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DETERMINATION OF THE STABILITY CONSTANTS OF SALICYLATO-BERYLLIUM COMPLEXES BY A DISTRIBUTION METHOD

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ABSTRACT

An investigation of the solvent extraction behaviour of salicylato–beryllium complexes is reported here. A simplified method for calculating the stability constants has been developed. The values obtained are $\beta_1 = 4.0 \times 10^{12}$ and $\beta_2 = 4.3 \times 10^{22}$ in 0.15M sodium perchlorate.

CONTENTS

1. INTRODUCTION

The beryllium salicylate system is interesting because of its suggested use in the selective dissolution of beryllium from spent fuel elements. A summary of previous work on salicylate complexes of beryllium has been given by Fardy (1961), who confirmed the existence of a neutral 1:1 chelate and determined its formation constant by cation exchange.

This complex appears to be soluble only in a restricted range of solvents. The present work was done using amyl alcohol. Solvents likely to form complexes with beryllium were avoided deliberately.

1.1 List of Symbols Used in the Text

Concentrations are indicated by round brackets, and charge signs are omitted.

M = metal atom

L = free ligand

(L_m) = free ligand concentration at maximum extraction

(L'), (L'') = free ligand concentration at conjugate points of equal extraction e.g. P' and P'' (See Figure 1).

k_1, k_2 = stepwise formation constants for ML and ML_2

β_2 = $k_1 \times k_2$ i.e. the overall stability constant for ML_2

q = distribution ratio of total metal = $(M_t)_o/(M_t)_a$

S = maximum possible number of ligands taken up by M

λ = distribution constant of the neutral extractable complex ML

$\bar{n}$ = average number of ligands bound to all central atoms M in an aqueous system

$\bar{A}_1$, $\bar{A}_2$ = association constants for H_2L, the protonated ligand. $\bar{A}_1 = 1/K_{a1}$, $\bar{A}_2 = 1/(K_{a1} K_{a2})$. See de Bruin and Florence (1961).

Subscripts o and a refer to organic and aqueous phases respectively.

The subscript t indicates the total quantity of a species present in the system.

The signs ' and '' indicate values of any variable at points of equal extraction.

2. THEORY

2.1 Determination of the Overall Stability Constant

It has been shown earlier (Rosenheim and Lehmann 1924; Jones et al., 1930; Fardy 1961) that beryllium and salicylate ions form two complexes ML and $ML_2^=$, which will be expected to have different extractabilities into a given solvent.

If the solvent is capable of extracting only the neutral intermediate complex, then we expect the extraction of the metal to pass through a maximum when expressed as a function of the free ligand concentration. The fall-off in extraction at high values of (L) is brought about by the increased formation of $BeL_2^=$, the non-extractable species. This is illustrated in the following figure.

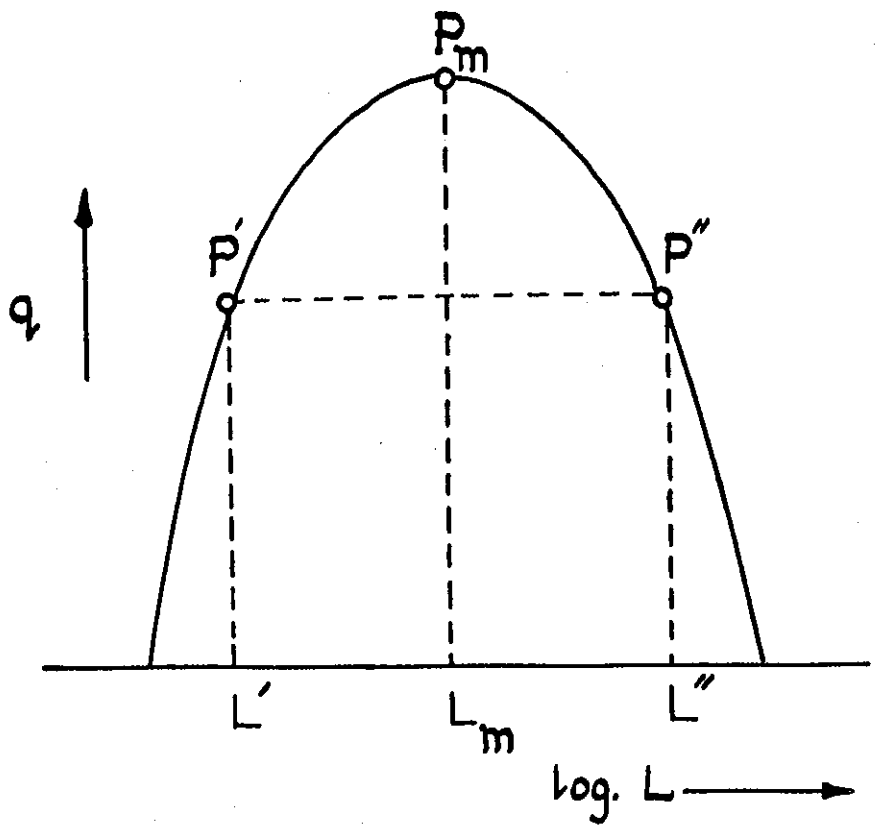

Figure 1 Extraction curve of a metal forming two complexes, where the 1:1 complex is neutral and the 1:2 complex is anionic.

In the following treatment, three assumptions are made:

(i) The only extracted species is monomolecular ML.

(ii) Hydrolysis and the formation of polynuclear complexes can be neglected.

(iii) The ratio of the volumes of the two phases and the quantity of total metal in the system are kept constant.

It is essential that the free ligand concentration at each point should be known. This can be calculated from the known total ligand concentration and pH measurements, if the association constants, and distribution coefficient, of the protonated ligand are known.

We now choose two points P' and P'' which have the same distribution ratio q (Figure 1) and let the free ligand concentrations at these points have the values (L') and (L'') respectively. The quantity of the neutral complex in the organic phase must then be the same at these two points and, according to Nernst's distribution law, the proportion $(ML)_o/(ML)_a$ is constant (λ). Therefore at the points P' and P'' we have:

$$\begin{aligned} (ML')_o &= (ML'')_o \\ (ML')_a &= (ML'')_a \\ (ML')_t &= (ML'')_t \end{aligned} \qquad (1)$$

As the total metal in the system is constant and is present in the forms M, ML, and ML_2 we can write

$$(M') + (ML_2') = (M'') + (ML_2'') \qquad (2)$$

M and ML_2 are assumed to exist in the aqueous phase only. By applying the law of mass action to the conditions at points P' and P'' we can therefore express their concentrations in terms of k_1 and k_2, the stepwise formation constants for ML and ML_2, and the concentrations (M'), (L'), and (L'').

Thus

$$(M') + k_1k_2(M')(L')^2 = \frac{(M')(L')}{(L'')} + k_1k_2(M')(L')(L'') \qquad (3)$$

and, rearranging,

$$k_1k_2(L')\{(L'')-(L')\} = \frac{(L'')-(L')}{(L'')}$$

and: $$k_1k_2 = \beta_2 = \frac{1}{(L')(L'')} \qquad (4)$$

or: $$\frac{1}{k_1(L')} = k_2(L'') \qquad (4a)$$

This derivation is not valid for the maximum at point P_m in Figure 1 where $(L'')-(L') = 0$, but as $q = f(L)$ is a continuous function, equation (4) will be valid at this point too, and then becomes:

$$\beta_2 = \frac{1}{(L_m)^2} \qquad (5)$$

This is in accordance with Bjerrum's equation (1941) for the average formation constant

$$k_{av} = \sqrt{k_1k_2} = \frac{1}{(L)} \qquad (6)$$

when the formation function $\bar{n} = 1$.

A similar expression can be obtained by Dyrssen and Sillén's (1953) two-parameter calculation. If (L_I) is the ligand concentration at the point of intersection of the asymptotes,

$$\beta_2 = \frac{1}{(L_I)^S} \qquad (7)$$

It can easily be shown that the conditions of equations 6 and 7 apply to point P_m of our graph. When equation 4a is substituted into the equation defining $\bar{n}$ (Bjerrum 1941), which in our case takes the form

$$\bar{n} = \frac{1 + 2k_2(L)}{\frac{1}{k_1(L)} + 1 + k_2(L)} ,$$

we get for points P' and P'':

$$\bar{n}' + \bar{n}'' = 2$$

At the point P_m this becomes $\bar{n} = 1$. The same can be shown to hold for the ligand number for the two-phase system.

With regard to equation 7 it will be sufficient to show that our curve of $\log q = f \log(L)$ is symmetrical with respect to a perpendicular line passing through P_m. This can be seen from the logarithmic form of equation 4, namely

$$\frac{\log(L') + \log(L'')}{2} = \text{const.}$$

The advantage of equation 4 for finding the overall stability constant lies in being able to use all experimental points. As the curve is usually rather flat about the maximum it is difficult to find the ligand concentration L_m.

2.2 Determination of the Stepwise Formation Constants, and the Distribution Ratio for the Neutral Complex

According to the method of Rydberg (1950),

$$q = \frac{\lambda k_1(L)}{1 + k_1(L) + k_1 k_2(L)^2} \qquad (8)$$

or at point P', $$q = \frac{\lambda}{\frac{1}{k_1(L')} + 1 + k_2(L')} \qquad (8a)$$

From (4a) and (8a) we get

$$q = \frac{\lambda}{1 + k_2\{(L') + (L'')\}} \qquad (9)$$

or

$$1/q = 1/\lambda + \frac{k_2}{\lambda}\{(L') + (L'')\} \qquad (10)$$

k_2/λ and $1/\lambda$ can be obtained by plotting $(1/q)$ as a function of $\{(L') + (L'')\}$.

The sum $(L') + (L'')$ has a minimum value of $2(L_m)$ at the point P_m in Figure 1 where q reaches its maximum. If we substitute the value $2(L_m)$ into equation 9 and express (L_m) by equation 5 we get

$$q_{max} = \frac{\lambda}{1 + 2\sqrt{\frac{k_2}{k_1}}} \qquad (11)$$

It will be seen that the maximum distribution ratio is a constant, independent of the total ligand concentration. However, there will be no maximum unless the free ligand concentration exceeds (L_m). Therefore, variations in the maximum obtained at different total ligand concentrations, may be taken as an indication of other species in the system. For example, hydrolysis of the metal ion will lower the maximum extraction obtainable.

The free ligand concentrations were calculated from the formula

$$(L) = \frac{(L)_{t,a}}{1 + \bar{A}_1(H) + \bar{A}_2(H)^2} \qquad (12)$$

$(L)_{t,a}$ was determined experimentally.

3. EXPERIMENTAL

3.1 Reagents

Reagents used were of analytical grade and were not further purified, except for the following:

Amyl alcohol was washed three times with 0.1N HCl, followed by three washings with 0.1N KOH. It was then distilled over potassium hydroxide pellets. The fraction boiling at 130 – 132°C was collected, washed with demineralized water, and used without drying.

Beryllium perchlorate was prepared from the sulphate by means of Serjeant's (1960) ion exchange method. The solutions used were not saturated with amyl alcohol.

3.2 Apparatus

The two phases were equilibrated by shaking in an apparatus described by Bishop, de Bruin, and Temple (1959). The glass containers used were coated with silicone resin and fitted with a ground standard tapered socket, closed by a tapered polythene stopper over which a tight fitting rubber cap was placed.

pH measurements were made with an EIL Model 23A direct–reading, mains–operated pH meter, with a type GMV 23 Microvol glass electrode. The electrode sheath was connected to a glass capillary by means of a polythene tube, thus allowing direct withdrawal of the aqueous phase into the Microvol assembly.

Be–7 counts were made in polythene containers of ½ inch diameter, by means of an EKCO type 550A well–crystal scintillation counter, used with an EKCO type 529 scaler and fast prescaler.

3.3 Preliminary Tests

The solvents tested were toluene, carbon tetrachloride, amyl alcohol, 2–ethyl–hexanol, and sec–octyl alcohol. Amyl alcohol gave the best extraction, while toluene and carbon tetrachloride failed to extract measurable activity. The effect of various buffers was tested using 4×10^{-5}M salicylic acid in amyl alcohol. When phosphate, phthalate, citrate, acetate, and borate buffers were used all experiments gave lower extractions than parallel experiments without buffers. In the latter case sodium hydroxide or perchloric acid were used for pH adjustment. When the ionic strength was raised by addition of sodium perchlorate to samples without buffer, the distribution ratio showed very little change. Buffers were omitted in further experiments.

Slight extraction was observed in the absence of salicylic acid, but the purified amyl alcohol did not extract more than 0.3 per cent. of the total beryllium. (A correction corresponding to this figure was made to all q values measured. The figures shown in Tables 1 – 3 are the corrected values).

The time required to reach equilibrium was not determined accurately, but no change in the distribution could be detected after 16 hours, even in the most dilute solutions.

3.4 Distribution Measurements

All equilibrations were carried out at 25 °C by shaking together 10 ml of each of the two phases for 16 hours. The ionic strength was kept at 0.15. The aqueous phase was composed of 8 ml of 1.25×10^{-5}M beryllium perchlorate, containing sufficient Be–7 to give approximately 10^5 disintegrations per ml per minute. The remaining 2 ml were made up from various sodium perchlorate solutions, each having an ionic strength of 0.75. The acid or alkali content was varied to give the desired pH. The organic phase consisted of salicylic acid dissolved in purified amyl alcohol. Three concentrations were used: 4×10^{-1}M, 4×10^{-3}M and 4×10^{-5}M.

The flasks were filled to about two–thirds and the air was swept out with nitrogen gas to remove CO_2. No stable emulsions were formed on shaking. The separation of the phases was achieved by settling in a thermostatically controlled water bath for 48 hours. This was much more satisfactory than centrifuging. Centrifuging caused variations of phase volumes due to changes of mutual solubility with fluctuations in ambient temperature. It also involved undue exposure of the weakly buffered solutions to the atmosphere.

After settling, the pH was determined by drawing a sample directly into the glass electrode assembly. The two phases were then sampled by means of hypodermic syringes, and the distribution of Be–7 was determined by gamma–counting. Some adsorption of gamma–activity on the containing vessels was noticed at high pH values, but was largely overcome by the silicone treatment. Only the last few experiments listed in Table 3 were significantly affected. The distribution of salicylic acid was measured spectrophotometrically by the method of Florence (1961).

To check the effect of possible polynuclear complexes, one series of experiments was made with 10^{-4}M beryllium perchlorate. The results were almost identical with those listed in Table 2, showing negligible formation of polynuclear complexes.

4. RESULTS

The distribution ratio values obtained at various pH values are listed in Tables 1 – 3, together with the calculated free ligand concentrations.

Figure 2 shows the percentage of salicylic acid extracted into 0.15M sodium perchlorate from its 4×10^{-3}M solution in amyl alcohol, as a function of pH. Figure 3 gives the corresponding – log (L) values plotted as functions of pH. They were calculated from equation 12, using the association constants $\bar{A}_1 = 2.78 \times 10^{13}$ and $\bar{A}_2 = 2.70 \times 10^{16}$. These correspond to data given by Euler (1928) and Larsson (1929).

Figure 4 shows q values plotted as functions of pH, with the three curves representing different concentrations. Each curve has limiting slopes of +2 and –1, supporting the assumptions that

(i) at high H^+ concentration the main overall reaction is

$$H_2Sal + Be^{++} \rightleftharpoons BeSal + 2H^+$$

and

(ii) at lower (H^+)

$$HSal^- + BeSal \rightleftharpoons BeSal^= + H^+$$

Figure 5 shows the same values of q as functions of pL.

Table 2 has been used for computing the following results:

Conditional constants at an ionic strength of 0.15 at 25 °C

From equation 4: $\beta_2 = 4.3 \times 10^{22}$

From equation 10: $\lambda = 0.70$

From equation 10: $k_2 = 1.1 \times 10^{10}$

and therefore $k_1 = 4.0 \times 10^{12}$

λ and k_2 were obtained by use of the method of least squares. The value of β_2 is an arithmetic mean of values obtained from equation 4, with the greatest weight at half of the maximum extraction. The same value may be obtained using equation 5 when $-\log(L_m)$ is found graphically from Figure 5.

TABLE 1

Distribution ratio q of beryllium at various pH values, when a 10^{-5}M beryllium perchlorate solution is at equilibrium with 4×10^{-1}M salicylic acid in amyl alcohol at 25 °C (ionic strength = 0.15)

pH	q	pL
3.25	0.416	12.25
3.55	0.558	11.73
3.80	0.623	11.27
4.00	0.607	10.90
4.18	0.553	10.55
4.43	0.437	10.14
4.60	0.340	9.83
4.72	0.284	9.64
4.93	0.176	9.33

TABLE 2

Distribution ratio q of beryllium at various pH values when a 10^{-5}M beryllium perchlorate solution is at equilibrium with 4 x 10^{-3}M salicylic acid in amyl alcohol at 25 °C

(Ionic strength = 0.15)

pH	q	pL	pH	q	pL
2.92	0.003	15.0	5.35	0.616	10.75
3.02	0.006	14.7	5.48	0.560	10.55
3.28	0.012	14.25	5.58	0.524	10.45
3.45	0.047	14.0	5.58	0.529	10.45
3.70	0.117	13.4	5.70	0.495	10.3
3.72	0.122	13.35	5.82	0.416	10.15
3.75	0.099	13.3	5.88	0.337	10.05
3.80	0.127	13.2	6.03	0.335	9.9
3.82	0.119	13.15	6.05	0.311	9.82
3.90	0.164	13.1	6.05	0.250	9.82
4.20	0.359	12.55	6.05	0.311	9.82
4.40	0.522	12.15	6.18	0.255	9.7
4.55	0.550	11.9	6.38	0.117	9.50
4.65	0.616	11.7	6.45	0.096	9.4
4.79	0.575	11.45	6.55	0.127	9.3
4.88	0.631	11.4	6.58	0.099	9.27
5.00	0.613	11.25	6.78	0.066	9.0
5.08	0.637	11.15	7.18	0.016	8.6
5.10	0.605	11.1	7.50	0.009	8.3
5.22	0.634	10.95	7.68	0.006	8.1

TABLE 3

Distribution ratio q of beryllium at various pH values, when a 10^{-5}M beryllium perchlorate solution is at equilibrium with 4 x 10^{-5}M salicylic acid in amyl alcohol at 25 °C.

pH	q	pL *
4.4	0.004	14.5
4.5	0.012	14.05
4.8	0.024	13.6
4.9	0.045	13.4
5.0	0.041	13.25
5.0	0.059	13.25
5.1	0.070	13.1
5.2	0.105	13.0
5.3	0.119	12.9
5.4	0.153	12.8
5.6	0.198	12.5
6.0	0.333	12.0
6.1	0.245	11.9
6.2	0.328	11.8
6.3	0.321	11.7
6.8	0.335	11.2
7.2	0.252	10.6
7.9	0.120	10.2
8.3	0.070	9.8
8.6	0.029	9.5
8.8	0.014	9.3

* corrected for depletion of H_2L (values under 13.0)

5. DISCUSSION OF RESULTS

The values for 4×10^{-3}M salicylic acid were used in preference to those for 4×10^{-1}M and 4×10^{-5}M because the highest acid concentration makes it impossible to maintain the ionic strength at 0.15, while the lowest concentration does not yield accurately reproducible results and requires pH values at which considerable hydrolysis occurs. For values in Table 3 an adjustment of the free ligand concentration was necessary to allow for depletion of H_2L due to complex formation. This meant a deduction of 0.1 units from the logarithm at maximum extraction (curve x Figure 5) and 0.3 at maximum concentration. Nevertheless the middle portion of the curve was considered sufficiently accurate to draw conclusions.

Tables 1 and 2 show all values measured, with the exception of q values at both ends of the pL range which were too low to be reliable. Values for β_2 calculated from Tables 1 and 3 are not appreciably different from the one given in Section 4 but the lower maximum value of q for the lowest salicylate concentration shows that hydrolysis occurs in this range.

It can be concluded that the assumptions used in making the present calculations substantially apply for most of the range investigated, and the values given are in good agreement with those found by Fardy (1961). The limiting slopes of the curves in Figure 5 are +1 and −1 respectively, as was expected.

The solubility of the neutral complex in water is given by Jones et al. (1930) as about 0.03M at 25 °C. Since $\lambda = 0.7$, this would indicate a solubility of this compound in amyl alcohol of the order of 0.02M. A greater solubility would be required for practical solvent extraction of beryllium. It is therefore recommended that the extraction be carried out using a ligand molecule in which the hydrocarbon radical is increased in size.

6. ACKNOWLEDGMENTS

The author owes particular thanks to H.J. de Bruin who has checked the mathematical treatment, and given valuable criticism and advice. The Analytical Chemistry Services Group has also helped with advice, in particular T.M. Florence, who also determined the distribution of total salicylate in the equilibrated samples. Thanks are also due to Dr. R.B. Temple for useful suggestions.

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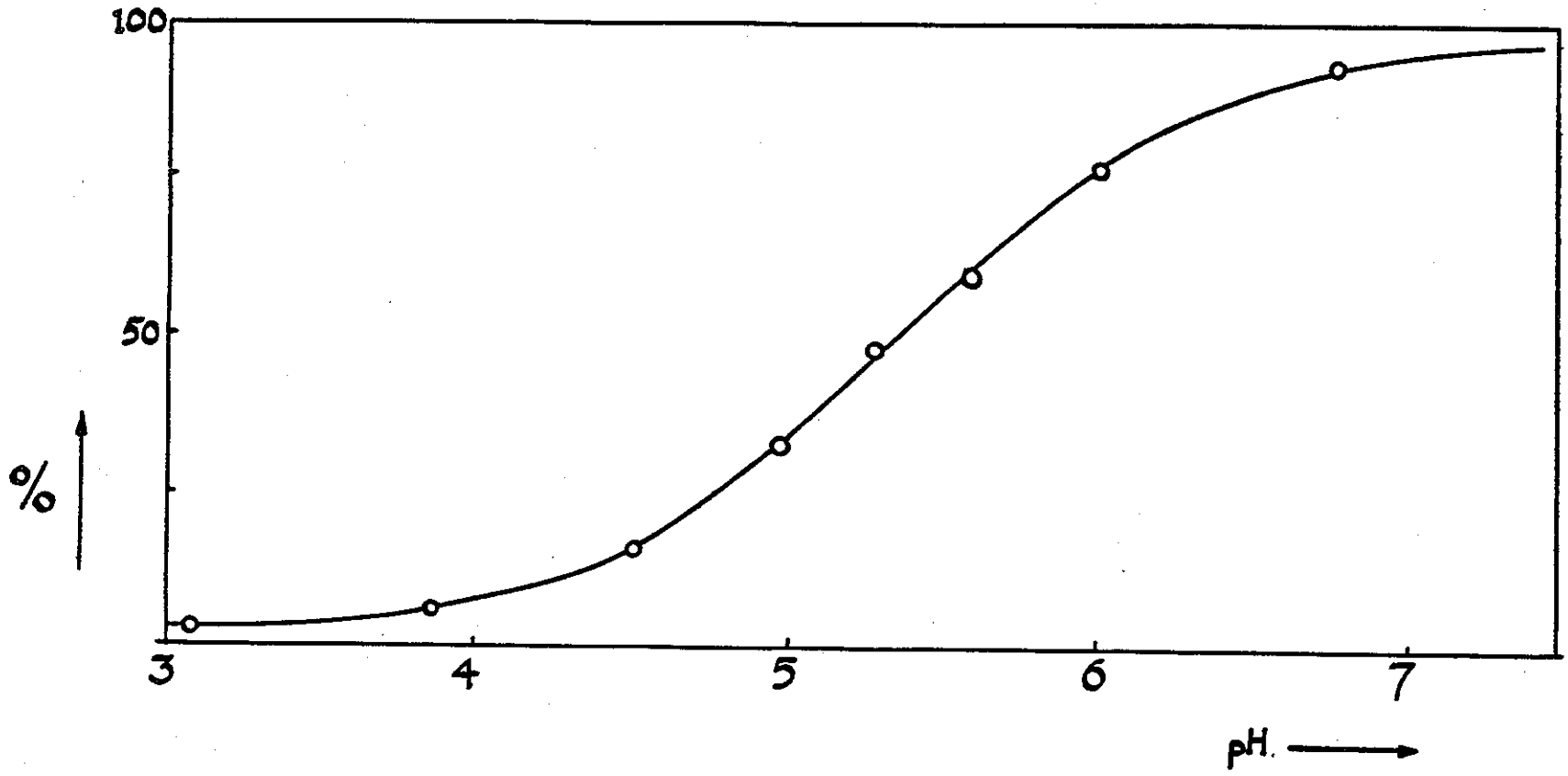

FIGURE 2 PERCENTAGE OF SALICYLIC ACID EXTRACTED INTO THE AQUEOUS PHASE (0.15M PERCHLORATE), FROM ITS 4×10^{-3}M SOLUTION IN AMYL ALCOHOL AT 25 °C.

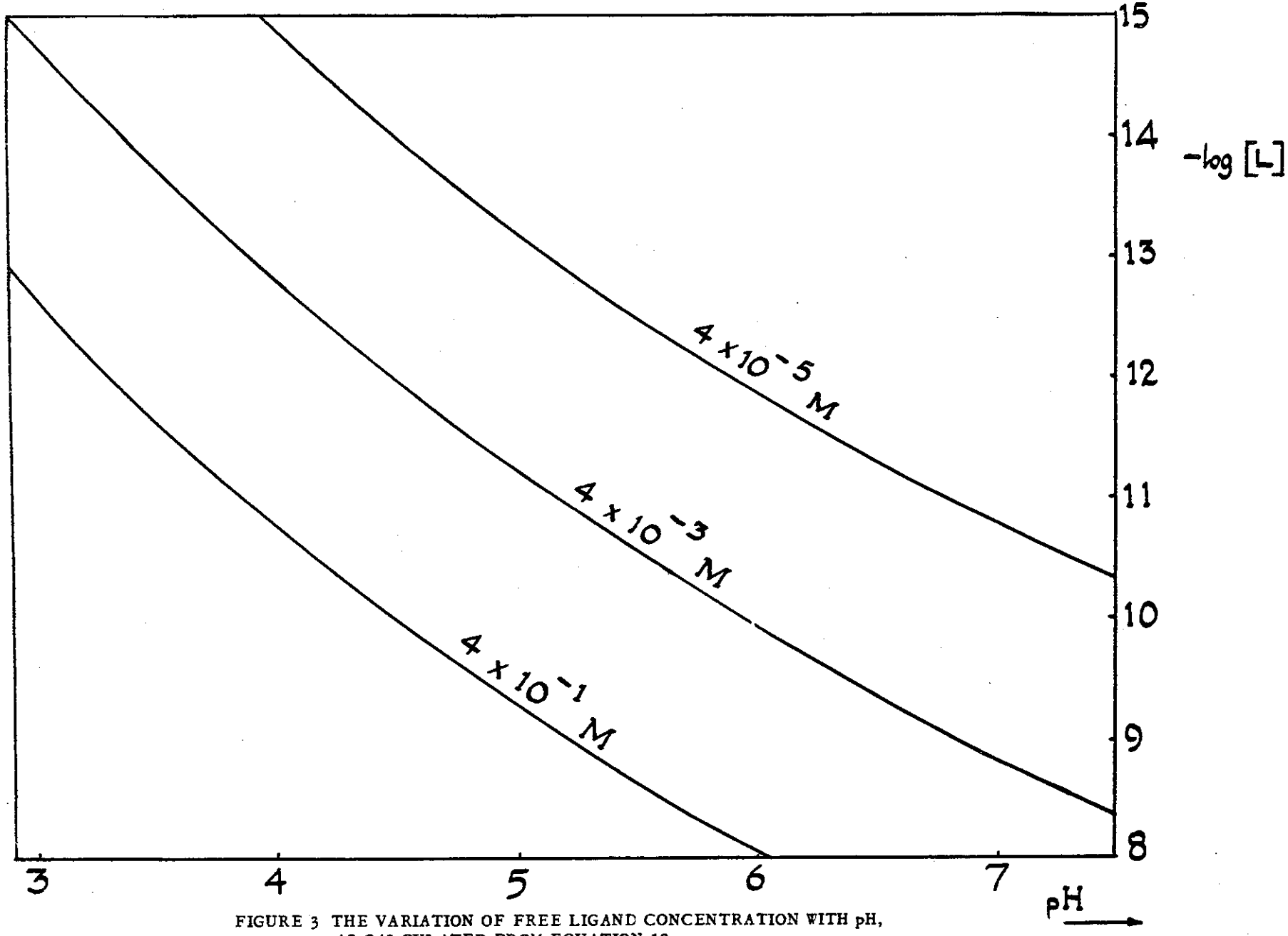

FIGURE 3 THE VARIATION OF FREE LIGAND CONCENTRATION WITH pH, AS CALCULATED FROM EQUATION 12.

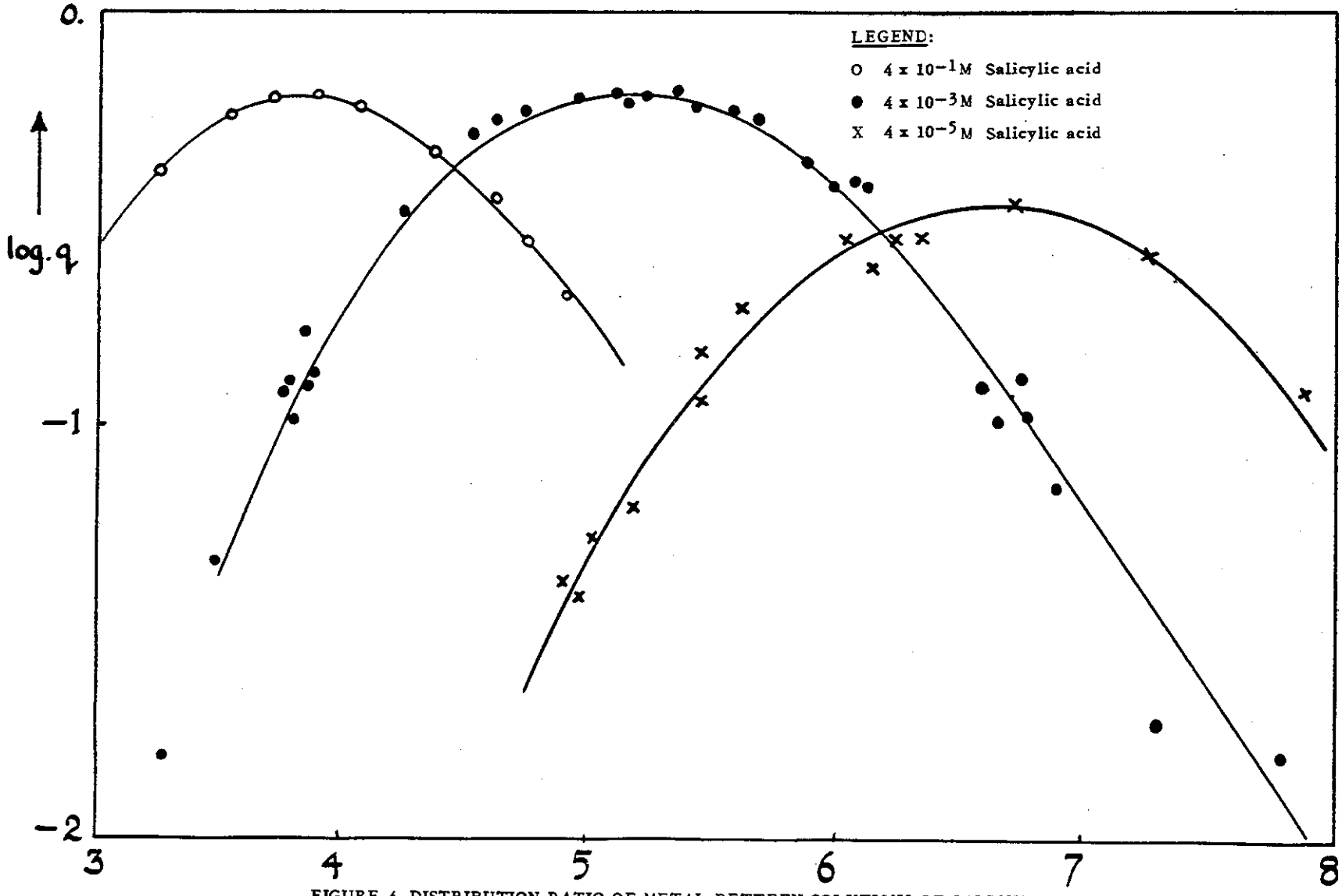

FIGURE 4 DISTRIBUTION RATIO OF METAL BETWEEN SOLUTIONS OF SALICYLIC ACID OF VARIOUS CONCENTRATIONS IN AMYL ALCOHOL AND A 10^{-5}M AQUEOUS BERYLLIUM PERCHLORATE SOLUTION AT 25°C (μ = 0.15), EXPRESSED AS FUNCTIONS OF pH.

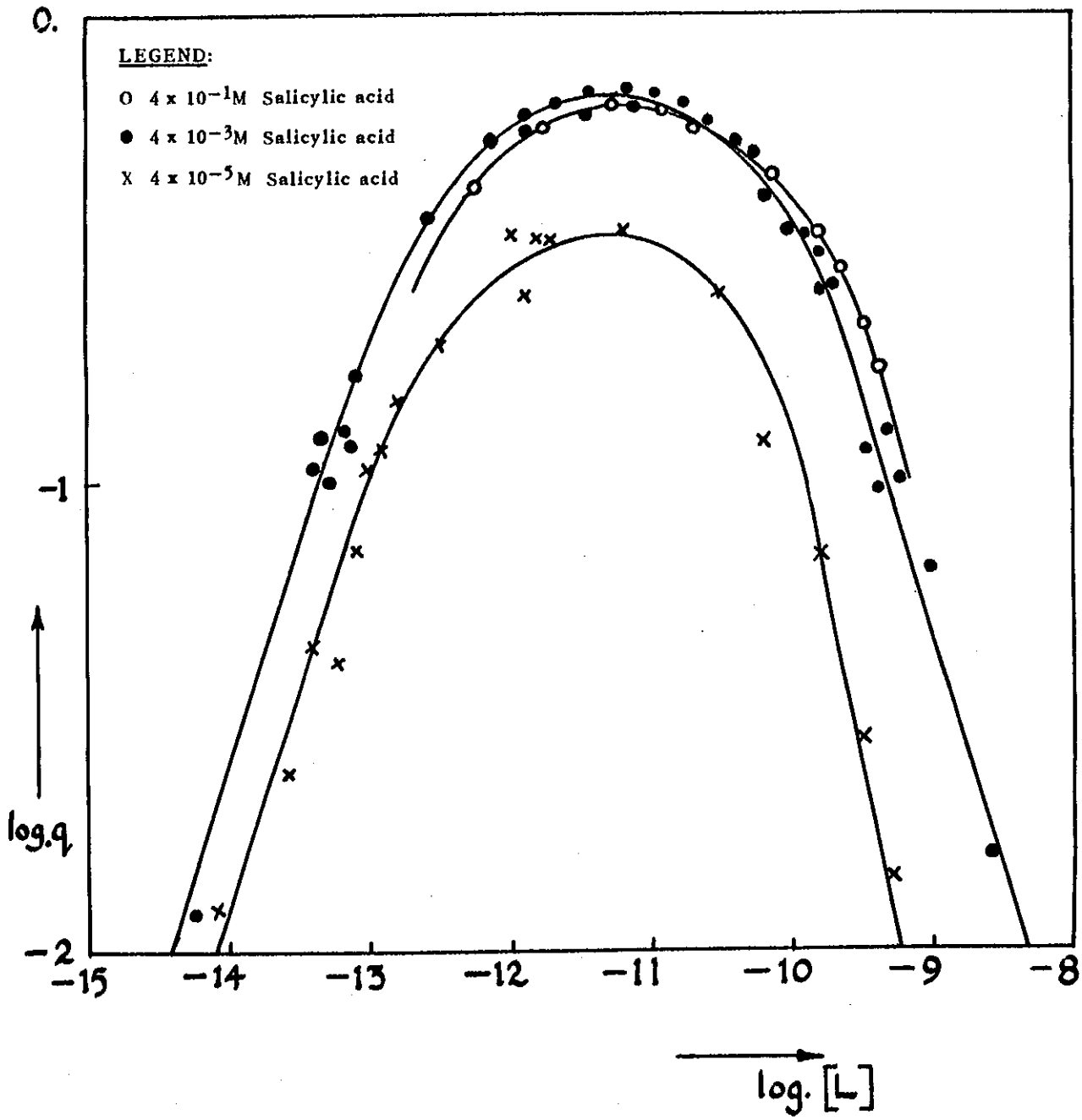

FIGURE 5 DISTRIBUTION RATIO OF METAL BETWEEN SOLUTIONS OF SALICYLIC ACID OF VARIOUS CONCENTRATIONS IN AMYL ALCOHOL AND A 10^{-5}M AQUEOUS BERYLLIUM PERCHLORATE SOLUTION AT 25 °C (μ = 0.15), EXPRESSED AS FUNCTIONS OF pL.