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THE ION EXCHANGE BEHAVIOUR OF BERYLLIUM SALICYLATE COMPLEXES

by

J. J. FARDY

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ABSTRACT

As part of a general study of the co-ordination chemistry of beryllium, the beryllium salicylate complexes have been investigated by ion exchange procedures. The evidence indicates that a neutral 1 : 1 and an anionic 1 : 2 chelate exist in solution under appropriate conditions, and their stability constants have been determined by ion-exchange methods. The values of the stability constants were found to be $\beta_1 = 4.97 \times 10^{12}$, and $\beta_2 = 2.63 \times 10^{22}$.

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GENERAL INTRODUCTION

The beryllium/salicylate system has been studied in detail because of its importance in a scheme proposed for processing homogeneous, beryllium-based fuel elements. (Farrell and Temple, 1962).

The identification of the complexes and the measurement of their stability constants by ion-exchange procedures are described here. The values obtained for the stability constants are in reasonable agreement with those determined by solvent extraction and pH – titration (de Bruin, Kairaitis, and Szego, 1962).

Part 1 of the paper deals with cation exchange experiments carried out at relatively low pH; Part 2 concerns anion exchange experiments in the alkaline region. It is believed that the results enable a choice to be made between the structures proposed for the beryllium-salicylate complexes by various authors (see Table 1).

EXPERIMENTAL

All reagents were of analytical grade. "Zeo-Karb 225" resin (100-200 mesh, 8% D.V.B.) was used in the cation exchange experiments. It was converted to the sodium form, and dried over anhydrous magnesium perchlorate at 60 °C under vacuum for 48 hours before use.

Beryllium concentrations were measured by scintillation counting on liquid samples, using Be-7 as a tracer. Stable carrier had been added to give a final beryllium concentration of approximately 10^{-9}M.

The pH was measured with an E.I.L. model 23A direct-reading pH meter using a glass indicator electrode and saturated KCl/calomel reference electrode. These were standardized with commercial buffer solutions. Measurements were reproducible to ± 0.02 pH unit.

Equilibrations were carried out at 25 °C in a shaker previously described by Bishop, de Bruin, and Temple, (1960). Polystyrene containers were used to minimize loss of beryllium by adsorption.

To determine distribution ratios, 20 ml aliquots of an aqueous beryllium solution, whose salicylate concentration had been adjusted to known values between 0 and 5.5×10^{-3}M, were shaken with 100 mg of the appropriate resins for 24 hours. For the cation exchange experiments the ionic strength was adjusted to 0.15 with sodium perchlorate. Similar procedures were followed in the anion-exchange work in which "De Acidite-FF" was used, but the ionic strength was adjusted to 0.15 with ammonium chloride.

PART 1 CATION-EXCHANGE INVESTIGATIONS

1. INTRODUCTION

In complex formation between a beryllium ion and salicylic acid, the ligand must be either a singly or a doubly charged anion, which may be represented as $HSal^-$ and $Sal^=$ respectively. Neglecting hydrolysis of the Be^{2+} ion, the generalized equation for the formation of beryllium complexes can therefore be written:

$$Be^{++} + nH_2Sal \quad = \quad Be(H_{2-p}Sal)_n^{2-np} + npH^+ \ , \qquad (1)$$

where p is the number of protons lost from salicylic acid, and n can be 1 or 2 for cationic, neutral or anionic complexes, or 2, 3, or 4 for anionic species (see Table 2).

Schubert (1948) developed the following cation exchange technique which can be used to determine n and p for a single complex formed from trace amounts of metal ion in a region where hydrolysis can be neglected.

The equilibrium constant for Equation 1 is given by

$$K \quad = \quad \frac{[Be(H_{2-p}Sal)_n] \ [H]^{np}}{[Be] \ [H_2Sal]^n} \ , \qquad (2)$$

omitting the charges on all species in the concentration terms.

In the absence of salicylate, the distribution of the beryllium between the resin and the solution is given by

$$\alpha_o = \frac{[\mathrm{Be_R}]_o}{[\mathrm{Be}]_o} ,$$

where Be, and $\mathrm{Be_R}$ are the concentrations of metal in solution and on the resin respectively, and the subscript refers to the absence of ligand. If it is assumed that the complex formed in the presence of the ligand is not adsorbed, a similar expression then holds, namely

$$\alpha = \frac{[\mathrm{Be_R}]}{[\mathrm{Be}] + [\mathrm{Be(H_{2-p}Sal)_n}]} ,$$

where absence of a subscript indicates the presence of ligand, and the other symbols correspond to those in the expression for α_o .

Substituting these in Equation 2 gives K in terms of α_o and α , that is

$$K = \frac{\left(\frac{\alpha_o}{\alpha} - 1\right) [\mathrm{H}]^{np}}{[\mathrm{H_2Sal}]^n} , \qquad (3)$$

so

$$\log \left\{ \frac{\left(\frac{\alpha_o}{\alpha} - 1\right)}{[\mathrm{H_2Sal}]^n} \right\} = -np \log [\mathrm{H^+}] + \log K , \qquad (4)$$

or, at a constant hydrogen–ion concentration,

$$\log \left(\frac{\alpha_o}{\alpha} - 1\right) = n \log [\mathrm{H_2Sal}] + \text{constant} . \qquad (5)$$

The graphical solution of Equations 4 and 5 will yield values for n and p.

If the values of n and p are integral, the stability constant β_n of a complex formed by the reaction

$$\mathrm{Be^{2+}} + n\,\mathrm{H_{2-p}Sal} = \mathrm{Be(H_{2-p}Sal)_n}^{2-np} ,$$

can be calculated from the experimental data, since

$$\beta_n = \frac{[\mathrm{Be(H_{2-p}Sal)}]_n}{[\mathrm{Be}]\,[\mathrm{H_{2-p}Sal}]^n} .$$

This equation can be put in the form

$$\beta_n = \frac{\left(\frac{\alpha_o}{\alpha} - 1\right)}{[\mathrm{H_{2-p}Sal}]^n} , \qquad (6)$$

and rearranged to

$$\frac{1}{\alpha} = \frac{1}{\alpha_o} + \beta_n \frac{[\mathrm{H_{2-p}Sal}]^n}{\alpha_o} , \qquad (7)$$

from which $\frac{1}{\alpha_o}$ can be found by extrapolating $\frac{1}{\alpha}$ to $[\mathrm{H_{2-p}Sal}] = 0$. This rearrangement minimizes errors which arise in the direct measurement of α_o.

2. CATION EXCHANGE BEHAVIOUR OF BERYLLIUM IN THE PRESENCE OF o–METHOXYBENZOIC ACID

Additional information about the role of the phenolic group in the formation of the mono–complex can be obtained by studying the adsorption of beryllium by a cation resin in the presence of o–methoxybenzoic acid.

If the high stability of the salicylate complex derives from a chelate ring formed by the loss of a proton from the phenol group, then little or no complex formation would be expected with the methoxy-benzoic acid, and the presence of this should have little effect on the cation exchange behaviour of beryllium.

3. RESULTS AND DISCUSSION

Although a buffer was necessary to control pH, preliminary experiments showed that acetate ion had a negligible effect on the salicylate equilibria in the cation exchange experiments.

Table 3 gives the results of cation exchange experiments in the pH region 3.6 – 4.3 in varying concentrations of salicylic acid. Errors arising from hydrolysis can be neglected, since below pH 5, hydrolysis of trace amounts of the simple beryllium ion is negligible (Feldman and Havill 1952; Schweitzer and Nehls 1953; Kakihana and Sillén 1956).

The experiments were repeated with o-methoxybenzoic acid. Results obtained for both acids are shown in Table 4. The negligible effect of o-methoxybenzoic acid on the adsorption of beryllium on "Zeo-Karb 225" contrasts with that obtained for salicylic acid. This is evidence for the formation of a chelate ring in the salicylate complex through the loss of the phenolic proton, which is of course not available in the methylated acid.

Since the above results imply that a neutral complex is formed with $Sal^{=}$ as the ligand, Equations 4 and 5 may be applied to the data in Table 3. The undissociated salicylic acid concentration can be calculated sufficiently accurately using the equation

$$[H_2\,Sal] = \frac{A_2[H]\ [Sal]_t}{A_2[H] + 1}\ , \qquad (8)$$

where $[Sal]_t$ is the total (initial) salicylic acid concentration, and A_2 is the second association constant of the acid (de Bruin and Florence 1961). The dissociation of the phenol group can be neglected. Figures 1 and 2 are graphs of Equations 4 and 5 respectively for the data of Table 3. There appears little doubt that $n = 1$ and $p = 2$, which is in accordance with Structure 1, Table 2.

To determine the stability constant according to Equation 6, it is necessary to calculate $[Sal]$.

From the definitions of the acid association constants A_1 and A_2 (Fuoss 1957; De Bruin and Florence 1961), it follows that

$$[Sal] = \frac{[Sal]_t}{1 + \bar{A}_1[H] + \bar{A}_2[H]^2}\ . \qquad (9)$$

The constants used are $\bar{A}_1 = 2.78 \times 10^{13}$, and $\bar{A}_2 = 2.70 \times 10^{16}$. (Euler 1898, Larsson 1929, Tananaev and Shcheglova 1957 , Adamovitch and Kravchenko 1957).

The extrapolated value for α_0 (Figure 3) has been used in calculating β_1. The extrapolated value increases slightly at pH values greater than 4. This is consistent with the slight complexing effect of the acetate buffer under these conditions, but the variation is trivial. The average value of β_1, obtained from Equation 6, was found to be 4.97×10^{12}. The agreement between the extrapolated values of α_0 and those measured directly shows that polymerization is unlikely (Feldman and Havill 1952). Furthermore, an increase in beryllium concentration from 10^{-9}M to 10^{-6}M failed to produce any change in the values of α.

PART 2 THE NATURE OF THE ANIONIC COMPLEX, AND ITS STABILITY CONSTANT

1. INTRODUCTION

Rosenheim and Lehmann (1924) prepared alkali metal salts which appeared to contain the complex salicylate beryllium anion $BeSal_2^{=}$.

Preliminary experiments with solutions 10^{-9}M in beryllium and not less than 2.5×10^{-4}M in salicylic acid showed that between pH 7 and 9 beryllium was not significantly adsorbed by a cation exchanger or by the polystyrene containers, but that it was adsorbed by "De-Acidite FF". An attempt was therefore made to determine the structure and stability constant of the anionic complex formed under these conditions.

If it is assumed that only one adsorbable complex is formed, then its charge can be measured by the method of Nelson and Kraus (1955). Following the treatment they proposed, the distribution of an anionic beryllium complex between a solution and an anionic exchange resin in the X^{b-} form may be represented by the equation:

$$b\,[\mathrm{Be(H_{2-p}Sal)_n(OH)_s}^{2-(np+s)}] + \{2-(np+s)\}\,[X^{b-}]_R \rightleftharpoons$$

$$b\,[\mathrm{Be(H_{2-p}Sal)_n(OH)_s}^{2-(np+s)}]_R + \{2-(np+s)\}\,[X^{b-}]\ , \qquad (10)$$

where the subscript R refers to the adsorbed species. The inclusion of $(OH)_s$ in the formula for the complex is intended to take account of the possible existence of partially hydrolyzed species. $s = 4-np$ and may be 0, 2 or 3.

Let $v = 2-(np+s)$. The equilibrium constant for this reaction will then be:

$$K = \frac{\alpha^b\,[\mathrm{Be}]_t^b\,[X]^v}{[\mathrm{Be(H_{2-p}Sal)_n(OH)_s}]^b\,[X]_R^v}\ , \qquad (11)$$

in which α has the same significance as before, $[\mathrm{Be}]_t$ is the total concentration of all beryllium species in the aqueous phase and the charges are omitted. If conditions are chosen so that all the metal in the aqueous phase is completely complexed and the supporting anion concentration $[X]$ is very much larger than the concentration of the anionic complex, then

$$\frac{[\mathrm{Be(H_{2-p}Sal)_n(OH)_s}]}{[\mathrm{Be}]_t} = 1$$

and

$$\alpha^b\,[X]^v = \text{constant}\ .$$

Hence

$$\frac{d\log\alpha}{d\log X} = -\frac{v}{b}\ , \qquad (12)$$

and v can be determined if the adsorption of beryllium on the resin is expressed as a function of the supporting electrolyte concentration.

The anionic exchange method of Nelson, Day, and Kraus (1960) can be used to measure the stability constant of this complex. According to this method, if all the metal is completely complexed, α, the distribution coefficient for beryllium between the resin and solution will be a maximum, and constant, above a limiting value of pH. Let this maximum value be α_m. Below this pH value the anionic complex will dissociate, with the result that the distribution coefficient for the metal will decrease. According to Nelson, Day, and Kraus (1960) the fraction of the metal existing as the complex, F_n, is given by

$$F_n = \frac{\alpha}{\alpha_m} = \frac{[\mathrm{Be\ (H_{2-p}Sal)_n(OH)_s}]}{[\mathrm{Be}]_t}\ . \qquad (13)$$

If F_n is known, it is possible to substitute the appropriate expressions for the stability constants and to determine these graphically.

2. RESULTS AND DISCUSSION

2.1 Charge of the Anionic Complex

As preliminary experiments revealed only slight anion exchange with solutions containing salicylate ion in a perchlorate medium, further investigations were carried out in a chloride medium. The results indicated that no anionic complex was formed between beryllium and the chloride anion under the conditions of our experiment. This is shown at the bottom of Table 7 by the constant adsorption coefficient obtained at different ionic strengths. Figure 4 shows α as a logarithmic function of chloride concentration at pH 8.9. This is a straight line, from which $v = -1.9$ according to Equation 12. This indicates that the complex has a charge of −2.

2.2 Nature of the Anionic Complex

It can be seen from Figure 5 that the distribution coefficient for beryllium in the presence of a large excess of salicylic acid reaches a maximum at pH 6.5. The maximum value of 3,800 was used in the calculations shown in Tables 5 and 6. The shape of the adsorption curve above pH 6.5 and the measured value of v both indicate that only one complex is formed in this region. It is therefore possible to examine individually the various anionic complexes that could form in the alkali region and to apply the appropriate form of Equation 13 to the formation of each.

As shown earlier, the general form of the anionic complex can be represented by

$$[\mathrm{Be(H_{2-p}Sal)_n\,(OH)_s}]^{2-(np+s)} ,$$

and from the data already obtained it is obvious that the following possibilities have to be considered:

(a,i) If $p = 2$, the ligand is the ion $\mathrm{Sal}^{=}$, and in the absence of hydrolysis ($s = 0$) only one mononuclear anionic complex, $\mathrm{BeSal_2^{2-}}$, can be formed. (Structure 2, Table 2).

Then from Equation 13

$$\frac{\alpha}{\alpha_m} = \frac{[\mathrm{BeSal_2}]}{[\mathrm{Be\,Sal_2}] + [\mathrm{BeSal}] + [\mathrm{Be}]} ,$$

and therefore

$$\left(\frac{\alpha_m}{\alpha} - 1\right)[\mathrm{Sal}] = \frac{1}{\beta_2\,[\mathrm{Sal}]} + \frac{\beta_1}{\beta_2} , \tag{14}$$

since $\beta_2 = \dfrac{[\mathrm{Be(Sal)_2}]}{[\mathrm{Be}]\ [\mathrm{Sal}]^2}$ and $\beta_1 = \dfrac{[\mathrm{BeSal}]}{[\mathrm{Be}]\ [\mathrm{Sal}]}$.

A graph of $\left(\dfrac{\alpha_m}{\alpha} - 1\right)[\mathrm{Sal}]$ versus $\dfrac{1}{[\mathrm{Sal}]}$ should therefore be a straight line with slope $1/\beta_2$ and intercept $= \beta_1/\beta_2$.

The results given in Table 5 and Figure 6 show that there is little variation in the value for $\left(\dfrac{\alpha}{\alpha_m} - 1\right)[\mathrm{Sal}]$. Since the slope of Figure 6 is very nearly zero, Equation 14 reduces to

$$\left(\frac{\alpha_m}{\alpha} - 1\right) = \frac{\beta_1}{\beta_2\,[\mathrm{Sal}]} ,$$

or

$$\frac{\alpha}{\alpha_m} = \frac{[\mathrm{Be\,Sal_2}]}{[\mathrm{Be\,Sal_2}] + [\mathrm{Be\,Sal}]} , \tag{15}$$

which indicates that in the pH range 5.5 – 6.5 the anion exchange complex dissociates to the neutral species BeSal, and a negligible concentration of beryllium cations. The results of similar experiments performed with cation exchange resins under identical conditions support this deduction.

(a, ii) If $p = 2$ and hydrolysis occurs, then again only one divalent anionic complex is theoretically possible. This would be $\mathrm{BeSal\,(OH)_2^{2-}}$. (Structure 9, Table 2).

However in this case the adsorption data could be complicated by the presence of the monovalent anionic complex $\mathrm{(Be\,Sal\,OH)^-}$ formed by the dissociation of the divalent species. Under the conditions of the experiment there is a high $[\mathrm{X^{b-}}] / [\mathrm{X^{b-}}]_R$ ratio, $\mathrm{X_R^{b-}}$ being the anion exchange resin in the X form, and only the doubly charged anionic complex should be adsorbed to any significant extent (Feldman et al. 1955; Li et al. 1957). The rapid fall in α as the pH is reduced (Figure 5) suggests that if the monovalent ion exists it does not have a significant affinity for the resin.

Application of Equation 13 to this system gives:

$$\frac{\alpha}{\alpha_m} = \frac{[\mathrm{Be\,Sal\,(OH)_2}]}{[\mathrm{BeSal\,(OH)_2}] + [\mathrm{BeSal\,OH}] + [\mathrm{BeSal}] + [\mathrm{Be}]}$$

and

$$\left(\frac{\alpha_m}{\alpha} - 1\right)[\mathrm{Sal}] = [\mathrm{Sal}]\left\{\frac{\beta_2}{\beta_3[\mathrm{OH}]} + \frac{\beta_1}{\beta_3[\mathrm{OH}]^2}\right\} + \frac{1}{\beta_3[\mathrm{OH}]^2} \qquad (16)$$

Therefore for a constant pH there should be a linear relationship between $\left(\frac{\alpha_m}{\alpha} - 1\right)[\mathrm{Sal}]$ and $[\mathrm{Sal}]$, as shown in Figure 7. However, since the slope is again very nearly zero, Equation 16 reduces to

$$\left(\frac{\alpha_m}{\alpha} - 1\right) = \frac{1}{\beta_3[\mathrm{OH}]^2[\mathrm{Sal}]} ,$$

or

$$\frac{\alpha}{\alpha_m} = \frac{[\mathrm{Be\,Sal\,(OH)_2}]}{[\mathrm{Be\,Sal\,(OH)_2}] + [\mathrm{Be}]} . \qquad (17)$$

It is therefore inferred from Equation 17 that if the salicylate concentration decreased at a constant pH, the anionic complex would dissociate into beryllium ions. However cation exchange studies at this pH, and the absence of surface adsorption of beryllium showed that no beryllium ions are present. We can therefore conclude that the complex represented by Structure 9 in Table 2 is not formed.

(b, i) If p = 1, the ligand is the ion HSal, and if no hydrolysis occurs, the mononuclear divalent anionic complex $\mathrm{Be(HSal)_4}$ would be formed. (Structure 6, Table 2).

From Equation 13 under these conditions

$$\frac{\alpha}{\alpha_m} = \frac{[\mathrm{Be(HSal)_4}]}{\sum_{n=0}^{n=4}[\mathrm{Be(HSal)_n}]}$$

and

$$\left(\frac{\alpha_m}{\alpha} - 1\right)[\mathrm{HSal}] = \frac{1}{\beta_4[\mathrm{HSal}]^3} + \frac{\beta_1}{\beta_4[\mathrm{HSal}]^2} + \frac{\beta_2}{\beta_4[\mathrm{HSal}]} + \frac{\beta_3}{\beta_4} . \qquad (18)$$

If Equation 18 holds for the system, then $\left(\frac{\alpha_m}{\alpha} - 1\right)[\mathrm{HSal}]$ would not be a linear function of $\frac{1}{[\mathrm{HSal}]}$. However since Figure 6 is a straight line, and the ratio $[\mathrm{HSal}]/[\mathrm{Sal}]$ is constant at a given pH, then the graph of $\left(\frac{\alpha_m}{\alpha} - 1\right)[\mathrm{HSal}]$ against $1/[\mathrm{HSal}]$ must also be a straight line (Figure 8). This shows that the complex adsorbed is not $\mathrm{Be(HSal)_4^=}$.

(b, ii) If p = 1, and hydrolysis occurs, then two possible mononuclear divalent anionic complexes could be formed. (Structures 7 and 8, Table 2).

If we consider the formation of the species $\mathrm{Be(HSal)_2(OH)_2}$ only, that is s = 2, then

$$\frac{\alpha}{\alpha_m} = \frac{[\mathrm{Be(HSal)_2(OH)_2}]}{[\mathrm{Be(HSal)_2(OH)_2}] + [\mathrm{Be(HSal)_2OH}] + [\mathrm{Be(HSal)_2}] + [\mathrm{BeHSal}] + [\mathrm{Be}]} ,$$

which is related to the stability constants by the expression

$$\left(\frac{\alpha}{\alpha_m} - 1\right)[\mathrm{HSal}] = [\mathrm{HSal}]\left\{\frac{\beta_3}{\beta_4[\mathrm{OH}]} + \frac{\beta_2}{\beta_4[\mathrm{OH}]^2}\right\} + \frac{1}{\beta_4[\mathrm{HSal}][\mathrm{OH}]^2} + \frac{\beta_1}{\beta_4[\mathrm{OH}]^2} . \qquad (19)$$

If this relationship were applicable, then again $\left(\frac{\alpha_m}{\alpha} - 1\right)$ [HSal] would not be a linear function of [HSal] at a constant pH. Therefore the results obtained rule out the formation $Be(HSal)_2(OH)_2$.

Finally, if the species adsorbed by the anion exchange resin is $Be\,HSal(OH)_3$, then

$$\frac{\alpha}{\alpha_m} = \frac{[Be\,HSal\,(OH)_3]}{[Be(HSal)(OH)_3] + [BeHSal\,(OH)_2] + [BeH\,Sal\,OH] + [BeHSal] + [Be]} \quad ,$$

from which

$$\left(\frac{\alpha_m}{\alpha} - 1\right)[HSal] = [HSal]\left\{\frac{\beta_3}{\beta_4[OH]} + \frac{\beta_2}{\beta_4[OH]^2} + \frac{\beta_1}{\beta_4[OH]^3}\right\} + \frac{1}{\beta_4[OH]^3} \quad . \qquad (20)$$

Since this is similar to Equation 17, and the remarks above are equally applicable here, the existence of Structure 7 can also be ruled out. The experimental results can therefore be regarded as strong evidence for the existence of the single anionic complex $(Be\,Sal_2)^{2-}$, indicated by Structure 2 in Table 2..

2.3 Ion Exchange in the Presence of o-Methoxybenzoic Acid

The anion-exchange behaviour was also investigated in the presence of o-methoxybenzoic acid (OMB), and when supporting electrolyte but no ligand was present. The pH range was from 7.3 to 8.4 (Table 7).

In the presence of salicylate ion, beryllium was adsorbed almost quantitively by the anion exchange resin, whereas negligible losses occurred in the complete absenceof resin. An increase of pH produced no change in the anion exchange adsorption, but increasing the ionic strength produced a large decrease in beryllium adsorption. This behaviour is characteristic of an ion exchange process, and indicates a negative charge on the anionic complex. As we have seen above, this is -2. On the other hand, markedly different behaviour was observed in the presence of o-methoxybenzoate ions. The sorption of beryllium in the presence of anion resin was lower than when salicylate was present and showed little change with increasing ionic strength. This behaviour was similar to that observed when only supporting electrolyte was present, and increased with increasing pH. The implication from these observations is that little or no anion exchange takes place in the presence of OMB, and they are further evidence against the existence of the hydrolyzed species represented by Structures 7 and 8 in Table 2, and the non-hydrolyzed species represented by Structure 6, Table 2. Unfortunately it was impossible to study the adsorption by the resin quantitatively in the pH region of interest, because of adsorption on the walls of the containers and on the surface of the resin.

2.4 Calculation of the Stability Constant

The gradient of the curve in Figure 6 cannot be obtained with sufficient accuracy to give a reliable figure for β_2, but by combining the value for the intercept (which is equal to β_1/β_2) with the value of β_1 obtained in Section 3, β_2 was found to be 2.63×10^{22}. This agrees reasonably well with the value of 4.3×10^{22} obtained by solvent extraction measurements (de Bruin, Kairaitis, and Szego 1962).

CONCLUSIONS

The evidence presented here strongly supports the structures proposed by Rosenheim and Lehmann (1924), Jones, Homer, Davies, and Bury (1930), and Varma and Mehrotra (1958), in contrast to those proposed by Asmussen and Madsen (1933), Schubert and Lindenbaum (1954), Zolotukhin (1957), Tananaev and Shcheglova (1957) and Adamovitch and Kravchenko (1957) (see Table 1).

Perhaps because of its very small covalent diameter, beryllium forms extremely stable six-membered cyclic structures with salicylate ion. On the other hand, non-chelate structures are formed with $HSal^-$ as the ligand by metals such as scandium, yttrium, cerium (III), and lanthanum, which have considerably greater covalent diameters. (Sudarikov, Zaytzev, and Puchkov 1959).

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TABLE 1. ~ SUMMARY OF BERYLLIUM ~ SALICYLATE STUDIES. ~ DESCRIBED IN THE LITERATURE. ~

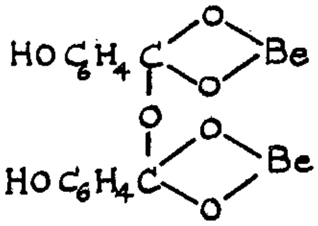
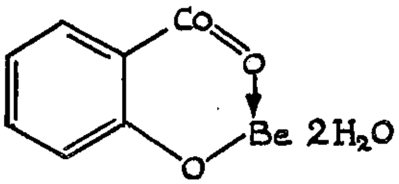
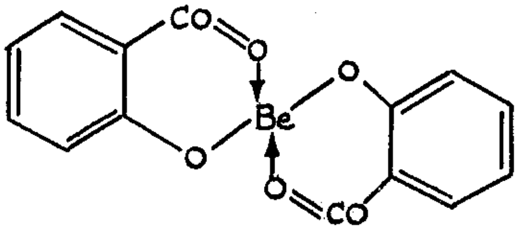
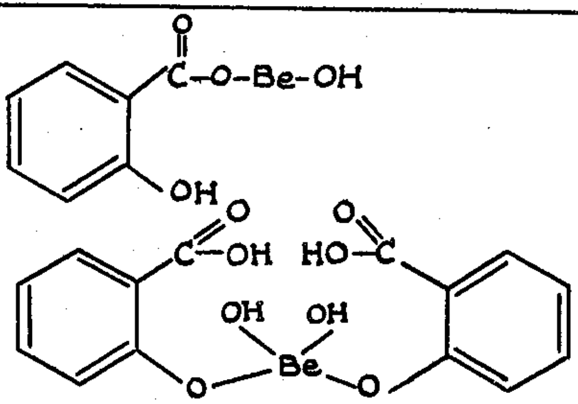
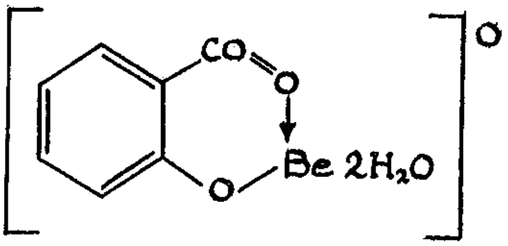
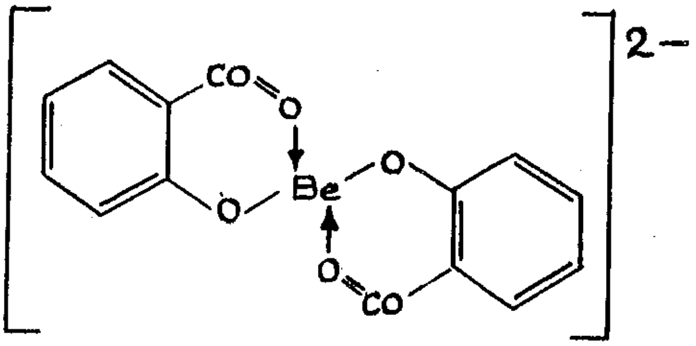
	PROPOSED FORMULA	FORMATION CONSTANT Method & Value.	REFERENCE.
1.			Glassman 1907
2.	 	Conductivity & pH measurements " "	Jones et al. 1930 Rosenheim & Lehmann 1924
3.	Confirms above two authors.	Potentiometric Titrations	Asmussen & Madsen · 1933
4.	$Be(C_6H_4OHCO_2)$	Enzyme Reactions $\log K^{Be}_{BeHSal} = 4.3$	Schubert et al. 1954.
5.	 $(C_6H_4OH\,CO_2)_4\,Be_2O(OH)_2$	Solubility & pH measurements stability constants :- 1.43×10^{12} 1.25×10^{22}	Zolotukhin. 1957
6.	Suggests existence of very weak complex	pH measurements.	Tananaev & Shcheglova. 1957.
7.	$Be\,OH(C_7H_4O_3)_2^{3-}$	Spectrophotometric. stability constant = 2.04×10^{17}	Adamovitch & Kravchenko. 1957.
8.	As No. 2.	Potentiometric & conductimetric titrations.	Varma & Mehrotra. 1958.

TABLE 2. ~ POSSIBLE STRUCTURES OF THE SALICYLATE -- BERYLLIUM COMPLEXES..



(n = 1 ; p = 2)

1.



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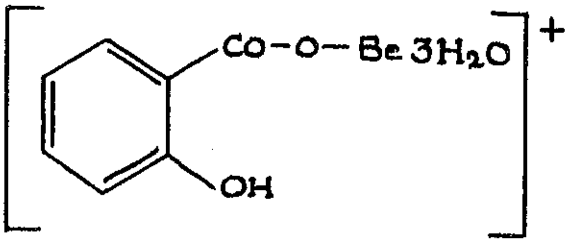

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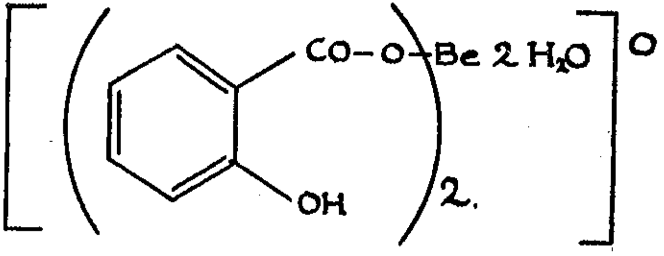

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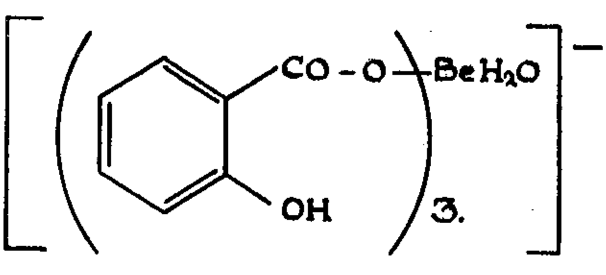
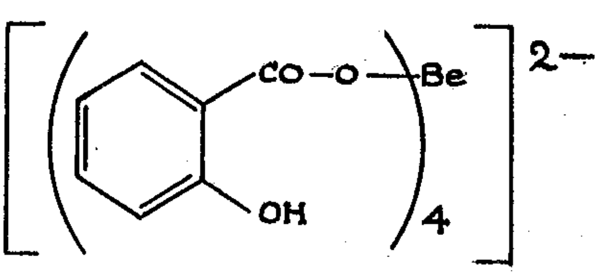


(n = 3 ; p = 1)

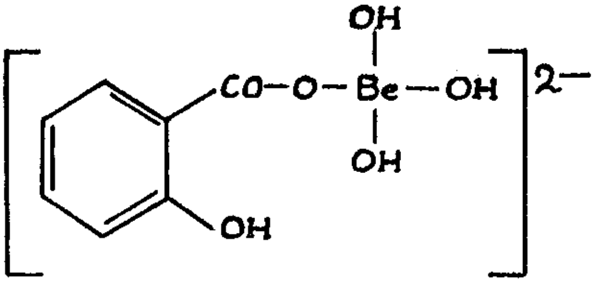
5.



(n = 4 ; p = 1)

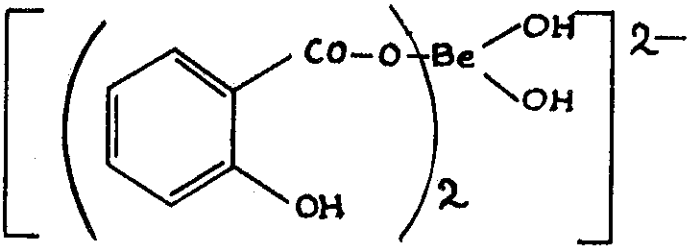
6.

TABLE 2 ~ Cont'd.



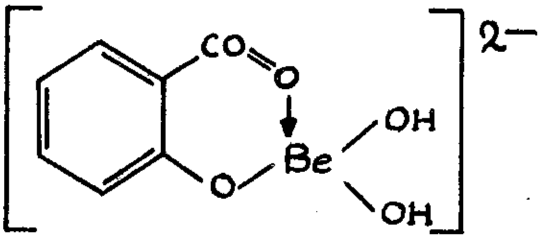
(n = 1 p = 1)

7



(n = 2 p = 1)

8



(n = 1 ; p = 2)

9

TABLE 3

CATION EXCHANGE DATA IN AN IONIC STRENGTH OF 0.15 WITH RESPECT TO Na^+

pH	Total Salicylic Acid Conc. M	α	$\log\left\{\frac{\frac{\alpha_0}{\alpha}-1}{[H_2Sal]}\right\}$	β_1 (α_0 by direct measurement)	α_0 By Extrapolation	β_1 (α_0 by Extrapolation)
	$\times 10^{-3}$			$\times 10^{12}$		$\times 10^{12}$
3.60	0	325.6			327.2	
	0.75	218.2	3.53	5.49		5.56
	1.25	191.2	3.46	4.56		4.63
	1.75	148.4	3.54	5.72		5.74
	2.75	120.6	3.51	5.01		5.07
	3.75	96.0	3.51	4.81		4.83
	5.50	72.4		5.82		5.41
	$\times 10^{-3}$			$\times 10^{12}$		$\times 10^{12}$
3.90	0	316.8			327.8	
	0.25	237.2		5.16		5.88
	0.75	145.4	4.07	4.95		5.26
	1.25	128.4	4.04	4.50		4.76
	1.75	100.8	4.05	4.69		4.95
	2.75	68.0	4.08	4.95		5.16
	3.75		4.04			
	$\times 10^{-3}$			$\times 10^{12}$		$\times 10^{12}$
4.30	0	306.0			322.60	
	0.5	117.2		4.58		4.99
	0.75	97.6	4.80	3.95		4.27
	1.25	64.8	4.90	4.27		4.37
	1.75	57.2	4.84	4.56		4.85
	2.75	32.6	4.82	3.95		4.18
	3.75	21.8	4.88	4.42		4.64

TABLE 4

CATIONIC ADSORPTION OF BERYLLIUM AT pH 3.90 ON CATION RESIN

(as a function of either o-methoxybenzoic acid or salicylic acid concentration)

Total Acid Concentration M	% Be Adsorbed by Resin	
	Salicylic Acid	o-Methoxybenzoic Acid
$\times 10^{-3}$		
0	61.3	62.4
0.75	54.3	59.4
1.25	42.1	59.3
2.75	33.5	58.7

TABLE 5

ANION EXCHANGE DATA

α_m = 3,800 Sal_t = $6.25 \times 10^{-3}M$

pH	Sal	α	$(\frac{\alpha_m}{\alpha} - 1)$ [Sal]	$(\frac{\alpha_m}{\alpha} - 1)$ [HSal]
	$\times 10^{-12}$		$\times 10^{-10}$	$\times 10^{-1}$
4.45	6.12	117.8	1.91	1.89
4.50	6.90	130.0	1.95	1.71
	$\times 10^{-11}$			$\times 10^{-2}$
4.90	1.76	332.2	1.89	6.45
5.00	2.23	364.4	2.10	5.84
5.03	2.39	444.0	1.81	4.68
5.10	2.81	478.0	1.95	4.31
5.50	7.09	936.0	2.17	1.90
5.80	0.14	1660.0	1.82	0.81
6.00	0.23	2120.0	1.78	0.49
6.20	0.36	2520.0	1.82	0.32
7.40		3940.0		
8.30		3820.0		
9.00		3600.0		

TABLE 6

ANION EXCHANGE DATA

Adsorption of Beryllium as a Function of Salicylic Acid
Concentration at a Constant pH

pH	$[Sal]_t$	α	[HSal]	$(\frac{\alpha_m}{\alpha} - 1)$ [HSal]	[Sal]	$(\frac{\alpha_m}{\alpha} - 1)$ [Sal]
	$\times 10^{-3}$		$\times 10^{-3}$	$\times 10^{-4}$	$\times 10^{-10}$	$\times 10^{-10}$
7.0 – 9.5	6.25	3800 = α_m				
6.65 ± 0.05	3.75	3176	3.75	7.35	6.03	1.18
”	2.50	3040	2.50	6.25	4.02	1.00
”	1.88	2774	1.88	6.92	3.01	1.11
”	1.25	2474	1.25	6.70	2.01	1.08
”	1.01	2190	1.00	7.35	1.61	1.18
”	0.16	1786	0.63	7.05	1.00	1.13

TABLE 7

ION EXCHANGE OF BERYLLIUM IN THE PRESENCE OF EITHER o-METHOXY-BENZOIC ACID (OMBA) OR SALICYLIC ACID (pH 7.30 - 8.40)

Acid	μ	% Be Taken up by Resin *		% Loss no resin	Final pH
		Anionic Resin	Cationic Resin		
Salicylic 6.25×10^{-3}M	0.15	95.2	1.6	0	7.4
		96.0	0.8	0	8.4
Salicylic 6.25×10^{-3}M	0.50	66	0	0	7.4
o-methoxy-benzoic (OMBA) 6.25×10^{-3}M	0.15	81.0	67.0	40	7.4
		78.0	65.4	20	7.3
		90.4	74.6	47	8.4
OMBA	0.50	68.6	52.4	29	7.4
		68.6		16	7.3
NH_4Cl only	0.15M	68.3	93	65	7.4
,,	0.5	65.9	86.3	95	7.5

(* Concentrations obtained by difference)

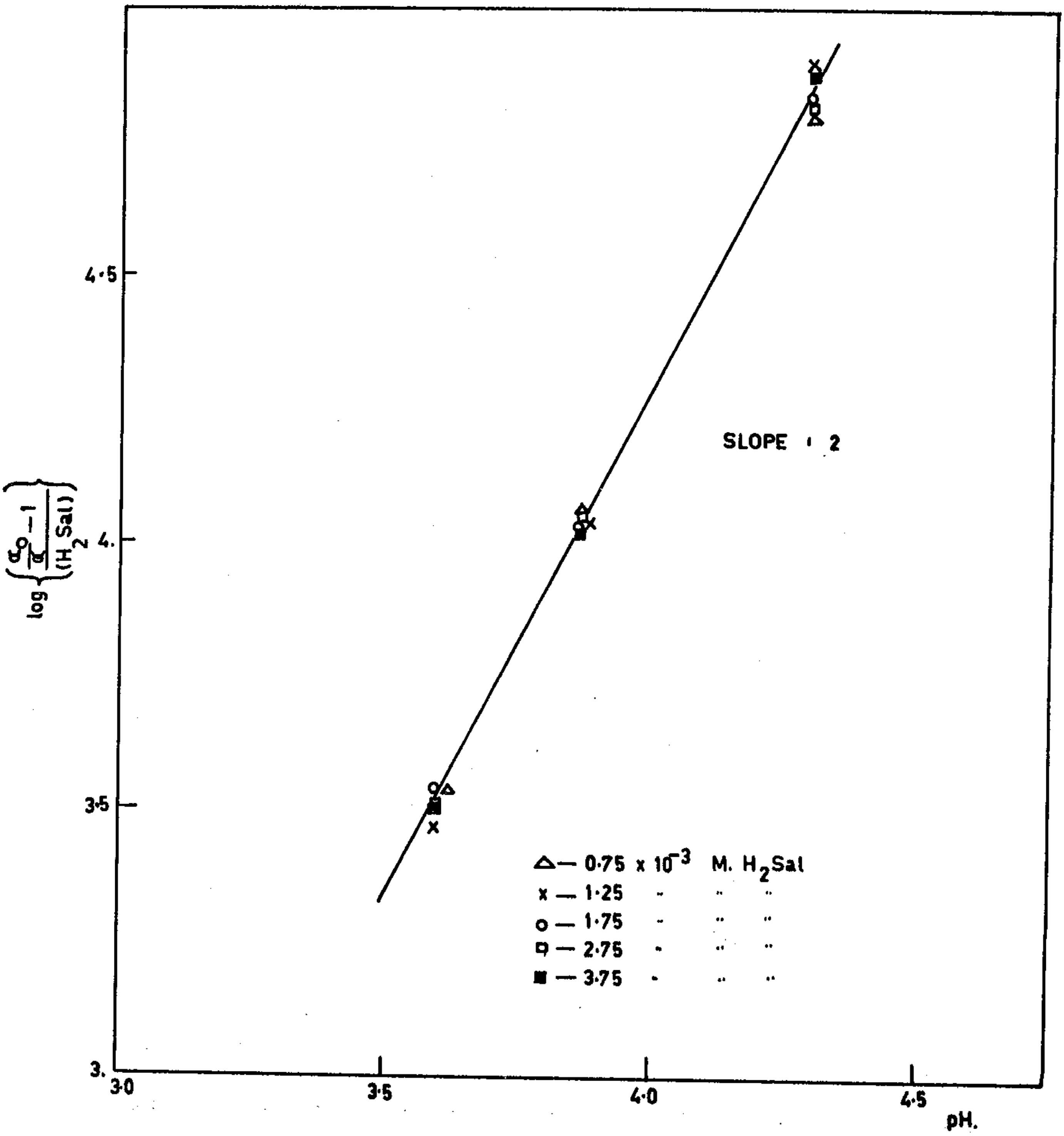


FIG.1 - CATION EXCHANGE STUDIES —— EVALUATION OF p.

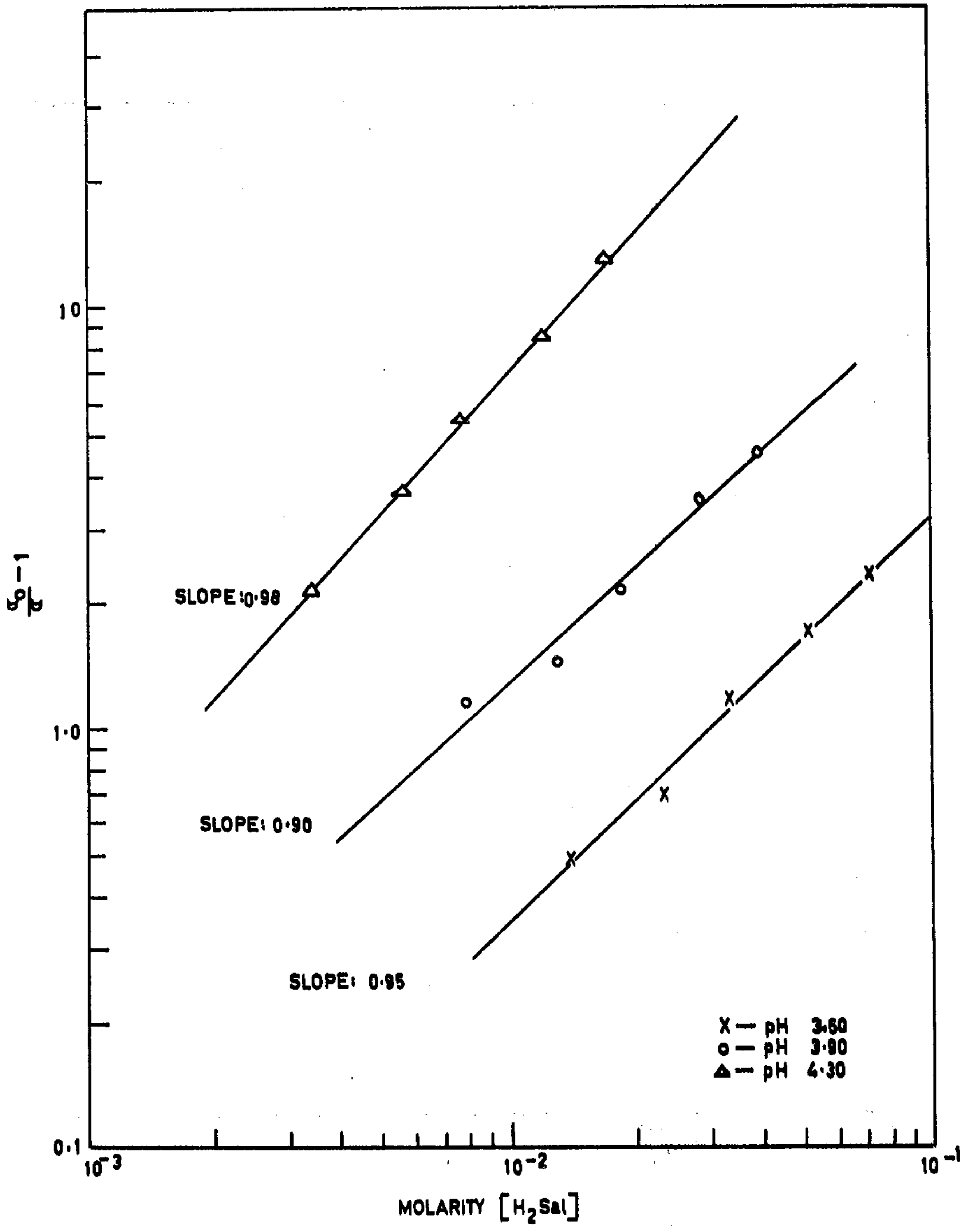


FIG. 2. CATION EXCHANGE STUDIES EVALUATION OF n.

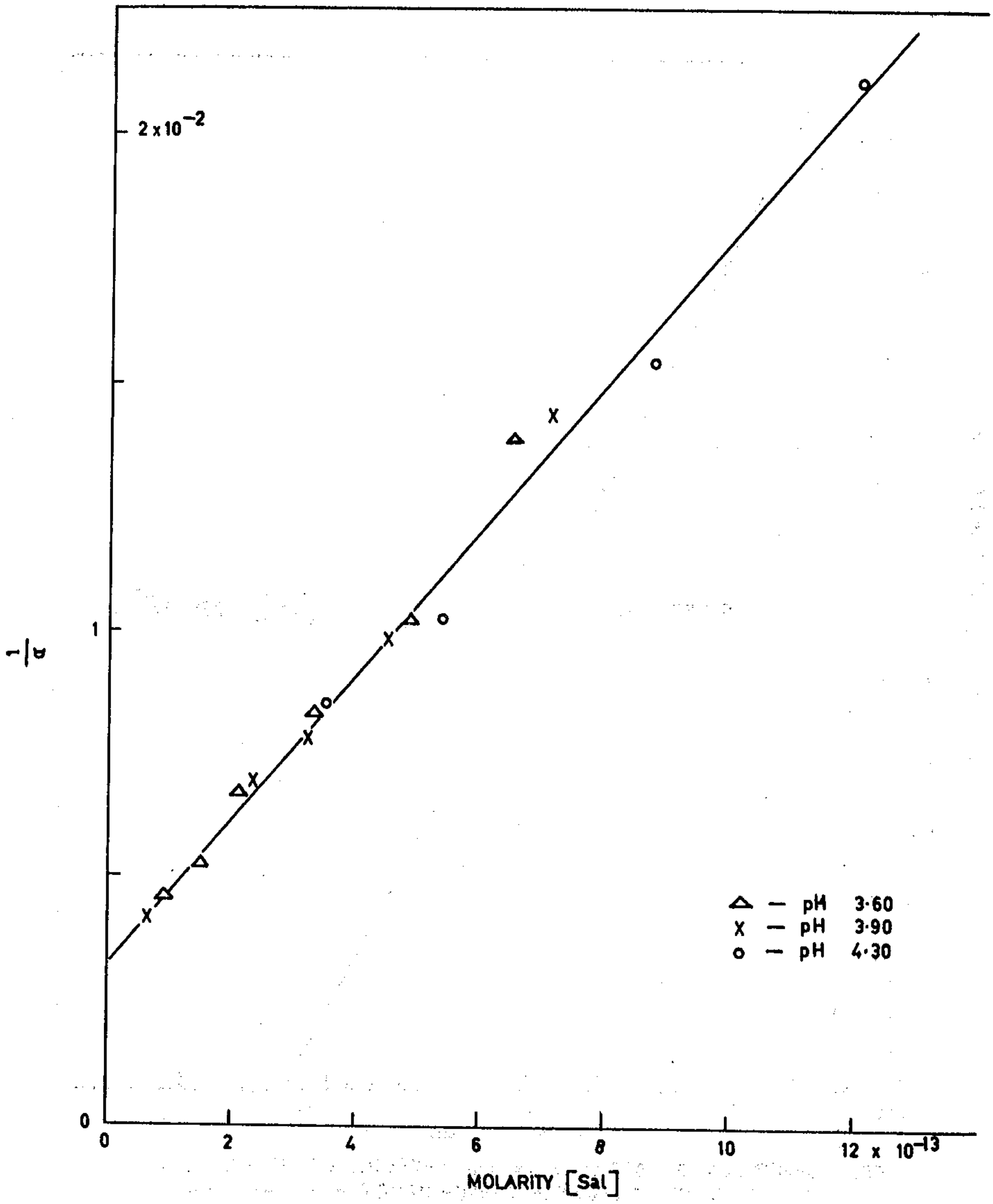


FIG. 3 EVALUATION OF α_o

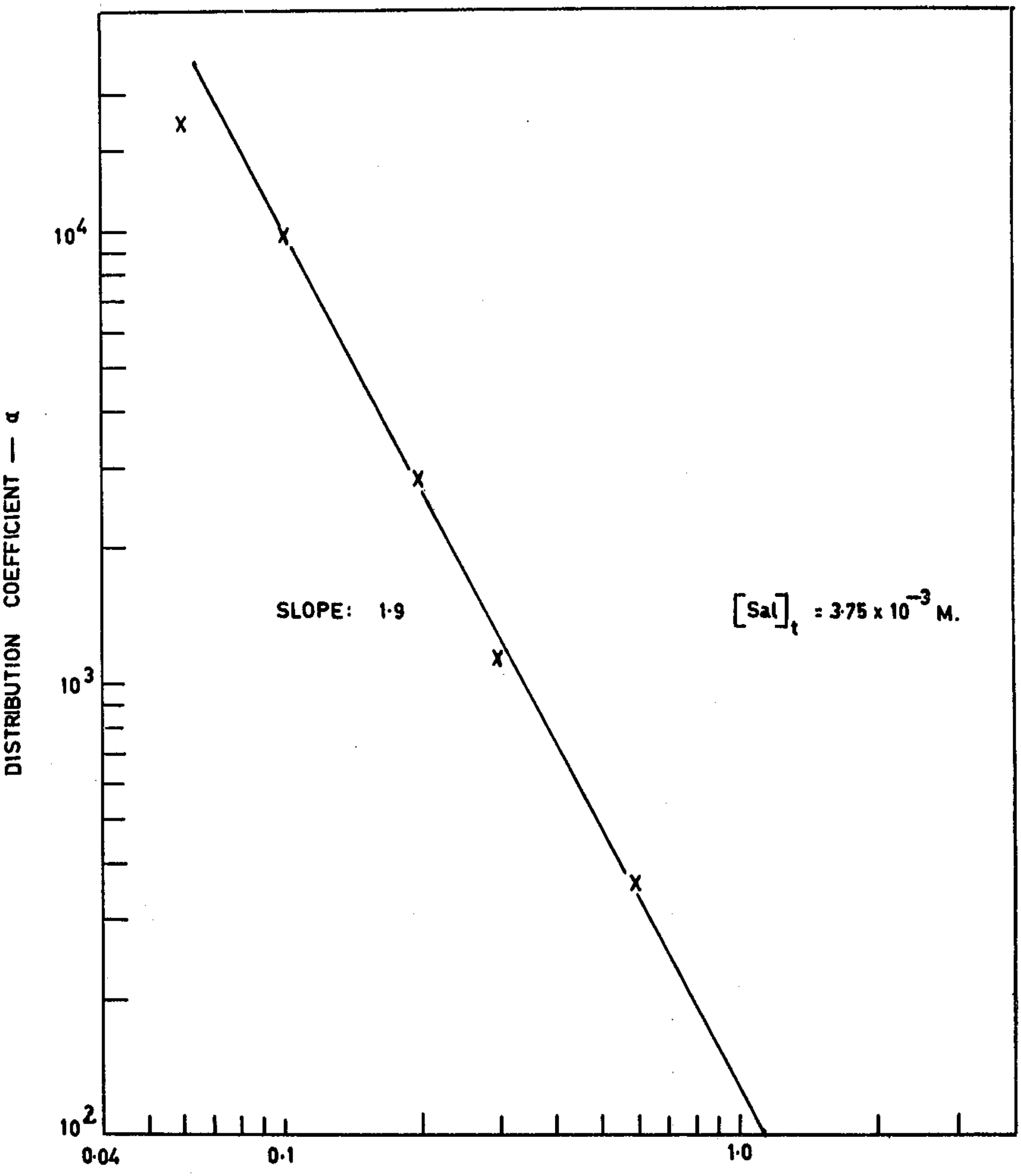


FIG. 4 ADSORPTION OF BERYLLIUM IN THE PRESENCE OF SALICYLATE AS A FUNCTION OF CHLORIDE CONCENTRATION.

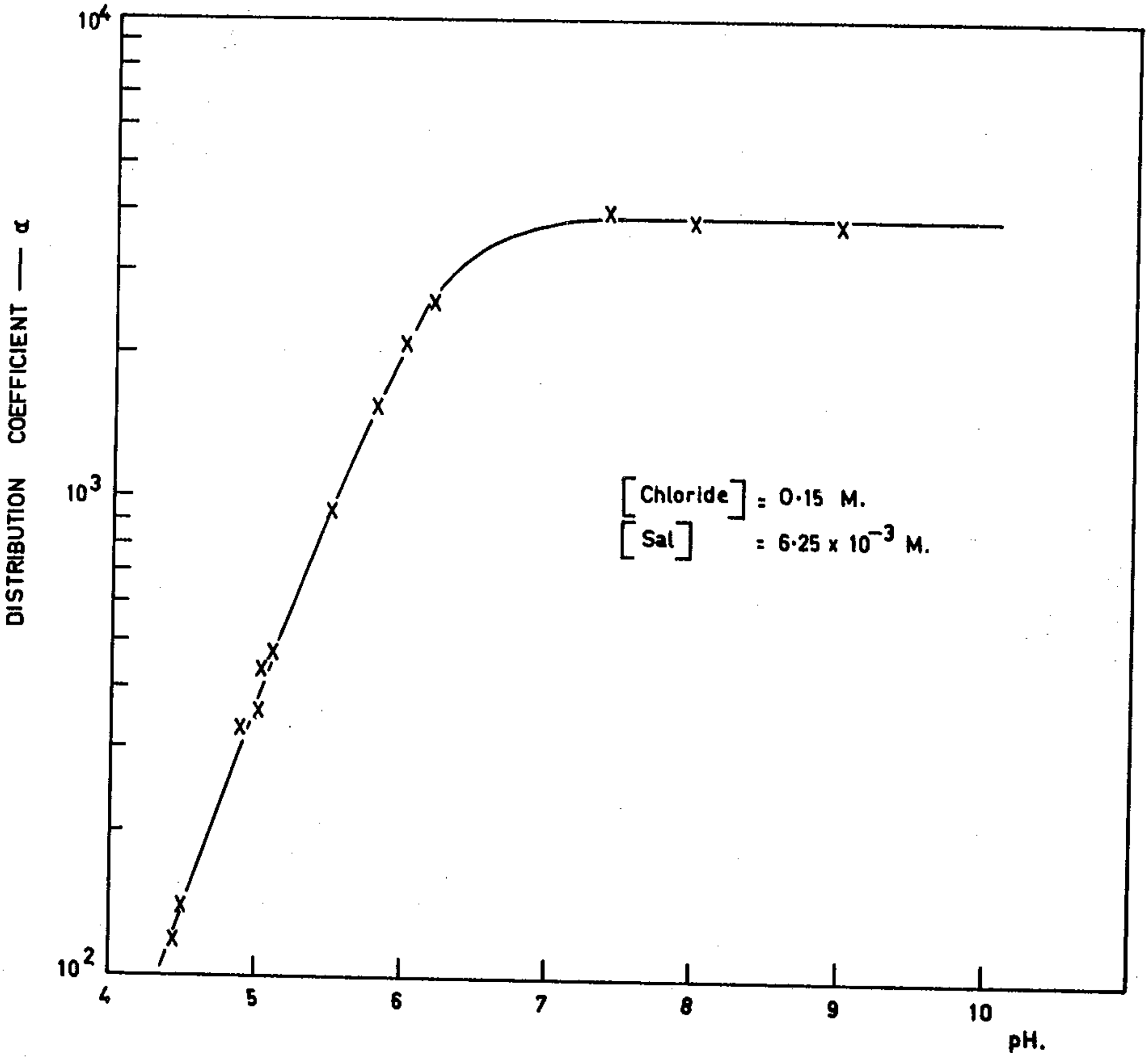


FIG 5. BERYLLIUM ADSORPTION ON ANION-EXCHANGE RESIN AS A FUNCTION OF pH

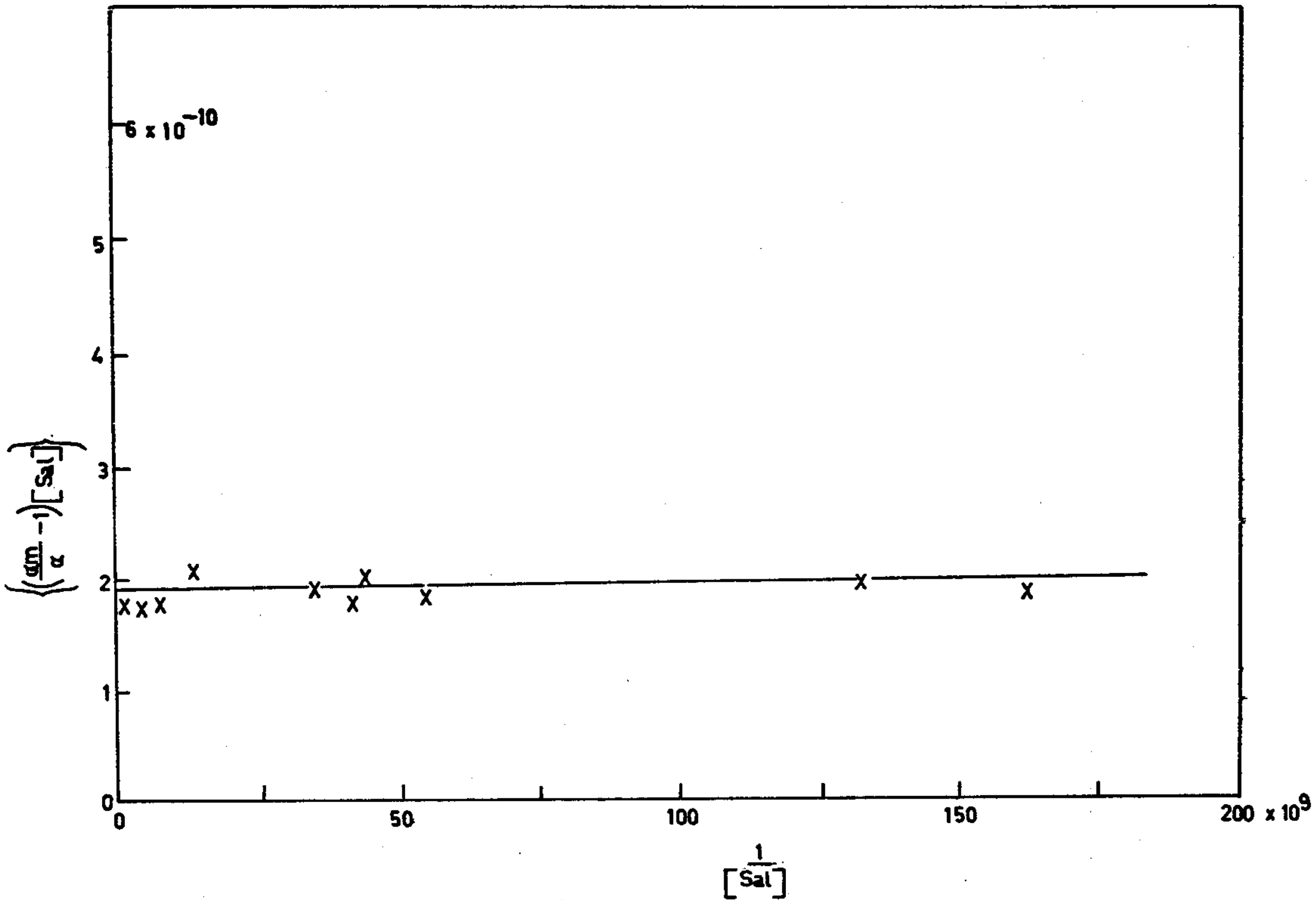


FIG. 6. VARIATION OF $\left(\frac{\alpha m}{\alpha}-1\right)[\mathrm{Sal}]$ WITH $\frac{1}{[\mathrm{Sal}]}$

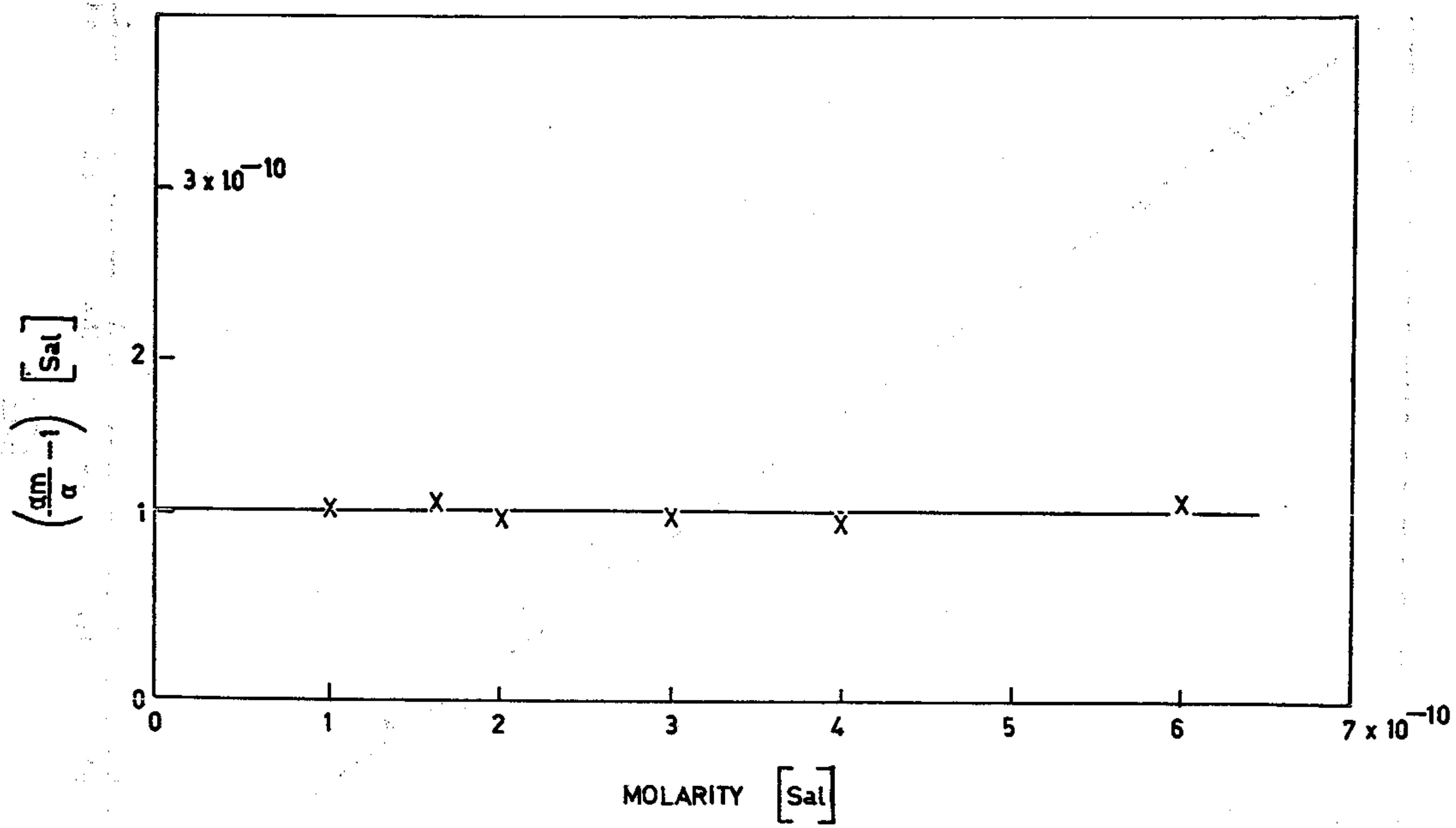


FIG. 7. VARIATION OF $\left(\frac{\alpha m}{\alpha} - 1\right)$ [Sal] WITH [Sal] AT CONSTANT pH (6·65±0·5)

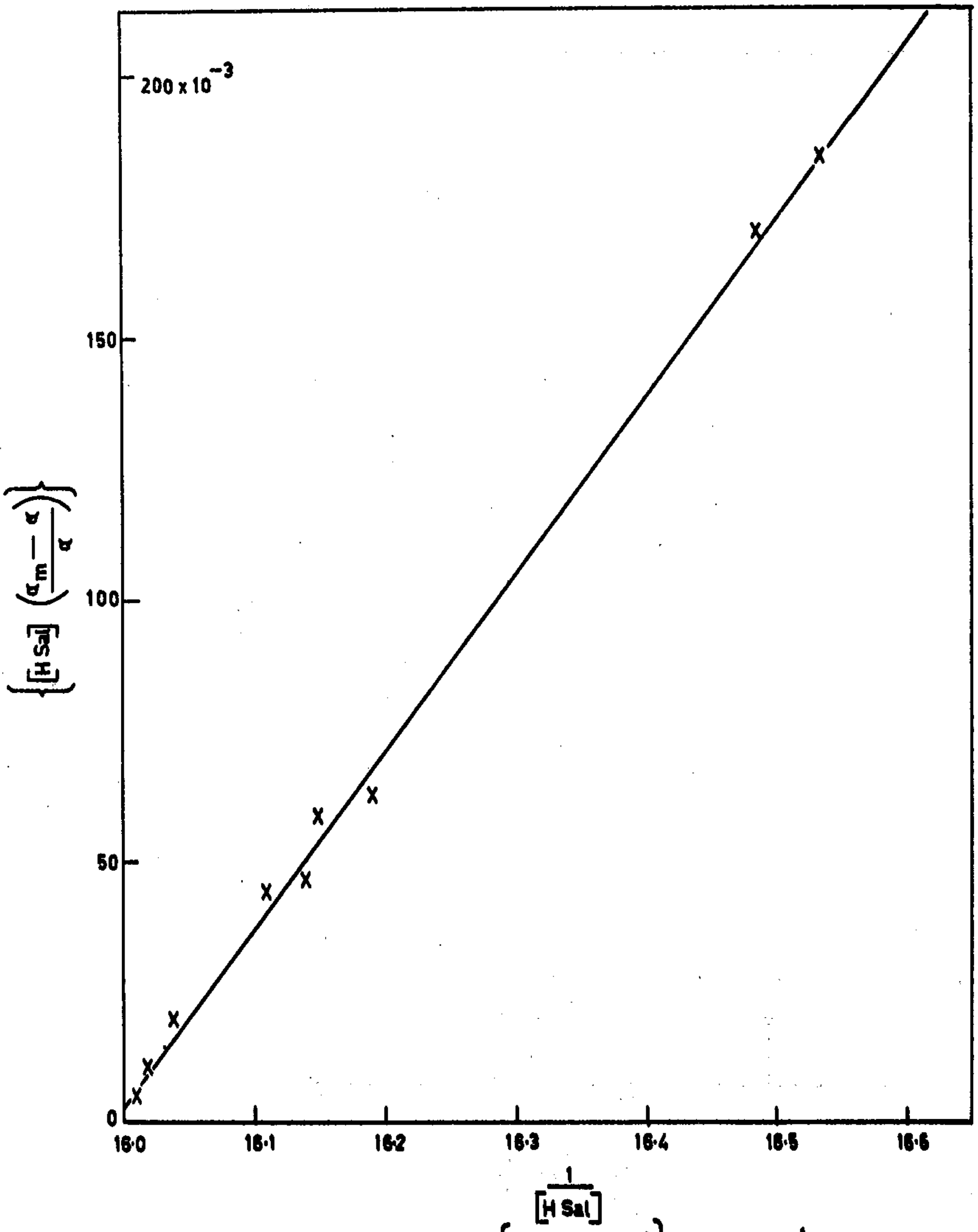


FIG. 8. VARIATION OF $\left\{[H\,Sal]\left(\frac{\alpha_m-\alpha}{\alpha}\right)\right\}$ ·WITH $\frac{1}{[H\,Sal]}$