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THE ADSORPTION OF BERYLLIUM ON ION-EXCHANGE RESINS FROM INORGANIC SYSTEMS

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ABSTRACT

Anion–exchange studies have revealed that beryllium forms anionic complexes with fluoride, phosphate, carbonate, and thiocyanate. The stabilities of these complexes lie in the order $F^- > H_2PO_4^- \approx CO_3^{=} >> CNS^-$. Under the conditions of this investigation BeF_4^{-2} and $Be(H_2PO_4)_4^{-2}$ have been identified. Attempts to identify the carbonate complex were prevented by hydrolysis. The anionic thiocyanate complex is very weak and no attempt was made to identify this species.

The anion–exchange data obtained in dilute nitric, hydrochloric, and sulphuric acid solutions showed some anionic complex formation but corresponding cation–exchange data have shown that in solutions of concentration up to 2.0M the extent of this reaction is negligible.

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1. INTRODUCTION

Kraus and Nelson (1955) were the first to study systematically the behaviour of metal ions on an ion–exchange resin. They showed that the chloride complexes of a number of metals possess large selectivities for strong–base anion–exchange resins. Their principal methods for measuring the adsorbabilities were column effluent analysis or column scanning, and batch equilibration. In the first method trace amounts of the metal ions were loaded in a tight band on the top of the column and eluted with hydrochloric acid solutions of 0.1 to 12M. This yielded an elution constant, E, from the relationship:

$$E = \frac{d\,A}{V} \quad , \tag{1}$$

where d is the distance moved by the band, A is the cross–sectional area of the column, and V is the volume of eluent passed through the column (Kraus and Moore 1951). The volume distribution coefficient α_v (amount per litre of ion–exchange resin/amount per litre of solution) can then be evaluated from the expression:

$$\alpha_v = 1/E - i = \bar{v} \quad , \tag{2}$$

where i is the fractional interstitial space and $\bar{v}$ is the actual number of column volumes of eluent necessary to elute the element under investigation in maximum concentration.

The batch equilibration method gives a value for α, the distribution coefficient (amount per kilogram of dry resin/amount per litre of solution). Since α and α_v are related by:

$$\alpha_v = \rho\,\alpha \quad , \tag{3}$$

where ρ is the bed density, the values for α may be readily correlated with the column behaviour.

An important concept in ion–exchange chromatography is the separation factor, K_b^a, defined as:

$$K_b^a = \frac{\alpha_a}{\alpha_b} = \frac{\bar{v}_a}{\bar{v}_b} \quad ,$$

where α_a and α_b represent the distribution coefficients of the two ions whose separation is being considered, and $\bar{v}_a$ and $\bar{v}_b$ are the numbers of column volumes needed for the respective ions to appear in the effluent in maximum concentration. An examination of the resulting adsorption isotherms, obtained by plotting log α_v against the concentration of the medium under investigation for each of the elements studied, quickly reveals possible separations.

Bunney and his associates (1959) measured the distribution coefficients of many elements in nitric and sulphuric acids with strong anion exchangers. Freiling, Pascual, and Delucchi (1959) extended this work to phosphoric acid solutions. A separation scheme for several metal ions in a mixed HCl – HF acid system was developed by Wish (1959) after measurement of the adsorption isotherms in this media. Kraus, Nelson, and Moore (1955) also extended their own studies to mixed acid solutions.

Strelow (1960), noting the absence of similar data for cation–exchange chromatography, made a comprehensive study of the adsorption of cations in hydrochloric acid using a sulphonic–acid–type cation–exchange resin. A selectivity scale was then assembled, based on the value of the distribution coefficient for each cation in 1.0N hydrochloric acid.

Although distribution data are available for a great many metal ions in different inorganic media, little information has been published for beryllium. If ion–exchange separation schemes for beryllium and fission products are to be pursued, this information is necessary. This report describes an investigation of the adsorption of beryllium by both cation– and anion–exchangers in various inorganic media.

2. EXPERIMENTAL

All reagents were of analytical grade. Zeo–Karb 225 and De–Acidite FF resins (100–200 mesh, 8% D.V.B.) were converted to a suitable form and dried under vacuum at 60 °C over anhydrous magnesium perchlorate for 48 hours before use.

Batch equilibrations were performed by shaking 100 milligrams of dried resin with 10 ml aliquots of the inorganic medium under investigation and containing tracer amounts of Be-7. After being shaken for 24 hours, the resin was allowed to settle to the bottom of the bottle and a one ml sample was withdrawn from the supernatant liquid, care being taken not to draw up any resin. Distribution coefficients were then calculated by activity differences in the solution before and after equilibration.

In cases where the high density of the solution made this method of sampling inaccurate, the resin was separated from the solution by filtering through glass wool. However, investigations showed this method to be unsatisfactory where the pH value of the solution exceeded 4.0 since Be-7 was lost from solution by adsorption on the surface of the glass wool. A more satisfactory method for separating the resin from the solution used a polythene pill pack in the bottom of which small holes had been made, and into which small shavings of polythene were packed. The solution was filtered under suction by using an adaptor to connect the pill pack to a Buchner flask.

Beryllium concentrations were measured by scintillation counting on liquid samples containing Be-7 tracer (no carrier).

Earlier experiments were performed by column elution techniques. After pretreatment of the resin with the solution under investigation, Be-7 was adsorbed in a tight band at the top of the ion-exchange column and then eluted with the same solution. Initially the effluent was collected by means of a fraction collector, Fractomat Y, and the activity of each fraction measured. In later measurements an Ecko Ratemeter Type N-600 was used to detect the activity in the eluate. The volume distribution coefficient was computed from the number of column volumes at which maximum activity occurred in the eluate. Determination of the bed density of the resin (Kraus and Moore 1951) allowed calculation of the distribution coefficient.

Although the column effluent method was used in the chloride system it was abandoned for the remaining studies in favour of the batch equilibration method. Continuous monitoring using a Type N-600 Ratemeter failed to give the desired performance, chiefly because the speed of the recorder motor was too fast to enable accurate estimation of the peak of the elution curve. Furthermore it was discovered that considerable tailing occurred in the elution of beryllium, even with a very small loading ($<<1$ per cent) and with care being taken to work the column under equilibrium conditions.

3. RESULTS AND DISCUSSIONS

3.1 Chloride System

Table 1 summarizes the results of beryllium adsorption obtained in chloride media. The results are the average values obtained from at least two equilibrations.

It is possible to verify that beryllium is involved in true cation exchange (Nelson et al. 1964) with hydrochloric acid by an appropriate plot of the values obtained in Table 1.

Consider the general ion-exchange reaction represented by the equation:

$$y\,M^{+x} + x\,A_R^{+y} \rightleftharpoons y\,M_R^{+x} + x\,A^{+y} \qquad (4)$$

with the equilibrium constant:

$$K = \frac{(M^{+x})_R^{\,y} \quad (A^{+y})^{x} \; G}{(A^{+y})_R^{\,x} \quad (M^{+x})^{y}} \qquad (5)$$

where parentheses indicate the concentration of the species, subscript R indicates the resin phase, and G is the proper activity quotient of the activity coefficients of the species.

The distribution coefficient is defined by:

$$\alpha = \frac{(M^{+x})_R}{(M^{+x})} \quad .$$

If G is constant, that is, if the Debye–Hückel term vanishes in dilute solution, and $(M^{+x})_R << (A^{+y})_R$, that is, tracer concentration of metal is used, Equation 5 can be written:

$$\text{Log } \alpha = -\frac{x}{y} \log (A^{+y}) + \text{constant} \quad .$$

Then

$$\frac{d \log \alpha}{d \log (A^{+y})} = -\frac{x}{y} \quad , \tag{6}$$

where x and y are the charges of the metal ion and the supporting medium cation respectively.

If, however, the anion of the supporting medium interacts with the metal ion to form complexes, the effective concentration of the metal ion in solution will be lowered, resulting in a deviation from the slope depicted by Equations 4–6. The limit of anion interaction is the formation of a 'stable' anionic complex over the concentration range under investigation. Here no cation exchange will be obtained.

The graph of log α versus log (HCl concentration) has a slope of −2 (Figure 1). This would be expected if x = 2 and y = 1 in Equation 6. This evidence of cation exchange indicates that below an acid concentration of 2.0M negligible beryllium chloro–complex formation occurs in hydrochloric acid.

In contrast with the above conclusion was the observed anion adsorption of beryllium by De–Acidite FF from hydrochloric acid solutions, shown in Table 1 and Figure 2. Analysis of the slope of this adsorption function using the method of Kraus and Nelson (1959) should yield information regarding complex formation in the aqueous phase.

Using the approach outlined above for the slope analysis of cation–exchange data, Kraus and Nelson were able to produce a general equation for the slope analysis of the anion–exchange adsorption function.

Consider a metal M^{+x} which forms a series of complexes MX_n with the anion of the supporting electrolyte X^{-b}, a total MX_i of which are adsorbed by an anion–exchange resin. Then it may be shown that:

$$\frac{d \log \alpha}{d \log (X^{-b})} = \sum_{n=o}^{q} \left[\frac{x - nb}{b} \right] F_n + \sum_{n=o}^{q} F_n \frac{d \log g_{MX_n} g_{X^{-b}}^{\frac{x-nb}{b}}}{d \log (X^{-b})}$$

$$- \frac{1}{\alpha} \sum_{i=o}^{q} \alpha_i \frac{d \log g_{MX_{i(R)}} g_{X^{-b}}^{\frac{x-nb}{b}}{}_{(R)}}{d \log (X^{-b})} - \frac{1}{\alpha} \sum_{i=o}^{q} \alpha_i \left[\frac{x}{b} - 1 \right] \frac{d \log (X^{-b})_{(R)}}{d \log (X^{-b})} \tag{7}$$

If the derivatives involving resin invasion and activity coefficients in the resin are zero then this equation will reduce to:

$$\frac{d \log \alpha}{d \log (X^{-b})} = \sum_{n=o}^{q} \left[\frac{x-nb}{b} \right] F_n + \sum_{n=o}^{q} \frac{d \log g_{MX_n} g_{X^{-b}}^{\frac{x-nb}{b}}}{d \log (X^{-b})} \quad , \tag{8}$$

which is the same relationship that can be developed if only a single species is adsorbed by the resin. In the above equations q is the maximum number of ligands which can be coordinated by M^{+x}, x is the charge of the uncomplexed cation, b is the charge on the anion of the supporting electrolyte, g is the activity coefficient of the individual species, and F_n is represented by:

$$F_n = \frac{MX_n}{m_t} \quad \text{and} \quad \sum_{n=o}^{q} F_n = 1 \quad ,$$

where m_t is the total metal concentration in solution. The definitions for the distribution coefficients in the above equations are:

$$\alpha_i = \frac{MX_{i(R)}}{m_t}$$

and

$$\alpha = \sum_{i=o}^{q} \alpha_i \quad ,$$

with conventions as in Equation 5.

Therefore under the above conditions the slope of the graph log α versus log (X^{-b}) yields the average charge of the metal ion in solution after correction for a weighted activity coefficient derivative. Equation 8 will simplify still further in dilute solutions in which a single 'stable' complex is formed, that is, $F_n = 1$. Then the familiar expression:

$$\frac{d \log \alpha}{d \log (X^{-b})} = - \frac{(x - nb)}{b} \qquad (9)$$

is obtained.

An inspection of the adsorption function for beryllium in hydrochloric acid (Figure 2) indicates the average charge of the species, in solutions with concentration greater than 0.001M, is negative. In the region 0.04–0.10M the curve appears to reach a constant slope of −2. However the true slope of the curve is in some doubt since difficulty was experienced in obtaining consistent results. In solutions with pH values $\leq$ 3.0, hydrolysis and/or polymerisation of trace amounts of beryllium can be neglected (Feldman and Havill 1952; Schweitzer and Nehls 1953; Feldman et al. 1955; Kakihana and Sillen 1956), so that no simple explanation seems to exist for this observation. Despite this uncertainity it is conclusive that anion exchange does occur and that the slope is negative. If it is assumed that the shape of the curve does not differ significantly from that obtained in Figure 2, then in the region 0.04–01M hydrochloric acid, the average charge of the species in solution is −2. Assigning values of +2 to x and −1 to b in Equation 9 shows the composition of the anionic complex is $BeCl_4^{-2}$. Furthermore the shape of the curve indicates the beryllium exists solely as the $BeCl_4^{-2}$ species. However this conclusion is in direct contrast to the cation–exchange data discussed earlier.

It is tempting to explain the anion–exchange data on the basis of the formation of a weak anionic chloro complex of low selectivity. The concentration range 0.001 – 0.01M of the curve would then depict the partial effect of chloride desorption of this weak complex, and the region 0.01 – 0.1M full desorption. However this conflicts with equations 7 , 8 , and 9 , which are based on the selectivity of the adsorbable species. The formation of the weakly–dissociated species H_2BeCl_4 with increasing hydrogen ion concentration can also be dismissed as a possible explanation since the cation–exchange data did not reflect this reaction. The only conclusion that can be drawn from these results is that dangers exist in applying the method of slope analysis to anion–exchange data in dilute solutions without supportin cation–exchange data.

Experimental results show that the anion–exchange behaviour of beryllium in the presence of ammonium chloride is similar to that in hydrochloric acid (Table 1). Some anion exchange was noted at chloride concentrations below 0.1M but not at higher concentrations. However, these tests were limited by hydrolysis of the beryllium ion, the pH value of the test solution being in the region of 5.0. The data did confirm that the formation of the undissociated acid beryllium complex does not occur in the region 0.001 – 2.0M chloride solution.

Kraus, Nelson, Clough, and Carlston (1955) found very large differences in the anion adsorption of a number of metals from HCl and LiCl solutions. Beryllium was one of the metals investigated and good anion–exchange adsorption was obtained in LiCl solution . Two explanations were given for this behaviour, the first involving differences in activity coefficients in the resin phase and the second based on the formation of undissociated complex acids at high HCl concentrations. Further evidence has been gathered in these systems by the same authors which tends to favour the latter explanation. However, efforts to reproduce the results in this laboratory have been unsuccessful. Although beryllium was adsorbed (Table 1) the results were inconsistent and supplementary experiments have shown the adsorp–tion to be essentially surface adsorption of hydrolysed species rather than ion exchange.

Beryllium adsorption by a cation exchanger was also studied as a function of loading. Table 2 shows it was constant whenever the load was < 2 per cent. of the resin capacity. Above this loading the distribution coefficient decreased. This is in accordance with the results obtained for other metal ions by Cornish (1958).

Since beryllium does not form significant amounts of sorbable anionic complexes in hydrochloric solutions with concentrations greater than 0.1M, Table 3 has been compiled showing the fission products, corrosion products, and canning materials that may be separated from beryllium.

3.2 Nitrate System

The results of this study are summarized in Table 4 and Figures 1 and 2. The similarity to the chloride system can be easily observed and the remarks made in the previous section apply here.

An increase of beryllium loading on the resin above about 2 per cent. of the resin capacity resulted in a marked decrease of beryllium adsorption (Table 2). This supports the previous findings in the chloride system.

Table 5 shows the possible separations from beryllium that may be realised in a nitric acid medium. The data of Bunney et al. (1959) have been used in compiling this table.

3.3 Sulphate System

The results obtained in this section of the work are given in Table 6 and Figures 1 and 2, and are very similar to those obtained in the chloride and nitrate systems.

Evaluation of the charge of the anionic complex from the anion-exchange data is difficult. As well as the doubts on the actual slope discussed previously, there is the further complication that the sulphate solutions contain both HSO_4^- and SO_4^{-2}. The slope of the adsorption function contained in Figure 2 is -2 in the region of 0.01-0.05M H_2SO_4. The concentration of the HSO_4^- in this region is such that it should be the dominant ion. If Equation 9 is applied to this system then $(Be(SO_4)_2)^{-2}$ appears to be the anionic complex species involved. The problem of the two competing ions can generally be overcome by studying the adsorption in ammonium sulphate solutions. Attempts to measure this have been prevented by hydrolysis of the Be^{+2} ion.

The cation-exchange study in sulphuric acid clearly shows a $Be^{+2} - 2H^+$ ion-exchange reaction (Figure 1). The data obtained from load experiments with Zeo-Karb 225 were similar to the data obtained in chloride and nitrate media (Table 2), a load of less than 2 per cent. being necessary for constant adsorption.

While Bunney et al. (1959) have measured the adsorption of many fission products by anion-exchange resins from sulphuric acid solutions, little information is available in the literature on the remainder of the Periodic Table. Table 7 therefore summarizes possible fission product separation from beryllium in sulphuric acid solutions.

3.4 Fluoride System

The data contained in Table 8 confirm the work of Faris (1960) and Nelson, Rush, and Kraus (1960) who obtained strong adsorption of beryllium by anion exchangers from hydrofluoric acid. Figure 3 shows that the adsorption function decreases linearly with increasing hydrofluoric acid concentration. This indicates that the average charge of the beryllium species in solution is negative, that is, beryllium exists as anionic complexes. The absence of cation exchange under identical conditions (Table 8) is further confirmation that the beryllium exists entirely as a strong anionic complex or complexes.

For the charge evaluation of the anionic species a log-log plot of the adsorption function was made (Figure 3). As hydrofluoric acid is a weak acid, fluoride concentrations were obtained from the relationship:

$$(F^-) = \frac{(HF)_t}{\left[\frac{H^+}{K_1} + 1\right]} \qquad (10)$$

where $(HF)_t$ is the total hydrofluoric acid concentration and K_1 is the dissociation constant of HF, which has a value of 3.53×10^{-4} (Hodgman 1959–60). The slope of −1.95 obtained for this graphical solution indicates the formation of a single anionic complex, BeF_4^{-2}, whose composition is obtained by suitable substitution of the respective values in Equation 6.

The strength of the fluoberyllate complex enabled this study to be extended to ammonium fluoride solutions. Anion–exchange studies in ammonium fluoride solutions gave results similar to those from the HF investigations. Since the fluoride concentration equals the total ammonium fluoride concentration, the average charge of the beryllium species was obtained by direct measurement of the beryllium adsorption function in NH_4F. The value of −2 obtained in Figure 3 substantiated the above results.

While a strong fluoberyllate complex of high adsorbability is formed in fluoride media, it changes markedly when other anions are introduced. Aveston and Milward (1959) found that the recovery of beryllium, as an anionic complex, from a fluoride leach process is impossible unless the concentrations of competing anions are small.

For separation procedures in fluoride media, cation–exchange resins are preferred to anion–exchange resins. This enables the separation of micro concentrations of the contaminants from macro concentrations of beryllium. Thus CsI, SrII, NiII, FeIII, CrIII, CrVI, and partially RuIV may be adsorbed while the complexed beryllium remains in solution.

3.5 Carbonate System

Aveston and Milward (1959) dissolved beryllium selectively from a precipitate containing beryllium, ferrous ion, and aluminium by leaching with 0.8M sodium bicarbonate at 55 °C for 6 hours. Equilibrium loadings with anion– and cation–exchange resins showed the beryllium was present principally as an anionic complex.

Misumi and Taketatsu (1959) reported the adsorption of macro amounts of beryllium (resin loading $\bar{L} = 0.30$) on Dowex–2 anion–exchange resin from ammonium carbonate solution in the concentration range 0.1M–1.2M. The capacity of the resin was known, and the charge of the complex formed in 0.1M ammonium carbonate was determined by saturation of the resin with the complex. This indicated that the formula of the complex anion was $(Be(CO_3)_2)^{-2}$.

Table 9 shows the result of anion–exchange studies with tracer amounts of beryllium, as well as tests performed with the cation–exchanger Zeo–Karb 225, and blank equilibrations in the absence of resin. In the region 0.001–0.1M ammonium carbonate, the beryllium seems to be present as one or more hydrolysed species and the adsorption on the resins is by a surface mechanism. However, when the carbonate concentration is greater than 0.2M the regularity of the decreasing adsorption function shows the average charge of the beryllium species in solution is negative (Figure 4). From the slope of −1.80 and Equation 9 the composition of the adsorbed species appears to be $(Be(CO_3)_3)^{-4}$. This is obviously incorrect. Columns 3 and 4 of Table 9 show that although there is a reduction in beryllium losses in the presence of a cation–exchange resin, and with no resin, in ammonium carbonate solutions of concentration greater than 0.2M, losses still occur. This effect could cause the curve to alter from the ideal slope of −1 for $(Be(CO_3)_2)^{-2}$ to −1.80. Alternatively Equation 9 may not be an accurate representation of the adsorption function in this medium. This means Equation 7 would apply, so necessitating correction for resin invasion and activity coefficients of the species in the resin phase for accurate determination of the slope.

The hydrolysis of the beryllium ion therefore renders invalid slope analysis of the adsorption function in ammonium carbonate solution. It also shows the futility of studying the ion exchange of beryllium in alkaline solutions unless a strong complexing agent is present, for example, salicylic acid (Fardy 1962).

3.6 Thiocyanate Medium

Biermann and McCorkell (1962, 1963) evolved a solvent extraction process for separating beryllium from aluminium in a thiocyanate medium. They concluded that the extractable beryllium species is $Be(CNS)_2$ although some of the data suggested some degree of anionic complex formation in solutions of high thiocyanate concentration.

Figures 4 and 5 summarize the data shown in Table 10. The anion-exchange data indicate that beryllium has an apparent adsorption minimum which changes to a rising adsorption function when the thiocyanate concentration is greater than 0.5M. Therefore the average charge of the beryllium is positive over the thiocyanate concentration range studied. It may be concluded then that under the conditions of this study negligible anionic complex formation occurs.

The slope of the cation-exchange adsorption isotherm contained in Figure 5 shows negligible interaction between the beryllium and thiocyanate ion in the range 0.01-2.0M. The value of -1.80 for this slope implies that the desorption of beryllium is an $NH_4^+ - Be^{+2}$ ion-exchange mechanism.

3.7 Phosphate System

Merrill, Honda, and Arnold (1960) studied the adsorption of beryllium by a cation exchanger in the presence and absence of phosphate ions. From this data they obtained the stability constants of the complex species $Be(H_2PO_4)^+$, $Be(H_2PO_4)_2^0$, and $Be(H_2PO_4)_3^-$.

The results obtained in the present study of the phosphate system are summarized in Table 11 and Figures 6, 7, and 8. The anion-exchange adsorption results are very similar to those from the HCl, HNO_3, and H_2SO_4 systems. As phosphoric acid is polybasic a log-log plot of the beryllium adsorption as a function of $H_2PO_4^-$ concentration is also included in Figure 6. The $H_2PO_4^-$ concentration can be calculated with sufficient accuracy by using the equation :

$$[H_2PO_4^-] = \frac{[H_3PO_4]_T}{\frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + 1} ,$$

where $[H_3PO_4]_T$ is the initial concentration of phosphoric acid added, and K_1 and K_2 are the first and second dissociation constants of the acid. Values of 1.1×10^{-2} and 7.5×10^{-8} respectively were used (Hodgman 1959-60).

As in the previous studies in nitrate, chloride, and sulphate media a decreasing adsorption function is observed in phosphoric acid solutions. However the curve does show a significant difference since the slope changes abruptly in solutions containing greater than 0.5M H_3PO_4 or 9.0×10^{-2}M $H_2PO_4^-$. The slope and linearity of Curve II Figure 6 indicate that before this the majority of the beryllium exists as $Be(H_2PO_4)_3^-$ complex. The sudden change in the slope may herald the formation of a weakly-dissociated complex acid $HBe(H_2PO_4)_3$.

Table 11 gives the results of similar ion-exchange studies performed in the presence of the cation-exchange resin Zeo-Karb 225. Since phosphoric acid is weak, pH measurements were made on all solutions after equilibrium had been attained. Figure 7 depicts the adsorption of beryllium as a function of H^+ concentration. The slope of -3.2 obtained for this relationship shows the interaction of phosphate with the beryllium. These data do not support the implications of the anion-exchange results that, in 0.01-0.1M H_3PO_4, beryllium exists in solution solely as the $Be(H_2PO_4)_3^-$ species.

An alternative interpretation of the anion-exchange data is that Curve II Figure 6 represents the formation of a weakly-dissociated acid complex of a higher order than $HBe(H_2PO_4)_3^-$, that is, $H_2Be(H_2PO_4)_4$. If this reaction does occur then anion-exchange studies in $NH_4H_2PO_4$ should yield a normal adsorption function with the added possibility of identifying the anionic species.

The results of this study are contained in Table 11 and Figure 6 (Curve III). Beryllium displays an adsorption maximum in this medium. The average charge of beryllium is positive in solutions 0.001M-0.02M, becoming approximately zero at the maximum of 0.03M, and predominating as a negatively-charged complex species in phosphate concentrations in excess of 0.2M. Applying Equation 9 to the slope of the curve in this latter region, where the slope is constant at -1.90, shows the composition of the anionic complex to be $(Be(H_2PO_4)_4)^{-2}$. The formation of this complex is supported further by the data obtained with the cation exchanger in this same medium. No cation exchange is observed at concentration greater than 0.1M. At lower concentrations the data show that the decrease in beryllium adsorption with increasing ammonium dihydrogen phosphate concentrations is markedly different from the ideal $Be^{+2} - NH_4^{+1}$ exchange.

The adsorption characteristics of this complex were measured finally as a function of pH in 0.1M ammonium dihydrogen phosphate (Figure 8). The linear decrease of the adsorption with decreasing pH denotes the dissociation of the complex. The absence of a constant adsorption plateau signifies the beryllium is not wholly complexed, that is,

$$F_{Be(H_2PO_4)_4^{-2}} \neq \frac{[Be(H_2PO_4)_4^{-2}]}{M_t} < 1 \ ,$$

where M_t is the total concentration of beryllium in solution. The strength of the complex makes determination of its stability constant by the method of Nelson, Day, and Kraus (1960) difficult since the solution must be maintained at low and constant ionic strength throughout the determination.

Little information is available in the literature on the adsorption of other metals by ion-exchange resins from phosphoric acid solution. However the work of Freiling, Pascuol and Delucchi (1959) indicates that the fission products can be divided into two classes depending on the extent of their adsorption by anion exchangers in H_3PO_4. Those that are strongly adsorbed constitute the first class and include Zr(IV), Nb(V), U(VI), and Mo(VI), while the weakly-adsorbed ions Sr(II), Ce(III), and Cs(I) fall into the second class. On the basis of the above data beryllium can be separated from the first group by adsorbing this group on an anion-exchange resin from 3.0M H_3PO_4. Separation from the second group is a little more difficult since a chromatographic type separation is required. Beryllium adsorbs strongly in 0.1M H_3PO_4 and separation factors of 7 for Be/Sr, 8 for Be/Ce, and 50 for Be/Cs indicate good separations are possible.

4. CONCLUSION

Anion-exchange studies have revealed that beryllium forms anionic complexes with fluoride, phosphate, carbonate, and thiocyanate. The relative stability of these complexes can be gauged by comparing the position of the maximum for each of the adsorption functions obtained in solutions of the ammonium salts of these anions. The stabilities of these complexes lie in the order $F^- > H_2PO_4^- \approx CO_3^{=} >> CNS^-$. Under the conditions of this study the complexes $(BeF_4)^{-2}$ and $(Be(H_2PO_4)_4)^{-2}$ have been identified. Attempts to identify the carbonate complex were prevented by hydrolysis. The anionic beryllium thiocyanato complex is very weak and no attempt was made to identify this species.

The anion-exchange data obtained in dilute nitric, hydrochloric, and sulphuric acids indicate that anionic complex species are formed in these solutions. No explanation can be given at present for the shape and similarity of the adsorption functions obtained in each of the solutions. However cation-exchange data have shown that the extent of anionic complex formation in solutions up to 2.0M is negligible.

As a result of the adsorption isotherms for beryllium it is possible to separate many metal ions, found in fuel processing solutions, from beryllium.

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TABLE 1

ADSORPTION OF BERYLLIUM BY ION-EXCHANGE RESINS FROM CHLORIDE MEDIA

Chloride Concn. (M)	Distribution Coefficient					
	HCl		NH_4Cl	LiCl		
				Anion Resin		
	Cation Resin	Anion Resin	Anion Resin	Run 1	Run 2	Run 3
0.001						
0.01		110	126			
0.02		50	46		56.3	
0.1	1430	24.5	21.2	94.8		
0.2	360	0.9	1.0			
0.5	53	<1	<1	25.4		
1.0	14					
2.0	3.8			74.0	46.3	
4.0	<1			80.8		
6.0				61.2	300	
8.0				75.2	235.1	160
10.0				455.0		123

TABLE 2

ADSORPTION OF BERYLLIUM BY CATION-EXCHANGE RESIN AS A FUNCTION OF RESIN LOADING

Acid (0.1M)	Distribution Coefficient				
	L* = Tracer	L = 0.002	L = 0.02	L = 0.1	L = 0.4
HCl	1500	1540	1488	1207	452
HNO_3	1600	1608	1494	760	156
H_2SO_4	2447	2539	2526	1729	428

$$*L = \frac{\text{Total quantity of beryllium in the equilibration}}{\text{Total capacity of the resin}}$$

TABLE 3

POSSIBLE SEPARATIONS OF FISSION PRODUCTS, CORROSION PRODUCTS, AND CANNING MATERIALS FROM BERYLLIUM USING ANION–EXCHANGE RESIN IN HCl SYSTEMS

Metal	Concentration Range for Adsorption	Optimum Concentration for Adsorption
U VI	8–12M	12M
U IV	8–12M	12M
Zr IV	10–12M	12M
Pa V	8–12M	12M
Fe III	5–12M	10M
Sn IV	4–12M	6M
Cr VI	Strong Adsorption	
Ru IV	0.1–2.0M	0.1M
Cr III	Weak Adsorption	
Be, Rare earths, Sr, Cs, Ni, Al, Mg, Th	No Significant Adsorption	

TABLE 4

ADSORPTION OF BERYLLIUM BY ION–EXCHANGE RESINS FROM NITRATE MEDIA

Nitrate Concn. (M)	Distribution Coefficient		
	Nitric Acid		Ammonium Nitrate
	Cation Resin	Anion Resin	Anion Resin
0.001		40	42
0.01		19.2	17
0.02		10.1	9.5
0.10	1600	0.5	0.9
0.2	359	<1	<1
0.5	57		
1.0	11.3		
2.0	2.5		
4.0–10.0	<1		

TABLE 5

POSSIBLE SEPARATIONS OF FISSION PRODUCTS, CORROSION PRODUCTS, AND CANNING MATERIALS FROM BERYLLIUM USING ANION–EXCHANGE RESIN IN HNO_3 SYSTEMS

Metal	Concentration Range for Adsorption	Optimum Concentration for Adsorption
U VI	4–12M	8M
Zr IV	Slight Adsorption	6M
Ru IV	0.1–1M	0.1M
Rare earths	4–8M	6M
Th IV	4–12M	8M
Sn IV	Slight Adsorption	
Be Cr III, Fe III, Al III, Sr II, Ni II, Mg II, Cs I	No Significant Adsorption	

TABLE 6

ADSORPTION OF BERYLLIUM BY ION–EXCHANGE RESINS FROM SULPHURIC ACID

Concentration of Sulphuric Acid (M)	Distribution Coefficient	
	Cation Resin	Anion Resin
5×10^{-4}		24.0
5×10^{-3}		8.0
2×10^{-2}		1.6
0.1	663	0.96
0.25	110.1	< 1
0.5	29	
1.0	9	
2.0	2.5	
4.0–10.6	< 1	

TABLE 7

POSSIBLE SEPARATIONS OF FISSION PRODUCTS FROM BERYLLIUM USING ANION-EXCHANGE RESINS IN SULPHURIC ACID SOLUTIONS

Metal	Concentration Range for Adsorption	Optimum Concentration for Adsorption
U VI	0.01 – 0.5M	0.1M
Pa V	0.1 – 1.0M	0.2M
Th IV	0.1 – 0.2M	0.1M
	6.0 – 8.0M	8.0M
Zr IV	0.1 – 1.0M	0.1M
Ru IV	0.1 – 0.2M	0.1M
	13.0 – 18.0M	18.0M
Be	No Significant	
Rare earths, Sr II, Cs I	Adsorption	

TABLE 8

ADSORPTION OF BERYLLIUM BY ION-EXCHANGE RESINS FROM FLUORIDE MEDIA

Hydrofluoric Acid				Ammonium Fluoride	
Concn. (M)	Cation Exchange Resin	Anion Exchange Resin		Anion Exchange Resin	
	α	Fluoride Concn. (M)	α	Concn. (M)	α
0.001		4.75×10^{-4}	46,400	6.5×10^{-4}	34,300
0.011		2.50×10^{-3}	30,600	9.4×10^{-2}	16,400
0.115	< 1	2.50×10^{-2}	2,990	0.1	1,940
0.46	< 1	5.67×10^{-2}	512	0.2	674
1.15	< 1	1.16×10^{-1}	126.6	0.5	114
2.30	< 1	1.90×10^{-1}	48.8	1.0	29.2
4.60		3.40×10^{-1}	15.8	2.0	6.8
10.0				4.0	1.9

TABLE 9

ADSORPTION OF BERYLLIUM BY ION–EXCHANGE RESINS FROM AMMONIUM CARBONATE SOLUTIONS

Carbonate Concentration (M)	α Anion Resin	% Loss from Solutions	
		Cation Resin	No Resin
0.001	717		89.0
0.01	4035	77	63.5
0.1	892	71	92.0
0.2	985		
0.5	254	7.0	5.0
1.0	82.5		
2.0	22.3	4.0	3.0

TABLE 10

ADSORPTION OF BERYLLIUM BY ION–EXCHANGE RESINS FROM AMMONIUM THIOCYANATE SOLUTIONS

Thiocyanate Concentration (M)	Distribution Coefficient	
	Cation Resin	Anion Resin
0.01	28,600	31.0
0.10	734.2	18.5
0.20	197.8	18.0
0.50	41.9	18.6
1.00	7.2	36.0
2.00	1.1	148.0
4.0	< 1	746.0

TABLE 11

ADSORPTION OF BERYLLIUM BY ION-EXCHANGE

RESINS FROM PHOSPHATE MEDIA

Total Phosphate Concn.	H_3PO_4					$NH_4H_2PO_4$			
	Cation Exchange Resin		Anion Exchange Resin			Cation Exchange Resin		Anion Exchange Resin	
	H^+ Concn. (M)	α	H^+ Concn. (M)	H_2PO_4 Concn.	α	NH_4^+ Concn. (M)	α	H_2PO_4 Concn.	α
0.001			1.59×10^{-3}	8.78×10^{-4}	661	0.001	63,900	0.001	398
0.01			5.01×10^{-3}	6.85×10^{-3}	148.2	0.01		0.01	1350
0.03								0.03	1850
0.1	2.51×10^{-2}	2130	2.04×10^{-2}	3.51×10^{-2}	50.4	0.1	9.34	0.1	1285
0.2								0.2	630
0.5	6.31×10^{-2}	103.4	9.03×10^{-2}	5.44×10^{-2}	16.7	0.5	<1	0.5	125
1.0	1.29×10^{-1}	23.4	1.20×10^{-1}	8.40×10^{-2}	3.8	1.0	<1	1.0	40
2.0	2.51×10^{-1}	1.7	2.51×10^{-1}	8.43×10^{-2}		2.0		2.0	18

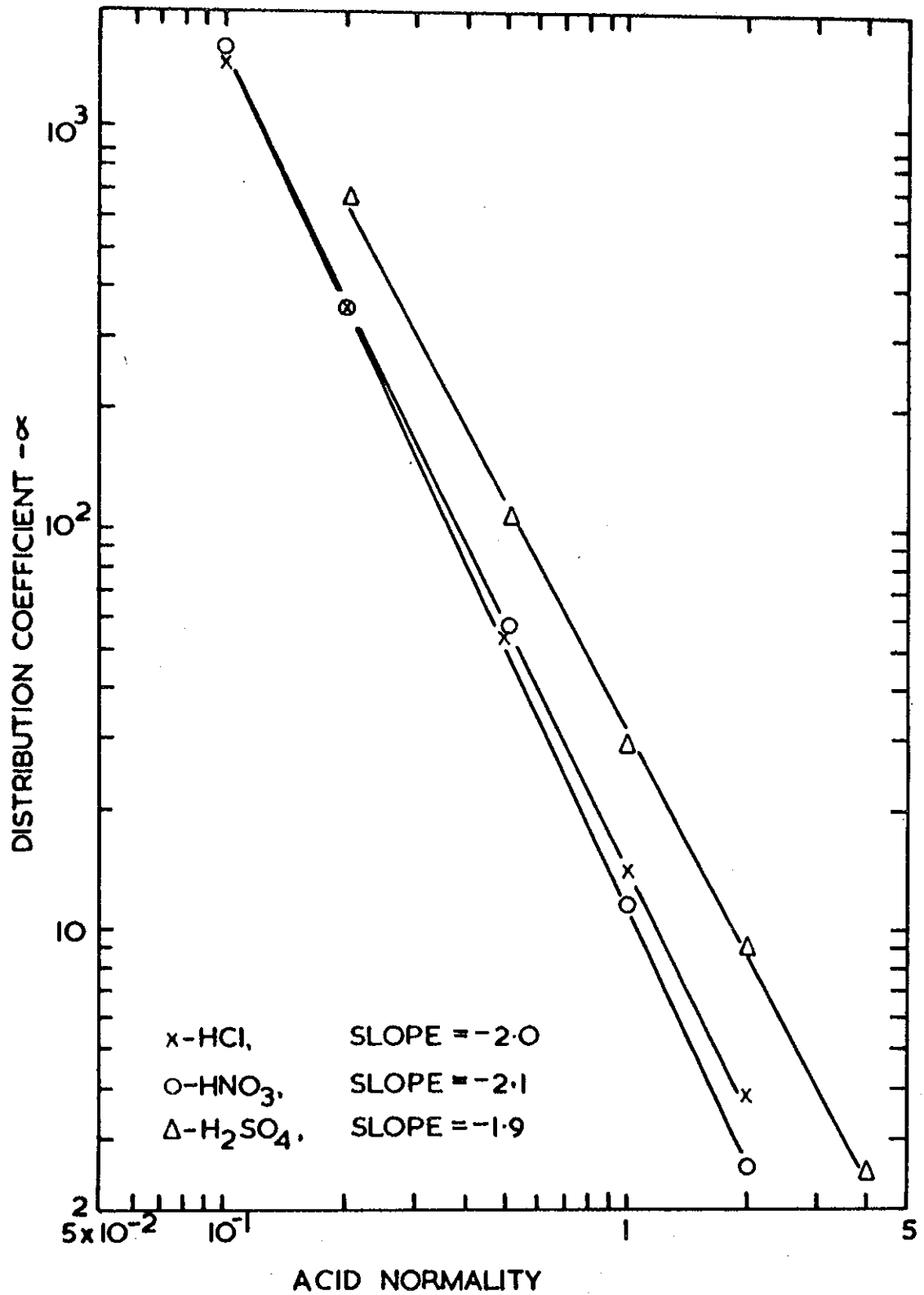

FIGURE I. ADSORPTION OF BERYLLIUM BY THE CATION EXCHANGER ZEO-KARB 225 FROM 0·1 <N ACID< 10

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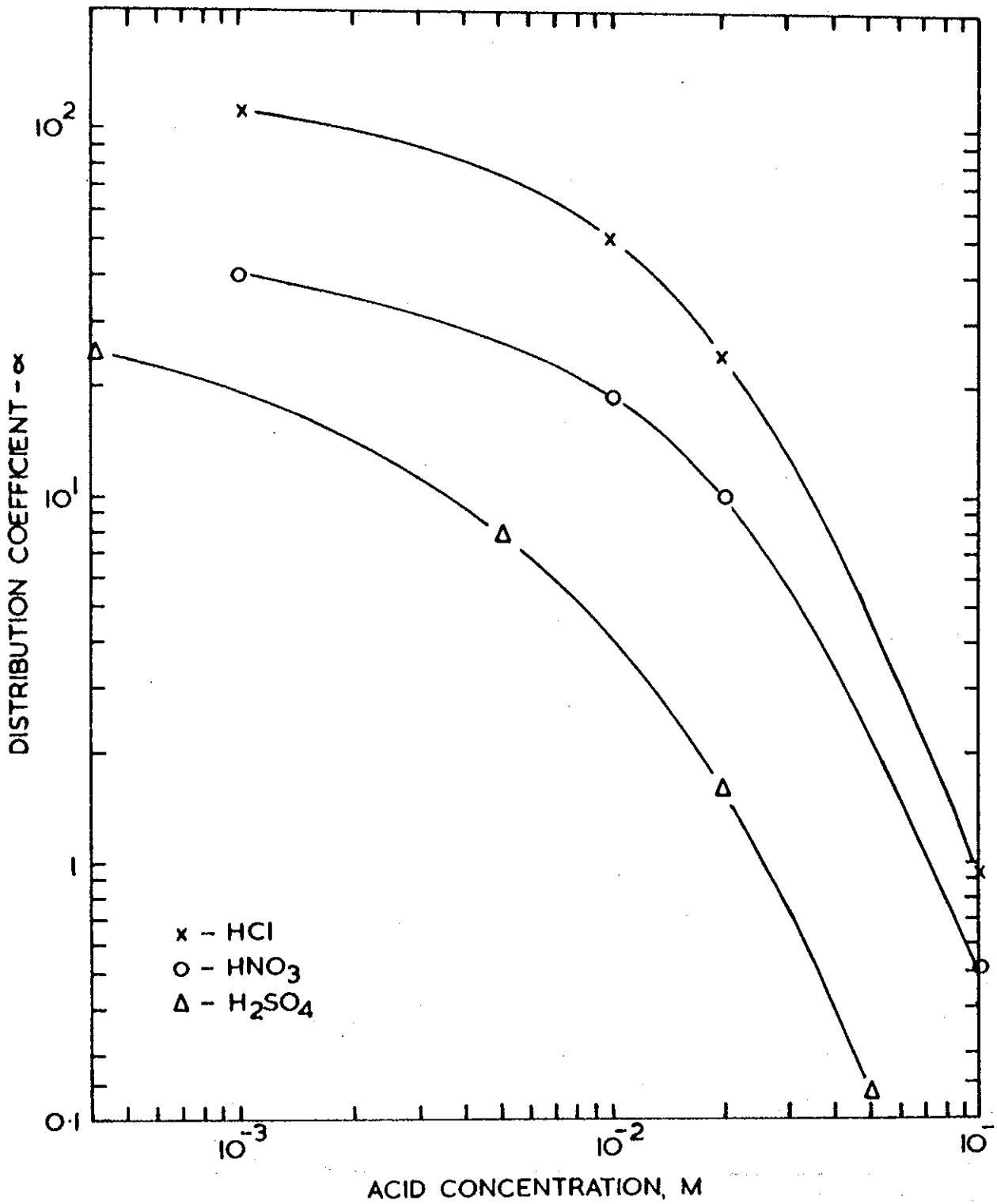

FIGURE 2. ADSORPTION OF BERYLLIUM BY THE ANION EXCHANGER DE-ACIDITE FF FROM 0·001 < M ACID < 4·0

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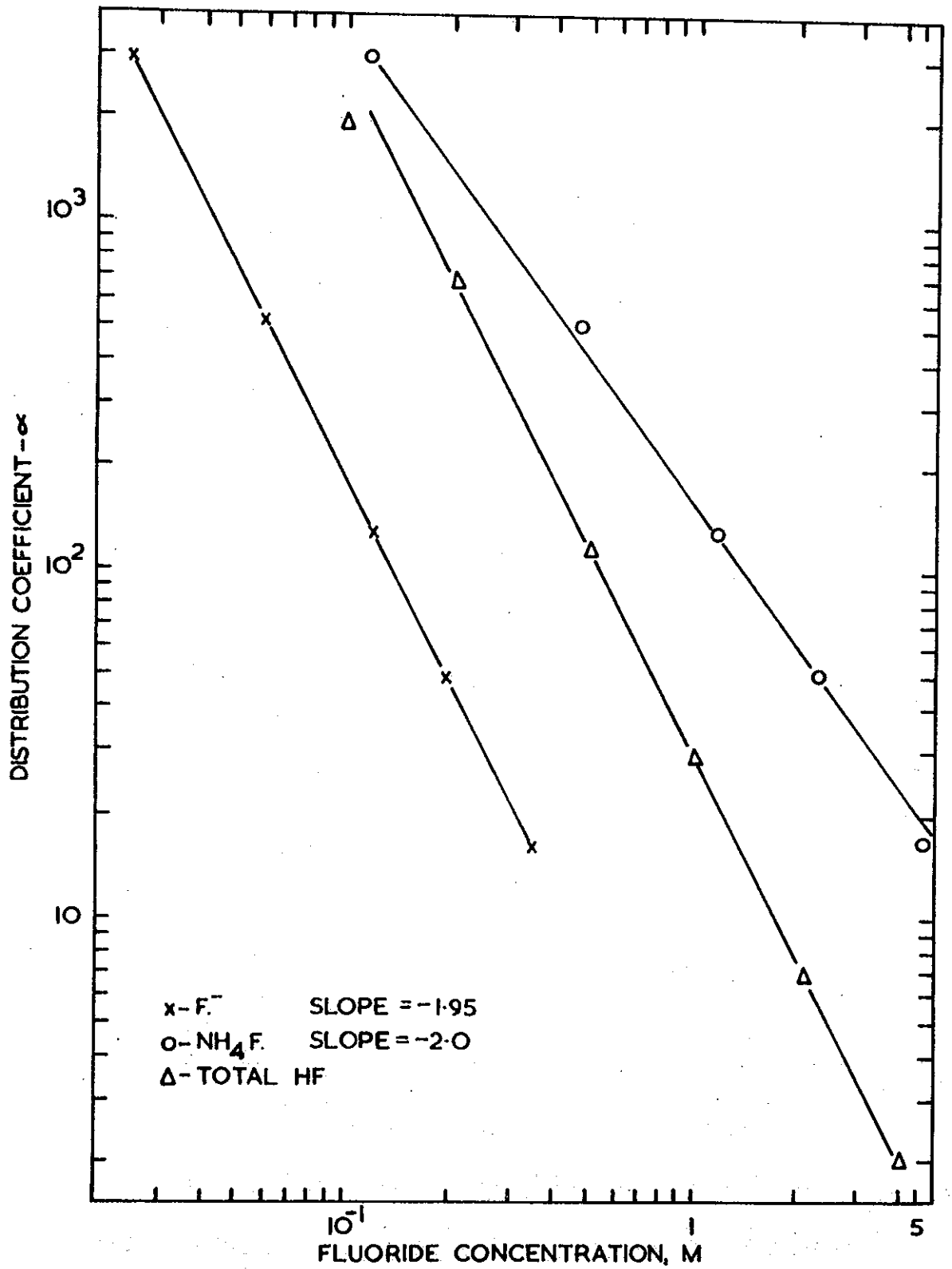

FIGURE 3. ADSORPTION OF BERYLLIUM BY THE ANION EXCHANGER DE-ACIDITE FF FROM 0·01 < M FLUORIDE < 10·0

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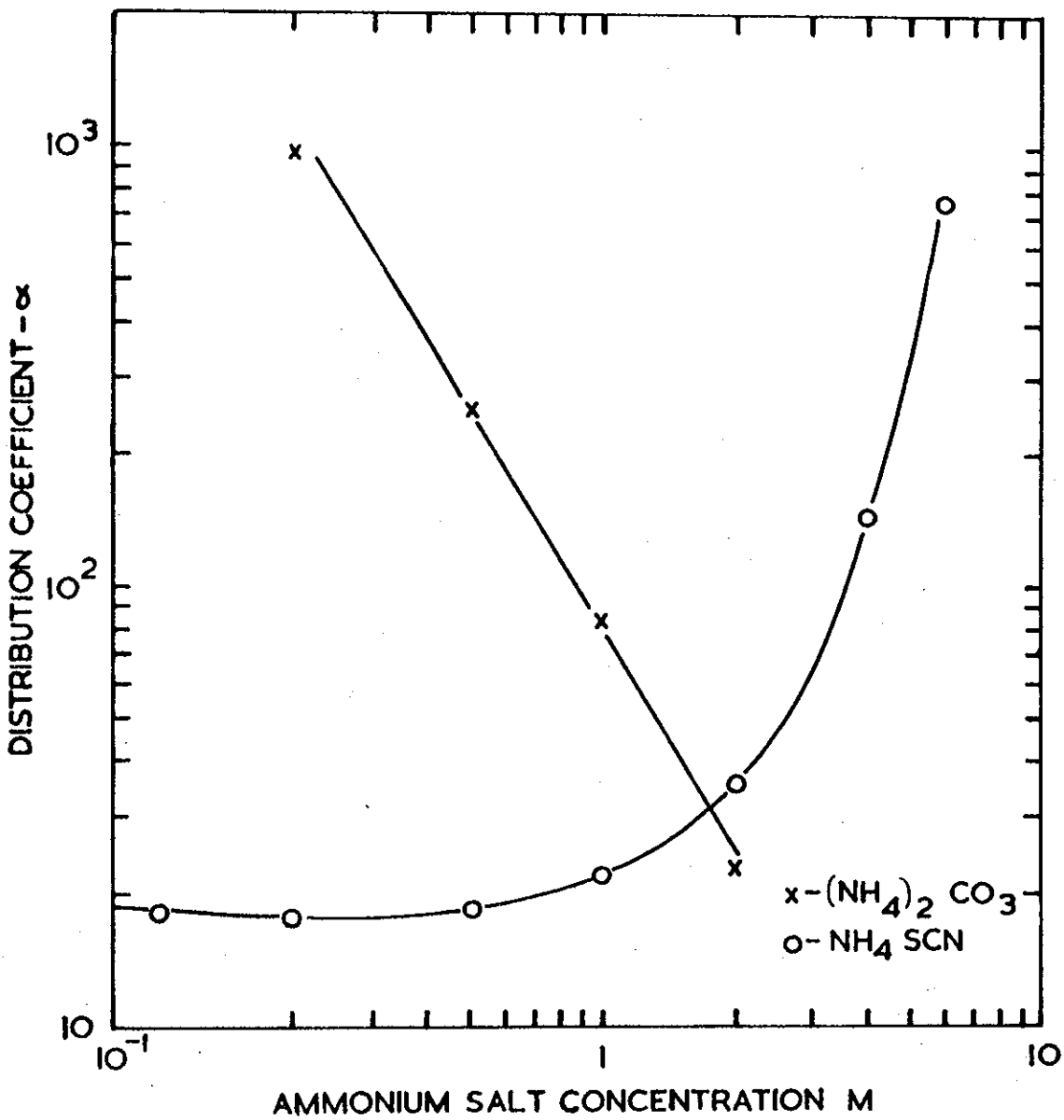

FIGURE 4. ADSORPTION OF BERYLLIUM BY THE ANION EXCHANGER DE-ACIDITE FF FROM 0·1<M NH_4X<6·0

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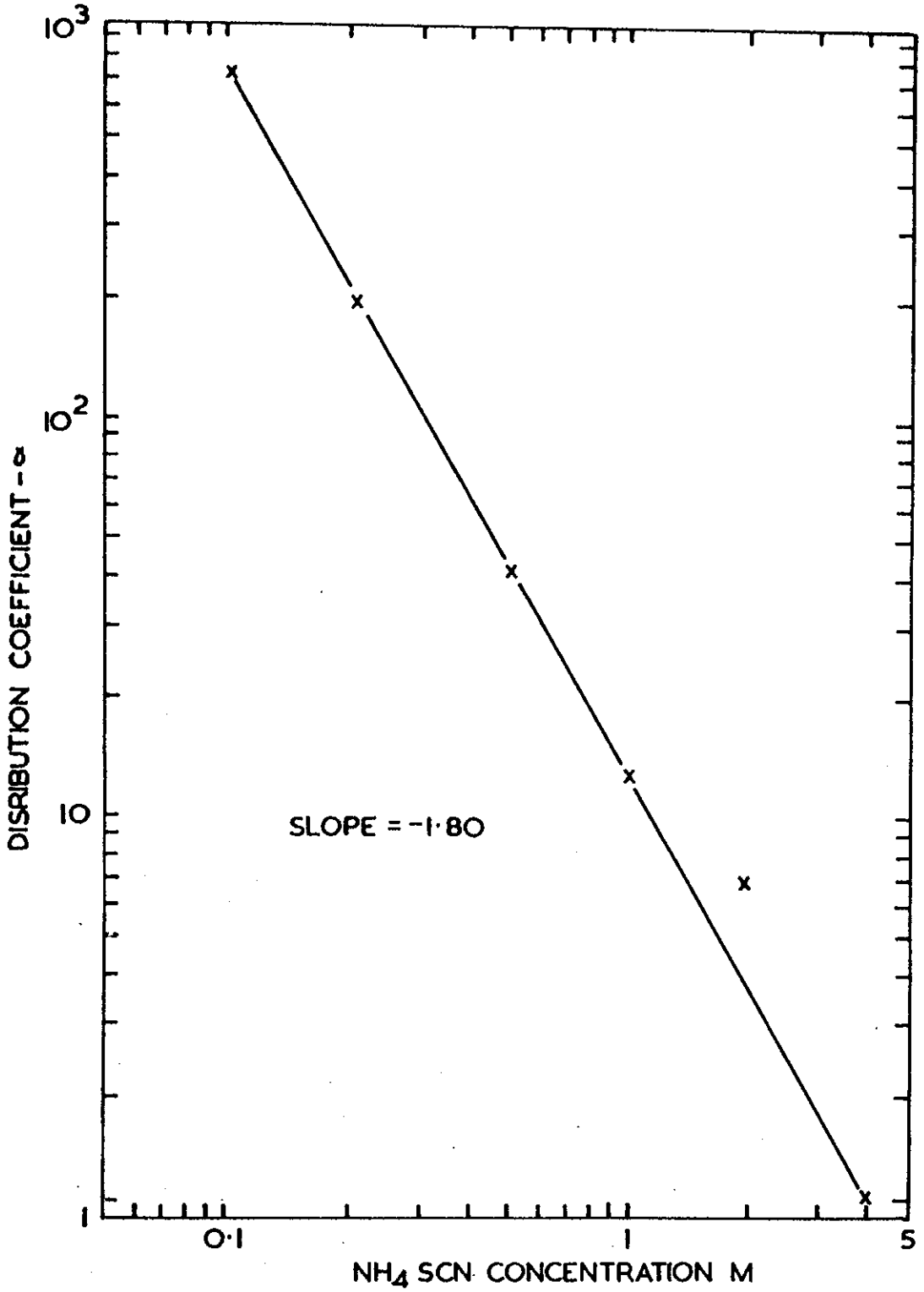

FIGURE 5. ADSORPTION OF BERYLLIUM BY THE CATION EXCHANGER ZEO-CARB 225 FROM 0·1 < M NH_4SCN < 6·0

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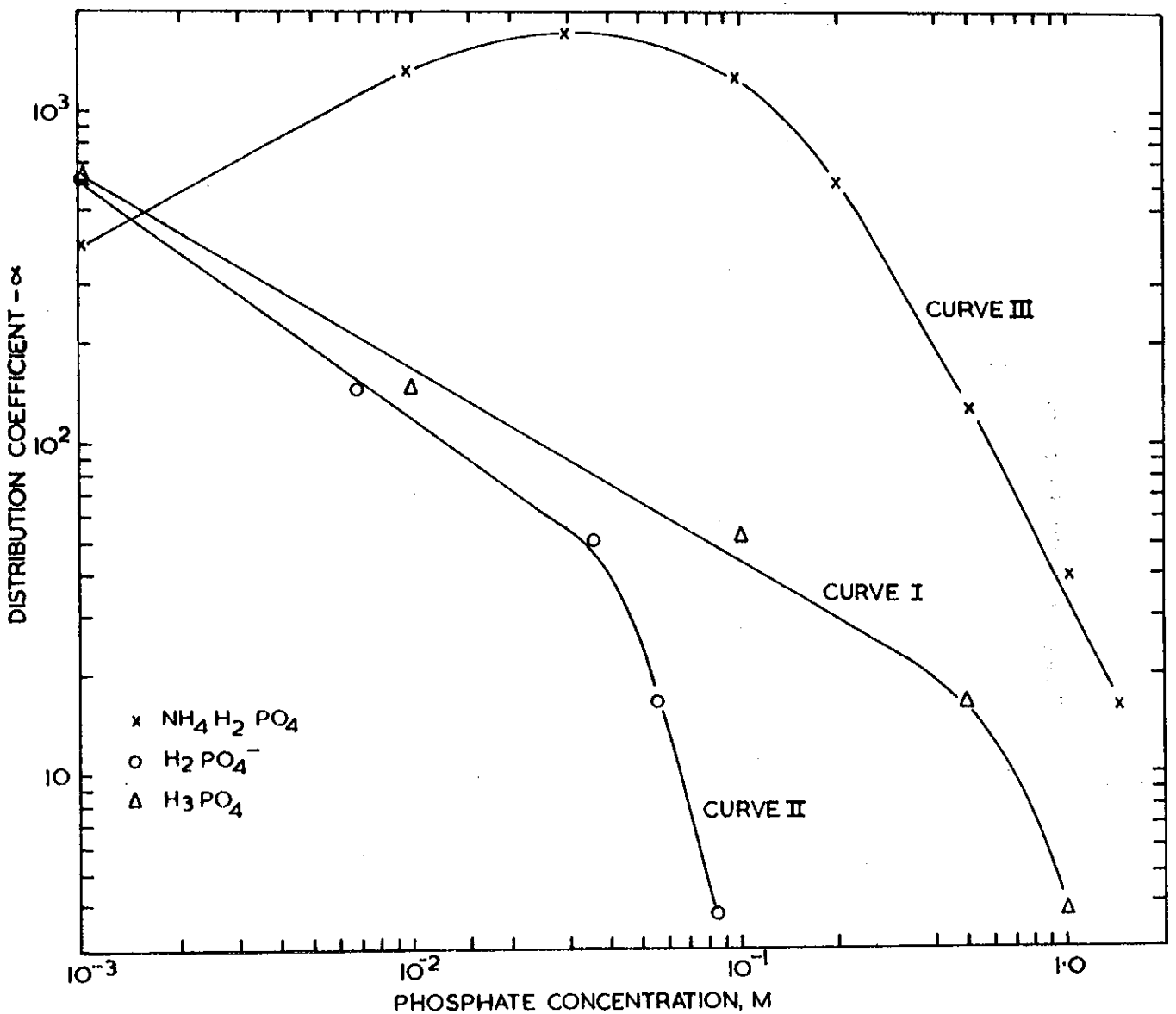

FIGURE 6. ADSORPTION OF BERYLLIUM BY THE ANION EXCHANGER DE-ACIDITE FF FROM 0·001 < M PHOSPHATE < 2·0

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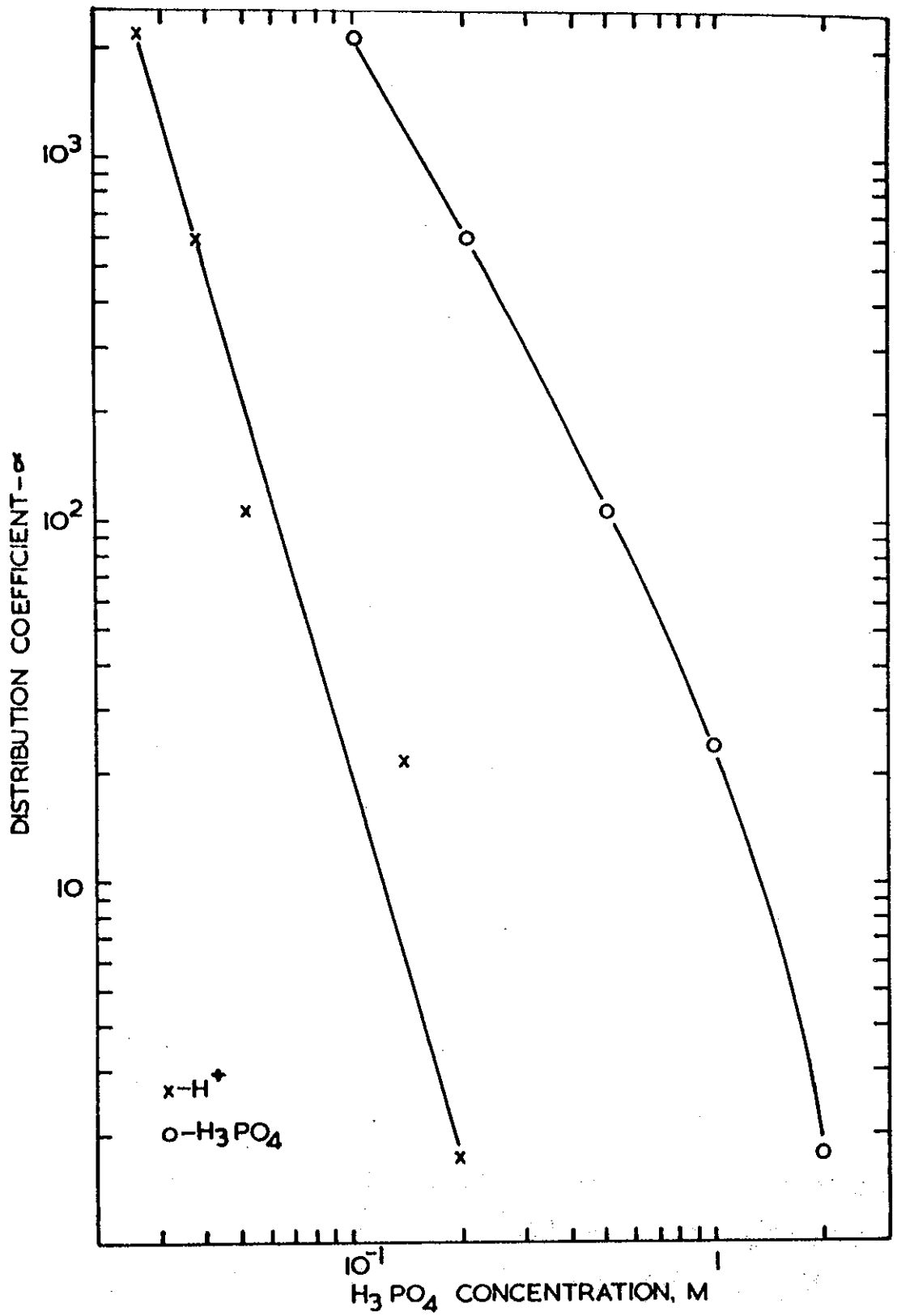

FIGURE 7. ADSORPTION OF BERYLLIUM BY THE CATION EXCHANGER ZEO-CARB 225 FROM 0·1 < M H_3PO_4 < 2·0

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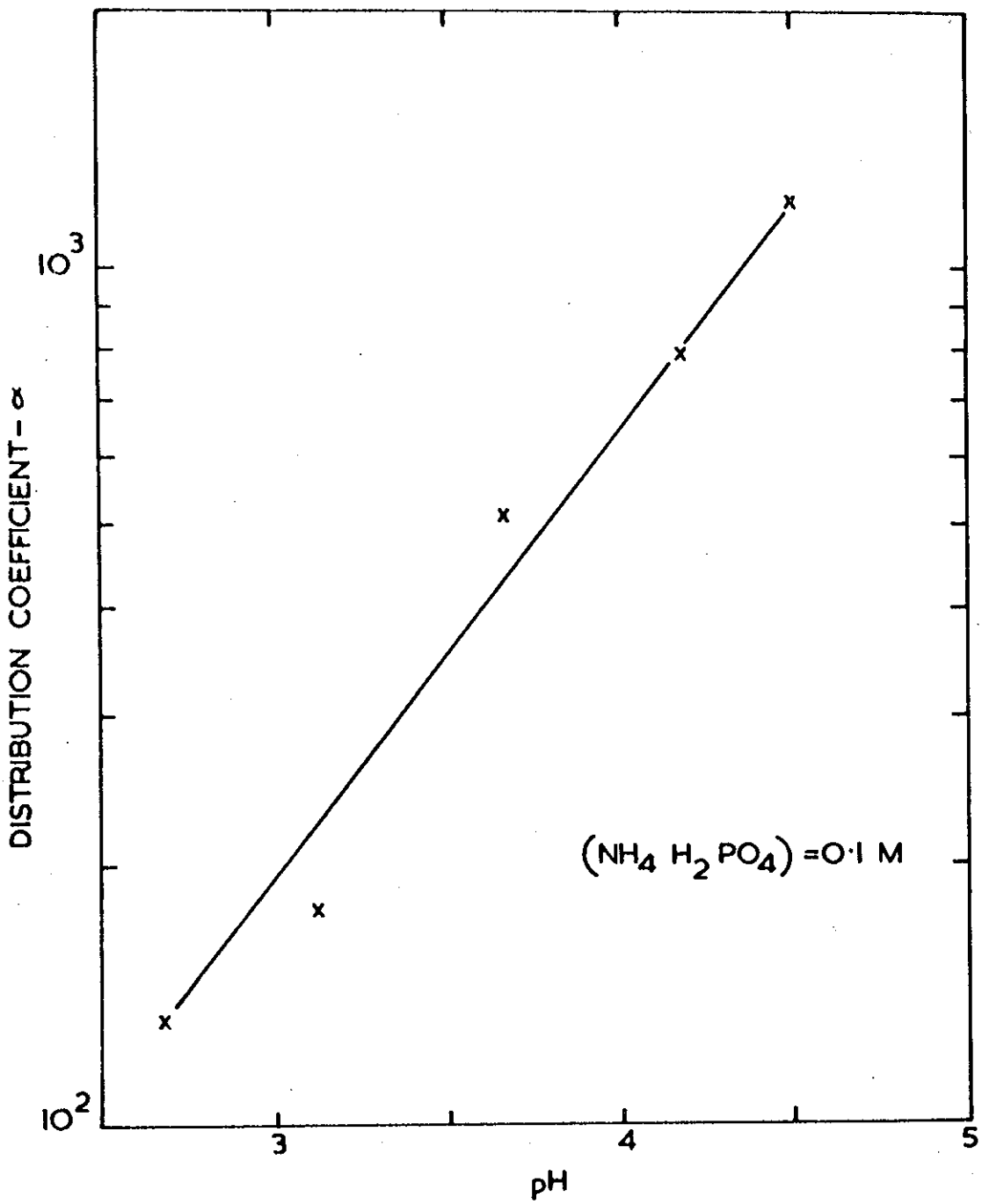

FIGURE 8. ADSORPTION OF BERYLLIUM BY THE ANION EXCHANGER DE-ACIDITE FF FROM 0·1 M $NH_4 H_2 PO_4$ AS A FUNCTION OF pH

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