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THE FORMATION CONSTANTS OF THE BERYLLIUM THENOYLTRIFLUOROACETONATES

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ABSTRACT

The formation constants of the mono– and bis–thenoyltrifluoroacetone complexes of beryllium have been measured by a solvent extraction method. The values found are

$$\beta_1 = 3.40 \times 10^5, \quad \text{and}$$

$$\beta_2 = 1.21 \times 10^{11},$$

in a medium of ionic strength 0.1, at a temperature of $25° \pm 0.1°$.

CONTENTS

1. INTRODUCTION

Although thenoyltrifluoroacetone (TTA) has been used in the solvent extraction of beryllium (Bolomey and Wish, 1950) the literature does not appear to contain any previous record of the formation constants of the Be–TTA complexes. We have now determined these at a constant ionic strength of 0.1 in sodium perchlorate, by measuring the partition of beryllium between the aqueous phase and an organic phase consisting of TTA at different concentrations in o–xylene.

In what follows, the undissociated form of TTA is represented by HT and the corresponding anion by T^-. The reaction between Be^{++} and T^- can then be represented by the stepwise equations

$$Be^{2+} + T^- = BeT^+ \qquad (1)$$

$$BeT^+ + T^- = BeT_2 \qquad (2)$$

if the pH is sufficiently low for hydrolysis to be negligible. Only the neutral BeT_2 complex would be expected to dissolve in a non–polar organic phase such as o–xylene.

According to Rydberg (1950) the distribution ratio for the metal between the two phases will be given by

$$q = \frac{\lambda_2 \beta_2 [T^-]^2}{1 + \beta_1 [T^-] + \beta_2 [T^-]^2} \qquad (3)$$

where λ_2 is the distribution ratio of the BeT_2 complex between the phases and β_1 and β_2 are the stability constants for the complexes formed in (1) and (2). If q is found experimentally at various values of $[T^-]$, then β_1, β_2, and λ_2 can be determined in several different ways. We have used two methods, due to Leden (1941) and to Dyrssen and Sillén, (1953) respectively, and have obtained closely similar results from each.

2. LEDEN'S METHOD OF COMPUTATION

By rearranging (3) we obtain

$$\frac{1}{q} = \frac{1}{\lambda_2} + \frac{\beta_1}{\beta_2 \lambda_2} \cdot \frac{1}{[T^-]} + \frac{1}{\beta_2 \lambda_2} \cdot \frac{1}{[T^-]^2} \qquad (4)$$

Alternatively

$$\left(\frac{1}{q} - \frac{1}{\lambda_2}\right) [T^-] = \frac{\beta_1}{\beta_2 \lambda_2} + \frac{1}{\beta_2 \lambda_2} \cdot \frac{1}{[T^-]} \qquad (5)$$

As $[T^-]$ increases, the dissociation of BeT_2 is correspondingly suppressed, so if we plot $\frac{1}{q}$ versus $\frac{1}{[T^-]}$ (equation 4) then in the limit when $\frac{1}{[T^-]}$ approaches zero the corresponding value of q will be the true distribution coefficient of the undissociated complex, because the intercept of the ordinate at $\frac{1}{[T^-]} = 0$ will be $\frac{1}{\lambda_2}$.

From equation 5 it can be seen that a graph of $\left(\frac{1}{q} - \frac{1}{\lambda_2}\right)[T^-]$ versus $\frac{1}{[T^-]}$ will be a straight line, with a slope of $\frac{1}{\beta_2 \lambda_2}$ and an intercept of $\frac{\beta_1}{\beta_2 \lambda_2}$. Therefore we can calculate β_1 and β_2 by measuring q, the distribution of the metal between the two phases, and relating it to the free ligand concentration $[T^-]$.

$[T^-]$ is calculated from the expression

$$[T^-] = \frac{[T]_t}{A(1+\lambda_T)[H^+]+1} \qquad (6)$$

$[T]_t$ being the initial concentration of TTA in the organic phase,

λ_T the distribution ratio of TTA between the phases, and

A the association constant of HT = 1.5×10^6 (Zebroski 1948).

3. DYRSSEN AND SILLÉN'S METHOD OF COMPUTATION

In the alternative method proposed by Dyrssen and Sillén (1953) the ratio of k_1 and k_2, the stepwise formation constants of the two complexes BeT^+ and BeT_2, is expressed in the form

$$\frac{k_1}{k_2} = 10^{2b} \qquad (7)$$

while their product is given by

$$k_1 k_2 = 10^{2a} \; (= \beta_2) \qquad (8)$$

By substitution in the logarithmic form of (3), we obtain the expression

$$\log q = \log \lambda_2 + 2a + 2 \log [T^-] - \log \left(1 + [T^-]10^{a+b} + [T^-]^2 10^{2a}\right) \qquad (9)$$

which represents the curve obtained by plotting the experimental values of q against the appropriate values calculated for $[T^-]$. This curve will have two asymptotes given by

$$\log q = \log \lambda_2 + 2a + 2 \log [T^-] \qquad (10)$$

$$\lim [T^-] \to o$$

and

$$\log q = \log \lambda_2 \qquad (11)$$

$$\lim [T^-] \to \infty \;,$$

intersecting at the point $(-a, \log \lambda_2)$.

To determine the ratio $\frac{k_1}{k_2}$, various values of b from $-\infty$ upwards are then inserted in turn into equation (9), together with the values of a and λ_2 just obtained. The curve which fits the experimental points most closely is assumed to have the correct value of b. It should be noted that $b = -\infty$ corresponds to a total absence of BeT^+, while $b = 0$ corresponds to $k_1 = k_2$, i.e. when the two ligands in BeT_2 are equally tightly bound.

4. EXPERIMENTAL WORK

The TTA, melting point 42.5° to 43°, obtained from L. Light and Coy., Colnbrook, Middlesex, England, was used without purification. The o-xylene used in these experiments was thiophene-free, Analytical Grade. Beryllium perchlorate solutions were prepared by the ion-exchange method of Sergeant (1960), and enough Be-7 tracer was added to allow the necessary analyses to be made by γ-scintillation counting.

The distribution ratio of TTA itself was measured between 10 ml of 0.2M TTA in the organic solvent and 10 ml of an aqueous phase adjusted to μ = 0.1 with sodium perchlorate. The two phases were shaken together for 24 hours at 25°, separated by centrifuging, and the concentration of TTA in the aqueous layer found spectrophotometrically in quartz cells on a Hilger "Uvispek", after diluting with 50 volumes of water. The band at 266 mμ (King and Reas, 1949) was found to obey the Beer-Lambert law over the concentration range studied. It was shown that small amounts of dissolved organic phase do not interfere with the optical density measurements.

The beryllium extraction experiments were made at 25° ± 0.1° in an apparatus described by Bishop, de Bruin, and Temple (1960). As preliminary experiments showed that a contact time of about 100 hours was necessary to reach equilibrium, the two phases were shaken continuously for a week. The pH was adjusted with either perchloric acid or sodium hydroxide as necessary.

For measuring the stability constants, 0.1 and 0.5M solutions of TTA in o-xylene were used. The aqueous phase was 10^{-5} M in beryllium and the ionic strength was adjusted to 0.1 with sodium perchlorate.

5. RESULTS AND DISCUSSION

The distribution coefficient for TTA between o-xylene and water was found to be independent of hydrogen-ion concentration over the pH range 1 – 5. The value obtained was 32.9. The results of the extraction experiments are shown in Table 1.

These data are plotted according to Leden's method in Figures 1 and 2, and according to Dyrssen and Sillén's method in Figure 3. From these curves the following results have been obtained:-

Figure 1. $\frac{1}{\lambda_2} = 8.0 \times 10^{-4}$

$\frac{\beta_1}{\beta_2\lambda_2} = 2.25 \times 10^{-9}$

Figure 2. $\frac{\beta_1}{\beta_2\lambda_2} = 2.25 \times 10^{-9}$

$\frac{1}{\beta_2\lambda_2} = 6.60 \times 10^{-15}$

From these relations it may be deduced that $\lambda_2 = 1250$

$\beta_1 = 3.40 \times 10^5$

$\beta_2 = 1.21 \times 10^{11}$

TABLE 1

Distribution of beryllium between water and TTA solutions in o-xylene

Initial TTA concentration 0.1M

pH	log q	$-\log T^-$	1/q	$1/T^-$	$(1/q-1/_2)\,T^-$
4.65	3.08	4.05	8.32×10^{-4}	1.12×10^{4}	2.85×10^{-9}
4.08	3.03	4.62	9.33	4.17	3.17
3.90	3.00	4.80	1.00×10^{-3}	6.31	3.17
3.86	3.00	4.84	1.00	6.92	2.88
3.70	2.95	5.00	1.12	1.00×10^{5}	3.20
3.60	2.92	5.10	1.20	1.26	3.17
3.51	2.88	5.19	1.32	1.55	3.36
3.29	2.75	5.41	1.78	2.57	3.81
3.07	2.54	5.63	2.88	4.27	5.12
2.96	2.38	5.74	4.17	5.50	6.13
2.95	2.33	5.75	4.68	5.62	6.90
2.91	2.26	5.79	5.50	6.17	7.61
2.70	1.90	6.00	1.26×10^{-2}	1.00×10^{6}	1.19×10^{-8}
2.60	1.70	6.10	2.00	1.26	1.53
2.41	1.35	6.29	4.47	1.95	2.25
2.22	0.88	6.48	0.132	3.02	4.37
2.08	0.58	6.62	0.263	4.17	6.31
1.72	-0.17	6.98	1.48	9.55	1.55×10^{-7}

Initial TTA concentration 0.5M

3.58	3.10	4.43	7.94×10^{-4}	2.69×10^{4}	
3.29	2.05	4.72	8.91	5.25	1.73×10^{-9}
2.73	2.80	5.28	1.59×10^{-3}	1.91×10^{5}	3.70
2.46	2.60	5.55	2.51	3.55	4.82
2.36	2.52	5.65	2.02	4.47	4.97
2.32	2.43	5.69	3.72	4.90	5.96
1.73	1.33	6.28	4.67×10^{-2}	1.91×10^{6}	2.41×10^{-8}

From Figure 3 on the other hand, $a = 5.56$

$\lambda_2 = 1260$

and using these values, the curves shown in Figure 3 were computed for $b = -\infty$, 0, and 0.25. The best fit with the experimental points appears to be obtained for $b = 0$. Hence

$$\beta_1 (=k_1) = 3.63 \times 10^5 \quad \text{and}$$

$$\beta_2 (=k_1k_2) = 1.32 \times 10^{11}.$$

There is no significant difference in accuracy between the two methods. The experimental errors in measuring the distribution coefficients are such that the extrapolation of the reciprocals in Leden's method is no more accurate than the extrapolation of the logarithms used by Dyrssen and Sillén.

Figure 4 summarizes the results of the calculations. The percentage distribution of the Be between Be^{++}, BeT^+, and BeT_2 has been plotted as a function of $[T^-]$. It will be seen that BeT^+ exists in appreciable proportions only over a small range of $[T^-]$.

The measurements were made at a pH at which hydrolysis of the Be^{++} could be ignored. Only a few measurements were made at pH values above 4.0, and since the initial metal concentration was 10^{-5} M and the distribution ratio about 10^3, the concentration of metal in the aqueous phase was about 10^{-8} M. At pH 4, the results of Kakihana and Sillén (1956) show that less than 1 per cent. of the Be^{++} is hydrolyzed in a solution of this concentration.

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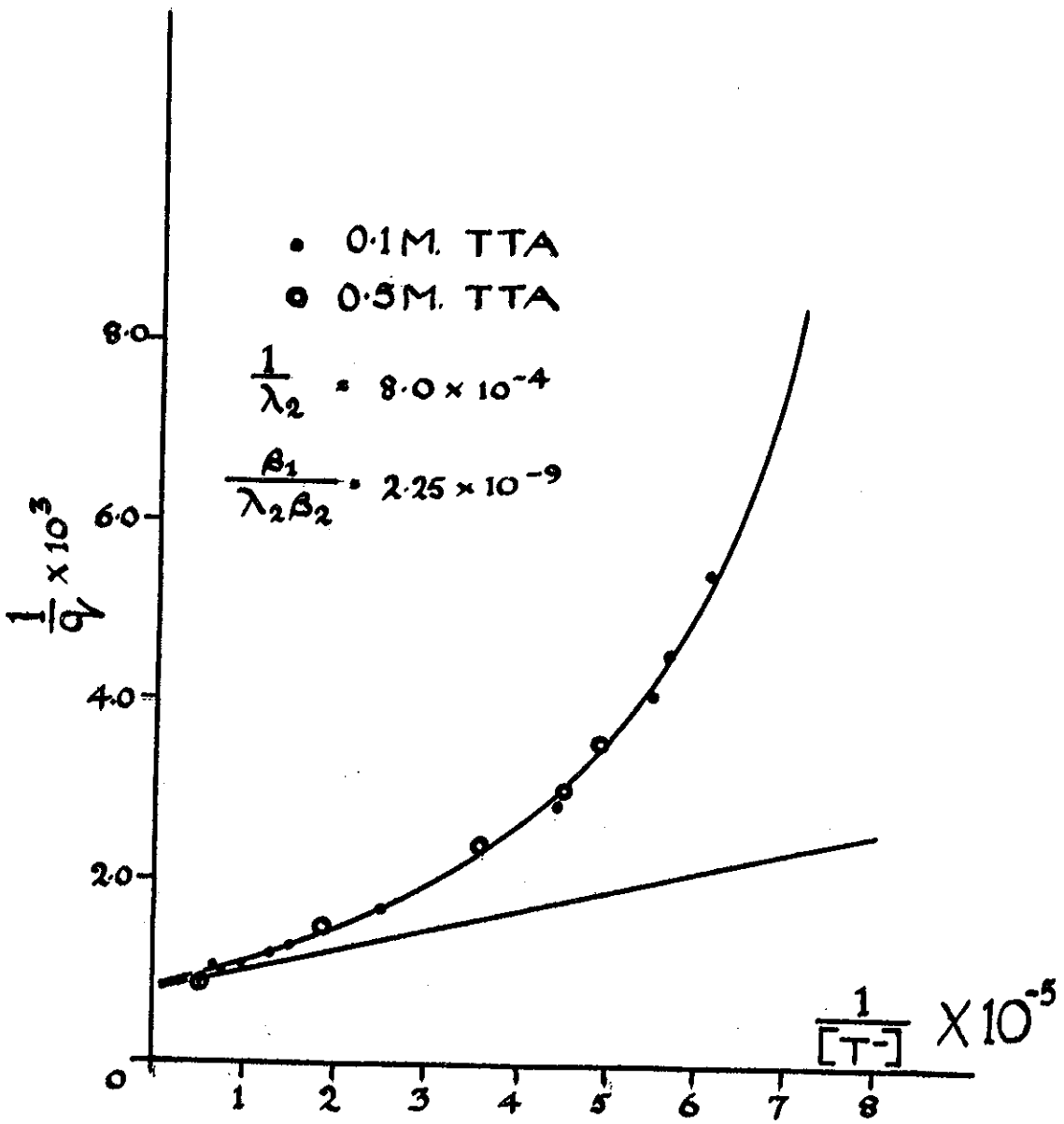

Fig. 1 ~ $\frac{1}{q}$ AS A FUNCTION OF $\frac{1}{[T^-]}$.

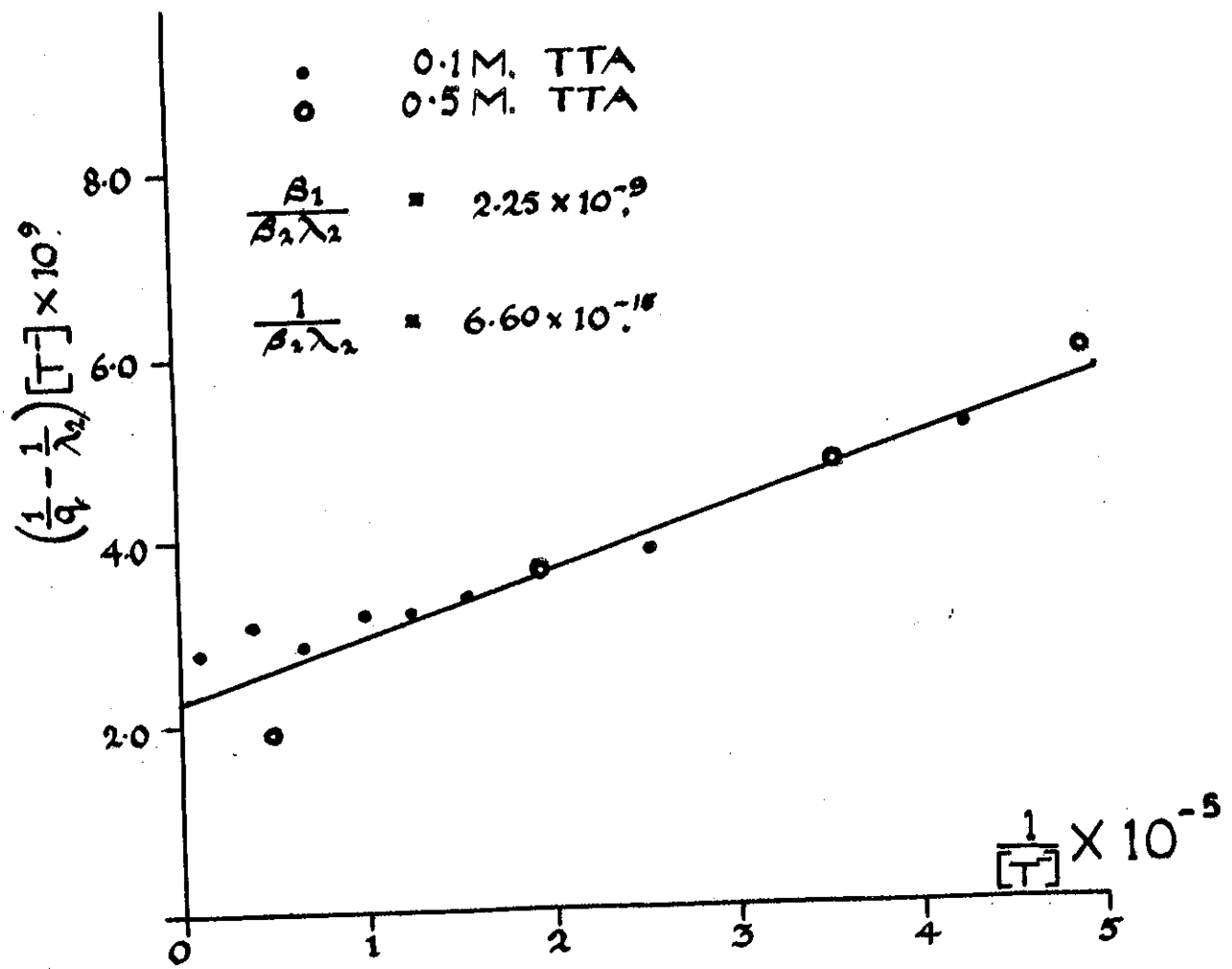

Fig 2. – $\left(\frac{1}{q}-\frac{1}{\lambda_2}\right)[T^-]$ AS A FUNCTION OF $\frac{1}{[T^-]}$

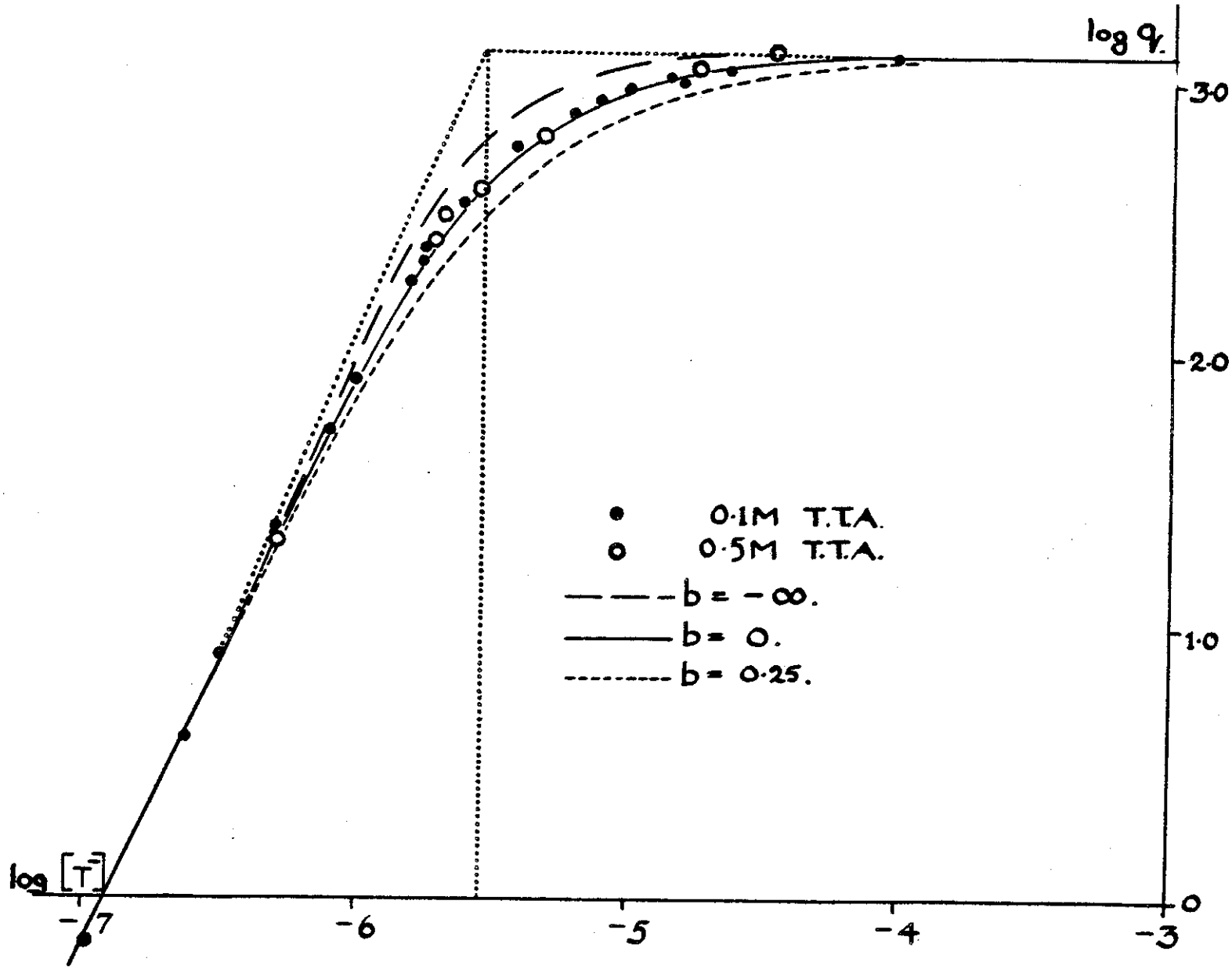

Fig 3. ~ EXTRACTION CURVE FOR BERYLLIUMTHENOYLTRIFLUOROACETONATE INTO O-XYLENE.

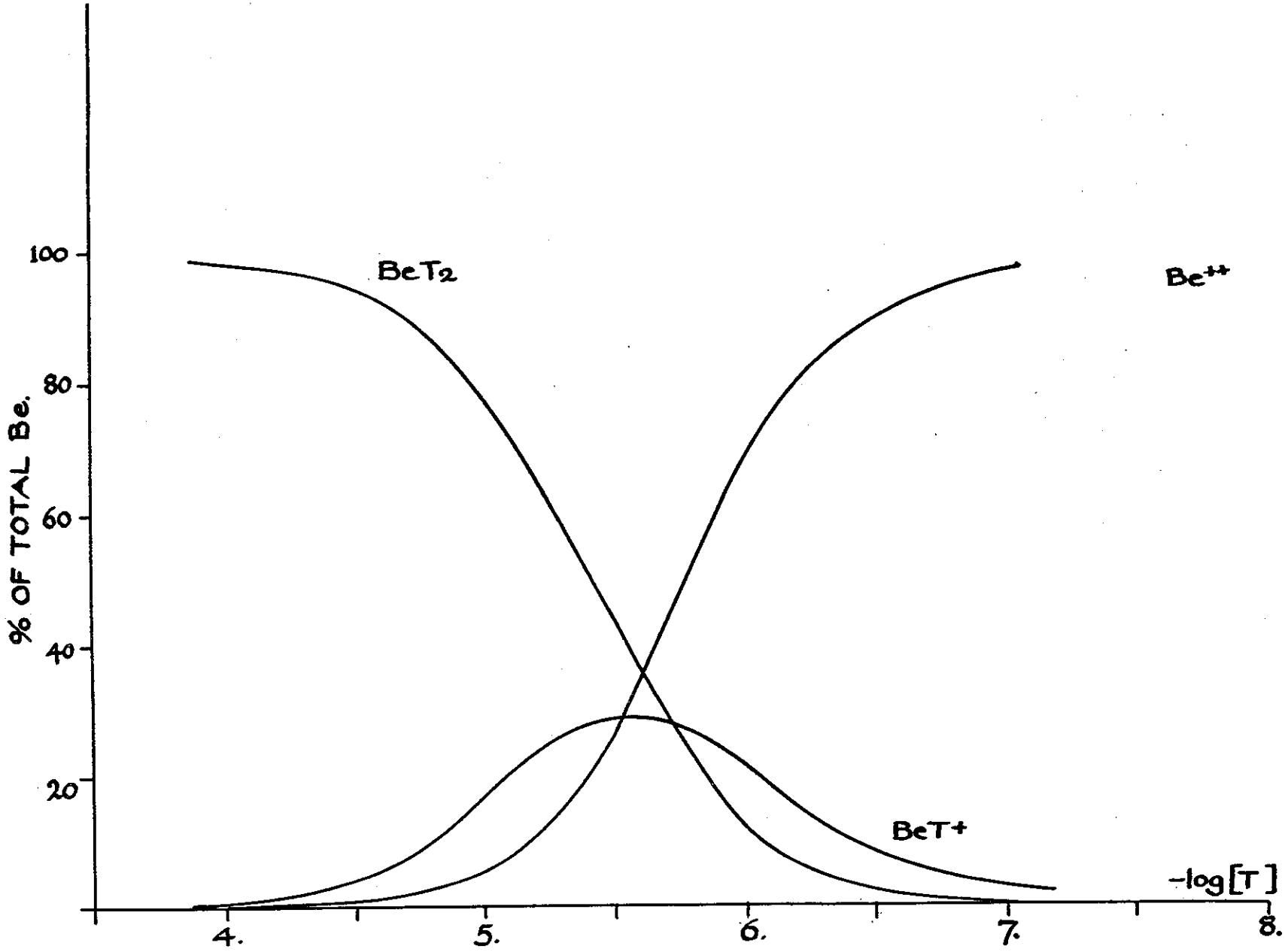

Fig 4. ~ FRACTIONAL DISTRIBUTION OF BERYLLIUM IN AQUEOUS TTA SOLUTION.