table 3, the two-parameter method described in Part V¹³ gave the following values:

$$a = \frac{1}{4} \log \kappa_4 = 9.45$$

$$b = 0.45$$

The two parameters a and b determine the mean complexity constant 10^a ($= \sqrt[N]{\kappa_N}$) and the mean spreading factor 10^{2b} ($= k_n/k_{n+1}$).

In order to estimate the limits of error of the parameters two curves are drawn in Fig. 2; the full curve has $a = 9.50$, $b = 0.40$ and $\log \lambda_4 = 3.50$, and the dashed curve has $a = 9.40$, $b = 0.50$ and $\log \lambda_4 = 3.40$. As all of the points do not fall inside these two curves, the errors in each of these constants may be somewhat larger than ± 0.05 .

The value of a for PBHA is definitely higher than for tropolone⁹ ($a = 8.14$), but somewhat lower than for oxine¹ ($a = 9.80$). All these reagents form five-membered chelate rings. A summary of our work will be published shortly¹⁴, where these values will be discussed together with data for other reagents.

In Part XXXI⁷ the overall equilibrium constant K was defined, and it was stated that the pH for 50 % extraction was approximately determined by the terms $\log [\text{HA}]_{\text{org}}$ and

$$\frac{1}{N} \log K = \frac{1}{N} \log \kappa_N \lambda_N - (pk_a + \log k_d) \quad (3)$$

The following values of $\frac{1}{N} \log K$ may be calculated using eqn. (3)

La(III):	—4.80
U(VI):	—1.57
Th(IV):	—0.17

If these values are compared with those for other reagents¹⁴, it is found that the values for La(III) and Th(IV) are rather favorable; aromatic N-substituted hydroxamic acids (keto hydroxylamines) may prove to be a very useful group of compounds for the extraction of tri- and tetravalent lanthanide and actinide ions.

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