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THE EXTRACTION OF BERYLLIUM BY TRIISOOCTYLAMINE IN THE PRESENCE OF OXALATE ION

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ABSTRACT

Beryllium ions can be extracted into organic solvents by tertiary amines, in the presence of compounds which give rise to anionic complexes. The nature of the extracted species has been investigated for the system beryllium/oxalate/triisooctylamine; it appears to be

$$Be(C_2O_4)_2\,[NH(i{-}C_8H_{16})_3]_2.$$

The beryllium/oxalate/water system has been examined by the method of pH titration in the absence of the organic phase. Under the conditions chosen, the dissociation constants for oxalic acid were found to be $K_1 = 4.64 \times 10^{-2}$ and $K_2 = 1.20 \times 10^{-4}$, and the stability constants for the beryllium oxalate complexes $\beta_1 = 6.32 \times 10^3$ and $\beta_2 = 3.91 \times 10^5$.

CONTENTS

ERRATA

Page 2 Equation should read $I \rightleftharpoons 2H^+ + III$

Page 6, line 7 abscissae

Page 7, Section 3.4 $[(HO)_2 BeOx]^{=} \cdot 2R_3NH^+$

Page 8 Reference de Bruin, H.J., and Florence, T.M. is AAEC/E72

1. INTRODUCTION

Organic reagents such as acetylacetone, containing one replaceable hydrogen atom, form neutral dichelate complexes with beryllium which can be extracted from aqueous solution by nonpolar organic solvents, for example benzene. Beryllium also forms negatively-charged chelate compounds with molecules containing two replaceable hydrogen atoms and these complexes cannot be extracted into neutral organic solvents. Such complexes are formed with catechol, salicylic acid, oxalic acid, and other dibasic acids. Their anionic character can be shown by their sorption on anion exchange resins, from which they can be eluted with NaCl or HCl, for example. We have found that under appropriate conditions these anionic complexes can be extracted into organic solutions of long chain amines such as tri-n-and triisooctylamine (Temple, 1960) although other amines are probably equally effective. The extraction of simple anions from aqueous solutions by these amines has been known for some time (Moore, 1952), and these reagents have been likened to "liquid ion-exchangers". Some discussion of the possible extraction mechanism for uranium anions has been given by Brown and collaborators (1958).

This paper describes the investigation of the complex which is extracted by triisooctylamine from beryllium solutions containing oxalate ions, in the pH range from 1.5 to 7.0. Owing to the relative weakness of the complexes formed, this system is extremely complicated. Therefore before studying the solvent extraction an investigation had to be made into the aqueous beryllium/oxalate system. This was done by the Bjerrum-Calvin method using pH-titration, which has been described in detail by de Bruin and Florence (1961).

2. EXPERIMENTAL

2.1 Investigation of the Aqueous Phase

Since the formation of the metal complex liberates protons from the complexing agent, the essence of the method is to titrate the complexing agent (in this case oxalic acid) with and without the addition of a known quantity of a metal salt, and to measure the accompanying changes of pH in each case. The results can be interpreted quantitatively to give numerical values for the stability constants of the complexes present in solution. A solution 0.05M in oxalic acid and 0.0063M in perchloric acid was prepared. Different amounts of 1N potassium hydroxide were added to aliquots of this solution so that the final concentrations covered the range from 0.0 to 0.15M in K^+ ion. The solutions were left at 25°C to come to equilibrium, after which the pH was measured with a Radiometer PHM3 meter, using a jacketed cell through which water at 25°C was circulated. A series of measurements were made on solutions similar to those above, which were 0.0269M in beryllium in addition to the specified concentrations of oxalic and perchloric acids.

The pH meter was standardized with a 0.03M potassium hydrogen tartrate buffer (pH 3.567), and with a 0.025M potassium dihydrogen - and disodium hydrogen phosphate buffer (pH 6.857), which were prepared from recrystallized AR grade reagents. The Hitchcock and Taylor (1937) standard pH scale was used. The results were reproducible to 0.005 pH unit.

2.2 Investigation of the Organic Phase

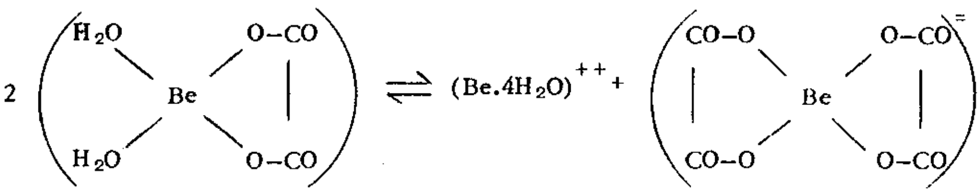
The variation of the distribution coefficient (D_A) of beryllium between an organic phase containing triisooctylamine (TIOA) and an aqueous phase containing oxalic acid was measured when the total oxalate concentration, total amine concentration, total beryllium concentration, and pH were each varied in turn, the others being kept constant. Beryllium-7 was used as an indicator with γ-scintillation liquid counting to simplify beryllium analyses. The extractions were carried out by stirring together 5 ml portions of each phase in a 20 ml centrifuge tube, contained in a constant temperature bath at 25° C. The pH was monitored and adjusted with acid or alkali if necessary during the stirring period, using an E.I.L. model 23A direct reading pH meter. The concentrations of the relevant reactants are shown in the Figures. The analysis of TIOA (Union Carbide, Inc.) was carried out by titration with perchloric acid in glacial acetic acid, using methylviolet as indicator.

Preliminary experiments showed that equilibrium was reached within 2 minutes. In subsequent work the phases were stirred together for 5 minutes, separated by centrifuging, the final pH of the aqueous phase measured, and the phases sampled for beryllium analysis.

3. DISCUSSION AND RESULTS

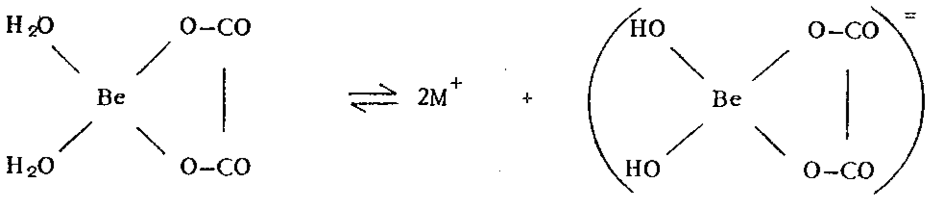
3.1 The Beryllium Oxalate Complexes

According to Sidgwick and Lewis (1926), beryllium oxalate gives evidence of being an internally complex molecule. Freezing-point measurements show it to be hardly dissociated in water and it has an abnormally low molecular conductivity which is almost constant over a wide range of concentration. Sidgwick and Lewis explained these facts by postulating an equilibrium between a non-ionized monochelate (I) and a highly-dissociated dichelate compound (II), i.e.:-



I II

They also drew attention to the existence of a series of "double oxalates" of general formula M_2BeOx_2, which appear to contain the $BeOx_2^{=}$ ion. All these conclusions are supported by the potentiometric investigations reported here. It is possible that under some circumstances the monoxalate complex (I) could ionize to form the dihydroxyoxalate complex III (below), which might be more extractable in a long chain amine than the hydrated monochelate.



I III

However, this ionization should be suppressed by the presence of H^+. Since extraction by the amine can only take place in acid solution where the cation R_3NH^+ is formed, it is unlikely that any appreciable amount of (III) is present in the organic phase.

Similarly it is unlikely that (I) would be extracted by an amine incorporating a long hydrocarbon chain. We would therefore expect that the beryllium species extracted by chloroform solutions of TIOA would be (II), which can form ion-pairs with the amine cations.

This assumption is supported by the fact that beryllium cannot be extracted from oxalate solutions by chloroform alone, and by the decrease in the distribution coefficient at higher pH values.

3.2 Stability Constants of the Beryllium Oxalate Complexes

Figure 1 shows the pH titration curve for oxalic acid, with and without the addition of beryllium perchlorate. The stabilities of the complexes and the association constants of the acid were calculated using the Bjerrum–Calvin technique and the Irving and Rossotti curve-fitting method as described elsewhere (de Bruin and Florence, 1961), in which the following notation has been used:

$\bar{p}$ = average number of protons bound to oxalate

$(Ox)_t$ = total oxalate concentration

(K^+) = concentration of potassium ions in the experimental solutions, due to the addition of standard potassium hydroxide solution.

K_1 = first acid dissociation constant of oxalic acid

K_2 = second dissociation constant of oxalic acid

$A_1 = 1/K_2$ = first association constant of oxalic acid

$A_2 = 1/K_1$ = second association constant of oxalic acid

$\bar{n}$ = average number of ligands bound per beryllium ion

β_1 = stability constant for the reaction:

$$Be^{++} + Ox^{=} = BeOx$$

β_2 = stability constant for the reaction

$$Be^{++} + 2Ox^{=} = BeOx_2^{=}$$

( ) are used to indicate concentrations

The dissociation constants for oxalic acid were calculated from the following expressions applied to the titration of oxalic acid against standard potassium hydroxide:

$$\bar{p} = \frac{2(Ox)_t - (H^+) - (K^+)}{(Ox)_t} \tag{1}$$

and

$$\frac{\bar{p}}{(1-\bar{p})(H^+)} = A_1 + A_1A_2 \frac{(2-\bar{p})\ (H^+)}{1-\bar{p}} \tag{2}$$

The results are shown in Figure 1 (pH–titration curve) and Figure 2 (the association curve for oxalic acid) from which the following values were calculated.

$A_1 = 8.33 \times 10^3$ or $K_2 = 1.20 \times 10^{-4}$

$A_2 = 21.5$ or $K_1 = 4.64 \times 10^{-2}$

These results agree favourably with those tabulated by Bjerrum, Schwarzenbach and Sillén (1957). It should be noted that these are "conditional constants", and are strictly applicable in the stipulated circumstances only.

The stability constants for the beryllium oxalate complexes were obtained by titrating solutions containing oxalic acid and beryllium perchlorate against standard potassium hydroxide, the necessary calculations being made by using the equations:

$$\bar{n} = \frac{(Ox)_t - (Ox^=)\{1 + A_1(H^+) + A_1A_2(H^+)^2\}}{(Be)_t} \qquad (3)$$

$$(Ox^=) = \frac{2(Ox)_t - (H^+) - (K^+)}{2A_1A_2(H^+)^2 + A_2(H^+)} \qquad (4)$$

and

$$\frac{\bar{n}}{(1-\bar{n})(Ox^=)} = \beta_1 + \beta_2 \frac{(2-\bar{n})}{1-\bar{n}} (Ox^=) \qquad (5)$$

The pH titration curve is shown in Figure 1, and the formation curve in Figure 3, from which the following results were obtained:

$$\beta_1 = 6.32 \times 10^3$$

$$\beta_2 = 3.91 \times 10^5$$

The distribution of each of the beryllium species as a percentage of the total beryllium present is shown in Figure 4 as a function of free oxalate concentration. This assumes that hydrolysis of beryllium is absent.

From the results it should be noted that:

1. Beryllium forms two weak complexes with oxalate ions, which are strongly hydrolyzed above pH 6. (Figure 1).
2. The titrations had to be performed in concentrated solutions to obtain a sufficiently high value of $\bar{n}$ at the high hydrogen ion concentration necessary to avoid hydrolysis of the beryllium ion (Kakihana and Sillén, 1956). All calculations were made using the results for pH $<$ 4.5.
3. Because of the already high concentrations of the reagents, the use of an excess of a non-interfering strong electrolyte to maintain a constant ionic strength would be impracticable. The constants obtained are therefore conditional concentration constants applicable only under the particular experimental conditions.

3.3 Solvent Extraction

If we assume the extracted species to be a neutral ion-pair, then the extraction of beryllium in the presence of oxalate by an organic solution of a tertiary amine can be represented by

$$Be^{++}_a + n\,Ox^=_a + (2n-2)R_3N_o + (2n-2)H^+_a = [BeOx_n(R_3NH)_{2n-2}]_o \qquad (6)$$

The subscripts a and o refer to the aqueous and organic phases respectively. This formation equation assumes that no polymeric beryllium species are formed. This assumption has been experimentally verified for the range of concentrations of Be covered by our experiments (see Section 3.3.1). The equilibrium constant for the formation reaction is then

$$K_{eq} = \frac{(\text{Complex})_o}{(\text{Be}^{++})_a \ (\text{Ox}^{=})_a^n \ (\text{R}_3\text{N})_o^{2n-2} \ (\text{H}^+)_a^{2n-2}} \qquad (7)$$

Hence

$$\log D_T = \log K_{eq} + n \log(\text{Ox}^{=})_a + (2n-2)\log(\text{R}_3\text{N})_o + (2n-2)\log(\text{H}^+)_a \qquad (8)$$

$$\text{where } D_T = \frac{(\text{Complex})_o}{(\text{Be}^{++})_a} \qquad (9)$$

From (8) it follows that

$$\log D_T = (2n-2)\log(\text{R}_3\text{N})_o + \text{constant} \qquad (10)$$

if the concentrations of oxalate and hydrogen-ion are kept constant. Under the appropriate conditions similar expressions can be written connecting D_T with the other variables, namely

$$\log D_T = n \log(\text{Ox}^{=})_a + \text{constant} \qquad (11)$$

$$\text{and } \log D_T = (2n-2)\log(\text{H}^+)_a + \text{constant} \qquad (12)$$

When the variable is the initial beryllium concentration, it is better to plot the expression

$$\log(\text{Complex})_o = \log(\text{Be}^{++})_a + \text{constant} \qquad (13)$$

For experimental convenience, we have measured the quantity D_A instead of D_T, where D_A is defined by

$$D_A = \frac{\text{Total concentration of beryllium species in the organic layer}}{\text{Total concentration of beryllium species in the aqueous layer}}$$

A rigorous mathematical treatment of the extraction to determine n in equation 6 is extremely difficult, because many species may be present as a result of the relative instability of the oxalate complexes. In the aqueous phase H_2Ox, HOx^-, $Ox^=$, BeOx, $BeOx_2^=$, R_3NH^+, and oxalate/amine complexes will all be present to some extent. In the organic phase the situation is less complicated, but species such as $R_3NH\,HOx$ and $(R_3NH)_2Ox$ must be accounted for, as well as beryllium/amine species. However, for the qualitative identification of the extractable beryllium/oxalate/amine complex, a number of simplifying assumptions are justifiable. These are as follows:

1. Only one beryllium species is extracted as shown in equation 6.
2. The species is electrically neutral.
3. No polynuclear Be complexes are formed.

Figure 5 shows the total Be concentration in the organic phase plotted versus the total Be concentration in the aqueous phase. Figures 6, 7 and 8 were obtained by plotting D_A versus pH, the initial oxalate concentration in the aqueous phase, and the initial amine concentration in the organic phase, respectively. The conventional procedure for determining n would be to use a large excess of the components whose concentrations are kept constant, to minimize any possible variation in their concentrations as the concentration of the variable component changes. However, this cannot be done in this instance, because the mechanism of extraction is similar to ion exchange, where there is competition between the adsorbable species for the available capacity of the resin. Because of this, the abcissae in Figures 7 and 8 are the initial oxalate concentration in the aqueous phase, and the initial amine concentration in the organic phase, respectively. These quantities are related to $(Ox^{=})_a$ and $(R_3N)_o$ (equations 11 and 10), and the relationship is most involved in the case of the oxalate concentration.

3.3.1 Variation of Initial Beryllium Concentration

In the concentration range used ($\leqslant 10^{-2}$ molar) polynuclear complexes appear to be absent. This was shown by a series of experiments measuring the distribution with different concentrations of beryllium in the aqueous phase, the initial concentrations of amine and oxalate being kept constant. The value of log $(Be)_o$ was found to vary linearly with $\log(Be^{++})_a$ below 0.01M. These experiments were made at both pH 2 and pH 5. The slope of the line in Figure 5 deviates very slightly from unity for initial aqueous beryllium concentrations above 0.01, and this may indicate the presence of polynuclear anionic beryllium complexes at higher concentrations.

3.3.2 Variation of Hydrogen Ion Concentration

Figure 6 shows the relation between the distribution coefficient for beryllium and the hydrogen-ion concentration. At low pH values extraction is low because there are few $Ox^{=}$ ions present to form the complex. The initial increase in extraction with rising pH is due to the increased dissociation of oxalic acid, with a consequent increase in the concentration of extractable complex present. The final rapid decrease in extraction above pH 4.5 is probably due to the falling-off in the concentration of the amine cation at higher pH values

$$(R_3NH^+)_a \rightarrow (R_3N)_o + (H^+)_a$$

but hydrolysis of the beryllium ion may also be responsible.

3.3.3 Variation of Initial Oxalate Concentration

The results obtained must be analysed bearing in mind that what was measured was D_A versus initial oxalate concentration instead of D_T versus $(Ox^{=})_a$, for the reason given above. To simplify the discussion we shall use only curves 2 and 3 in Figure 7, in order to avoid complications which might arise from the hydrolysis of Be^{++} at higher pH values. The slope of these curves is 1.64. From the definition of D_A and D_T, namely

$$D_A = \frac{(Complex)_o}{(Be^{++})_a + (BeOx)_a + (BeOx_2^{=})_a}$$

$$D_T = \frac{(Complex)_o}{(Be^{++})_a}$$

it follows that their ratio is given by

$$\frac{(Be^{++})_a}{(Be^{++})_a + (BeOx)_a + (BeOx_2^{=})_a} = \frac{1}{1 + \beta_1 (Ox^{=}) + \beta_2 (Ox^{=})_a^2} = \Delta \qquad (14)$$

Therefore $$D_T = \frac{D_A}{\Delta} \qquad (15)$$

If Δ is known, D_T can be calculated. The Be^{++} curve in Figure 4 is actually a plot of 100 Δ versus free oxalate concentration.

The extraction data obtained here are insufficient for an accurate calculation of the free oxalate concentration in the aqueous phase, and hence D_T cannot be obtained. However, it can be said that Δ approaches unity for low values of $(Ox^{=})_a$ and that it will decrease as the free oxalate concentration increases. In other words the use of D_A instead of D_T in Figure 7 will give too low a slope to the line at pH 2. There can therefore be no doubt that the real slope should be 2, and not unity.

3.3.4 Variation of the Initial Amine Concentration

The results shown in Figure 8 obtained when the initial amine concentration in the organic phase was varied, can be interpreted similarly to those in Figure 7. The experimental slope of log D_A versus log $(R_3N)_t$ deviates from the theoretical value given by equation 10 to an extent depending on Δ, and hence on the free oxalate concentration, as indicated by equation 14. No allowance is made for the variation of $(Ox^{=})$ with total amine concentration in plotting Figure 7, but if the total oxalate is in excess with respect to the other reagents in equation (6), the free oxalate concentration in the aqueous phase, and hence the ratio D_A/D_T, should remain approximately constant. Curve 3 in Figure 7 shows the results obtained under such conditions; the slope is seen to be 2.0.

3.4 Nature of the Extracted Species

Since it is generally held that only neutral species dissolve to a significant extent in organic liquids, we would expect the species extracted by TIOA in these experiments to be either

$$(BeOx_2)^{=} \,.\, 2\, R_3NH^+$$

or

$$(HO_2BeOx)^{=} \,.\, 2R_3NH^+$$

The experimental results given above enable us to say that the beryllium is present in the organic layer almost entirely as the first of these alternatives, viz. that the extracted species has the empirical formula $Be(C_2O_4)_2 \; \{ NH\,(i\text{-}C_8H_{16})_3 \}_2$.

4. ACKNOWLEDGMENTS

We would like to express our grateful thanks to Miss P.M. Beach, who conscientiously carried out the protracted extraction experiments, and to Professor R. Green of the University of Sydney for very valuable discussions.

The analysis of TIOA was developed and carried out by Mr. T.M. Florence of the Analytical Chemistry Group.

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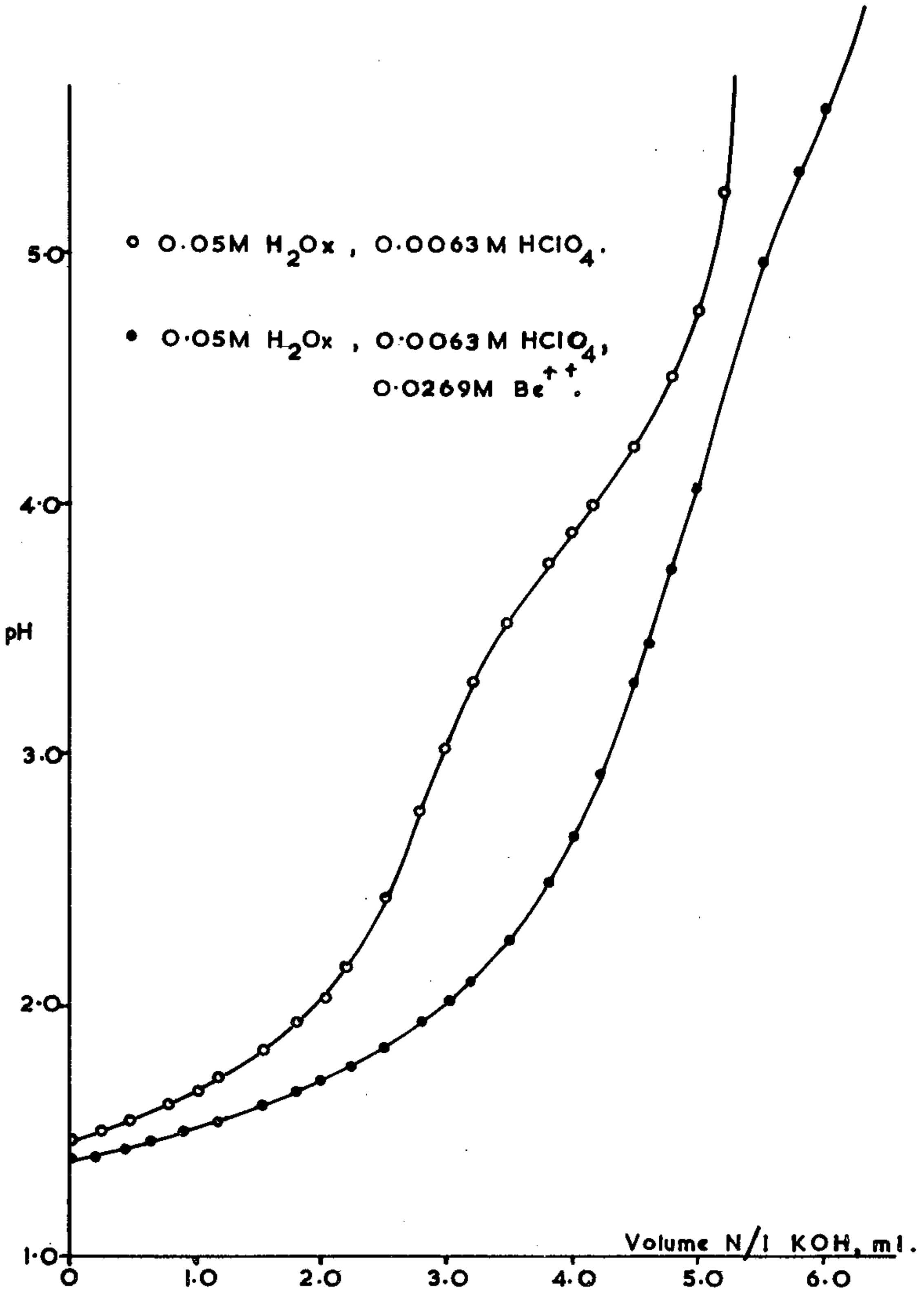

Figure I. pH Titration of Beryllium Oxalates.

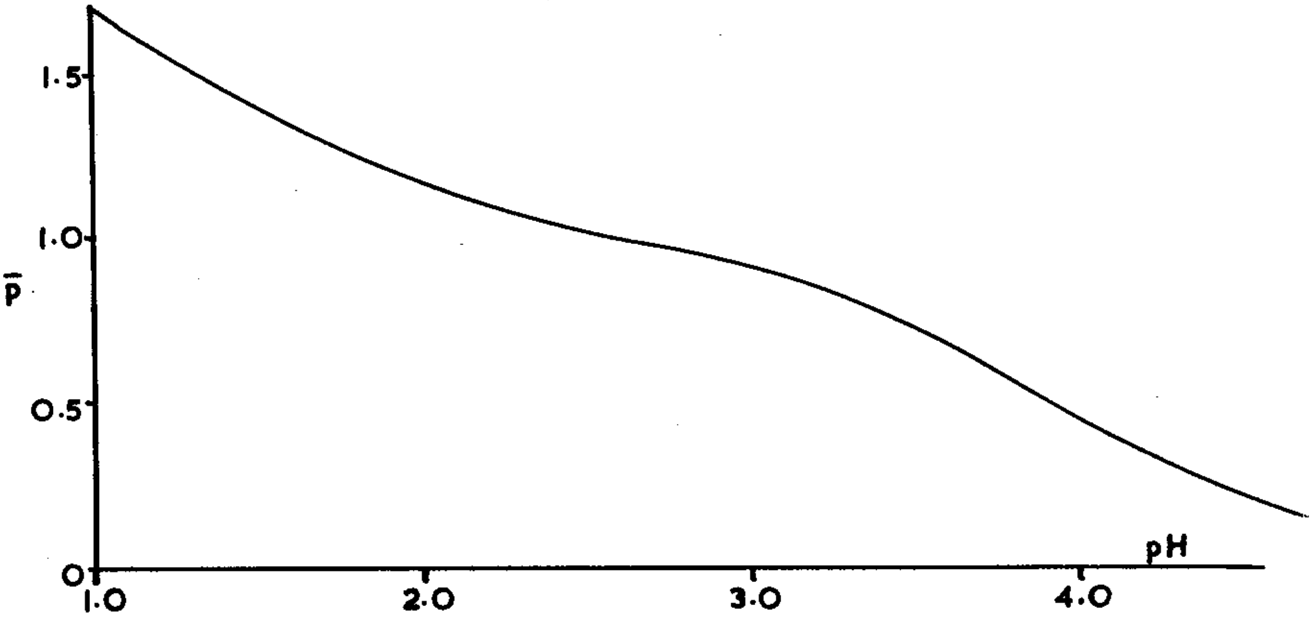

Figure 2 Association Curve of Oxalic Acid.

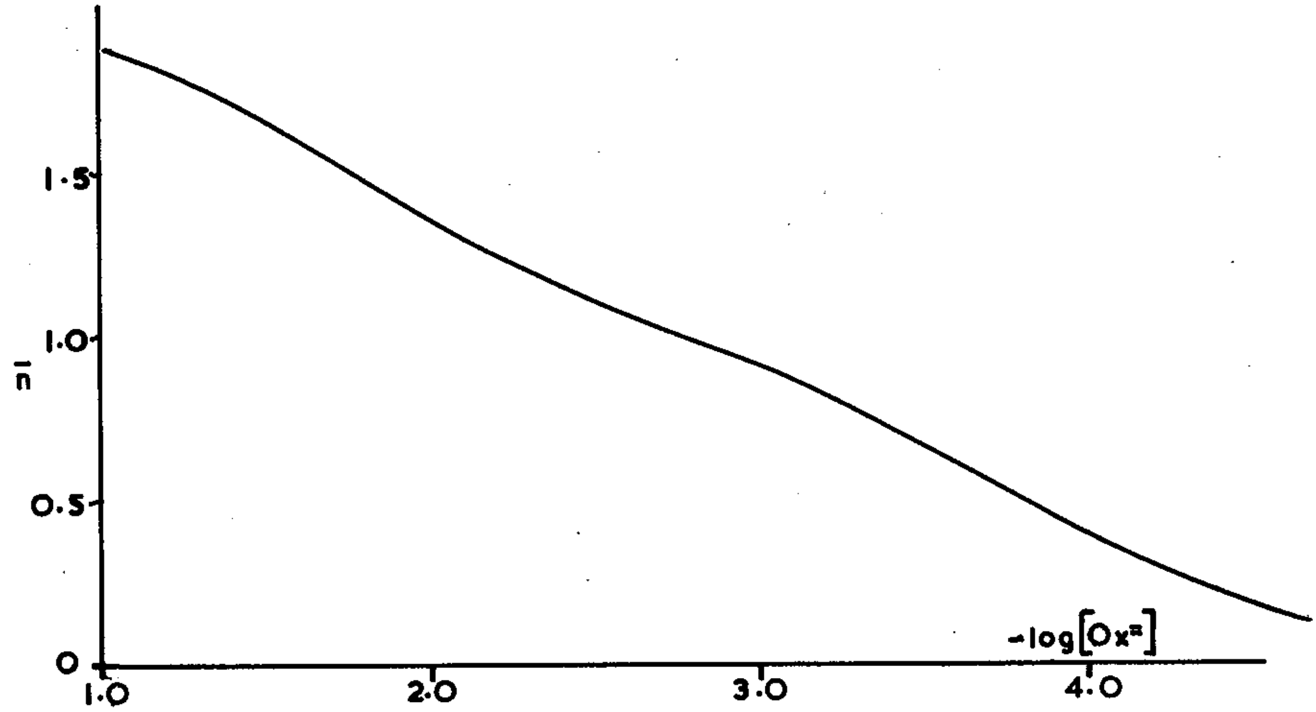

Figure 3. Formation Curve of Beryllium Oxalates.

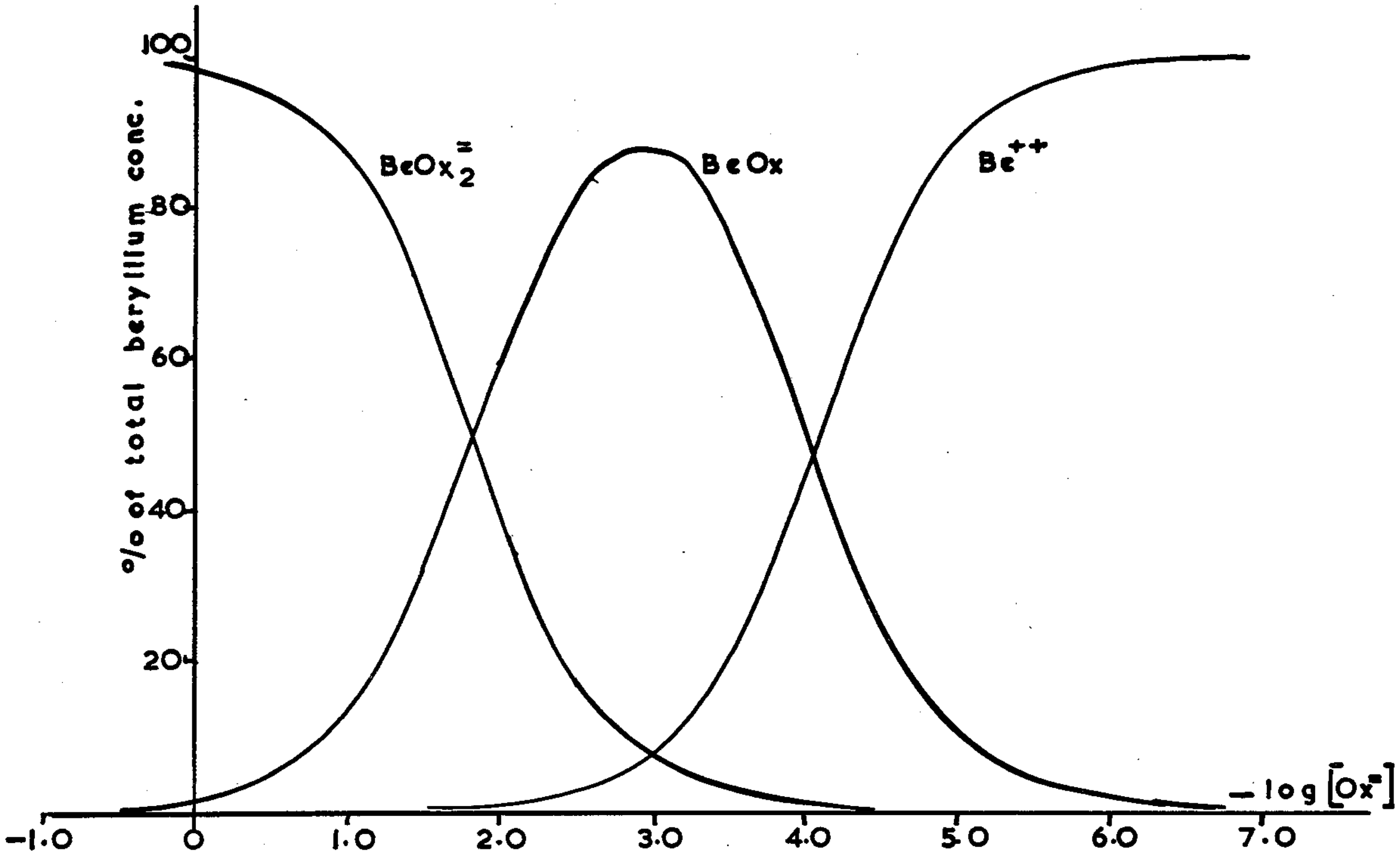

Figure 4. Distribution of Beryllium Species.

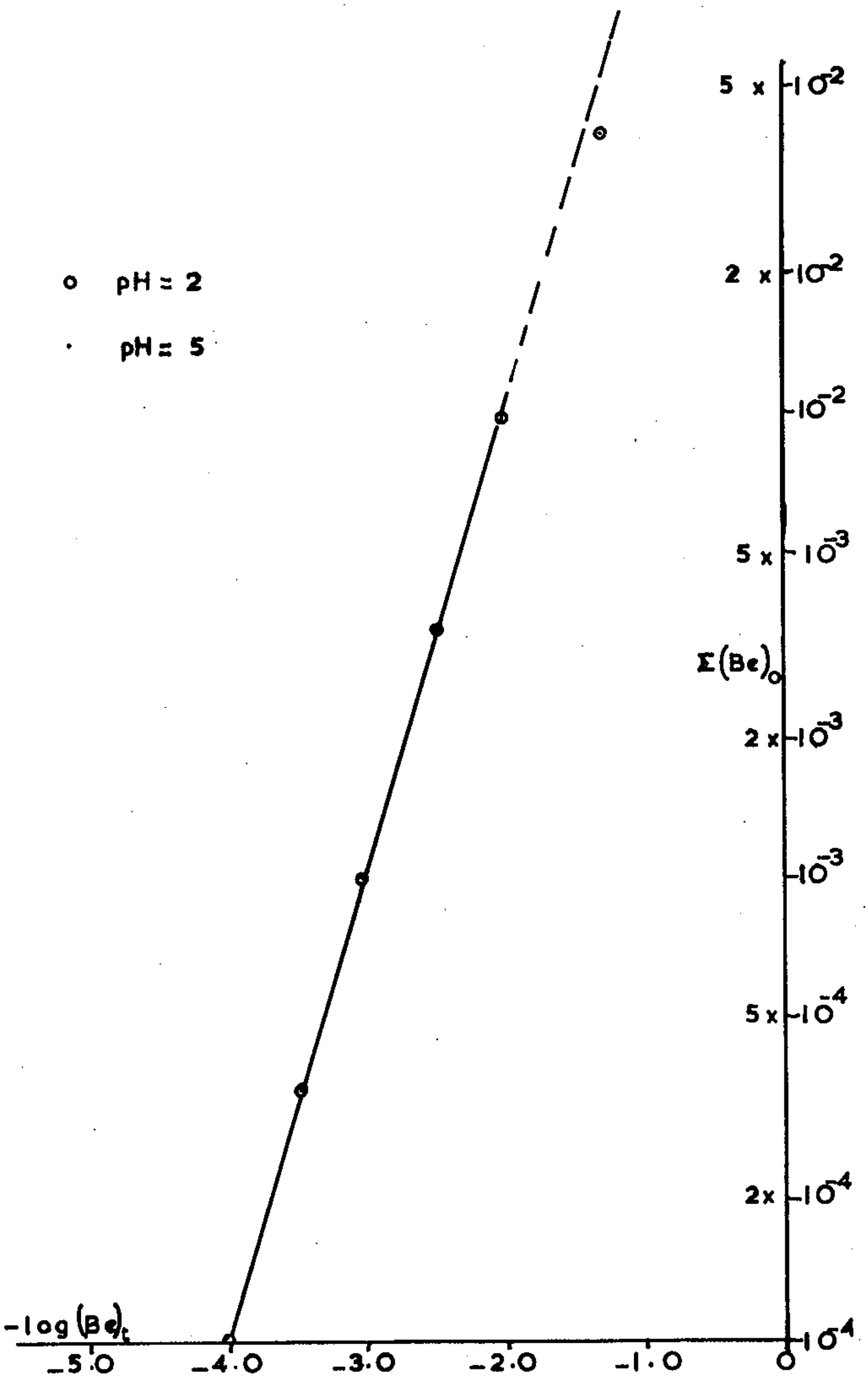

Figure 5. Extraction as a Function of the Total Beryllium Concentration.

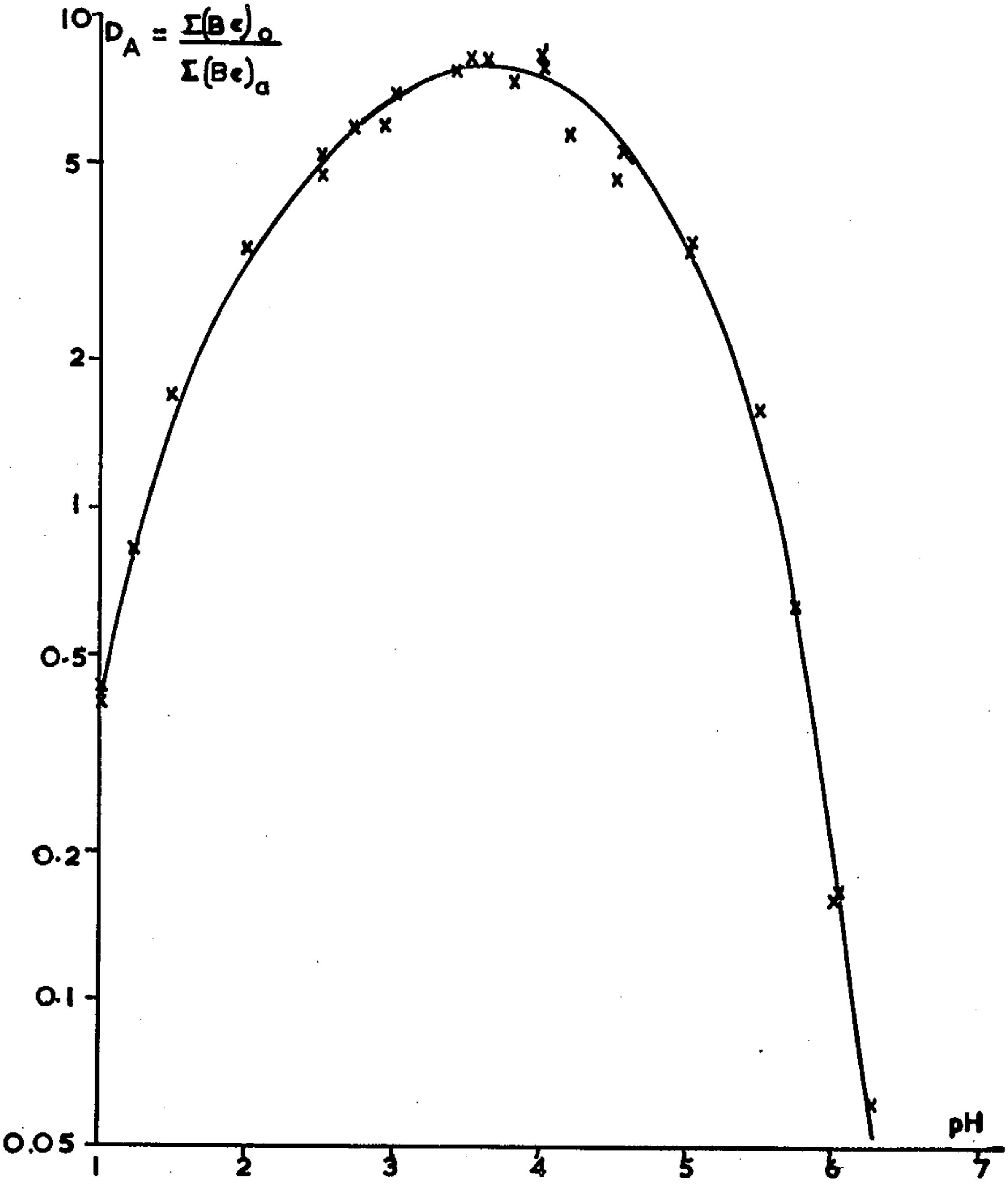

Figure 6. Extraction as a Function of pH.

0.05M Be^{++}, 0.1M H_2Ox, 0.1M TIOA in $CHCl_3$.

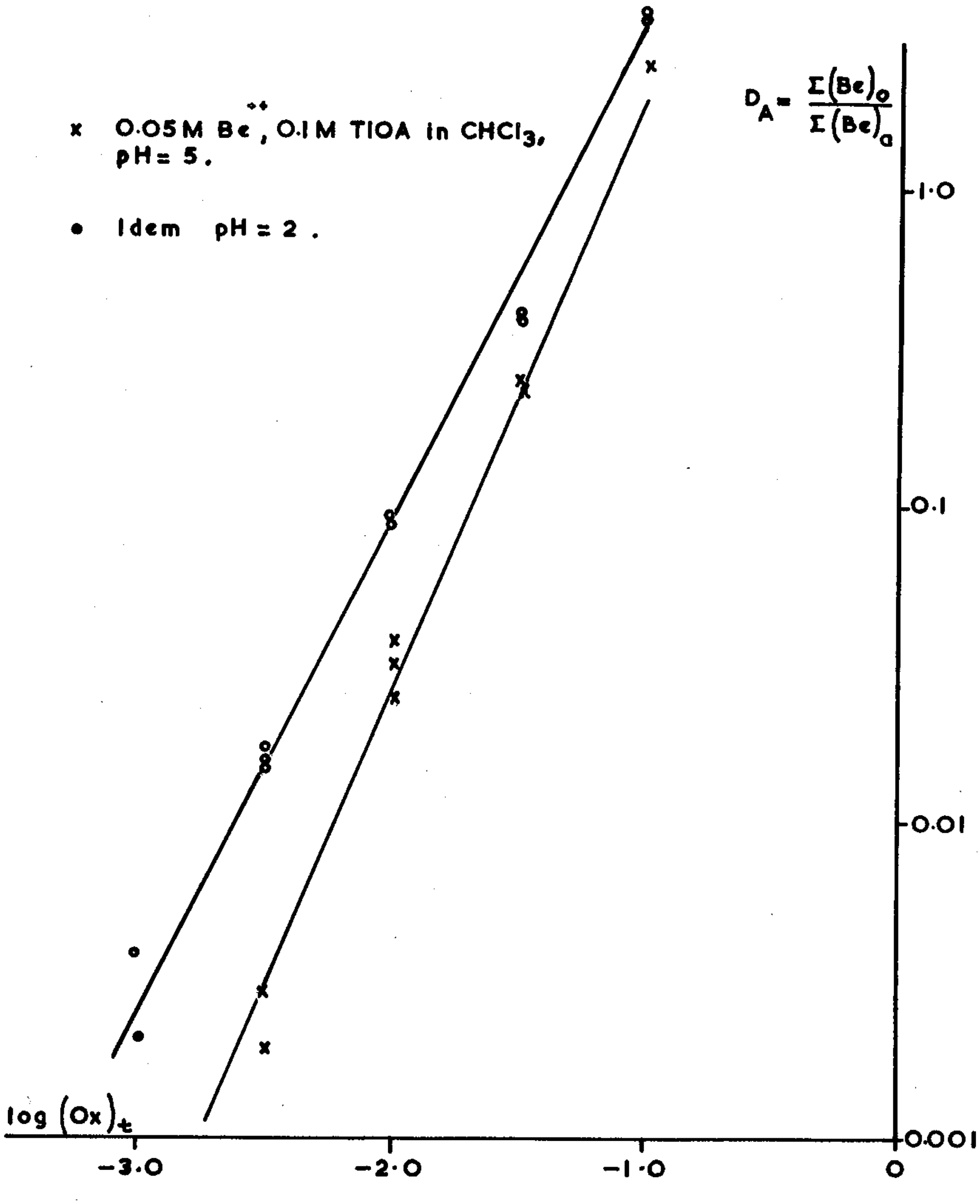

Figure 7. Extraction as a Function of the Initial Oxalate Concentration.

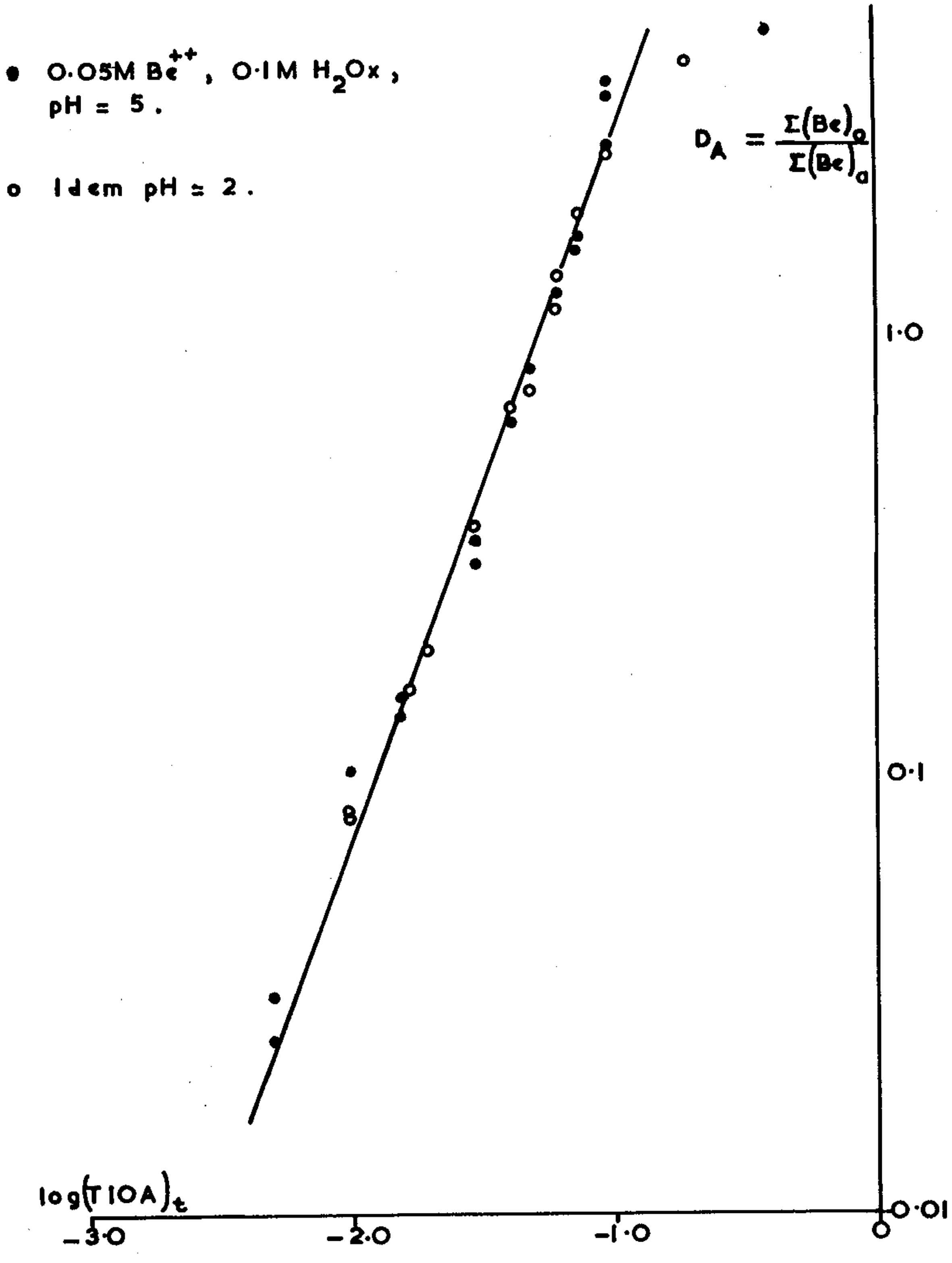

Figure 8. Extraction as a Function of the Initial TIOA Concentration.