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THE EXTRACTION OF BERYLLIUM BY TRIISOOCTYLAMINE

THE EFFECT OF THE ANIONIC COMPLEXING AGENT

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ABSTRACT

The extraction of beryllium by triisooctylamine was measured over the pH range from 1 to 10, in the presence of malonic, maleic, succinic, phthalic, and salicylic acids. Values were obtained for the stability constants of the various metal–acid complexes by potentiometric titration. Values for these constants have not hitherto been published.

The degree of extraction is dependent on the abundance of the anionic complex present in the aqueous phase and this is in turn dependent on the strength of the corresponding acid and the stability of the complex.

CONTENTS

1. INTRODUCTION

It has already been established that in the presence of oxalate ions, beryllium can be extracted into an organic solvent containing triisooctylamine (TIOA) as the "triple-ion" $Be(C_2O_4)_2\{NH(i-C_8H_{17})_3\}_2$, (de Bruin and Temple 1961). These studies were continued by measuring the extraction when the oxalate ions are replaced by other complexing agents. Malonic, maleic, succinic, phthalic, and salicylic acids have been investigated.

It has proved possible to interpret the extraction data from a knowledge of the stability constants of the complexes and the association constants for the acids concerned. The constants were measured by potentiometric titration (de Bruin and Florence 1961).

2. EXPERIMENTAL

2.1 Extraction Experiments

The techniques used have already been described by de Bruin and Temple (1961). Equal volumes of an aqueous and an organic phase were stirred together mechanically for 5 minutes, after adjustment of the pH to the required value. The hydrogen ion concentration in the aqueous phase was measured after equilibrium had been reached. In the original aqueous phase the concentrations of beryllium and of the relevant organic acid were 0.05 and 0.1 molar, respectively. The organic phase consisted of a 0.2 molar TIOA solution in o-xylene. The distribution of beryllium was measured by gamma scintillation counting using Be^7 as a tracer, after separation of the phases by centrifuging. Equilibrations were performed at a temperature of 25.0 ± 0.1°.

2.2 Acid Association Constants and Complex Stability Constants

Acid association constants and conditional stability constants of the complexes were determined by normal procedures (de Bruin and Florence 1961). Analytical reagent grade chemicals were used without further purification. The pH-titration curves were obtained using the concentrations shown in Table 1:

TABLE 1

Concentrations Used in pH Titrations; (moles/litre)

Organic acid	Organic acid concentration	Total beryllium concentration	Perchloric acid concentration
Oxalic	0.050	0.0135	0.0063
Malonic	0.0513	0.0135	0.0156
Succinic	0.0499	0.0135	0.0163
Maleic	0.0532	0.0135	0.0153
Phthalic	0.0253	0.0068	0.0081
Salicylic	0.0076	0.0019	0.0153

Hydrogen-ion concentrations were measured in a thermostatted cell, using a Radiometer PHM3 pH meter, standardized between measurements against a 0.03 molar potassium hydrogen tartrate buffer (pH = 3.567). Solutions were kept at 25.0 $\pm$ 0.1° under a nitrogen atmosphere during equilibration.

3. RESULTS AND DISCUSSION

3.1 Extraction Experiments

Figure 1 includes the results of a large number of extractions in which the beryllium distribution was studied as a function of hydrogen-ion concentration, in the presence of the various organic acids under the conditions already stipulated. The highest extraction (90 per cent.) was obtained with oxalic acid, although malonic and salicylic acids gave peak extractions of 60 and 65 per cent. respectively.

Precipitates were formed in all the systems (with the exception of the salicylate) at pH values above 5.7, but the solid phases were not investigated. They probably consisted of hydrolyzed beryllium species.

There was no significant difference between the extraction of maleate and succinate complexes below pH 5. It should be noted that the limiting slopes of all the extraction curves were approximately two at low pH values.

3.2 Acid Association Constants and Complex Stability Constants

The pH-titration curves are shown in Figures 2 and 3. From these the acid association constants and the conditional stability constants of the beryllium complexes were calculated, with the exception of the first association complex of salicylic acid, for which a value was obtained from the literature (Larsson 1929). The method of Irving and Rossotti (1953) was used, and the necessary computations were made with the aid of an IBM 650 computer. Only the portions of the titration curves below pH 3.5 were used in calculating the stability constants, in order to avoid significant hydrolysis of the beryllium ion.

Table 2 is a summary of values obtained for these constants.

TABLE 2

Conditional Association and Stability Constants

Acid	$\log \bar{A}_1$	$\log \bar{A}_2$	$\log \beta_1$	$\log \beta_2$
Oxalic	2.59	3.92	4.08	5.91
Malonic	5.34	8.19	5.73	9.28
Maleic	5.91	7.83	4.33	6.46
Succinic	4.88	8.93	4.69	6.43
Phthalic	5.13	8.04	3.97	5.69
Salicylic	13.44*	16.32	12.61	22.60

*Larsson (1929)

From data in Table 2 it can be seen that all the complexes formed (with the exception of the salicylate complexes) are relatively weak.

The data in Table 2 also appear to show that complexes with 6-membered rings (for example malonate) are more stable than the 5-membered (oxalate) or 7-membered ring systems (for example maleate). The maximum stability of 6-membered beryllium chelates is in contrast to the maximum stability of 5-membered ring structures for metal ions with much larger radii (see for example West 1960).

3.3 Interpretation of the Results

The degree of extraction of the anionic complexes cannot be explained solely by reference to their stabilities; for example, the highest extraction coefficient is exhibited by the oxalate complex, which is one of the weakest. The extraction coefficient is in fact determined by competition between Be^{++} and H^+ for $L^=$, the anion of the complexing agents. It can be shown that in any given system the proportion of the total beryllium which is present as the anionic complex is a function both of the stability of the complex, and of the strength of the appropriate acid.

Figures 4 to 9 show the relative abundance of the various beryllium species present in solution. In the calculations, the influence of hydrolysis has been ignored. The concentration of each beryllium species, Be^{++}, BeL, and $BeL_2^=$ has been calculated as a fraction of the total beryllium concentration. The following expressions were used; they follow simply from the definitions of β_1 and β_2.

$$\% [Be^{++}] = \frac{100}{1 + \beta_1 [L^=] + \beta_2 [L^=]^2} \quad (1)$$

$$\% [BeL] = \frac{100}{\frac{1}{\beta_1 [L^=]} + 1 + \frac{\beta_2}{\beta_1} [L^=]} \quad (2)$$

$$\% [BeL_2^=] = 100 - \% [Be^{++}] - \% [BeL] \quad (3)$$

$$\text{where } (L^=) = \frac{[L]_t}{1 + \bar{A}_1 [H^+] + \bar{A}_2 [H^+]^2} \quad (4)$$

where $[L]_t$ is the initial acid concentration in moles per litre.

Table 3 shows the relative concentrations of the various anionic beryllium complexes, calculated from equations 1, 2, 3, and 4 at several hydrogen ion concentrations for a value of 0.1 for $[L]_t$. This was the concentration of the organic acids in the aqueous phase of the extraction experiments.

TABLE 3

Comparison of Extraction Efficiency with Relative Abundance of the Anionic Complex

Acid	pH = 2			pH = 3			pH = 4		
	$p[L^=]$	% $[BeL_2^=]$	% Extr.	$p[L^=]$	% $[BeL_2^=]$	% Extr.	$p[L^=]$	% $[BeL_2^=]$	% Extr.
Oxalic	1.76	49	78	1.15	80	88	1.02	87	85
Malonic	5.25	1.5	4.8	3.57	48.5	36	2.66	88	60
Maleic	5.17	<0.1		3.94	1.1	0.10	2.92	14	1.86
Succinic	5.93	<0.1		3.96	0.5	0.04	2.23	23	1.86
Phthalic	5.09	<0.1		3.39	1.6	0.20	2.19	24	4.12
Salicylic	13.37	<0.1		11.68	1.9	2.0	10.47	25	21.9

It will be seen that the extractability of beryllium in a given system bears a close relation to the fraction which is present as the $BeL_2^=$ complex. From this we can deduce that the extraction of beryllium should be accomplished most easily in the presence of a strong dibasic acid giving rise to stable Be complexes. To test this hypothesis we hope to synthesize some difluoromalonic acid, $CF_2\langle{}^{COOH}_{COOH}$, at a later date.

There are some anomalies in Table 3 at pH 4.

(a) The extraction for both oxalate and malonate should be about the same, according to data in column 9. However in the presence of malonate, extraction is only 75 per cent. of that in the presence of oxalate.

(b) The efficiency of salicylate in the extraction is considerably better than its concentration suggests. Comparison of the relative abundances of the anionic complexes $BeL_2^=$ would suggest approximately equal extraction efficiencies in the presence of salicylate, phthalate, or succinate. In actual fact the salicylate extraction is well over four times greater than the phthalate, and ten times greater than the succinate.

These and other minor discrepancies can be explained by considering the effects of hydrolysis in the aqueous phase at this pH. As mentioned earlier the influence of hydrolysis was ignored in calculating the data on which Table 2 and Figures 4 to 9 are based. In actual fact the proportion of $[BeL_2^=]$ in these figures will never reach 100 per cent. if the side reactions are taken into account. They will increase to a maximum, after which rapid decomposition of the anionic complex will take place with subsequent precipitation. This maximum is not merely a function of the free ligand concentration, but also of total metal- and hydrogen-ion concentrations in the aqueous phase. It is possible that a comparison of stability constants, determined in a region where hydrolysis can be ignored, could be combined with the extraction data obtained over a considerable pH range to give valuable information about metal hydrolysis. For example, the negligible amount of hydrolysis in the case of the very stable salicylate complexes is shown by an increase in extraction efficiency up to pH 6. Here the maximum is not due to hydrolysis as with the other acids, but to a decrease in the amine cation concentration as the pH increases.

4. ACKNOWLEDGMENT

We gratefully acknowledge the assistance of Miss P.M.Beach, who patiently carried out the extraction experiments.

5. REFERENCES

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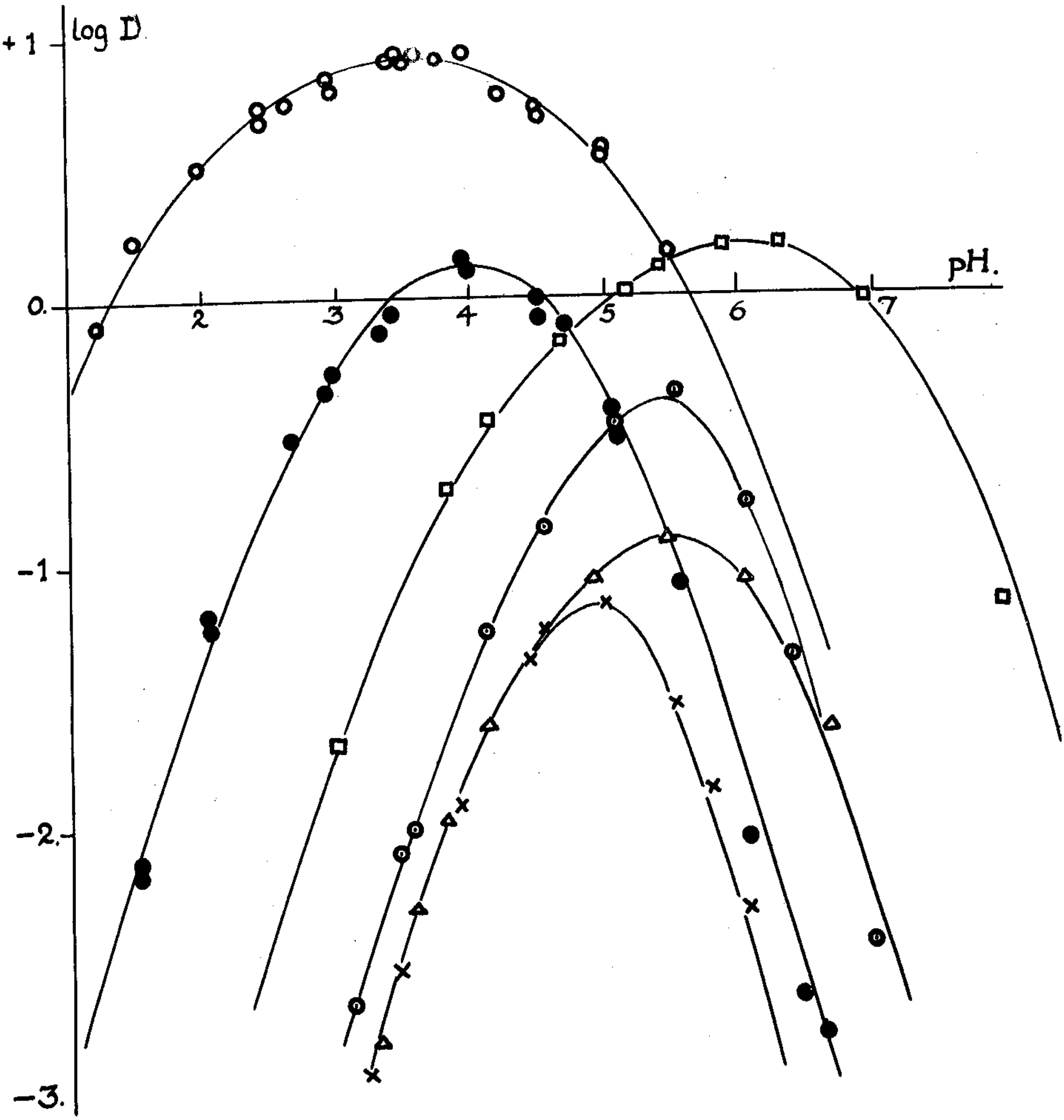

Fig 1. ~ Extraction Curves for Beryllium by TIOA using Dibasic Organic Acids. ~

○ = Oxalic : ● = Malonic : × = Succinic : △ = Maleic :
⊙ = Phthalic : □ = Salicylic Acids. ~

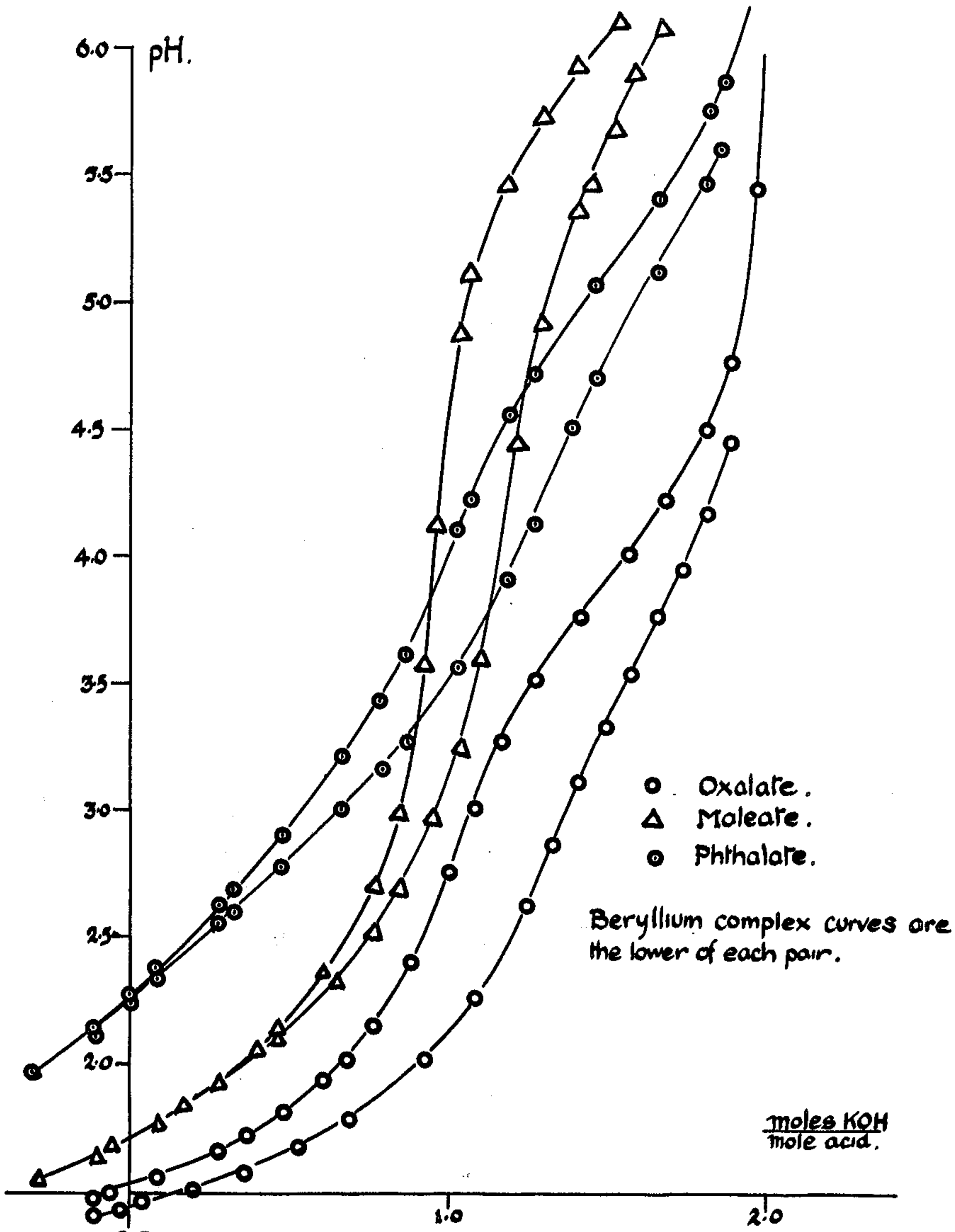

Fig 2. ~ pH Titration Curves for Oxalate. Maleate and Phthalate Systems.

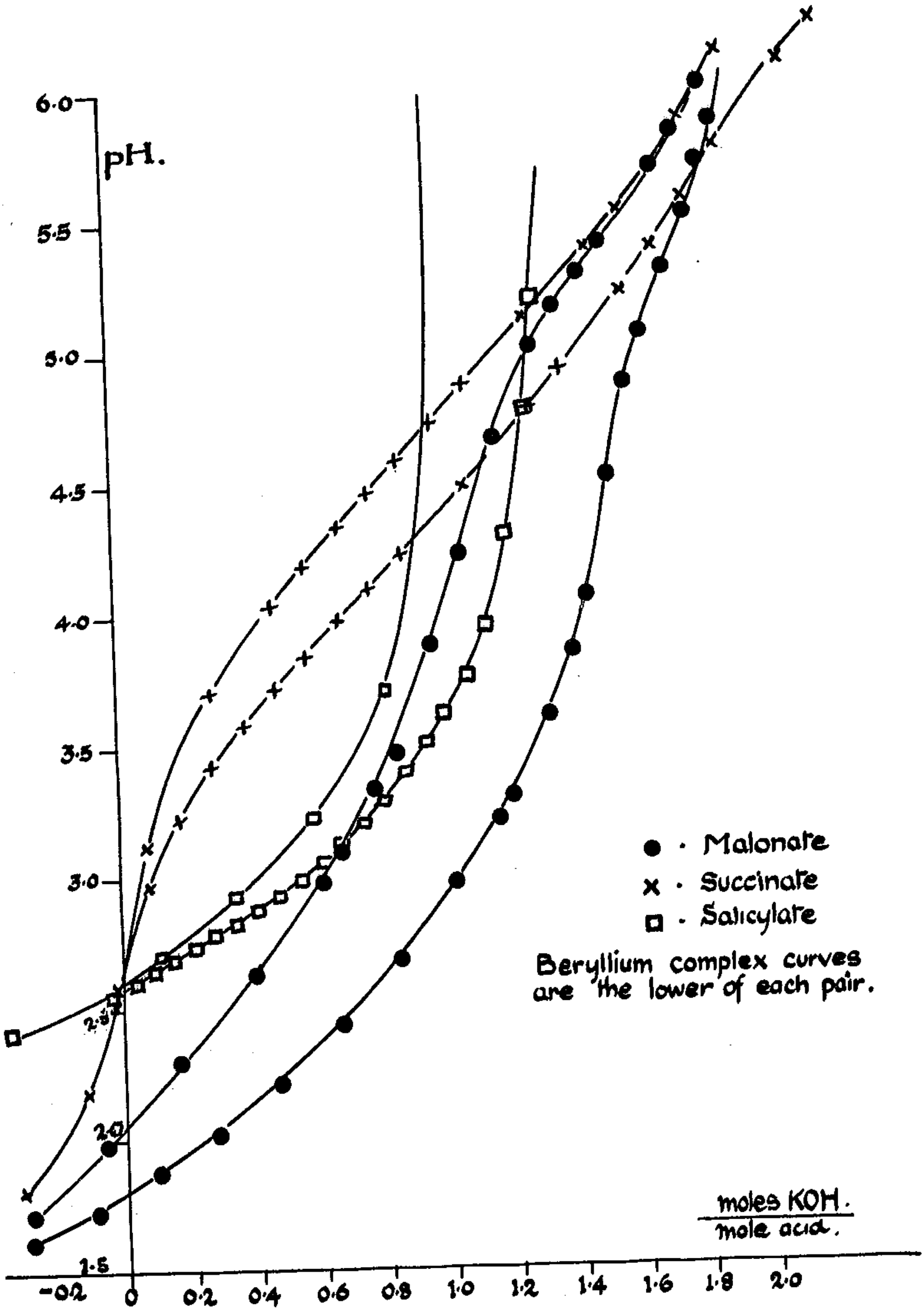

Fig 3. ~ pH Titration Curves for Malonate, Succinate and Salicylate Systems.

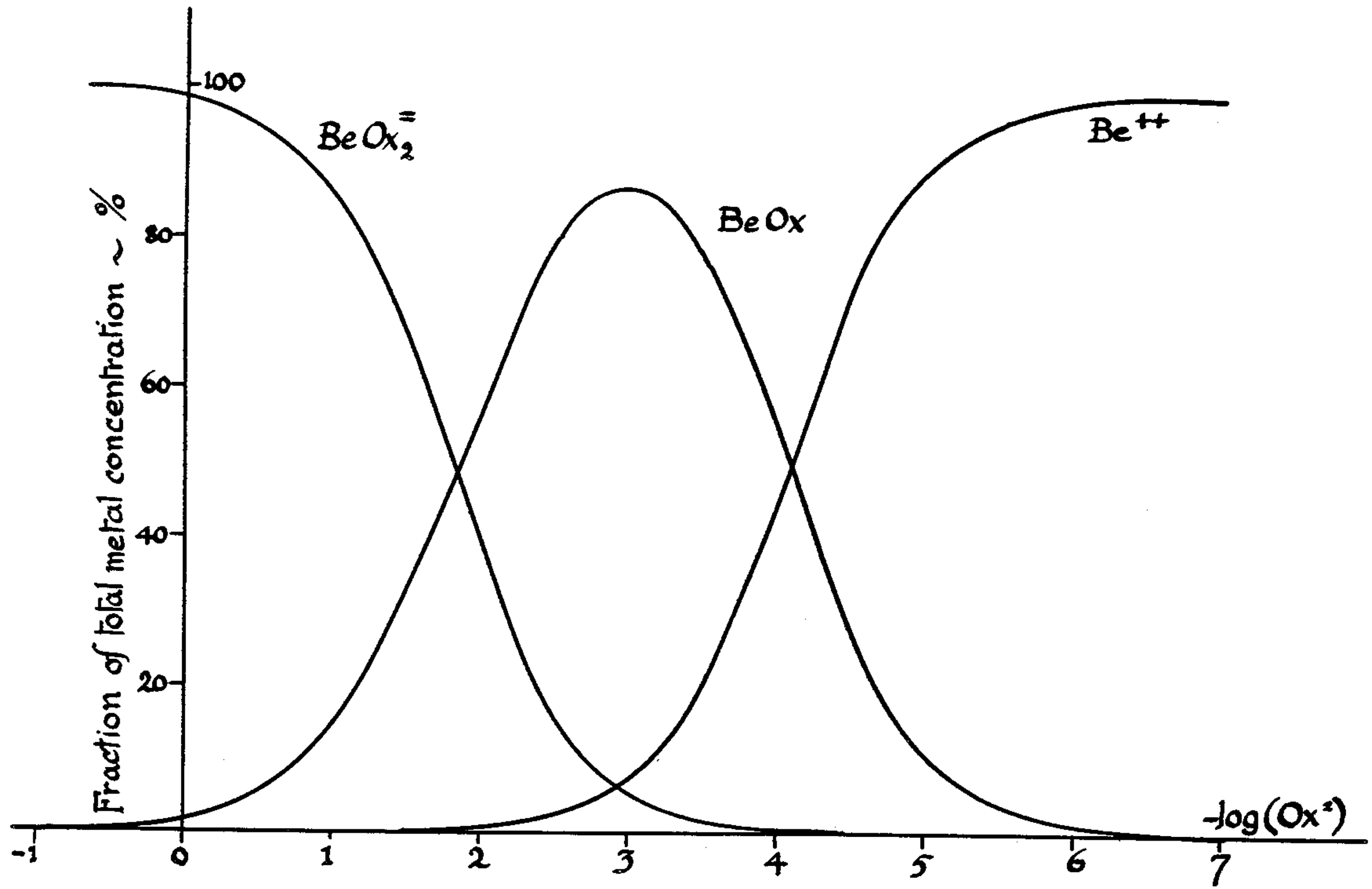

Fig 4 ~ Fractional Distribution of Beryllium Species in Aqueous Oxalate Solutions. ~

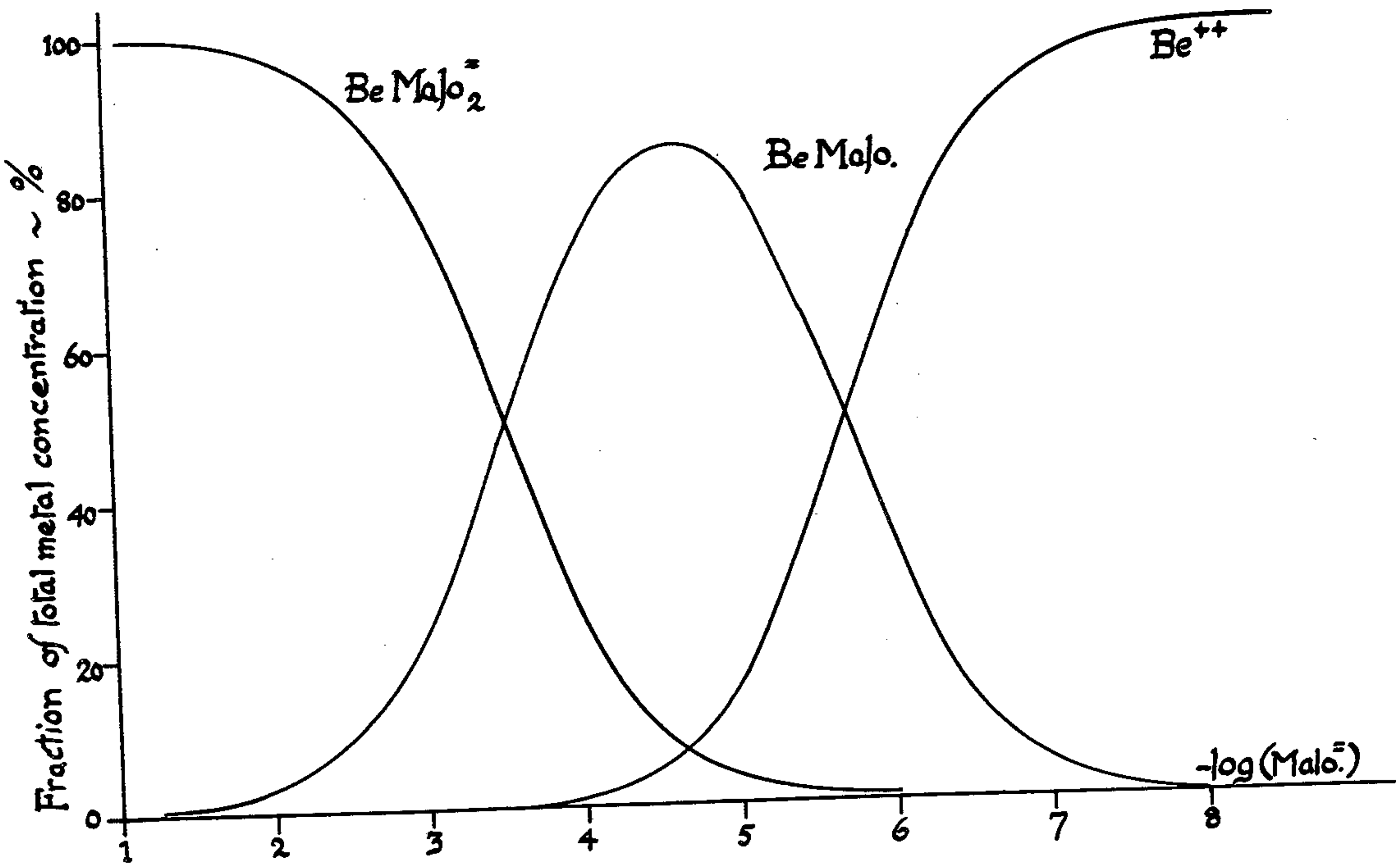

Fig 5. ~ Fractional Distribution of Beryllium Species in Aqueous Malonate Solutions. ~

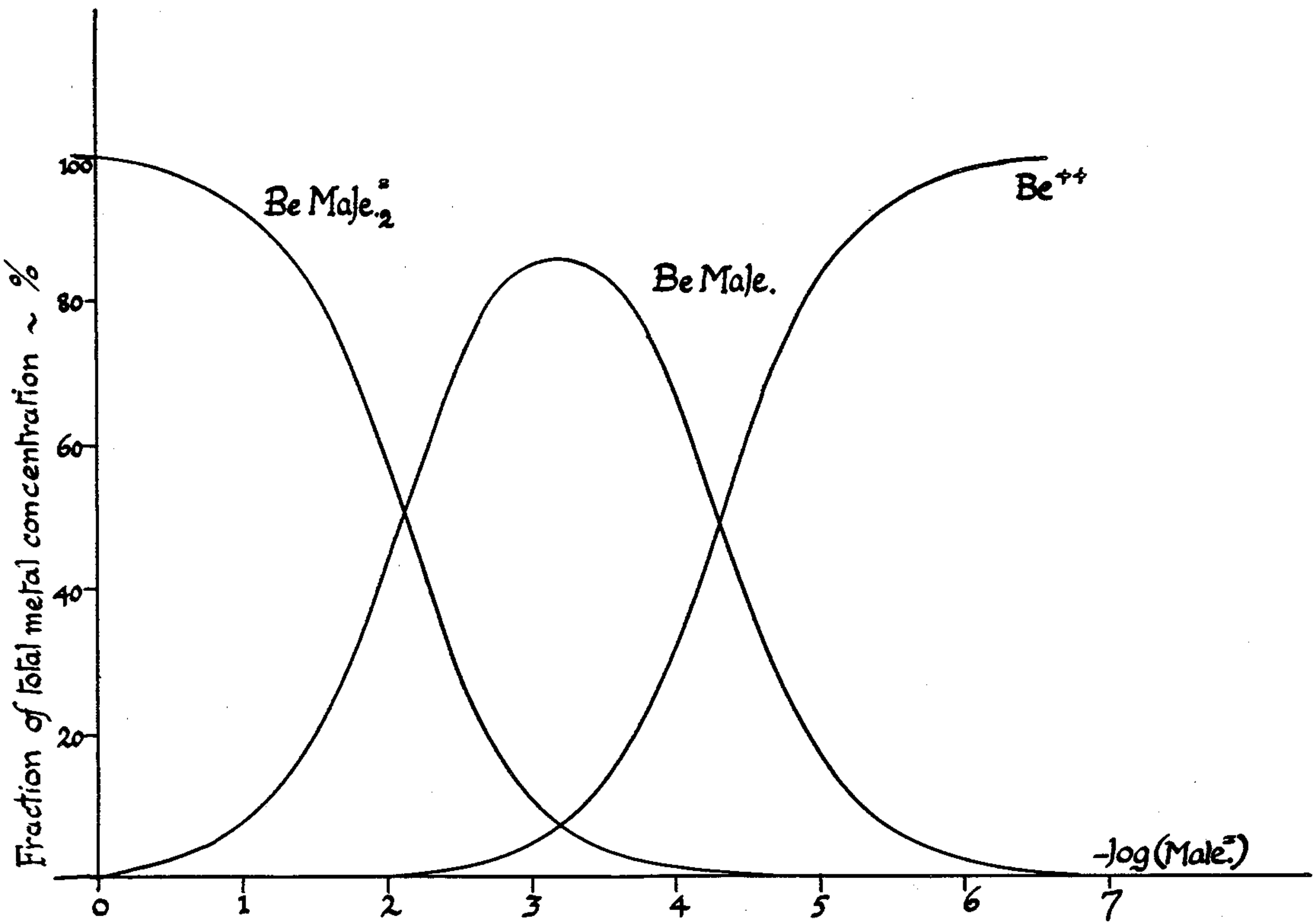

Fig 6 ~ Fractional Distribution of Beryllium Species in Aqueous Maleate Solutions. ~

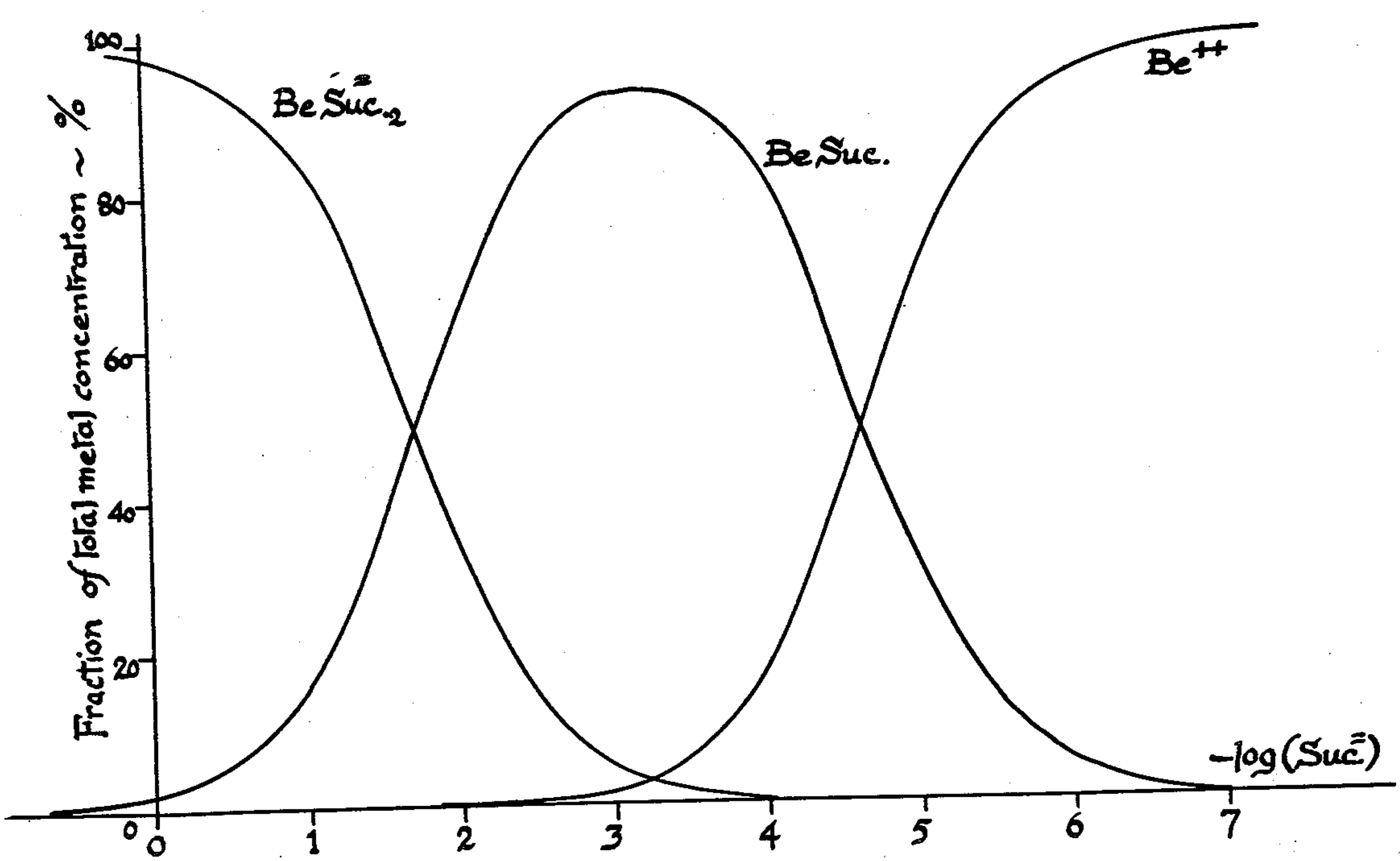

Fig 7. ~ Fractional Distribution of Beryllium Species in Aqueous Succinate Solutions. ~

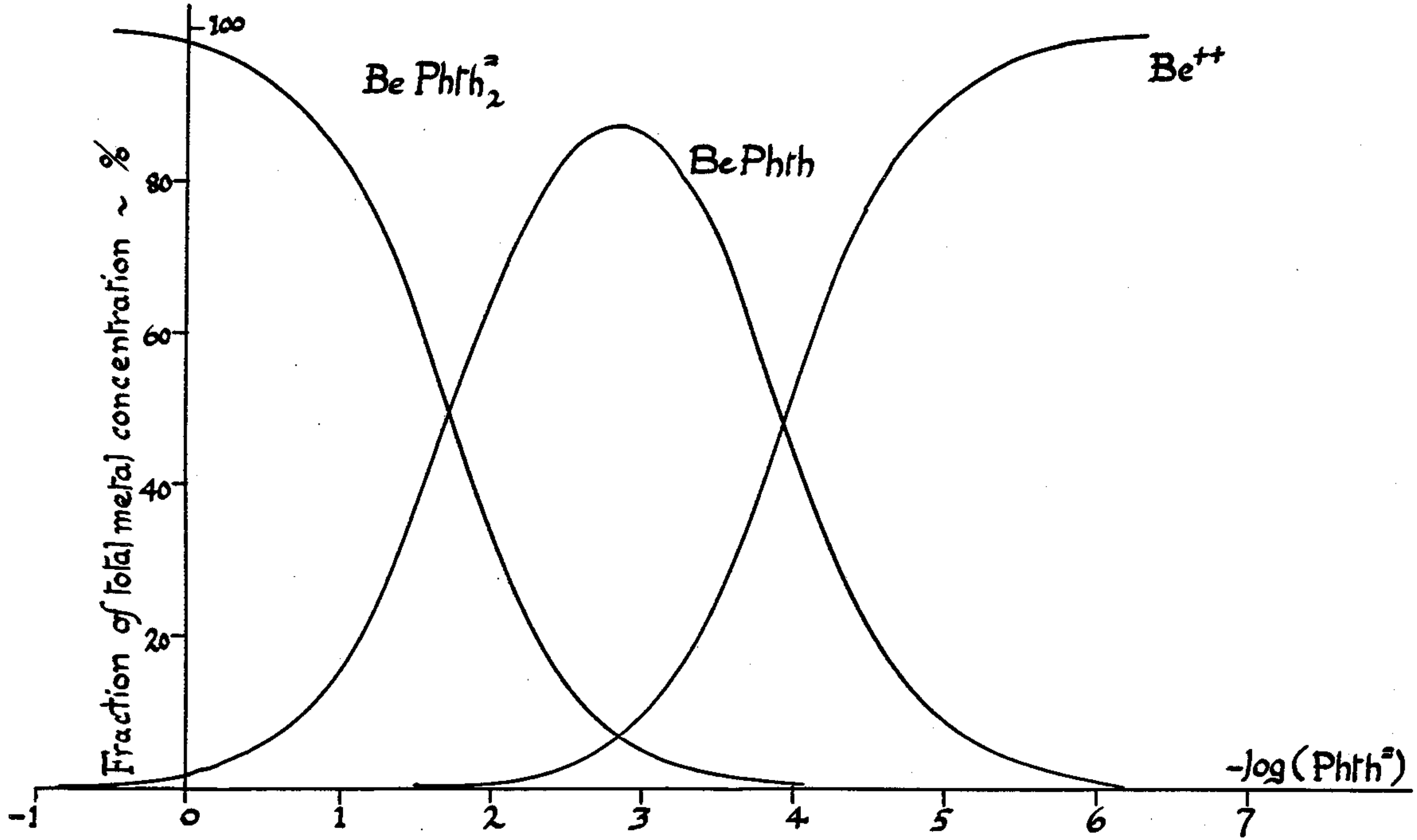

Fig 8. ~ Fractional Distribution of Beryllium Species in Aqueous Phthalate Solutions. ~

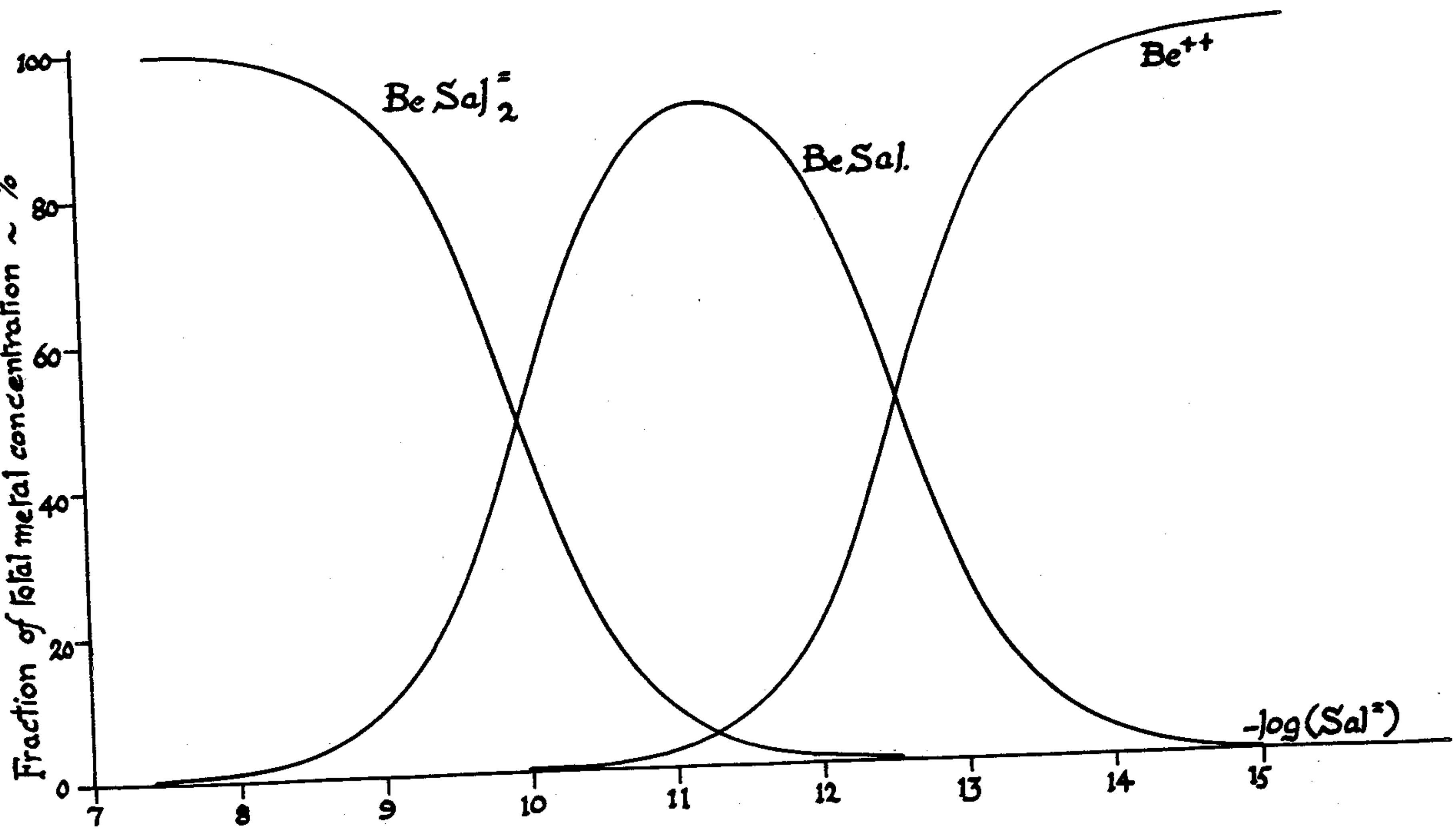

Fig 9 ~ Fractional Distribution of Beryllium Species in Aqueous Salicylate Solutions. ~