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fulvic acid**

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1983-03-31

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The Complexation of Eu(III) by Fulvic Acid

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Summary

It has been determined that fulvic acid (FA) at concentration levels as low as 10^{-4} molar (~ 20 ppm), on a monomer basis, exists in aqueous media as a well-defined molecular aggregate which exhibits microgel properties. This property of the fulvic acid was not discovered earlier because complication by inadvertent CO_2 dissolution occurred; the consequent disturbance of the acid dissociation equilibrium in these studies was not suspected. It was observed (and reported) earlier, for example, that, during extended examination of potentiometric data obtained in these fulvic acid systems during their stepwise neutralization in batch equilibration studies, pH values slowly drifted with time. Time intervals of 30 to 40 days, at which point pH readings approached a plateau, were considered necessary for equilibration of these systems. As a consequence data analysis was prejudiced by the pH-leveling potential of the additional and unaccounted for reaction between CO_2 , H_2O and OH^- ion when pH measurements, obtained after this prolonged interval, were used to characterize the potentiometric behavior of the FA.

The unambiguous deduction that FA exists as a separate phase (microgel) when dispersed in aqueous media is based on the following observations: (1) In studying the distribution of Eu^{154} between 8% crosslinked Dowex 50 resin in the Na^+ -ion form and fulvic acid at several different NaCl concentration levels and over an extended pH range from 4 to as high as 10 it has been shown that only one FA-complexed species of Eu^{+3} , $[\text{Eu}(\text{COOR})]_n^{++}$, is formed, the magnitude of its apparent constant of formation, $\beta_{\text{Eu}(\text{COOR})^{++}}$, being roughly proportional to the

third power of the NaCl concentration employed in the study (a direct proportionality is blurred by expansion or contraction of the microgel as experimental parameters change) and (2) although the apparent pK of the fulvic acid, because of significant aberration of the pH data by CO₂ sorption has been quantitatively measured in only a few instances, an inverse relationship between apparent pK and ionic strength has been conclusively demonstrated.

Observations (1) and (2) can only correlate with the fact that the concentrations of free mobile ion counterions in solution are a reflection of the equilibrium between H⁺, COOR⁻, Eu⁺⁺⁺, HCOOR and Eu(COOR)⁺⁺ in the microgel defined by the FA aggregate which controls the concentration ratio of H⁺, Eu⁺⁺⁺ and Na⁺ in the aqueous phase. Thus, if Na⁺, the potential determining ion, is reduced or raised in solution by a factor of 10 in parallel sets of experiments, the quantity of H⁺ and Eu⁺⁺⁺ in solution is reduced or raised, about a factor of $\sim 10^1$ and $\sim 10^3$, respectively, so that the Donnan equilibria between these diffusible components in the microgel and aqueous phases (Eu Cl₃ and NaCl, and HCl and NaCl) can be fulfilled; the exact proportionality is effected by microgel flexibility.

With the unique description of the FA, Eu(III), NaCl system provided by this useful gel model it has been possible to compare the complexation potential of CO₃⁼ and FA as a function of ionic strength, the particular FA source, pH, and total CO₃⁼. It is quite apparent that some FA sources can be expected to complex Eu(III) so selectively in the presence of CO₃⁼ ion that even as little as 2 ppm of FA can preferentially bind to the Eu(III) in typical ground water systems.

Introduction

In the scheme developed for the disposal of radioactive waste the multiple barrier system devised to prevent its leakage from the burial site¹ must reduce the eventual rate of transport of radioactivity sufficiently so that decay to a level that is not hazardous to man can be reached before any release to the biosphere occurs. The negatively charged sites of the bedrock barrier and the bentonite used to plug fissures and cracks in the bedrock barrier in order to block as effectively as possible the movement of ground water into and through these barriers are expected, as well, to provide a sorption sink for the radioactive elements eventually leaking from the burial site into the ground water. In the tortuous traversal of the cracks and fissures by the ground water the transport of the radioactive waste elements should be retarded by their sorption thereby contributing to the attainment of the goal of the disposal scheme.

There are, however, certain factors which can be expected to interfere with the sorption process thereby promoting the migration of the radioactive elements. The possibility of their occurrence and the magnitude of their adverse effects must be examined. For example, the presence of dissolved or colloiddally dispersed organic substances, such as humic and fulvic acids (HA and FA) in the ground water, could have a detrimental effect on the barrier performance if the elements comprising the radioactive waste form negatively charged or uncharged complexes with them to prevent their sorption.

It has been the objective of this feasibility study to examine this aspect. For this purpose we have studied the potentiometric properties

of FA as a function of (a) ionic strength (b) initial FA concentration and (c) time of equilibration. With this program we expected to show whether FA exists as a small molecule, a two-dimensional polyelectrolyte or a three dimensional aggregate. This information was essential for facilitating quantification of the complexation reactions of the rare earth nuclide, ^{154}Eu , with FA, the primary objective of this investigation.

Theoretical Basis of Research

A. The Protolytic Properties of Weakly Acidic Polyelectrolytes and their Gel Analogs

Potentiometric titrations of weakly acidic polyelectrolytes with identical functional groups yield results which depend strongly on the ionic strength of the aqueous medium and the physical state of the macromolecule.^{2,3} For linear polyelectrolytes, plots of $\text{pH} - \log \frac{\alpha}{1-\alpha}$ versus α , based on data obtained at different ionic strengths, result in a series of curves that converge at $\alpha=0$ (where α is the degree of neutralization of the polyacid). This characteristic property of linear polyelectrolytes is illustrated² by Fig. 1* and is explained as follows: The intrinsic microscopic acid dissociation constant of the repeating functional group HA (ν groups per macromolecule) is defined by

$$K_{(\text{HA})_\nu}^{\text{int}} = \frac{(\text{H}_a^+)(\text{A}^-)}{(\text{HA})} = \frac{(\text{H}_a^+)(\alpha)}{(1-\alpha)} \quad (1)$$

where (H_a^+) represents the activity of the hydrogen ions at the charged cylindrical surface of the polyelectrolyte. One can consider the assembly of macromolecules in these systems as a parallel arrangement of charged cylindrical rods which define a surface whose electrical properties may be expressed by Gauss' law.

By assuming Boltzmann statistics apply, the activity of H^+ ion, (H^+) , in the bulk of the solution can be related to (H_a^+) with eq. 2:

$$(\text{H}_a^+) = (\text{H}^+) e^{-F\psi_a/Rt} \quad (2)$$

*Convergence of the curves to a unique point as shown in Fig. 1 may be somewhat of an exaggeration. However, any deviation of the intercept value with ionic strength can be expected to be quite small.

where ψ_a is the difference in potential between the charged polymer surface and the bulk of the solution. With this definition of $(H^+)_a$ employed in eq. 1, one obtains eq. 3:

$$K_{(HA)_v}^{int} = (H^+) \frac{\alpha}{1-\alpha} e^{-F\psi_a/RT} \quad (3)$$

By introducing the relationship:

$$K_{(HA)_v}^{app} = \frac{(H^+)\alpha}{1-\alpha} \quad (4)$$

we obtain eq. 5:

$$K_{(HA)_v}^{int} = K_{(HA)_v}^{app} e^{-F\psi_a/RT} \quad (5)$$

Eq. 4 can be restated as follows:

$$\begin{aligned} pK_{(HA)_v}^{app} &= pH - \log \frac{\alpha}{1-\alpha} \\ &= pK_{(HA)_v}^{int} - F\psi_a/RT \ln(10). \end{aligned} \quad (6)$$

and a plot of $pH - \log \frac{\alpha}{1-\alpha}$ versus α extrapolated to intercept the ordinate axis at $\alpha=0$ ($\alpha \rightarrow 0, \psi_a \rightarrow 0$) will, for any ionic strength, yield $pK_{(HA)_v}^{int}$. The effect of ionic strength upon such a plot comes from its influence upon the value of ψ_a as α is varied.

With crosslinked polyelectrolytes (gels) the pH of the gel is inaccessible to direct measurement. As a consequence, study of the potentiometric properties of weakly acidic gels has had to be based upon the pH of the external solution phase in equilibrium with the gel phase. The net result has been that these properties are observed to be a sensitive function of (1) the water content of the gel (which depends on the flexibility of its matrix) and (2) the ionic strength of the aqueous medium.

At a fixed ionic strength and α value, the $pK_{(HA)_v}^{app}$ of the repeating monomer unit appears to increase with the matrix rigidity which is in turn controlled by the quantity of crosslinking agent used in the gel manufacture. Indeed, it becomes possible to estimate the percent divinyl benzene employed in the crosslinking of a polymethacrylic acid gel from the effect of the resultant matrix flexibility on the value of pK . The effect of increasing ionic strength, on the other hand, is to decrease the measured pK .

In both instances, plots of $pK_{(HA)_v}^{app} (pH - \log \frac{\alpha}{1-\alpha})$ versus α parallel each other, the value of pK as a function of α being higher the lower the ionic strength and the higher the rigidity (crosslinking) of the gel. Unlike the linear polyelectrolyte, no convergence of such curves is observed^{4,5} as α approaches zero (Fig. 2) and a unique microscopic pK cannot be resolved for the repeating functional unit of the macromolecule.³

To understand this result we must return to our earlier analysis of the protolytic behavior of the weakly acidic linear polyelectrolyte. Again let us define the intrinsic microscopic acid dissociation constant of the repeating functional group, HA , with eq. (1). However, at this point, it is important to realize that this system is most closely comparable in its equilibrium properties to a solution of the linear polyelectrolyte separated from simple salt solution at various concentrations by a membrane impermeable only to the macromolecule. By restricting partially the osmotic entry of water to the polyelectrolyte solution by the tension of a flexible spring attached to the membrane, the gel-simple salt system is approximated. In this situation, (H_a) must be related with eq. 2 to (H^+) , the activity of H^+ ion in the polyelectrolyte containing compartment. With the gel (H_a) is therefore

related to (H_g^+) the activity of H^+ ion in the gel phase as shown:

$$(H_a^+) = (H_g^+) e^{-F\psi_a/RT}, \quad (2a)$$

where ψ_a is now the potential difference between the charged polyelectrolyte framework and the bulk solution of the gel. Since (H_g^+) is not directly accessible experimentally, it must be calculated. Marinsky and Slota³ have recently shown that in a system consisting of a solution of strong acid, HX, and its salt, MX, in equilibrium with a gel, the distribution of M^+ and H^+ between the solution and gel phases is given by⁶:

$$\frac{(H^+)}{(M^+)} = \frac{(H_g^+)}{(M_g^+)}. \quad (7)$$

From eqs. (1), (2a) and (7) one then obtains:

$$K_{(HA)_v}^{int} = (H^+) \frac{(M_g^+)}{(M^+)} \times \frac{\alpha}{1-\alpha} \times e^{-F\psi_a/RT}, \text{ or}$$

$$pK_{(HA)_v}^{int} = pH - \log \frac{\alpha}{1-\alpha} + p(M_g^+) - p(M^+) + F\psi_a/RT \ln 10. \quad (3a)$$

The value of (M_g^+) , like the value of (H_g^+) , is not measurable and must be calculated. For this purpose, $[M_g^+]$, the concentration of M^+ in the gel phase is obtained first in the following way:³ The volume of the gel phase is measured and a charge balance, based on (1) the stoichiometry of the neutralization reaction and (2) the requirement that the condition of electroneutrality be satisfied, is made to define the quantity of M^+ entering the gel during neutralization of $(HA)_v$. Imbibement of the gel phase by MX, presumed accountable by a simple Donnan equilibrium,⁹ corrects for the introduction of additional M^+ . By introducing the value of $[M_g^+]$, so computed, into eq. 3a

$$pK_{(HA)_v}^{int} = pH - \log \frac{\alpha}{1-\alpha} + p[M_g^+] - \log \gamma_{M_g^+} - p(M^+) + F\psi_a/RT \ln (10) \quad (3b)$$

$$\text{and } pK_{(HA)_v}^{app} = pH - \log \frac{\alpha}{1-\alpha} + p[M_g^+] - \log \gamma_{M_g^+} - p(M^+) \quad (6a)$$

then

$$pK_{(HA)_v}^{int} - \log \gamma_{M_g^+} - F\psi(a)/RT \ln (10) = pK_{(HA)_v}^{app} \quad (6b)$$

Plots of $pK_{(HA)_v}^{app}$ versus α obtained from experiments at low ionic strength (and thus negligible imbibement of the gel by MX), when extrapolated to intercept the ordinate axis at $\alpha=0$, will yield the $pK_{(HA)_v}^{int}$ value of the repeating monomer unit, deviations from ideality being expected to vanish when the gel surface charge is zero.

The procedure, as outlined, has been applied to a crosslinked polymethacrylic acid gel (Amberlite/RC-50, Rohm and Haas Company) and to a Sephadex gel (C-50-120, Sigma Chemical Company), using dilute sodium polystyrenesulfonate solution in place of simple dilute electrolyte (MX).³ The $pK_{(HA)_v}^{int}$ values of 4.83 and 3.25, respectively, that were resolved are in excellent agreement with the $pK_{(HA)_v}^{int}$ values obtained for their linear analogs^{2,10,11} demonstrating the validity, as well as the utility, of this approach. Indeed, this approach, when applied to the potentiometric data obtained with a Sphagnum peat, NaCl system⁴ leads as shown in Fig. 3 to convergence of the parallel lines (Fig. 2) that resulted when these data were examined earlier with eq. 6.

To demonstrate how great the discrepancy between $pK_{(HA)_v}^{app}$ values computed directly from the measured solution pH (eq. 6) and the model-deduced $pH_{(g)}$ (eq. 6a) can be these two sets of values obtained for the polymethacrylic acid gel system are plotted in Fig. 4 as a function of α .³

The potentiometric behavior of the flexible Sephadex gel at different ionic strengths (I) is especially interesting. When the value of $pK_{(HA)_v}^{app}$ is based on the solution phase pH plots of this function versus α for data obtained at different I values yield curves which, as expected, do not converge to a unique intrinsic $pK_{(HA)_v}^{int}$ value at $\alpha=0$. However, neither do they parallel each other, their slope, as a function of α , being greater the lower the ionic strength. These data are presented in Fig. 5 and are based on potentiometric measurements made with solutions whose ionic strength was defined by high molecular weight polyelectrolyte, sodium polystyrene sulfonate, as mentioned above.¹² Use of this fully dissociated polyelectrolyte led to minimization of sodium imbibement so that accurate assessment of the quantity of Na^+ ion entering the gel phase at each neutralization value could be based on the stoichiometry of the neutralization reaction. Reexpression of the potentiometric data with equation 6a and replotting $pK_{(HA)_v}^{app}$, so obtained, in Fig. 6 yields curves typical of a linear polyelectrolyte. The curves converge at $\alpha=0$ to yield the $pK_{(HA)_v}^{int}$ value characteristic of carboxymethyl dextran, its linear analog. The increasing divergence of $pK_{(HA)_v}^{app}$ with α as I decreases is typical of the potentiometric behavior of linear polyelectrolytes as their concentration in solution decreases. The more expanded the gel the less concentrated it is in its gel phase solution and the lower is the counterion density. Screening of counterions from the charged polymer surfaces is less with a consequent enhancement of counter-ion density near the polymer sites.

B. Identification of the True Physical State of Colloidal and Particulate Suspensions

We can see from the above that the potentiometric properties of weakly acidic polymeric substances dispersed in aqueous solution as colloidal or particulate suspensions can yield special insight with respect to their physical configuration in these dispersions. The shape of plots of $\text{pH} - \log \frac{\alpha}{1-\alpha}$ versus α from the data obtained during their titration in the presence of different concentrations of simple salt can differentiate, as we have pointed out, between their existence in the system as a variably charged surface (two dimensional) or an ordered three-dimensional arrangement (gel) of functional units repeated in the macromolecule and can even yield insight with respect to their rigidity or flexibility if a gel. Indeed this capability for easily and simply distinguishing these physical states in these kinds of systems is quite important and useful to the eventual understanding of the various equilibria encountered (eg., metal-ion binding) with these substances.

C. An Example of the Utility of this Approach

The anomolous results that had been reported in earlier potentiometric studies of alginic acid^{13,14} led to the selection of this substance for examination with the above approach. Chowdhury and Roman¹⁵ had already suggested that the potentiometric properties observed by them for alginic acid might in some way be attributed to phase separation and it seemed a most appropriate material to use for this purpose.

A representative compilation of potentiometric data obtained with alginic acid in the presence of various concentrations of simple neutral electrolyte (NaCl, and in a few instances NaClO₄) are presented in Fig. 7 as plots of $pK_{(AA)}^{app}$ ($pH - \log \frac{\alpha}{1-\alpha}$) versus α . The data points collected in 0.01 M salt are from three separate experiments at this ionic strength.¹⁶ Because of their scatter three straight lines have been drawn to represent these separate results, with the center line presumed to yield a reasonably averaged result of the three sets of data. The scatter in these data are somewhat greater than at the higher ionic strength values where the deviation range is approximately 0.06 pK units.

From this figure we see that the potentiometric behavior of alginic acid as a function of ionic strength, like the Sephadex gel, seems to possess characteristics associated with both polyelectrolyte and gel behavior. For example the vertical displacement of $pK_{(AA)}^{app}$ as a function of α , decreases with ionic strength as it would with a polyelectrolyte. However the data points do not converge to a unique value when extrapolated to intercept the ordinate axis at $\alpha=0$. This result suggests that gel configuration is a factor in determining the observed $pK_{(AA)}^{app}$ behavior as a function of ionic strength as it was with the Sephadex.

One can attribute the tendency to convergence of the curves with decreasing α to screening of the charged polymer aggregate surface by imbibed salt. At low concentrations of neutral salts the surface charge in these loosely aggregated lattices is not as effectively screened as it is when larger concentrations of salt are used to define the ionic strength.

The imbibement of salt by the highly flexible arrangement of the three dimensional assembly of alginic acid can also account for the smaller than expected vertical displacement of the intercept with ionic strength that is observed. The pK value resolved from analysis of the potentiometric data obtained in 0.3 M NaCl is 3.1. At this ionic strength the invasion of the AA microgel is such that the concentration and acidity of Na^+ ion inside and outside the lattice aggregate are essentially the same. As a result $pH_{(g)} \approx pH$ and the computed value of $pK_{(HA)_v}^{app}$, essentially invariant with α because of effective screening of the AA surface charge by the imbibed NaCl, should correspond to the $pK_{(HA)_v}^{int}$ of the AA.

Further supporting evidence for the estimate that AA exists as a microgel in the presence of simple salt is difficult to develop by any straightforward analysis of the data that are presented in Fig. 7. Indeed, in order to provide any additional arguments for the presumed conformational property of AA in simple salt, reasonable estimates of $pH_{(g)}$ for a proper evaluation of $pK_{(AA)_v}^{app}$ on the basis of its presumed gel conformation must be sought. In our first attempts to accomplish this objective the "gel" volume and the pattern of volume change with neutralization of the alginic acid was based on volume measurements made earlier on the very flexible Sephadex gel.³ This procedure was believed justified by the fact that both Sephadex (carboxymethyl dextran) and alginic acid are polysaccharides of similar structure.

The $pK_{(AA)_v}^{app}$ values resolved at the various degrees of neutralization by this approach are listed in Table I for the four ionic strengths examined.

Table I. Estimates of $\overline{pK}_{(HA)_v}^{app}$ Assuming Sephadex Gel Behavior Directly
Applicable to Alginic Acid

0.01 M NaCl		0.03 M NaCl		0.10 M NaCl		0.30 M NaCl	
α	$pK_{(AA)_v}^{app}$	α	$pK_{(AA)_v}^{app}$	α	$pK_{(AA)_v}^{app}$	α	$pK_{(AA)_v}^{app}$
0.22	2.96	0.25	3.07	0.3	3.14	0.36	3.05
0.34	2.90	0.38	3.15	0.4	3.14	0.46	3.08
0.63	2.87	0.61	3.03	0.48	3.13	0.61	3.08
0.76	2.87	0.84	3.02	0.73	3.12	0.78	3.05
0.91	2.85	0.98	3.02	0.87	3.11	0.87	3.05

It is quite apparent from the results listed that initial estimates of $A_{(g)}^-/V_g$ may be (1) a little too high at the lowest ionic strength and (2) that $A_{(g)}^-/V_g$ apparently does not increase as α increases. Both these observations are not inconsistent with the discrepancy expected between the behavior of our model gel (Sephadex) and the more flexible "microgel" presumed to control the potentiometric properties of AA in simple salt media. First one could expect more solvent to enter the "microgel" phase at the lowest ionic strength (highest solvent activity) and second the volume of the more flexible microgel could be expected to expand sufficiently to maintain A^-/V_g essentially constant whereas the small degree of crosslinking in Sephadex resists somewhat such expansion through solvent entry to accommodate the increased ionic content during neutralization.

With this revised estimate of the situation the plot of $pK_{(AA)_v}^{app}$ versus α at the four-different ionic strength values converge as shown in Fig. 8 yielding (1) the expected $pK_{(HA)_v}^{int}$ value of 3.1 and (2) the increased variability of $pK_{(v)}^{app}$ with α . The sensitivity of $pK_{(HA)_v}^{app}$ to increasing α is most noticeable as well at the lowest ionic strength of the solution phase as expected.

On the basis of the above it can be concluded that the alginic acid employed in the studies described (1) exists as a microgel in the presence of simple salt and (2) is characterized by a $pK_{(HA)_v}^{int}$ of 3.1.

Corroboration of these deductions was obtained from the separate potentiometric studies carried out on AA samples after their conversion to inflexible water insoluble gels through crosslinking effected by reaction with epichlorohydrin. Analysis of the potentiometric behavior of the alginic acid gel with eq. 6a was facilitated by gel volume measurements directly accessible with this material. The $pK_{(HA)_v}^{app}$ values

computed as a function of α during equilibration in 0.1 and 0.3 M NaCl, respectively are presented in Fig. 9. The two curves converge to intercept the ordinate at a $pK_{(HA)}^{int}$ value of 3.1 to substantiate our earlier estimate of this parameter by assuming the existence of alginic acid dispersed in simple salt solution as a three dimensional aggregate (microgel).

From the above it is apparent that it is of utmost importance that the potentiometric properties of FA be carefully examined as a function of ionic strength to determine whether it is present in the systems of interest as a simple, mononuclear molecule, as a two-dimensional linear polynuclear molecule or as a three dimensional aggregate of molecules which defines a separate phase in the system.

Experimental^{17,18}

A. Potentiometric Studies

(a) Materials: The Armadale Bh Horizon FA^{19,20,21} prepared by A. W. Underwood (Chemistry Department, Carleton University, Ottawa, Canada) and received from D. Gamble (Chemical and Biological Research Institute, Department of Agriculture, Ottawa, Canada) was employed in the majority of experiments. Two other FA source (Waterton Pumphouse, June 1981) and (Suwanee River) received separately from R. L. Wershaw and M. Reddy (U. S. Geological Survey, Denver, Colorado), were used in a limited number of experiments for comparison. Reagent grade HCl, NaCl and NaOH were used in the experiments.

(b) Preparation, Standardization and Handling of Materials: Care was taken to keep the standard base free of CO₂ during storage and sampling. During addition of base to the various FA samples and the subsequent potentiometric measurements nitrogen gas was passed continuously over the surface of the solution. For standardization of the NaOH potassium acid phthalate, dried to constant weight, was used. The equivalence point of the titration was measured potentiometrically. Standardization of the HCl was performed potentiometrically as well using the standardized NaOH. The preparation of solutions at specified NaCl concentrations was affected by weighing the correct quantity of salt previously dried overnight at 105°C.

In the preparation of all solutions attempts were made to minimize bacterial growth. All water was boiled before use, the polyethylene bottles used to contain the equilibrating solutions were sterilized as

well before use. In some experiments a small quantity of toluene was added to the FA solutions.

c) Procedure: In the earlier studies¹⁷ fixed quantities of the Armadale FA and NaCl, weighed into polyethylene bottles were dissolved in 30.0 ml of triply distilled, deionized water. Solutions 1.5 to 3.0×10^{-3} M in FA and 0.001, 0.01, 0.1 and 1.0 M in NaCl, respectively were obtained in this way. Aliquot portions of 0.100 M NaOH were added to define the degree of dissociation of the FA in each sample. Equilibration time in these preliminary experiments prior to pH measurement was usually for 48 to 60 hours. In the later experiments¹⁸ approximately 0.1, 0.03 and 0.01 g samples of the Armadale FA were dissolved in 60.0 ml of triply distilled, deionized water. Five gram portions of these solutions, accurately weighed, were then diluted to 50 ml, reweighed, and made 0.10, 0.030, 0.010 and 0.0050 M in NaCl. Controlled amounts of standard sodium hydroxide (also weighed) solution containing the correct quantity of NaCl to maintain the ionic strength of the experiment were then added to eleven of the twelve samples to define a neutralization range from $\alpha = 0.3$ to $\alpha = 0.8$. A 2.5 ml Roger-Gilmont ultra precision micrometer buret was used to dispense the titrant. The samples were equilibrated for a period of greater than thirty days with pH measurements being made at three to four day intervals, after the first 24 hours. The samples were agitated continuously during equilibration at the ambient temperature, $25 \pm 2^\circ\text{C}$. The solution pH was measured with an Orion Research Microprocessor Ion Analyzer (901) instrument using a Radiometer combination electrode (GK 2321 C) as in the earlier experiments.¹⁷ Prior to and after the potentiometric measurements the glass electrode was calibrated as before¹⁷ with standard buffer solutions over the pH

range of the study. A Precision Scientific Model 154 constant temperature bath maintained the temperature of the solution at $25.0 \pm 0.1^\circ\text{C}$ during a measurement. A CO_2 -free atmosphere over the sample was, as mentioned above, affected by covering the surface of the solution with N_2 gas.

Because of the small quantity of Waterton Pumphouse and Suwanee River FA accessible to us (~ 0.05 g and 0.02 g) only a few experiments could be performed with this material to compare its potentiometric properties with those of the Armadale FA. About 0.01 g of these materials were dissolved in 60 ml of distilled, deionized water and divided into 12 five gram portions further diluted to 50 ml as before. The solutions were made 0.005 M in NaCl and equilibrated for one week with the first potentiometric measurements made after a 24 hour interval. Re-assessment of the potentiometric properties of these samples at the higher ionic strength of 0.10 M required only the controlled addition of NaCl crystals to each of the samples and another week of equilibration.

FA capacities employed in the final analysis of the data were eventually based on pH measurements made after a 24 hour equilibration period, the maximum change in pH with increment of base defining the equivalence point.

B. Europium Complexation Studies

(a) Materials: Analytical grade Dowex 50 W-X8, 50-100 mesh was obtained from the Bio-Rad Company. The radioactive isotope - Eu^{154} - was purchased from the New England Nuclear Corporation of Boston, Mass.

(b) Preparation, Standardization and Handling of Materials: The resin was prepared for use in the experimental program by recycling it once

after conversion to the Na^+ -ion form with excess 0.1 M NaOH in 0.1 M NaCl. The resin, in the Na^+ ion form was washed with distilled, deionized water to remove imbibed salt. It was then returned to the H^+ ion form by using progressively more concentrated HCl (0.1 M, 0.3 M, 1.0 M, 3.0 M) solutions for its conversion. The resin was then eluted with progressively more dilute HCl solutions (1 M, 0.3 M, 0.1 M, 0.05 M, 0.01 M) and finally triply distilled water until the pH of effluent and influent were the same. With each progressive dilution and concentration of reagents employed when necessary during the resin recycling operation rapid expansion and contraction of the resin column was avoided. Neglect of this aspect could have resulted in shattering of the column. The resin was then reconverted to the Na^+ -ion form with a sizeable excess of 0.1 M NaOH in 0.1 M NaCl. After complete conversion to the Na^+ -ion form the resin was washed with triply distilled, deionized water until the pH of the influent and effluent were the same and a test of the effluent with acidified AgNO_3 showed the complete absence of Cl^- ion. This resin product was then transferred, after suction filtration through a coarse glass frit, to evaporating dishes with large surfaces. These dishes were stored over saturated NH_4NO_3 in closed desiccators until the water content of the resin reached isopiestic equilibrium with the saturated NH_4NO_3 solution.

Upon equilibration, the resin was transferred to wide-mouthed polyethylene bottles and stored stoppered in the same desiccators over the saturated NH_4NO_3 solution. Their capacity was measured by the isotope dilution method: Accurately weighed one half to one gram resin samples were equilibrated with accurately measured quantities of 0.100 M NaCl already containing the radioactive nuclide, Na^{22} . Previously weighed one gram samples of this initial solution were sampled for

comparison of their Na^{22} content with the Na^{22} content of the same quantity of solution measured precisely after equilibration with the resin for at least a 24 hour period.

Concurrent with the transfer of one half to one gram resin samples for Na^+ -ion capacity measurement with the isotope dilution method additional samples were removed from the polyethylene storage bottles for water content measurement. These samples, precisely weighed, were dried to constant weight at 60°C by placing them in a vacuum oven maintained at a reduced pressure ($\sim 10^{-1}$ to 10^{-2} Hg) by the continuous action of a vacuum pump.

To assure accuracy in water content assay during the course of the research program these measurements were repeated periodically to accompany later sampling of resins for the Eu^{154} distribution measurements. Such regular reassessment of resin water content was considered a necessary precaution to monitor any loss of solvent from the resin during its periodic exposure to the ambient atmosphere of the laboratory during sampling.

Solvent and solute uptake by the resin as a function of the NaCl concentration employed in an experiment were known from earlier studies in our laboratory.²² These data could be used to estimate water and solute uptake by the resin, the water content of all resin samples being always smaller at the start of an experiment because of the lower water activity of the saturated NH_4NO_3 solution used in their preparation. In most cases, however, the stoichiometry of the system was not strongly affected by neglect of such correction of the data.

(c) Procedures: The Eu^{154} distribution studies in the presence and absence of FA were carried out using the batch equilibration method. First the distribution of Eu^{154} was examined as function of NaCl concentration to obtain a plot of $\log D_0$, where $D_0 = \frac{\text{activity Eu}^{154}/\text{g dry resin}}{\text{activity Eu}^{154}/\text{g NaCl soln}}$, versus the logarithm of the activity of the sodium chloride. To affect these measurements accurately weighed resin samples were equilibrated with measured quantities of NaCl solution at different concentrations ranging from 1.00 M to 0.100 M and containing Eu^{154} at an appropriate activity level. The activity of previously weighed one gram aliquots of these solutions, prior to and after equilibration with the resin for at least 24 hours, were then measured.

In the first experiments designed to compare the distribution, D_0 and D , of the Eu^{154} between resin and, respectively, FA-free and FA-containing NaCl solutions, accurately weighed resin samples were quantitatively transferred to weighed portions of the NaCl solutions at the predetermined molarity and an appropriate Eu^{154} activity level. These solutions, containing accurately measured quantities of FA, neutralized with standard base to define their degree of neutralization, were allowed to equilibrate for various periods of time prior to addition of the resin. After at least a 48 hour interval of equilibration with the resin, accurately measured one gram aliquot portions of each solution were removed for Eu^{154} measurement. One gram samples of each of the solutions were collected for activity measurement before contact with the resin to facilitate determination of the quantity of Eu entering the resin phase at equilibrium.

Attempts to study the complexation behavior of Eu^{+3} in the presence of HCO_3^- and $\text{CO}_3^{=}$ ion for comparison with its complexation behavior in the presence of FA were unsuccessful. The Eu^{154} slowly precipitated out of solution during the interval of a distribution measurement. Attempts to eliminate this irreversible behavior by addition of Eu carrier (10^{-7} to 10^{-6}M) did not succeed.

Finally in a series of experiments designed to simulate ground water conditions FA, at a concentration level of ~ 17 mg/l, was contained together with Eu^{154} in NaCl solutions where the total carbonate ($\text{CO}_3^{=} + \text{HCO}_3^-$) varied from 10^{-2}M to $2 \times 10^{-4}\text{M}$ and the pH from ~ 7.5 to 9.5; the total Na^+ ion was kept constant at 0.10 M or 0.010 M. The Eu^{154} distribution between measured quantities of Na^+ -ion form resin added to these solutions after their equilibration for up to 30-40 days was determined by measuring the level of Eu^{154} activity in these solutions before and after a greater than 48 hour interval of contact with the resin. In these systems the Eu^{154} remained in solution over the time interval of the experiment.

In the later experiments the concentration level of the FA solutions studied was at the ~ 20 ppm level as well. Their pH during equilibration with the resin was adjusted in most instances by the addition of standard base at the same concentration level as the NaCl medium employed in order to facilitate examination of an extended pH range without changing the concentration level of Na^+ ion. The pH measured at the time of sampling for radioactive assay of Eu^{154} was used to compute the quantity of dissociated (A^-) and undissociated FA(HA) by employing a pH versus A^- plot of the most reliable potentiometric data available for the FA

at the experimental ionic strength from measurements made after a 24 hour equilibration period. By this approach a reasonable assessment of A^- and HA in the resin, solution mixture could be made in spite of the presence of additional dissolved CO_2 inadvertently introduced during the extra handling of samples.

d) Miscellaneous: The measurement of the specific gamma ray activity of both Eu^{154} and Na^{22} in a particular solution was accomplished with a Canberra multichannel analyzer using a 3" x 3" Tl activated NaI crystal as the detector.

In all Eu^{154} distribution measurements a particular experimental condition was examined by splitting each solution under investigation into two approximately equal aliquot portion and contacting each of them with sizeably different quantities of resin. The objective of this experimental approach was to test the reliability of the procedures employed by the reproducibility in a D or D_0 measurement. If the ion-exchange process, presumed to be the basis of the measurement, was accompanied by anomolous sorption behavior of the Eu^{154} the extent of this problem was indicated by the lack of agreement in the measured D parameter. By maintaining the sample size the same to within a few percent, reproducibility in the geometry of each active source was assured to eliminate this experimental operation as a possible source of error in the estimate of Eu^{154} removal from the solution by the resin sample.

To minimize statistical error in assessment of the specific activity of Eu^{154} and Na^{22} , respectively, in a particular solution each measurement was continued until greater than 100,000 disintegration events had been detected. To assure reproducibility in counting the

gamma ray spectrometer was set at a voltage sufficiently high to assure detection of the complete spectrum of gamma rays characterizing the decay of both Na^{22} and Eu^{154} . This approach proved most accurate. Earlier attempts to confine the detection to a particular gamma ray were too sensitive to small drift in the voltage setting.

Results and Discussion

The great majority of experiments performed to examine the protolytic properties of FA were made with the Armadale FA source and estimates of the present state of understanding of these properties in FA are necessarily influenced most by the experimental results obtained with this material.

A. Potentiometric Studies: The potentiometric data compiled with the Armadale FA over the period of this study were not sufficiently reproducible to yield, with any certainty, the parameters of behavior sought. In our examination of the potentiometric properties of FA solutions it was observed that the capacity per gram of FA varied from sample to sample. In addition, the initial capacity of a FA sample, did not appear to persist over the equilibration period of thirty to forty days.

Studies of the potentiometric properties of a particular FA solution neutralized to different degrees showed that the pH of each sample increased on standing with each subsequent measurement, the change in pH being increasingly larger the greater the degree of neutralization. These increments in pH were eventually absent or barely noticeable after a thirty to forty day period. The highest pH reached in these studies, however, did not exceed a value of ~ 6.6 . In later experiments when the pH range was extended upward it was observed that the positive increments in pH with each subsequent measurement became smaller as the pH increased from ~ 6.8 to 7.1 eventually reaching a point beyond which the pH decreased increasingly in value with each subsequent measurement.

On the basis of these observations it was reported that the capacity of the FA appeared to change with time. Also when the 40-day measurements were analyzed using the new capacity the potentiometric properties of the FA appeared to be essentially unaffected by ionic strength or FA concentration. If based on the 24-hour measurement and the initial capacity the potentiometric properties appeared to be sensitive to both the ionic strength of the solution and the concentration of FA.

A less confusing determination of the dependence of the potentiometric properties of FA on (1) ionic strength (2) FA concentration and (3) time of equilibration than was accessible from these studies continued to be essential for the meaningful interpretation of the physical chemical properties of FA. With reliable information of this kind the physical state of the FA could be deduced to permit the educated examination of the FA-H^+ and FA-M^{n+} equilibria sought with the model described in the theoretical section of this report.

In our most recent attempt to remedy this situation a Fisher Isolator glove box was renovated to insure a capability for chemical manipulations in a CO_2 -free atmosphere. Solutions 20 ppm in FA and 0.0010, 0.010, 0.10 and 0.30 M in NaCl were prepared, as described earlier in the experimental section, with all operations carried out in the glove box. In one additional experiment the FA solution, 0.10 M in NaCl, was made eight times more concentrated. A flow of N_2 gas through the previously evacuated glove box defined the atmosphere during all manipulations with these samples. Twelve FA samples at each selected ionic strength were then neutralized with standard

CO₂-free NaOH to different degrees with the highest pH in each series of samples exceeding a value of 8. A 24-hour equilibration of all samples was affected by transferring the sealed samples from the glove box for storage in desiccators whose CO₂-free atmosphere was assured by ascarite granules spread over the bottom of each desiccator.

The only time these samples were not in a desiccator or the glove box was during their periodic pH measurement, our glove box being too small to carry out the pH measurements conveniently.

To monitor the above series of experiments a series of acetic acid solutions at the same concentration level as the FA (1.3 x 10⁻⁴M and 1.3 x 10⁻³M) was examined in exactly the same way. The potentiometric results obtained with these samples provided an accurate assessment of the efficiency of CO₂ elimination from our systems with the refined experimental procedures.

At the higher concentration elimination of CO₂ was sufficient to permit a correct analysis of the potentiometric data obtained with the acetic acid. The literature pK_A value for the acetic acid was obtained over the complete neutralization range after appropriate correction for non ideality at I=0.1. This was not the case at the lower concentration level. The pattern of pH change with time that was noted in our earlier studies continued to be observed, however, in both sets of acetic and fulvic acid samples but only at the higher pH values; at a pH ≤ 5.3 in the more dilute acid and at a pH ≤ 6.3 in the more concentrated acid samples. Since such potentiometric behavior in the acetic acid samples can only occur through introduction

of CO_2 into the samples it became quite apparent that our earlier studies at the 20 ppm concentration level had been unduly influenced by the presence of CO_2 . The extent of CO_2 contamination encountered in the improved potentiometric measurement program was accurately accessible in the acetic acid samples. An attempt was made to correct for CO_2 imbibement by projecting the observed uptake of CO_2 by the acetic acid samples to be duplicated in the FA samples. However, it was still not possible to resolve with precision the apparent pK pattern of the FA at the higher degrees of dissociation at each ionic strength examined. The equivalence point of the FA titration is approached more slowly than with the acetic acid. As a consequence, CO_2 sorption by the sample is a much more severe problem in the FA solutions at high neutralization values to explain this result.

That this is indeed the case may be seen from the comparison of the direct and 24-hour batch equilibration titration of the more concentrated FA sample that is presented in Fig. 10. Until a pH of 6.26 the titration curves are identical. Beyond this point the curves diverge. The equivalence point deduced from the direct titration is 11.5% lower than the value resolved from the batch equilibration measurements. With a parallel examination of the potentiometric titration of acetic acid at the same concentration level such divergence of pH beyond a value of 6.25 becomes unimportant since the equivalence point is reached rapidly enough to escape error from this source.

Apparently direct titration of FA samples for capacity measurement is more reliable than the batch-wise approach used almost exclusively in this research program. In the direct titration of the FA the pH

of the sample over most of the course of the titration is low enough to keep CO_2 sorption by the sample at a lower level eventually than can be achieved in the pH-measurement of the batch-equilibrated sample at an elevated pH.

(a) The capacity of Armadale FA - The concentration of the dilute acetic acid samples employed in the potentiometric measurement program was found to be 8.2% greater by direct titration with standard NaOH than the value based on analysis of their 10 and 75-fold more concentrated solutions. This discrepancy is attributable to the sorption of CO_2 during potentiometric titration of the more dilute acid sample. The quantity of CO_2 sorption, while insufficient to affect analysis of the more concentrated solution, was not reduced enough by the experimental procedures employed to remove it as an interference in the higher pH region.

We have presumed that the 8.2% error encountered in the dilute acetic acid samples was encountered in the dilute FA samples as well. The capacity measured for these samples has been reduced by this factor for estimate of the apparent pK of FA as a function of α but probably should be reduced more because of the greater sensitivity of the FA samples to error introduced by CO_2 in the equivalence point region.

(b) The Apparent pK of the Armadale FA as a Function of Ionic Strength - The exclusion of CO_2 by our refined experimental procedures has been shown to be sufficient to permit a precise analysis of potentiometric data obtained with acetic acid at a concentration level as low as $1.42 \times 10^{-3}\text{M}$ over the complete neutralization range.

The potentiometric data obtained with FA in 0.1 M NaCl at this same concentration level was shown to be equally accurate using the data obtained during direct titration. We believe we have obtained an accurate description of the apparent pK behavior of the FA as a function of α in this instance. The results of these computations are presented in Fig. 11.

With the most dilute acetic acid it was also possible, by using the corrected concentration value, to obtain the literature pK value of 4.75, over a part of the pH range of the titration. However above a pH value of 5.6 the computed pK became progressively smaller and a correction for the concurrent formation of bicarbonate ion with acetate ion had to be made to obtain the correct pK value of 4.75. With this approach it was possible to obtain an accurate estimate of the contribution as a function of pH, of CO_2 sorption to neutralization of the standard base. The logarithm of the quantity of HCO_3^- computed to be formed in these samples in this way is plotted in Fig. 12 versus the pH measured for each sample and demonstrates the exponential increase in CO_2 , ie, HCO_3^- involvement, as the neutralization of the acid progressed. These data show where CO_2 becomes a complicating factor in the computation of the apparent pK of FA as a function of degree of neutralization and only those pH measurements which are unaffected have been employed to compute the apparent pK of the FA in these samples. These points are plotted in Fig. 11 together with the apparent pK values compiled with the 8-fold more concentrated FA sample. The other pH data obtained with the more dilute FA samples are not used because the estimate of CO_2 involvement that

was necessary for their proper analysis could not be made with sufficient accuracy as we have already pointed out. When it was assumed that CO_2 involvement in the acetic acid samples was exactly duplicated in the FA samples as the pH increased the pK values so obtained deviated seriously from the pattern expected.

In comparing the apparent pK values plotted in Fig. 11 it must be remembered that the capacity used to evaluate the apparent pK values for the more dilute FA samples may still be overestimated. However, qualitatively the pattern of apparent pK values as a function of ionic strength is probably correct. There is a sizeable displacement downward of the curves with ionic strength; ~ 0.5 pK units going from $I=0.01$ to 0.1 and ~ 0.1 pK units going from 0.1 to 0.3 . The effect of ionic strength on the apparent pK of the FA reaffirms our earlier estimate that this parameter is a sensitive function of ionic strength. From this behavior the existence of FA in these solutions as a separate phase, ie, as a three dimensional molecular aggregate, is further substantiated. However the direct proportionality between K_A and ionic strength that was suggested from earlier potentiometric data obtained after a 24 hour interval is not fully substantiated in these somewhat more accurate studies. More precise assessment of FA capacity in future studies are necessary to quantify this aspect.

The effect of FA concentration, at a fixed ionic strength, is, however, most surprising. By increasing the concentration of FA a factor of approximately eight the apparent pK parameter is reduced by ~ 0.7 pK units over the α range that such a comparison can be made. This experimental variable apparently deserves careful study.

It is interesting to note that for the system where the complete potentiometric response is believed to be known quite precisely over the complete neutralization range an S-shaped curve continues to characterize the plot of apparent pK versus α . This result was attributed earlier to heterogeneity of the FA samples that could result from as few as three acidic groups with different dissociation properties. To examine this explanation of the S shape an experimental potentiometric plot is compared in Fig. 13 with points synthesized by presuming the existence of three different acidic groups with pK values of 3.0, 4.0 and 6.0 to be present at a molar ratio of 3 to 2 to 5, respectively. The agreement between the experimental curve and the position of the calculated points is sufficient to lend some credence to the suggestion that such heterogeneity in FA samples may be the primary reason for the S-shaped curves.

(c) Summary of Present State of Knowledge - Our present state of knowledge with respect to the potentiometric properties of the Armadale FA (as well as our other FA sources) is summarized below:

- i) The Armadale FA source is heterogeneous and its capacity varies from sample to sample.
- ii) Analysis of potentiometric behavior of the FA after a 24 hour equilibration period indicates that the apparent pK, based upon the solution pH, is affected by ionic strength and FA concentration. At a low ionic strength the apparent pK is higher than at a high ionic strength. The existence of FA in our solutions as a separate phase, i.e., as a molecular aggregate or "microgel" seems to be unambiguously demonstrated by this result. The fact that the pK is lowered by increasing

FA concentration appears to indicate the formation of a more compact aggregate.

iii) The shapes of all but one of the potentiometric plots in Fig. 11 cannot be accurately defined, even in the limited α range that this is attempted, but there is sufficient precision in the data to deduce that the FA gel aggregate is flexible. At a fixed ionic strength of 0.10 the gel apparently contracts with increasing concentration of FA; the absence or presence of a linear polyelectrolyte effect that would be discernible in a flexible gel through the divergence of such curves with increasing α cannot be excluded as a possibility since this aspect would be most noticeable of course, in the high α region that is least susceptible to accurate analysis. A more precise estimate of gel flexibility has to come from studies in which CO_2 is more completely excluded from the system.

iv) Our most recent examination of the capability for CO_2 exclusion from samples in the potentiometric measurements program has shown that CO_2 absorption by each sample during the pH measurements led, at least in part, to (1) overestimate of the capacity of FA samples in the earlier studies; to (2) the shifts in potential over equilibration periods of thirty to forty days that were observed during each periodic measurement; and to (3) the apparent change in capacity of the FA over this time interval.

To resolve the ambiguities and unresolved questions listed in the above summary of results, i.e., the effect of FA concentration at a fixed ionic strength, the quantitative effect of ionic strength at a fixed FA concentration and the effect of equilibration time on the

observed potentiometric properties; and to deduce from a comparison of the shapes of the apparent pK versus α curves compiled over the complete neutralization range for FA at the several different ionic strength levels examined the flexibility and the extent of expansion or contraction of the FA molecular aggregates into a separate phase at least an order of magnitude more effective exclusion of CO_2 from the FA solutions than has been obtained in the course of the most recent potentiometric measurements must be achieved. Future potentiometric measurement programs must strive for the performance of all operations in the CO_2 -free atmosphere of our glove box.

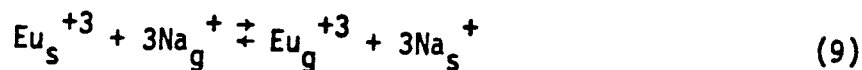
B. Complexation Studies.

In order to examine the complexation behavior of Eu^{+3} in the presence of FA it was necessary to be able to evaluate, with accuracy, the relative concentration of free (Eu_f^{+3}) and complexed (Eu_b^{+3}) europium in the various FA, NaCl systems selected for study. Such information could be reliably deduced from a comparison of the distribution of trace-level concentrations of Eu^{+3} between a cation exchange resin in the Na^+ -ion form and FA-free, D_0 , and FA-containing, D , NaCl solutions at the same chloride concentration level. In the FA-containing solutions the quantity of FA was kept low enough to assure that the Na^+ -ion concentration level was close enough to that of the FA-free solution to keep the effect of salt concentration differences well within the experimental error range of the measurement.

The ratio of complexed and free Eu^{+3} was calculated as shown:

$$\frac{\text{Eu}_b^{+3}}{\text{Eu}_f^{+3}} = \frac{D_0 - D}{D} \quad (8)$$

This relationship is derived as follows:²³ The exchange of trace levels of Eu^{+3} for Na^+ in the resin can be expressed by the reaction



the subscripts s and g referring to the solution and gel phases, respectively. At equilibrium

$$\frac{(\text{Eu}_g^{+3}) (\text{Na}_s^{+3})}{(\text{Eu}_s^{+3}) (\text{Na}_g^{+3})} = K \quad (10)$$

$$\text{where } \frac{\text{Eu}_g^{+3}}{\text{Eu}_s^{+3}} = \frac{\text{Eu activity/second/g NaR (dry)}}{\text{Eu activity/second/g solution}} = D_0 \quad (11)$$

By using trace level concentrations of Eu^{+3} the composition of the resin phase is unchanged in all equilibria studied so that Na_g^+ as well as K are constant parameters of the system. The ratio of Eu^{+3} in the resin and solution, i.e., D_0 , is then an inverse function of $(\text{Na}^+)^3$ and

$$\log D_0 = \log K (\text{Na}_g^+) - 3 \log (\text{Na}^+) \quad (11a)$$

as long as the invasion of the resin phase by NaCl is negligible compared to the value of (Na_g^+) . That this is indeed the case can be seen from a plot (Fig. 13) of $\log D_0$ values measured in this study versus the logarithm of the mean molal activity of the FA-free sodium chloride employed. The slope of -3.1 resolved for the resultant straight line is sufficiently close to the value of -3.0 that is predicted to attest to the reliability of both the measurements and the assumptions made in the development of eq. 11a.

In the presence of FA the measured distribution, D, of the carrier-free radioactive isotope of europium, Eu^{154} , between resin and solution

is equal to the ratio of Eu^{+3} in the resin and the sum of Eu^{+3} species, free and FA-complexed, in solution:

$$D = \frac{\text{Eu}_g^{+3}}{\text{Eu}_s^{+3} + \text{Eu}_{bs}^{+3}} \quad (12)$$

where the subscript bs refers to the europium-complexed species in the solution. If the numerator and denominator of eq. 12 is divided by Eu_s^{+3}

$$D = \frac{\frac{\text{Eu}_g^{+3}}{\text{Eu}_s^{+3}}}{\frac{\text{Eu}_s^{+3}}{\text{Eu}_s^{+3}} + \frac{\text{Eu}_{bs}^{+3}}{\text{Eu}_s^{+3}}} = \frac{D_o}{1 + \frac{\text{Eu}_{bs}^{+3}}{\text{Eu}_s^{+3}}} \quad (13)$$

This equation can, in turn, be transformed to

$$\frac{D_o - D}{D} = \frac{\text{Eu}_{bs}^{+3}}{\text{Eu}_s^{+3}} \quad (14)$$

the function essential to our study of the complexation of Eu^{+3} by FA.

(a) Eu^{154} Distribution Studies in the Presence of FA

Initially, the complexation of Eu^{154} by FA was studied as a function of FA concentration, pH and ionic strength. At the highest ionic strength (1.0 M NaCl) the sorption of Eu^{154} by the resin was not responsive to either variation in the degree of FA neutralization or the quantity of resin employed. Such anomalous distribution behavior was encountered less frequently in the 0.30 M NaCl system and was completely absent at the lowest ionic strength of 0.10 employed in these preliminary studies. Only those distribution data which were appropriately sensitive, in duplicate experiments, to variation in resin quantities employed are presented in Table II. In this table we have listed the solution pH

Table II. The Complexation of Eu^{+3} by FA as deduced from Ion-Exchange Distribution Studies with Armadale FA

A. System: 1.8×10^{-3} M FA; 1.0M NaCl; $D_0 = 2.20 \times 10^2$

Sample No.	pH	α	D	K_{Ex}
1A	3.179	0.44	21.8	6.0
8B	3.090	0.422	50.5	2.6
8B	3.084	0.421	56.6	2.3

B. System: 9.0×10^{-4} M FA; 0.30 M NaCl; $D_0 = 8.15 \times 10^3$

Sample No.	pH	α	D	K_{Ex}
2	3.604	0.417	45.5	8.5×10^1
3	3.678	0.424	32.5	1.0×10^2
4	3.747	0.441	32.6	8.9×10^1
5	3.831	0.455	38.8	6.3×10^1
6	3.82	0.455	34.9	7.1×10^1

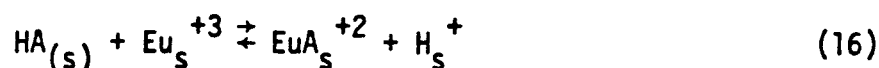
C. System: 9.0×10^{-4} M FA; 0.10 M NaCl; $D_0 = 2.2 \times 10^5$

Sample No.	pH	α	D	K_{Ex}
15A,15B	3.917	0.352	42.4	1.03×10^3
1A,1B	3.89	0.345	48.8	9.38×10^2
2A,2B	3.964	0.363	43.7	9.21×10^2
3A,3B	4.064	0.375	35.8	9.11×10^2
4A,4B	4.104	0.382	34.4	8.73×10^2
5A,5B	4.282	0.432	26.0	8.50×10^2
6A,6B	4.243	0.426	22.4	1.07×10^3
7A,7B	4.453	0.460	16.0	9.71×10^2
8A,8B	4.469	0.462	14.7	1.02×10^3
9A,9B	4.662	0.489	9.44	1.08×10^3
10A,10B	4.795	0.525	9.50	8.45×10^2
11A,11B	4.999	0.560	3.15	1.69×10^3

at equilibrium, the degree of neutralization, α , the measured distribution coefficient, D , and the exchange coefficient, K_{Ex} , where

$$K_{Ex} = \frac{D_0 - D}{D} \frac{(H^+)}{(HA)} = \frac{(Eu_{bs}^{+3})(H_s^+)}{Eu_s^{+3}(HA_s)} \quad (15)$$

Such treatment of the experimental data allows consideration of the interaction of Eu^{+3} with FA by the following simplest reaction path



by identifying Eu_{bs}^{+3} with $EuA_{(s)}^{+2}$.

In further examinations of the Eu^{154} (III), FA NaCl system the NaCl concentration seldom exceeded 0.1 M and the FA concentration was always kept lower than 1.0×10^{-3} M. These concentration boundary limits were defined by the incidence of anomolous distribution behavior of Eu^{154} (III) when these concentration levels were exceeded in the earlier study. In the later studies the Waterton Pumphouse FA and the Suwannee River FA, as well as the Armadale FA, were employed. The data compiled and their correlation with eq. 15 are presented in Tables III through IX.

The distribution and K_{Ex} data obtained with the Armadale and Waterton FA are listed in Tables III and IV. A limited set of data obtained with the Suwannee River FA is listed in Table V. The Suwannee River samples used in this part of the study were prepared from FA initially dissolved in 0.005 M NaCl for potentiometric study. Solid NaCl was added to these samples to increase the salt concentration to 0.010 M. After Eu^{154} was added aliquot portions were removed for equilibration with accurately weighed quantities of resin. The pH was adjusted in all but two of the samples by adding 0.010 M NaOH to obtain the higher pH values reported in Table IV. To obtain Table VI some of the samples used for

Table III. The Complexation of Eu(III) by FA as Deduced from Ion-Exchange Distribution Studies.

System: 1.80×10^{-4} M FA (Armadale); 0.010 M NaCl; $D_0 = 2.20 \times 10^8$

Sample No.	pH	HA Molarity	D	K_{EX}
1a	4.758	1.10×10^{-4}	337	1.04×10^5
1b	4.705	1.11×10^{-4}	354	1.10×10^5
2a	5.653	8.43×10^{-5}	47.3	1.23×10^5
2b	5.625	8.84×10^{-5}	49.0	1.20×10^5
3a	4.908	1.07×10^{-4}	160	1.61×10^5
3b	5.008	1.04×10^{-4}	129	1.61×10^5
4a	5.905	7.49×10^{-5}	35.7	1.02×10^5
4b	5.821	7.89×10^{-5}	35.3	1.19×10^5
5a	4.958	1.04×10^{-4}	156	1.50×10^5
5b	4.992	1.03×10^{-4}	158	1.40×10^5
6a	6.603	3.29×10^{-5}	10.1	1.66×10^5
6b	6.390	5.49×10^{-5}	8.10	2.01×10^5
7a	5.332	9.62×10^{-5}	62.7	1.70×10^5
7b	5.269	9.31×10^{-5}	49.3	2.58×10^5
8a	6.909	1.99×10^{-5}	12.0	1.13×10^5
8b	7.249	9.95×10^{-6}	10.3	1.21×10^5
9a	8.140	1.46×10^{-6}	7.23	1.51×10^5
9b	7.725	3.83×10^{-6}	9.33	1.16×10^5
10a	9.128	1.51×10^{-7}	7.41	1.47×10^5
10b	10.321	9.67×10^{-9}	8.10	1.34×10^5
11a	8.426	7.56×10^{-7}	6.76	1.61×10^5
11b	7.960	2.19×10^{-6}	9.67	1.14×10^5
12a	7.460	7.99×10^{-6}	9.25	1.04×10^5
12b	7.168	1.19×10^{-5}	13.7	0.91×10^5
13a	7.526	4.93×10^{-6}	9.13	1.45×10^5
13b	7.956	2.39×10^{-6}	9.08	1.12×10^5
14a	7.652	2.96×10^{-6}	8.35	1.98×10^5
14b	7.665	2.96×10^{-6}	8.51	1.96×10^5

Table III. (Continued)

15a	7.572	3.94×10^{-6}	8.15	1.84×10^5
15b	7.835	3.13×10^{-6}	6.83	1.50×10^5
16a	7.869	2.93×10^{-6}	6.52	1.56×10^5
16b	7.657	4.73×10^{-6}	6.27	1.63×10^5
17a	7.716	3.83×10^{-6}	5.28	2.07×10^5
17b	8.445	7.33×10^{-7}	4.23	2.54×10^5
18a	9.914	1.12×10^{-8}	4.22	2.58×10^5
18b	9.611	4.95×10^{-8}	3.59	3.03×10^5
19a	8.818	3.08×10^{-7}	4.13	2.63×10^5
19b	9.084	1.67×10^{-7}	4.89	2.22×10^5
20a	9.400	8.07×10^{-8}	2.90	3.74×10^5
20b	9.314	9.84×10^{-8}	3.36	3.23×10^5

Table IV. The Complexation of Eu(III) by FA as Deduced from Ion-Exchange Distribution Studies.

System: 9.90×10^{-5} M FA (Waterton); 0.010 M NaCl; $D_0 = 2.20 \times 10^8$

Sample No.	pH	HA Molarity	D	K_{EX}
1	4.433	6.54×10^{-5}	4.39×10^4	2.82×10^3
2	4.462	6.50×10^{-5}	4.70×10^4	2.49×10^3
3	4.540	6.30×10^{-5}	3.90×10^4	2.58×10^3
4	4.565	6.22×10^{-5}	3.70×10^4	2.60×10^3
5	4.623	6.05×10^{-5}	2.20×10^4	3.94×10^3
6	4.646	6.00×10^{-5}	2.90×10^4	2.86×10^3
7	4.727	5.80×10^{-5}	1.70×10^4	4.18×10^3
8	4.726	5.80×10^{-5}	1.40×10^4	5.09×10^3
9	4.824	5.55×10^{-5}	1.50×10^4	3.96×10^3
10	5.321	4.32×10^{-5}	1.30×10^4	1.87×10^3
11	5.011	5.10×10^{-5}	1.70×10^4	2.47×10^3
12	4.834	5.55×10^{-5}	1.50×10^4	3.87×10^3
13	5.355	4.22×10^{-5}	5.70×10^3	4.04×10^3
14	4.879	5.40×10^{-5}	5.80×10^3	9.28×10^3
15	5.193	4.60×10^{-5}	6.00×10^3	5.11×10^3
16	5.297	4.38×10^{-5}	6.50×10^3	3.90×10^3
17	6.072	2.70×10^{-5}	1.50×10^3	4.60×10^3
18	6.568	1.78×10^{-5}	1.30×10^3	2.57×10^3
19	6.413	2.06×10^{-5}	8.80×10^2	4.69×10^3
20	6.872	1.28×10^{-5}	8.00×10^2	2.89×10^3
21	5.667	3.50×10^{-5}	2.30×10^3	5.88×10^3
22	5.610	3.65×10^{-5}	3.00×10^3	4.93×10^3
23	6.065	2.68×10^{-5}	1.09×10^3	6.43×10^3
24	6.804	1.40×10^{-5}	5.70×10^2	4.33×10^3
25	6.668	1.60×10^{-5}	6.80×10^2	4.34×10^3
26	6.784	1.47×10^{-5}	4.70×10^2	5.24×10^3
27	7.262	6.60×10^{-6}	4.70×10^2	3.88×10^3
28	7.010	1.10×10^{-5}	5.60×10^2	3.49×10^3
29	7.545	3.40×10^{-6}	5.00×10^2	3.69×10^3
30	7.174	9.00×10^{-6}	4.20×10^2	3.90×10^3

Table IV. (Continued)

Sample No.	pH	HA Molarity	D	K_{EX}
31	7.195	8.00×10^{-6}	3.40×10^2	5.16×10^3
32	7.258	6.00×10^{-6}	3.20×10^2	6.33×10^3
33	7.131	9.20×10^{-6}	4.10×10^2	4.31×10^3
34	8.009	1.23×10^{-6}	3.90×10^2	4.62×10^3

Table V. The Complexation Behavior of Eu(III) as Deduced from Ion-Exchange Distribution Measurements.
(Suwannee R. FA, 1.5×10^{-4} M; 0.01 M NaCl; $D^0 = 2.2 \times 10^8$).

Sample No.	pH	HA Molarity	D	E_{EX}
D-1	4.595	9.30×10^{-5}	2.58×10^3	2.33×10^4
D-2	4.530	9.45×10^{-5}	3.05×10^3	2.25×10^4
D-3	7.367	9.00×10^{-6}	4.93×10^1	2.13×10^4
D-4	7.667	4.80×10^{-6}	3.37×10^1	2.92×10^4
D-5	8.019	2.24×10^{-6}	1.75×10^1	5.37×10^4
D-6	8.944	2.69×10^{-7}	3.64×10^1	2.56×10^4
Europium Carrier Added: 1.0×10^{-7} M EuCl_3				
D-11	8.880	3.11×10^{-7}	3.48×10^1	2.68×10^4
D-12	7.595	5.56×10^{-6}	4.17×10^1	2.41×10^4

Table VI. The Complexation of Eu(III) by FA as Deduced from Ion-Exchange Distribution Studies.

A: System: 9.90×10^{-5} M FA (Waterton); 0.10 M NaCl; $D^0 = 2.2 \times 10^5$

Sample No.	pH	HA Molarity	D	K_{EX}
1	4.323	4.21×10^{-5}	6.74×10^3	3.68×10^1
2	4.196	4.59×10^{-5}	5.44×10^3	5.72×10^1
17	4.667	3.56×10^{-5}	1.21×10^3	1.10×10^2
18	4.963	3.02×10^{-5}	8.99×10^2	8.83×10^1
27	6.676	2.97×10^{-6}	1.96×10^2	8.63×10^1
28	5.977	1.24×10^{-5}	2.52×10^2	7.39×10^1
29	7.109	1.19×10^{-6}	2.16×10^2	6.66×10^1
30	6.708	2.67×10^{-6}	2.25×10^2	6.68×10^1
31	6.449	4.95×10^{-6}	1.82×10^2	8.69×10^1
32	6.444	4.95×10^{-6}	2.15×10^2	7.44×10^1

Table VII. The Complexation of Eu(III) by FA as Deduced from Ion-Exchange Distribution Studies.

System: 9.0×10^{-5} M FA (Armadale) 0.010 M NaCl; $D_0 = 2.20 \times 10^8$

Sample No.	pH	HA Molarity	D	K_{EX}
1a	5.118	4.92×10^{-5}	1.04×10^2	3.28×10^5
1b	4.969	5.11×10^{-5}	1.76×10^2	2.63×10^5
2a	5.081	4.97×10^{-5}	1.03×10^2	3.57×10^5
2b	4.988	5.08×10^{-5}	1.65×10^2	2.68×10^5
3a	5.122	4.92×10^{-5}	1.05×10^2	3.22×10^5
3b	5.061	4.99×10^{-5}	1.16×10^2	3.30×10^5
4a	5.157	4.89×10^{-5}	8.04×10^1	3.90×10^5
4b	5.088	4.97×10^{-5}	1.05×10^2	3.44×10^5
5a	5.184	4.85×10^{-5}	8.24×10^1	3.61×10^5
5b	5.143	4.90×10^{-5}	1.10×10^2	2.93×10^5
6a	5.190	4.84×10^{-5}	9.48×10^1	3.10×10^5
6b	5.183	4.85×10^{-5}	1.39×10^2	2.14×10^5
7a	5.266	4.73×10^{-5}	2.76×10^6	4.15×10^5
7b	5.310	4.67×10^{-5}	7.00×10^1	3.30×10^5
8a	5.043	5.02×10^{-5}	1.06×10^2	3.75×10^5
8b	4.954	5.12×10^{-5}	1.65×10^2	2.89×10^5

Table VIII. The Complexation of Eu(III) by FA as Deduced from Ion-Exchange Distribution Studies.

System: 1.30×10^{-4} M FA (Armadale); 0.050 M NaCl; $D_0 = 1.8 \times 10^6$

Sample No.	pH	HA Molarity	D	K_{EX}
1a	4.470	7.41×10^{-5}	2.85×10^2	2.83×10^3
1b	4.544	7.22×10^{-5}	1.88×10^2	3.70×10^3
2a	4.385	7.48×10^{-5}	3.79×10^2	2.55×10^3
2b	4.628	7.09×10^{-5}	2.86×10^2	2.41×10^3
3a	4.496	7.35×10^{-5}	2.43×10^2	3.15×10^3
3b	4.483	7.35×10^{-5}	3.16×10^2	2.49×10^3
4a	4.476	7.41×10^{-5}	3.27×10^2	2.43×10^3
4b	4.894	6.57×10^{-5}	2.18×10^2	1.57×10^3
5a	4.631	7.09×10^{-5}	2.01×10^2	2.89×10^3
5b	4.739	6.89×10^{-5}	2.02×10^2	2.30×10^3
6a	4.541	7.22×10^{-5}	2.30×10^2	3.05×10^3
6b	4.616	7.11×10^{-5}	2.25×10^2	2.67×10^3
7a	4.616	7.11×10^{-5}	2.28×10^2	2.62×10^3
7b	4.801	6.72×10^{-5}	2.05×10^2	2.02×10^3
8a	4.525	7.28×10^{-5}	1.37×10^2	5.27×10^3
8b	4.854	6.63×10^{-5}	1.50×10^2	2.47×10^3
9a	4.347	7.54×10^{-5}	2.47×10^2	4.26×10^3

Table IX. The Complexation of Eu(III) by FA as Deduced from Ion-Exchange Distribution Studies.

System: 1.50×10^{-4} M FA (Waterton); 0.10 M NaCl; $D_0 = 2.2 \times 10^5$

Sample No.	pH	HA Molarity	D	K_{EX}
1a	4.255	6.68×10^{-5}	3.44×10^3	5.32×10^1
1b	4.150	7.05×10^{-5}	3.28×10^3	6.74×10^1
2a	4.174	6.98×10^{-5}	3.73×10^3	5.66×10^1
2b	4.185	6.90×10^{-5}	3.26×10^3	6.39×10^1
3a	4.235	6.72×10^{-5}	2.91×10^3	6.55×10^1
3b	4.218	6.75×10^{-5}	3.51×10^3	5.62×10^1
4a	4.207	6.68×10^{-5}	2.95×10^3	6.93×10^1
4b	4.297	6.53×10^{-5}	3.66×10^3	4.65×10^1
5a	4.264	6.60×10^{-5}	3.30×10^3	5.51×10^1
5b	4.306	6.50×10^{-5}	3.03×10^3	5.52×10^1
6a	4.223	6.72×10^{-5}	3.24×10^3	6.04×10^1
6b	4.367	6.38×10^{-5}	2.84×10^3	5.22×10^1
7a	4.228	6.71×10^{-5}	2.66×10^3	7.30×10^1
7b	4.200	6.86×10^{-5}	2.74×10^3	7.39×10^1
8a	4.388	6.23×10^{-5}	2.55×10^3	5.66×10^1
8b	4.521	5.85×10^{-5}	2.63×10^3	4.30×10^1
9a	4.461	6.00×10^{-5}	2.54×10^3	4.99×10^1
9b	4.246	6.60×10^{-5}	2.73×10^3	6.94×10^1
10a	4.300	6.53×10^{-5}	2.68×10^3	6.30×10^1
10b	4.204	6.84×10^{-5}	2.94×10^3	6.84×10^1
11a	4.274	6.56×10^{-5}	2.51×10^3	7.11×10^1
11b	4.494	5.94×10^{-5}	1.31×10^3	9.08×10^1
12a	4.458	6.00×10^{-5}	2.01×10^3	6.35×10^1
12b	4.419	6.20×10^{-5}	1.87×10^3	7.23×10^1

radioactive assay in the distribution study of the Waterton (Table IV) FA systems at 0.010 M NaCl were returned to their original containers. The correct quantity of oven-dried NaCl was then added to each of the selected mixtures to make the aqueous medium 0.10 M in NaCl. Additional distribution and K_{EX} data are presented in Tables VII to IX. In these studies there was no readjustment of the system pH after the first equilibration with the resin. The trace of H^+ ion in the resin from the CO_2 -saturated water used to elute the remnants of imbibed electrolyte from its preparation and the variable quantity of HA (and H^+) introduced with the NaCl for equilibration had to accommodate the Na^+-H^+ ion exchange isotherm. This resulted in a smaller pH range of study than was accomplished in the experiments reported on in Tables III to VI.

Analysis of the data in these Tables with eq. 15 used HA concentration estimates deduced either (1) from pH versus α curves obtained from potentiometric measurements on 24-hour batch equilibrated aliquots of the FA at the same ionic strength and FA concentration by weight used in the distribution study (Tables III, IV and VII) or (2) from apparent pK versus α estimates projected from one ionic strength (0.010) to another (0.050, Table VII; and 0.10, Tables VI and IX). The HA molarity reported in Table V for computation of K_{EX} used the 24-hour potentiometric data obtained for the Waterton FA in 0.010 M NaCl, no comparable data being available for the Suwannee R. FA. This did not seriously effect the computation since the Waterton and Suwannee R. potentiometric data in 0.0050 M NaCl are quite similar.

The computation of HA concentrations from the 24-hour pH measurements or from synthesis of potentiometric data based on our earlier observation (Fig. 14) that the value of K_{app} , obtained from pH measurements made with Armadale FA after a 24 hour interval of equilibration, increased

proportionately with ionic strength from 0.01 to 0.1 over the complete neutralization range ($0.3 \leq \alpha \leq 0.9$) is undoubtedly subject to considerable error. We have seen that FA capacity measurements, when based on potentiometric examination of 24-hour batch equilibrated samples, are significantly in error because of CO_2 involvement. As a consequence HA concentration based on these flawed estimates are consistently exaggerated. The evaluation of HA concentrations by attempting to project potentiometric properties is of course doubly flawed since the effect of ionic strength on the apparent pK has not yet been precisely determined.

To eliminate inconsistencies introduced in this way to the correlation of the data we have reexamined all of the distribution data presented in Tables II to IX by a direct comparison of measurable parameters through plots of $\log \left(\frac{D_0 - D}{D} \right)$ versus pH for each system studied. These data and more recently compiled data are presented in Figures 15 to 18 and can be directly compared to examine the effect of ionic strength, FA concentration, FA source (Armadale, Waterton Pumphouse, Suwannee River) and total carbonate content of solutions of FA on the complexation of $\text{Eu}^{154}(\text{III})$ by the FA. For example, in Fig. 15, we can examine the effect of ionic strength and FA concentration, respectively, on the relative amounts of bound and free $\text{Eu}^{154}(\text{III})$ over an extended pH range. Considering first the effect of FA concentration on the binding parameter at two different ionic strength levels (0.10 and 0.30 M) we see that at an ionic strength of 0.1 the logarithmic binding function, over a large pH range, increased by a constant factor of 1.4 when the FA concentration was increased five fold. There was thus a 25-fold increase in the ratio of bound to free $\text{Eu}^{154}(\text{III})$ when the concentration of FA was increased

only by a factor of five. At the ionic strength of 0.3 the change of the ratio of bound to free $\text{Eu}^{154}(\text{III})$ for a similar five fold increase in FA concentration was much smaller, the logarithmic factor of 0.3 corresponding to a two-fold increase in the ratio of bound to free $\text{Eu}^{154}(\text{III})$.

Had we not observed the large decrease in apparent pK of FA in Fig. 11 when the FA concentration was increased eight-fold while keeping I equal to 0.1 we would have expected the change in $\log \frac{D_0 - D}{D}$ to have been directly proportional to the change in concentration of FA at every solution pH value. The increase in the complexed species would have been expected to be exactly compensated by the increase in dissociated FA to keep the apparent formation constant of the complexed species formed unchanged at that pH.

The observed property of the binding parameter was on the basis of our potentiometric study expected; it has to be attributed to the existence of FA as a flexible microgel which forms as a result of the strong tendency for FA molecules to aggregate. At the lower ionic strength of 0.1 the aggregate arrangement is apparently more compact the higher the concentration of FA because cohesive forces originating in the polar sites of the FA molecule are enhanced by the higher concentration of these sites. At the higher ionic strength an even more compact assembly of FA molecules becomes somewhat less compact with increasing concentration of FA because repulsive forces originating in the positive charge on the partially dissociated FA molecule become slightly disruptive. Because of the closer approach of neighbor molecules due to the more compact arrangement of the FA microgel an increase in FA concentration apparently leads to a slight expansion of the microgel because of such repulsion.

The occurrence of gel contraction ($I = 0.1$) or expansion ($I = 0.3$), presumed to prevail with increasing concentrations of FA at the respective ionic strength values examined, can explain the respectively greater and smaller increase of bound species relative to the free, mobile counterion concentration in solution. While the ratio of mobile counterions in both phases remain unchanged the quantity of bound species relative to the mobile free counterion in solution increases or decreases with contraction or expansion of the gel phase.

The effect of ionic strength on the ratio of bound to free Eu^{154} (III) is observable in Figs. 15 and 16 from examination of distribution data obtained with a fixed quantity of Armadale FA (0.02 g/L) in 0.010, 0.050, 0.10 and 0.30 M NaCl. In the pH range from ~ 4 to ~ 6 the binding function increases as a function of ionic strength by the constant logarithmic factors of 1.9, 1.0 and 0.3, respectively as the logarithmic ratio of ionic strength changes from -0.70, -0.30, and -0.48. Over a pH range from ~ 6 to ~ 8 a plateau is reached in the logarithmic value of $\left(\frac{D_0 - D}{D_0}\right)$ in the 0.010 and 0.10 M systems with the ratio of the distribution functions maintained constant at the same value of 2.9 to 3.0 (1.9 plus 1.0; the 0.050 M system was not examined over this pH range). Even beyond this plateau region, where the distribution function rises slowly with pH from a pH of ~ 8 to ~ 10 this ratio of the distribution functions continues to be maintained at these two ionic strengths.

At the highest ionic strength of 0.3 M the plateau in the value of $\log \left(\frac{D_0 - D}{D_0}\right)$ is reached earlier at a pH of ~ 5.5 to 6 and persists over the additional pH range examined (up to 9.85).

The data obtained in the 0.01, 0.05, 0.1 and 0.3 M systems in the pH range of ~ 4 to ~ 6 can be qualitatively explained by our estimate

that the FA exists as a gel whose solvent uptake results in a counterion concentration of $\sim 0.2M$. In the most dilute salt system then the ratio of bound to free $\text{Eu}^{154}(\text{III})$ measured is extremely large because of the fact that the concentration of free $\text{Eu}^{154}(\text{III})$ ion, to which the quantity of bound europium should be related, is so much larger than observed in the aqueous phase. The ratio of $\text{Eu}^{154}(\text{III})$ in the gel and solution phases on this basis is predicted to be about 8000 in the most dilute system

studied as shown:
$$\frac{\text{Eu}_{(g)}^{+3}}{\text{Eu}_{(s)}^{+3}} \approx \left(\frac{\text{Na}_{(g)}^{+}}{\text{Na}_{(s)}^{+}} \right)^3 \approx \left(\frac{.2}{.01} \right)^3 \approx 8.0 \times 10^3$$
. This ratio

drops to ~ 80 , 14, and 3 in 0.05, 0.1 and 0.3 M NaCl to resolve constant logarithmic binding ratios of 2, 0.76 and 0.67 for comparison with the values of 1.9, 1.0 and 0.3 actually observed.

To explain the divergence from predicted behavior in the 0.30 M NaCl where there is an earlier appearance of a plateau in the $\log \left(\frac{D_0 - D}{D} \right)$ function which persists over the pH range from ~ 6 to ~ 10 we suggest that the FA aggregate expands over this pH range in the higher ionic strength system.

The plateau observed for the distribution function in 0.010 and 0.10 M NaCl is seen to coincide with the pH range in which the availability of carboxylic acid groups of the FA has reached its maximum value. This result would indicate that the complexed species of $\text{Eu}(\text{III})$ is exclusively associated with the carboxylic acid constituents of the FA.

The gentle increase in $\log \frac{D_0 - D}{D}$ with pH beyond the carboxylic acid equivalence point may signal the binding of another functional unit of the FA, e.g. phenol, or may just be a reflection of gel phase contraction in this pH range.

To examine the possibility that carbonate ion could complex $\text{Eu}^{154}(\text{III})$ more strongly than the FA in the pH range from 7.5 to 9.5 the distribution

pattern of $\text{Eu}^{154}(\text{III})$, i.e., the ratio of $\text{Eu}^{154}(\text{III})_{\text{bs}}$ to $\text{Eu}^{154}(\text{III})_{\text{s}}$, was examined over a pH range from 7.5 to 10.5 in 20 ppm Armadale FA solutions 5.0×10^{-3} , 2.5×10^{-3} , 1.0×10^{-3} and 2.5×10^{-4} molar in total carbonate and 0.010 M in Na^+ -ion content. This experimental approach had to be selected because earlier experiments designed to study the complexation of the $\text{Eu}^{154}(\text{III})$ by carbonate ion in solutions free of FA failed because of the instability of the $\text{Eu}^{154}(\text{III})$ in these solutions. Controls for comparison of the radioactivity at the start of an experiment with the radioactivity remaining after equilibration of the solutions with resin did not retain all of the $\text{Eu}^{154}(\text{III})$ in solution. Attempts to circumvent this instability by addition of macro quantities of Eu carrier did not stabilize the controls. In the presence of 20 ppm FA such instability of controls was no longer encountered.

The data obtained in these experiments are presented in Fig. 17. In three of the four sets of data the distribution pattern is essentially duplicated. In the fourth set the curve is displaced by a logarithmic factor of 0.6 while its shape is preserved. The pattern is the same as was obtained for the 20 ppm Armadale FA distribution study in 0.010 M NaCl that is presented in Fig. 16. The curve in Fig. 16 over the pH range from 7.5 to 9.5 is ~ 0.3 units lower than the upper curve of Fig. 17 and ~ 0.3 units higher than the lower curve.

We do not believe that the displacement of curves is any indication of differences in the complexation of Eu in the carbonate-free and carbonate-containing systems. First the separation of one set of points from the three other sets in the carbonate containing systems may be due to irreproducibility of the FA gel volume in this particular system. The discrepancy between the upper curve of Fig. 17 and the curve of

Fig. 16 is probably a consequence of gel volume differences arising from the fact that while maintaining the concentration of Na^+ ion in the carbonate containing systems the ionic strength differed from the 0.01 value used in the experiment summarized in Fig. 16.

The conclusion from the preceding data has to be that carbonate complexation of $\text{Eu}^{154}(\text{III})$ is not competitive in the presence of 20 ppm FA.

In Fig. 18 the complexation of $\text{Eu}^{154}(\text{III})$ by 20 ppm of Waterton Pumphouse FA in 0.10 and 0.010 M NaCl has been compared. The distribution data are plotted as before versus the equilibrium pH. Over the pH range of ~ 4.3 to ~ 5.5 the logarithmic ratio of distribution functions obtained at these two salt concentrations is ~ 1.8 . A value of 1.9 was obtained for this ratio in the Armadale FA system.

Agreement in the relative distribution behavior of the $\text{Eu}^{154}(\text{III})$ in the Waterton Pumphouse and the Armadale FA at the two ionic strength values of 0.01 and 0.1 M does not, however, persist beyond a pH value of ~ 5.5 . In the higher pH region the distribution behavior patterns diverge much as they did in the Armadale FA equilibrated with 0.1 and 0.3 M NaCl. We assigned the divergence earlier to gel contraction in the higher ionic strength system.

Finally the shape of plots of $\log \frac{D_0 - D}{D}$ versus pH obtained for $\text{Eu}^{154}(\text{III})$ with solutions 20 ppm in Suwannee River FA (Fig. 18), 20 ppm in Waterton Pumphouse FA (Fig. 18), and 20 ppm in Armadale FA (Fig. 16) in 0.010 M NaCl are comparable to show their equivalent complexation behavior and the gel volume constancy in these systems.

Concluding Remarks

i. The Complexation of Eu(III) by FA. We believe that use of eq. 15 to correlate the ion-exchange data compiled in this study provides a meaningful path to the analysis of this system even though some precision is lost through error in estimates of the equilibrium concentration of undissociated FA (HA). Even when hydrogen capacity determinations are in error by as much as 15% the error in HA over the α range of study (0.4 to 1.0) will initially be no higher than +30%. This error will eventually reduce to +15% as α approaches unity at a pH value of ~ 8 . Beyond this pH value use of eq. 15 to analyze the distribution data has to be somewhat less reliable. In addition to the 15% error introduced in the assignment of concentrations to the fully dissociated fulvic acid (from faulty H capacity measurements) for computation of the concentration of HA formed by computation hydrolysis at or beyond the equivalence point additional error is likely from faulty assignment of the plateau value of the apparent pK as the equivalence point is reached. Recall that K_h , the equilibrium constant for the hydrolysis reaction,



is expressed as shown:

$$K_h = \frac{K_w}{K_a} \quad (18)$$

The fact that the K_{EX} value obtained with eq. 15 is constant within the error limits of 15 to 30% for HA over a pH range from ~ 4 to at least 8 is significant. Since K_{EX} , as defined, is equal to the ratio of apparent stability constants, $\beta_{EuA}^{app} / \beta_{HA}^{app}$, this success in the use of eq. 15 must arrive from the fact that the statistical factor leading to the characteristic

S-shape in the plot of the apparent pK ($\text{pH} - \log \frac{A^-}{HA}$) versus A^- curves for FA is conveniently cancelled by the same statistical term encountered in the formation of EuA^{++} .

Beyond a pH of 8 the positive deviation of K_{EX} values from the constant obtained with eq. 15 in the lower pH range is believed to exceed sizeably the limits of uncertainty that can be logically expected to have been introduced into its computation from incorrect assignment of HA concentration values.

Earlier analysis of the distribution data from plots of $\log \left(\frac{D_0 - D}{D} \right)$ versus pH have led us to the same conclusion: The binding of $\text{Eu}^{154}(\text{III})$ appears to increase after saturation of carboxylate ligands is reached at a pH value of 8. This result could be due to contraction of the gel aggregate in this pH region; binding of $\text{Eu}^{154}(\text{III})$ to another site is also a possibility.

ii. The Aggregation of FA.

In our analysis of the $\text{Eu}^{154}(\text{III})$ distribution parameter as a function of ionic strength, FA concentration, FA source and pH we were able to rationalize the data by postulating aggregation of the FA to form a separate phase. For example the effect of FA concentration on the value of $\log \left(\frac{D_0 - D}{D} \right)$ at an ionic strength of 0.10 (Fig. 15) was attributed to extra contraction of this gel. The five fold greater enhancement of the distribution parameter than expected could be accounted for by the increase in concentration of gel component species affected by such contraction of the gel. On the basis of this modelling of the system this factor of 5 can be equated with the cubed ratio of Na^+ -ion gel concentrations in the two systems being compared (eq. 7). Consistent with this the ratio of K_{EX} in the two systems

should then be equal to $(5)^{2/3}$ or about three. The ratio of the averaged K_{EX} values obtained for the two systems over the pH range where such a comparison can be made (~ 4 to ~ 5.5) is $1 \times 10^3 / 2.6 \times 10^2$ or 3.8. This agreement with prediction is quite acceptable. In the other example ($I = 0.3$) of Fig. 15 K_{EX} at the higher FA concentration should be reduced by a factor of ~ 0.5 because of the gel expansion deduced from the lower than expected value of $\log \frac{D_0 - D}{D}$ at the increased FA concentration. This was indeed the case. The K_{EX} of $\sim 1.5 \times 10^2$ observed at the lower FA concentration in 0.3 M NaCl decreased to $\sim 8 \times 10^1$.

An interesting aspect of this interpretation of the effect of FA concentration on the ion-exchange distribution behavior of $\text{Eu}^{154}(\text{III})$ at a fixed ionic strength is that it can explain the ion-exchange distribution results obtained by Bertha and Choppin²⁴ in their study of the interaction of (HA) humic and fulvic acids with $\text{Eu}(\text{III})$ and $\text{Am}(\text{III})$. In their examination of the complexation of these trivalent ions in a cation-exchange distribution study they determined the distribution behavior of trace level concentrations of these metal ions at a fixed pH (4.50) and ionic strength ($I = 0.10$) by varying the HA or FA concentration in the system. They observed, as we have, that the ratio of bound to free metal ion ($\frac{D_0 - D}{D}$) increased more rapidly than the concentration of FA; their enhancement factor was 2.6 instead of 5 as observed by us. Apparently volume contraction of their HA and FA gels at $I = 0.1$ with increasing humic and fulvic acid concentrations was somewhat less than in our FA aggregates.

Not recognizing the tendency for humic and fulvic acids to aggregate and form a separate phase Bertha and Choppin incorrectly attributed the

above pattern of behavior to the binding of Eu(III) and Am(III) to two types of sites with 1:1 and 1:2 stoichiometry.

These instances where divergence of $\log \left(\frac{D_0 - D}{D} \right)$ versus pH patterns was observed (0.1 and 0.3 M NaCl, Armadale FA; 0.01 and 0.1 M NaCl, Watertown Pumphouse FA) when examining the effect of ionic strength at a fixed FA concentration value (~ 20 ppm) were attributed earlier to changes in volume of one FA gel relative to the other when the pH reached a value of 5 to 5.5. The ratio of $\frac{D_0 - D}{D}$ in one region divided by the ratio of $\frac{D_0 - D}{D}$ in the other and raised to the 2/3 power should, as we pointed out above, be equal to the ratio of K_{EX} in one region divided by the ratio of K_{EX} in the other if our proposed explanation of the divergence of the Eu¹⁵⁴(III) distribution pattern is correct. Although our K_{EX} values are not very accurate because of uncertainty in the evaluation of HA concentrations for use in eq. 15 they do support qualitatively our estimate of the situation in these instances. For the first system a seven-fold increase in the ratio of K_{EX} ratios was predicted; the experimental increase in the ratio of K_{EX} ratios was by a factor of 14. In the second system the predicted increase in the ratio of K_{EX} ratios was by a factor of three while the experimental ratio of K_{EX} ratios increased only by a factor of two.

The variation in K_{EX} with ionic strength, where $\log \frac{D_0 - D}{D}$ versus pH curves parallel each other to suggest gel volume stability at the different ionic strength levels, should be qualitatively predictable as well from the ratios of $\frac{D_0 - D}{D}$ at these ionic strengths taken to the 2/3 power. In the Armadale FA the relative magnitudes of K_{EX} going from

$I = 0.01$ to 0.05 to 0.1 to 0.3 are predicted on this basis to be 20, 5 and 2. Experimentally, relative magnitudes of K_{EX} are ~ 45 , ~ 10 , and ~ 2.5 . With the Waterton FA the K_{EX} ratio, going from $I = 0.01$ to 0.1 in the region where the $\log \frac{D_0 - D}{D}$ versus pH plots parallel each other, is predicted to be 20 while a ratio of ~ 70 is experimentally observed.

Additional independent confirmation of the existence of FA as an aggregate is available from small angle X-ray scattering measurements of the Armadale FA by R. L. Wershaw of the U. S. Geological Survey. R. Wershaw is collaborating with us in the examination of the physical chemical properties of FA. A brief summary of this research is included in an appendix to this manuscript.

iii. The Competitive Complexation of Eu(III) by FA and $\text{CO}_3^{=}$ Ion.

One can expect $\text{CO}_3^{=}$ ion and FA to be the most likely inorganic and organic species to interact strongly with any traces of Eu(III) that may be present in natural water systems at pH values ranging from 8 to 9. As a consequence a comparison of the Eu(III)-complexation potential of these substances is essential for evaluating their relative importance in migratory patterns that may derive from such interaction with any Eu(III) in radioactive waste leaking from its burial site into the ground water. With the unambiguous interpretation of the FA-Eu(III) binding data that we have been able to achieve in this research this objective is now accessible. To demonstrate this we have considered the complexation of Eu(III), present in trace quantity, by both $\text{CO}_3^{=}$ ion and FA in a water sample containing 20 ppm of organic carbon as fulvic acid ($\sim 1.5 \times 10^{-4} \text{M}$) with 200 ppm of HCO_3^- ion ($3.3 \times 10^{-3} \text{M}$) and 50 or 550 ppm (10^{-3} or 10^{-2}M) of NaCl as the other important constituents.

The effect of pH and FA source on the formation tendency of the most likely complexed species, i.e., $\text{Eu}(\text{CO}_3)_3^+$, $\text{Eu}(\text{CO}_3)_2^-$ and EuFA^{++} , has been examined at two pH levels, 8 and 9, in these two systems. The results of these computations are listed in Table X and the FA complexation projections are based on the data presented in Tables II to IX and Figures 15 to 18. In order to compute the ratios, $\text{EuCO}_3^{+1}/\text{Eu}^{+3}$ and $\text{Eu}(\text{CO}_3)_2^{-1}/\text{Eu}^{+3}$, listed in Table X, the respective stability constants for $\text{Ce}(\text{CO}_3)_3^+$ and $\text{Ce}(\text{CO}_3)_2^{-1}$, corrected to zero ionic strength from experimental data obtained at an ionic strength of 3.0, were employed.²⁵ Estimate of the quantity of $\text{CO}_3^{=}$ ion to use in the computation of these ratios resorted to the use of the thermodynamic carbonic acid and water dissociation constants as well. Non-ideality in these systems considered (ionic strength of 4.35×10^{-3} and 1.35×10^{-2} M, respectively) were neglected. The $\text{EuFA}^{+2}/\text{Eu}^{+3}$ values listed in the Table were resolved from data obtained at an ionic strength of 0.010 and 0.10 M, respectively and no consideration was given to perturbation introduced by non-ideality at these concentration levels, as well, in the computation of these ratios. It was considered that uncertainty introduced into the β values used for computation of $\text{Eu}(\text{CO}_3)_n^{(3-2n)}/\text{Eu}^{+3}$ by (1) correction for deviations from ideality on going from an ionic strength of 3.0 to zero and (2) the use of these data for Ce(III) as fully representative of Eu(III) was far greater than any uncertainty introduced to the calculations by neglecting non-ideality; we believe the approach used in preparing this Table is fully justified as a consequence.

From these computations we can conclude that (1) at a pH of 8, the Eu(III) is more strongly complexed by each of the three fulvic acid sources studied at both concentrations of NaCl examined and that (2)

Table X. The Competitive Complexation of Eu^{154} by FA and CO_3^{2-} .System: 20 ppm FA; 200 ppm HCO_3^- (3.3×10^{-3} M HCO_3^-).55 ppm NaCl

pH	(CO_3^{2-})	Eu(III) Species	Eu(III)(Bound)/Eu ⁺³ (Free)
8	1.55×10^{-5} M	$\text{Eu}(\text{CO}_3)^+$	3.9×10^3
8	1.55×10^{-5} M	$\text{Eu}(\text{CO}_3)_2^-$	1.2×10^4
9	1.55×10^{-4} M	$\text{Eu}(\text{CO}_3)^+$	3.9×10^4
9	1.55×10^{-4} M	$\text{Eu}(\text{CO}_3)_2^-$	1.2×10^6
8,9		$\text{Eu}(\text{FA})^{++}$ (Armada le H)	2.1×10^8
8,9		$\text{Eu}(\text{FA})^{++}$ (Suwanee R)	2.9×10^7
8,9		$\text{Eu}(\text{FA})^{++}$ (Waterton P)	2.7×10^6

550 ppm NaCl

8	1.55×10^{-5} M	$\text{Eu}(\text{CO}_3)^+$	3.9×10^3
8	1.55×10^{-5} M	$\text{Eu}(\text{CO}_3)_2^-$	1.2×10^4
9	1.55×10^{-4} M	$\text{Eu}(\text{CO}_3)^+$	3.9×10^4
9	1.55×10^{-4} M	$\text{Eu}(\text{CO}_3)_2^-$	1.2×10^6
8,9		$\text{Eu}(\text{FA})^+$ (Armada le H)	2.3×10^7
8,9		$\text{Eu}(\text{FA})^+$ (Suwanee R)	3.2×10^6
8,9		$\text{Eu}(\text{FA})^+$ (Waterton P)	2.7×10^5

at a pH of 9 the preference of Eu(III) for FA relative to $\text{CO}_3^{=}$ ion is reduced so that the least strongly binding (Waterton) FA source is only slightly more strongly complexed than the $\text{CO}_3^{=}$ ion in the more dilute NaCl system; at the higher concentration of NaCl Eu(III) is predicted to be 4 times more strongly bound to the $\text{CO}_3^{=}$ ion than the Waterton FA source, while the Armadale and Suwannee River FA sources still bind the Eu(III) a factor of ~20 and 3 times more strongly than the $\text{CO}_3^{=}$ ion.

Indeed, from these studies we can deduce that at a pH of 8, Eu(III) can be expected to be complexed more strongly than $\text{CO}_3^{=}$ ion by as little as 2 ppm of FA when the HCO_3^{-} concentration does not exceed 250 ppm.

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- (5) The data for Fig. 2 are from reference 4.
- (6) A more rigorous expression for this equilibrium includes a pressure-volume term⁷ as shown:

$$\frac{(H^+)}{(M^+)} = \frac{(H_g^+)}{(M_g^+)} + \exp \left(\frac{\pi(V_H - V_M)}{RT} \right) \quad (7a)$$

In this equation π is the osmotic pressure and V_H and V_M represent the partial molal volume, at infinite dilution, of the respective exchanging ions. In the case of H^+ and Na^+ ($V_H - V_{Na}$) = 0.0012 l/mole⁸ and there is little error introduced, even when π is large, from neglect of the pressure, volume term.
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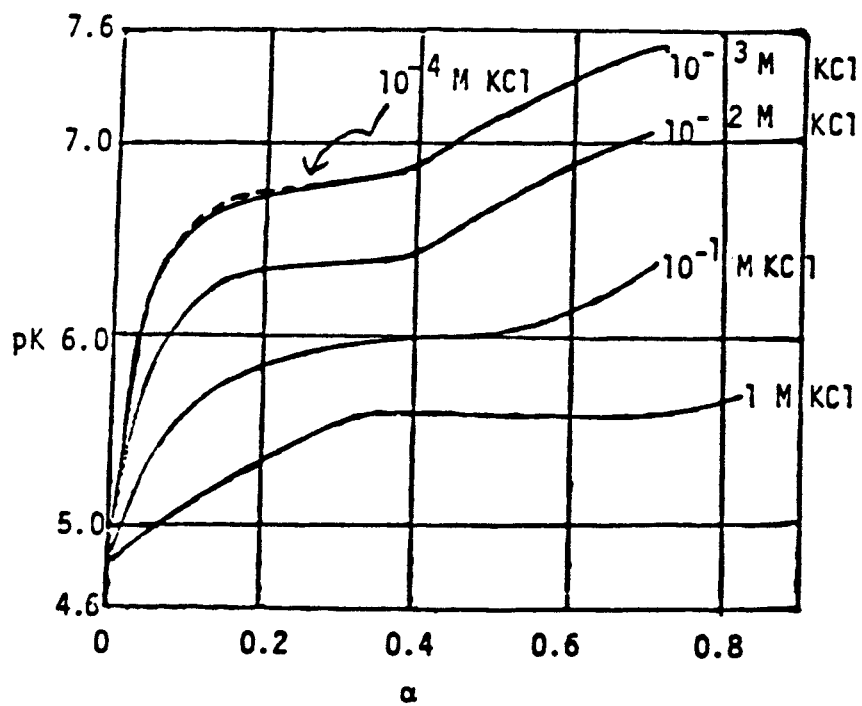


Figure 1. Potentiometric Titrations of Polymethacrylic Acid (Polymer Concentration = 0.01 equiv./liter).

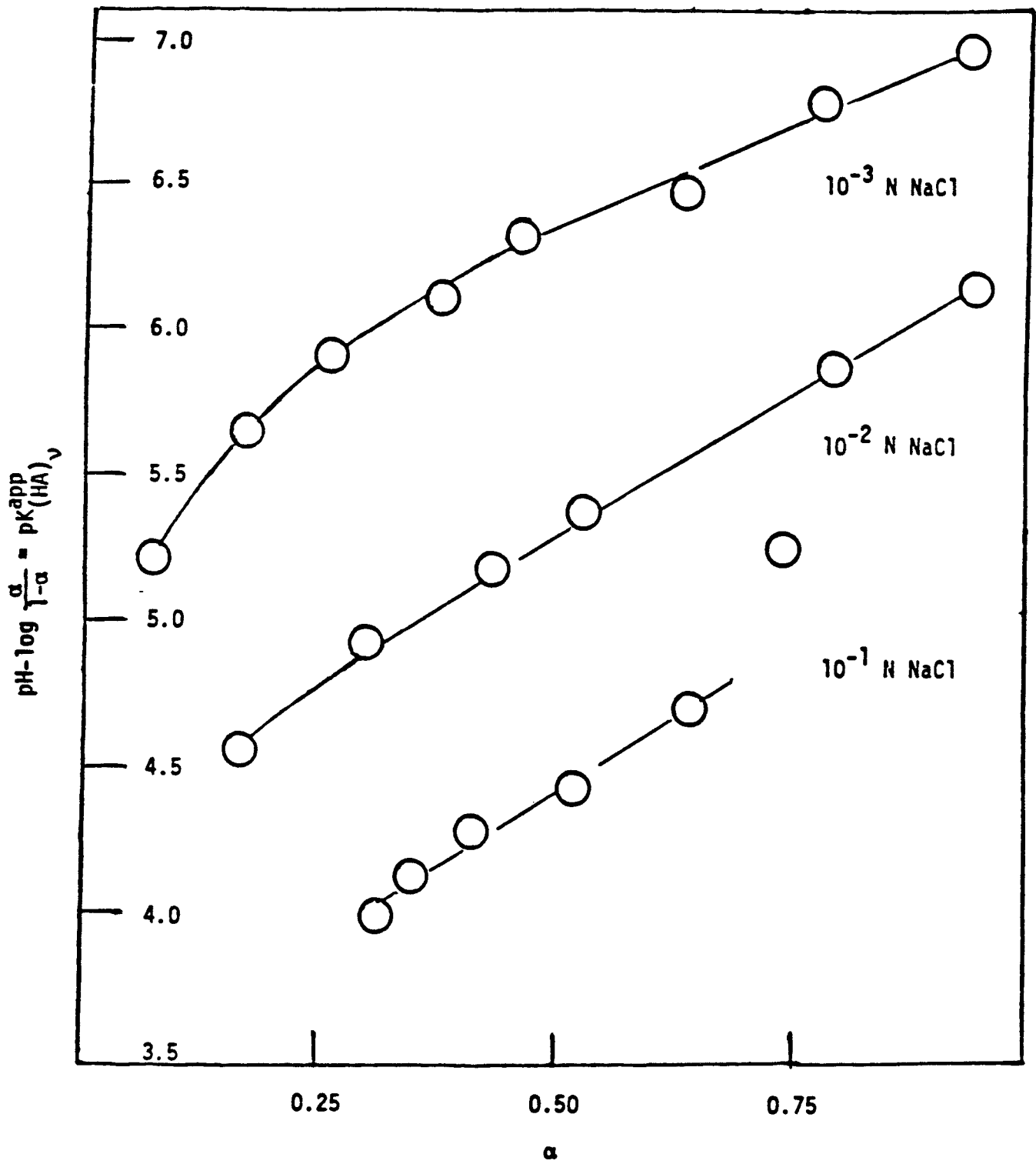


Figure 2. Potentiometric Titrations of Sphagnum Peat (Eq. 6).

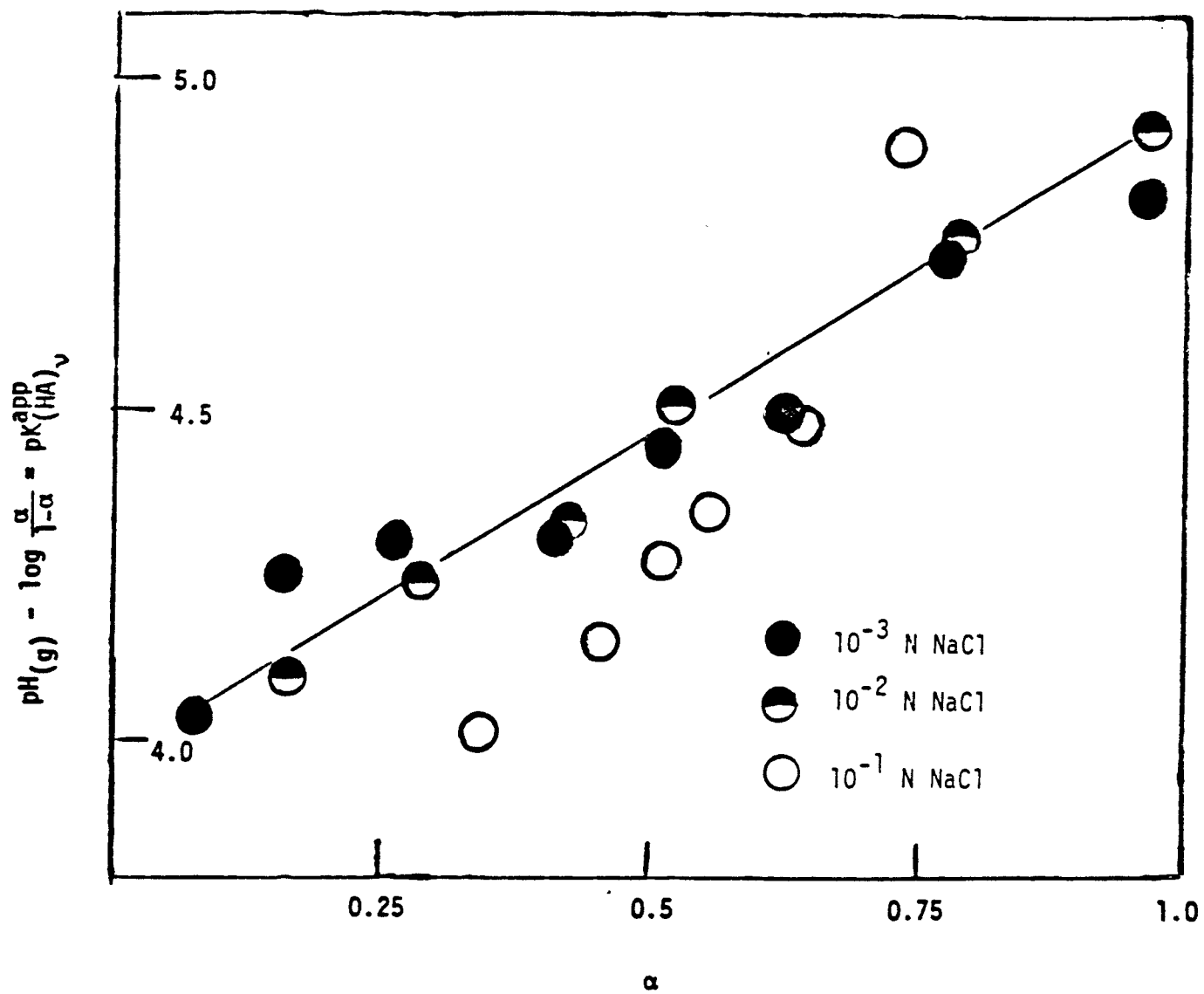


Figure 3. Potentiometric Titrations of Sphagnum Peat (Eq. 6a).

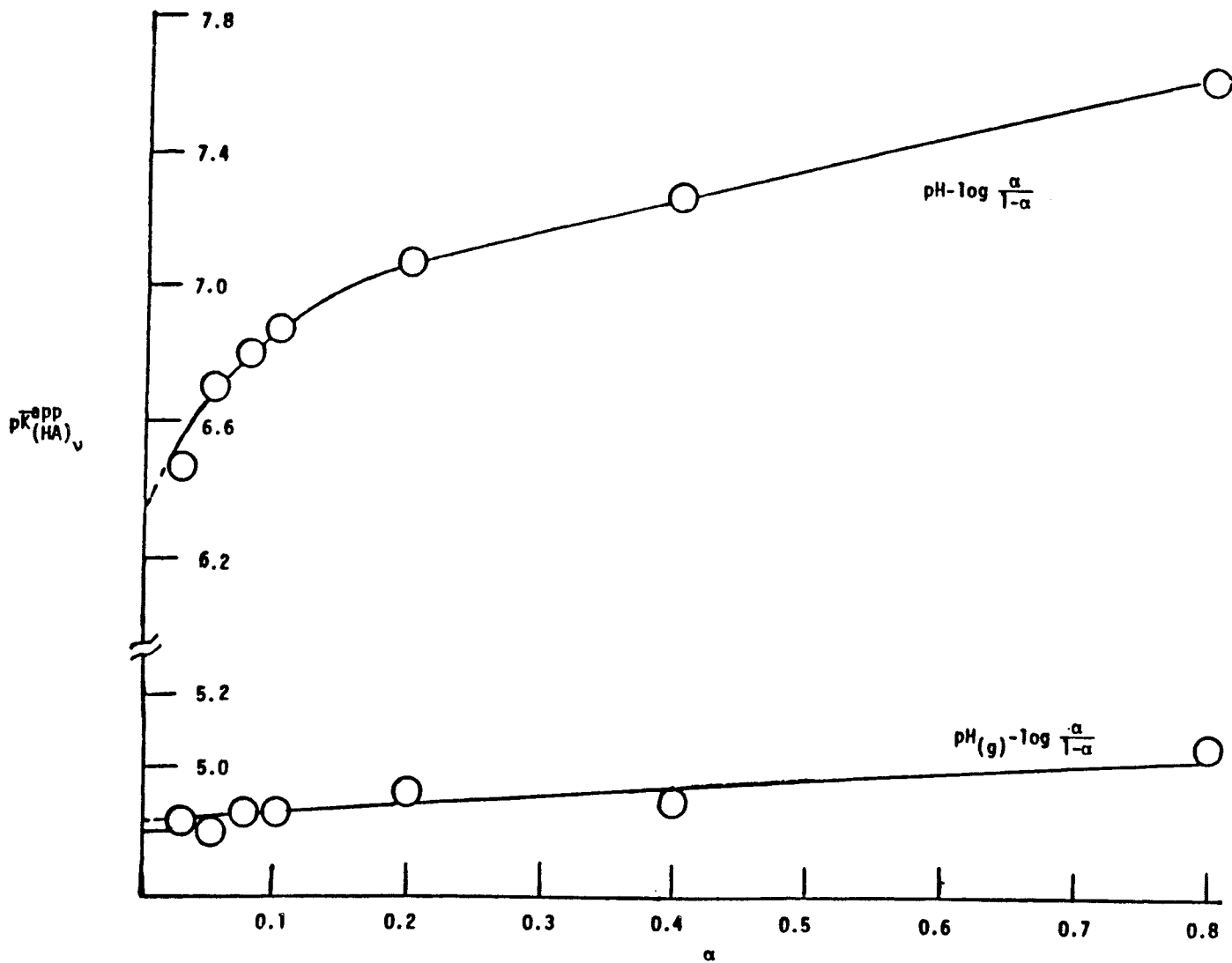


Figure 4. Potentiometric Study of Amberlite IRC-50 in 0.03 N NaPSS Solution.

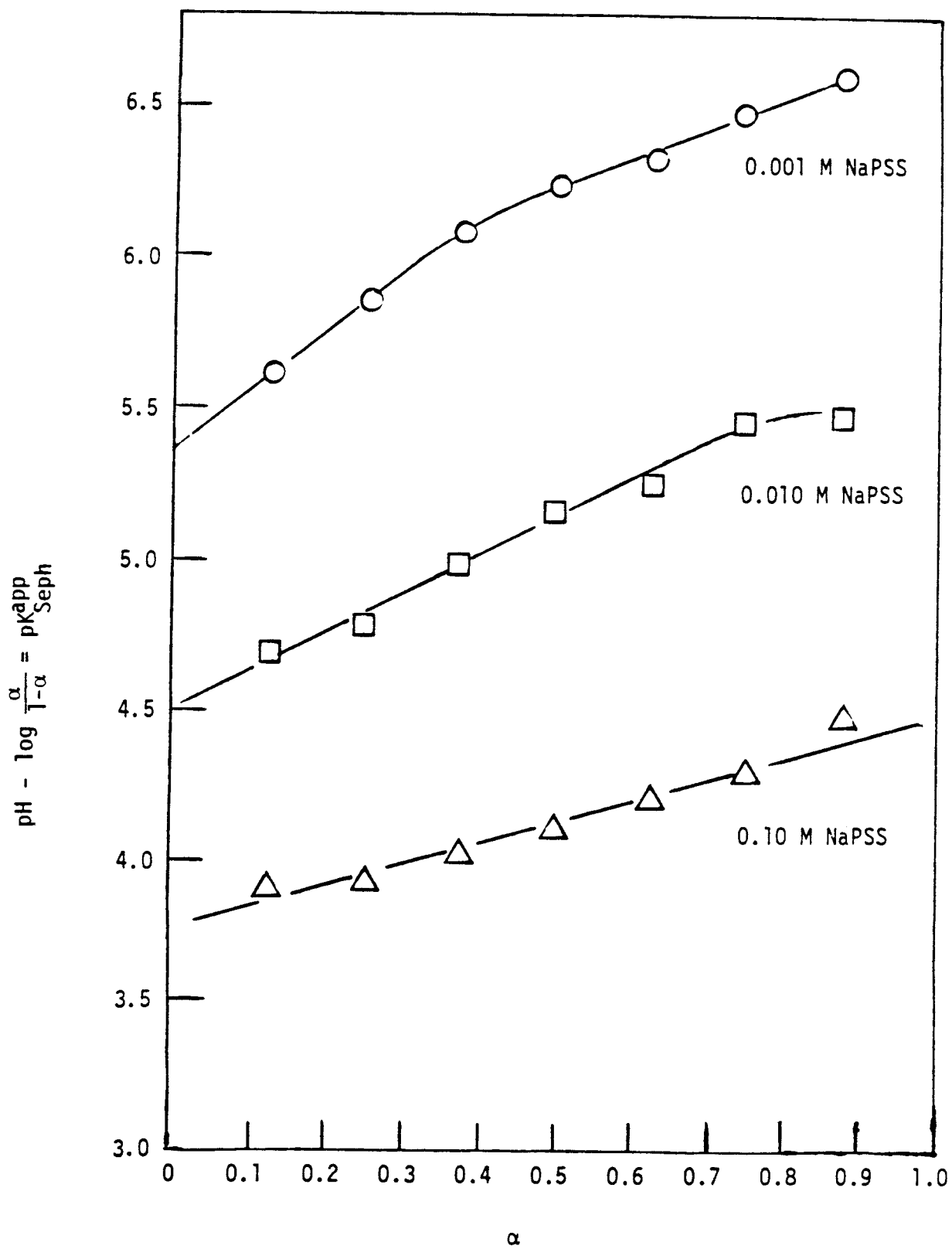


Figure 5. Potentiometric Titration Curves for Sephadex C-M-50-120 (Eq. 6).

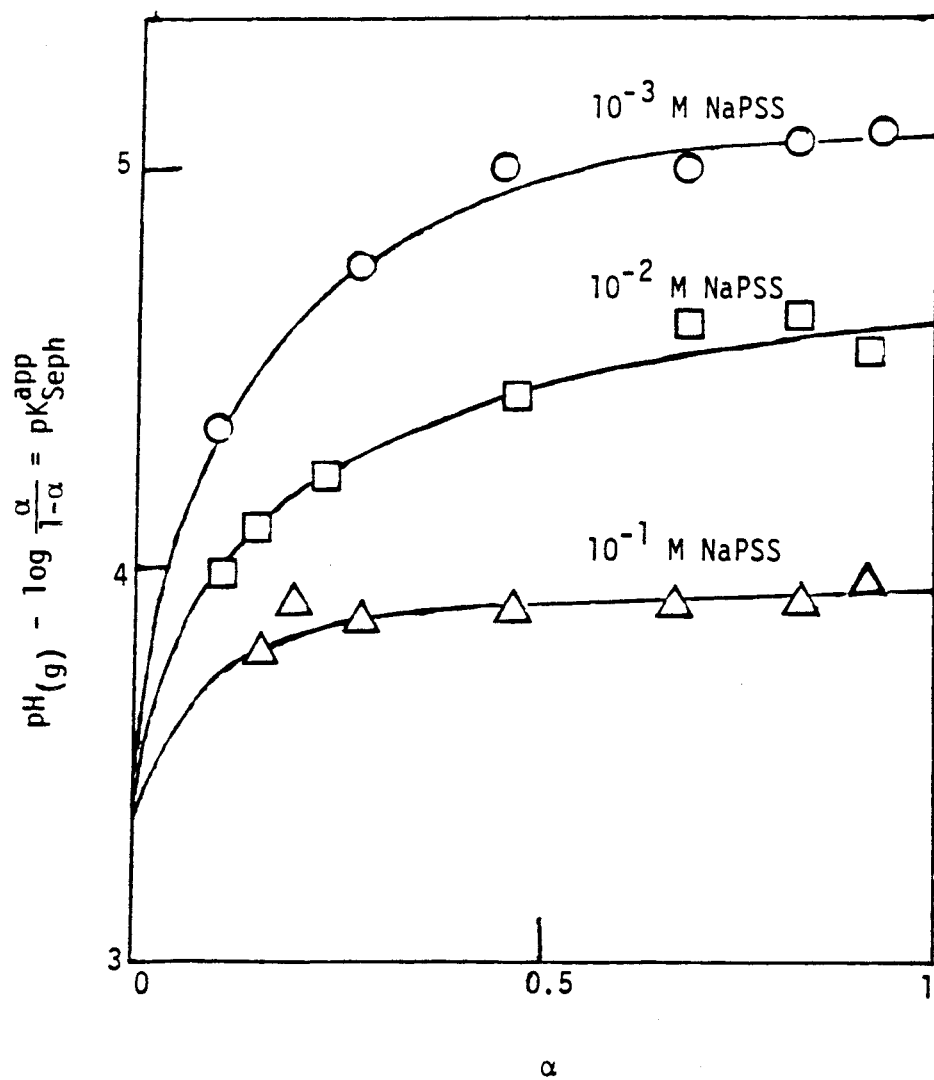


Figure 6. Potentiometric Titration Curves for Sephadex CM-50-120 (Eq. 6a).

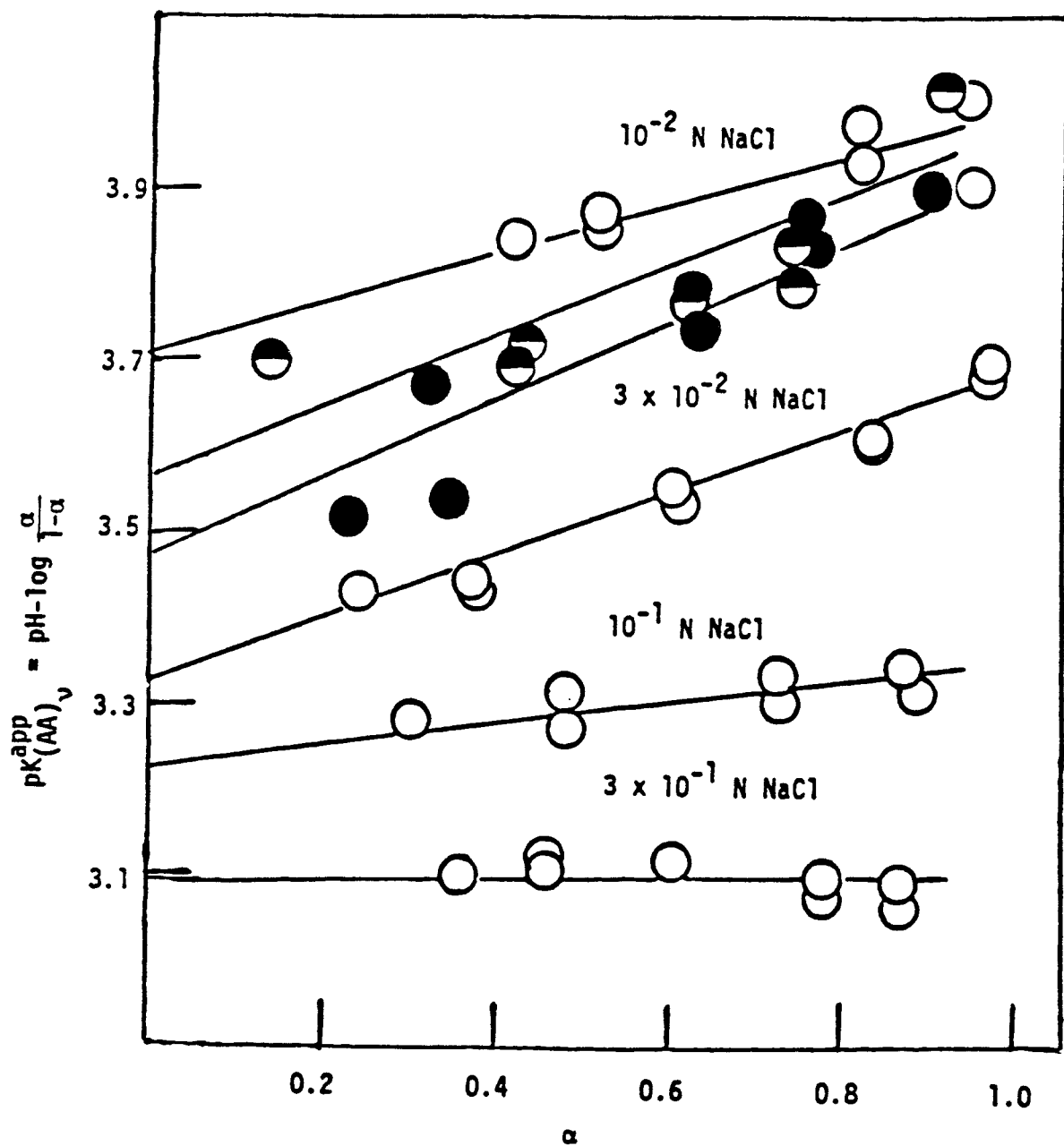


Figure 7. Potentiometric Titration Curves for Alginic Acid (Eq. 6).

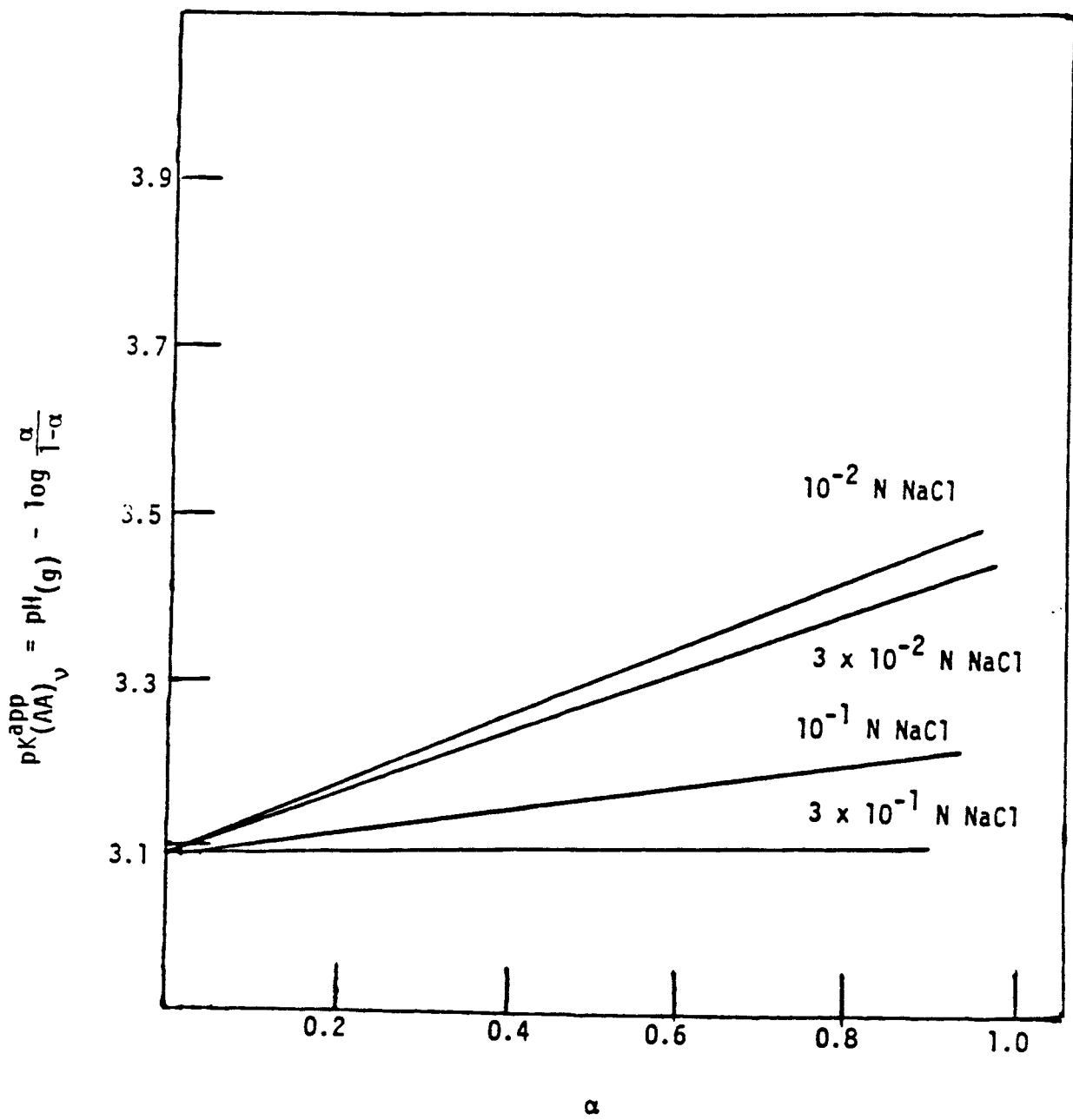


Figure 8. Potentiometric Titration Curves for Alginic Acid (Eq. 6a).

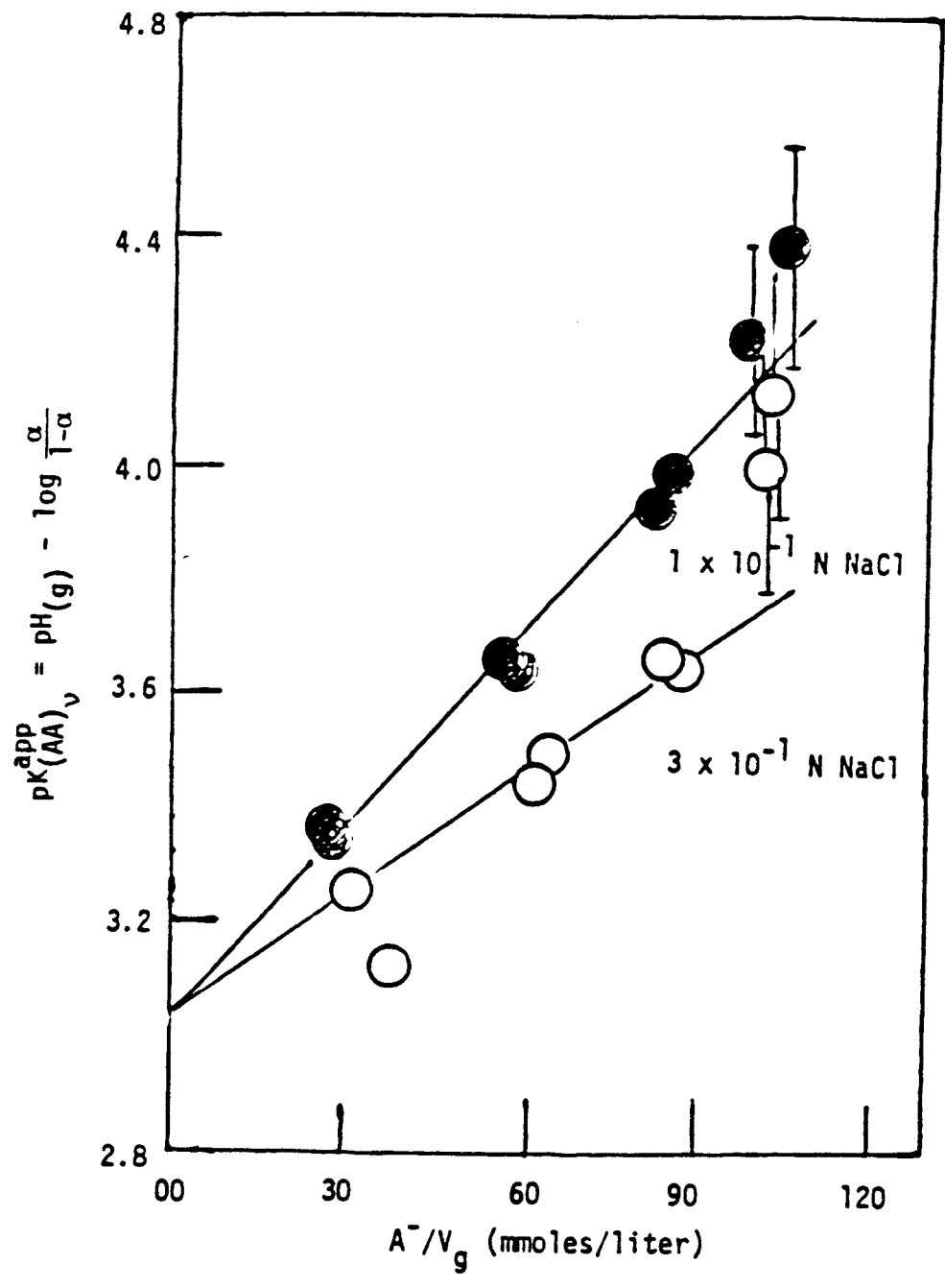


Figure 9. Potentiometric Titration Curves for Alginic Acid Gel (Eq. 6a).

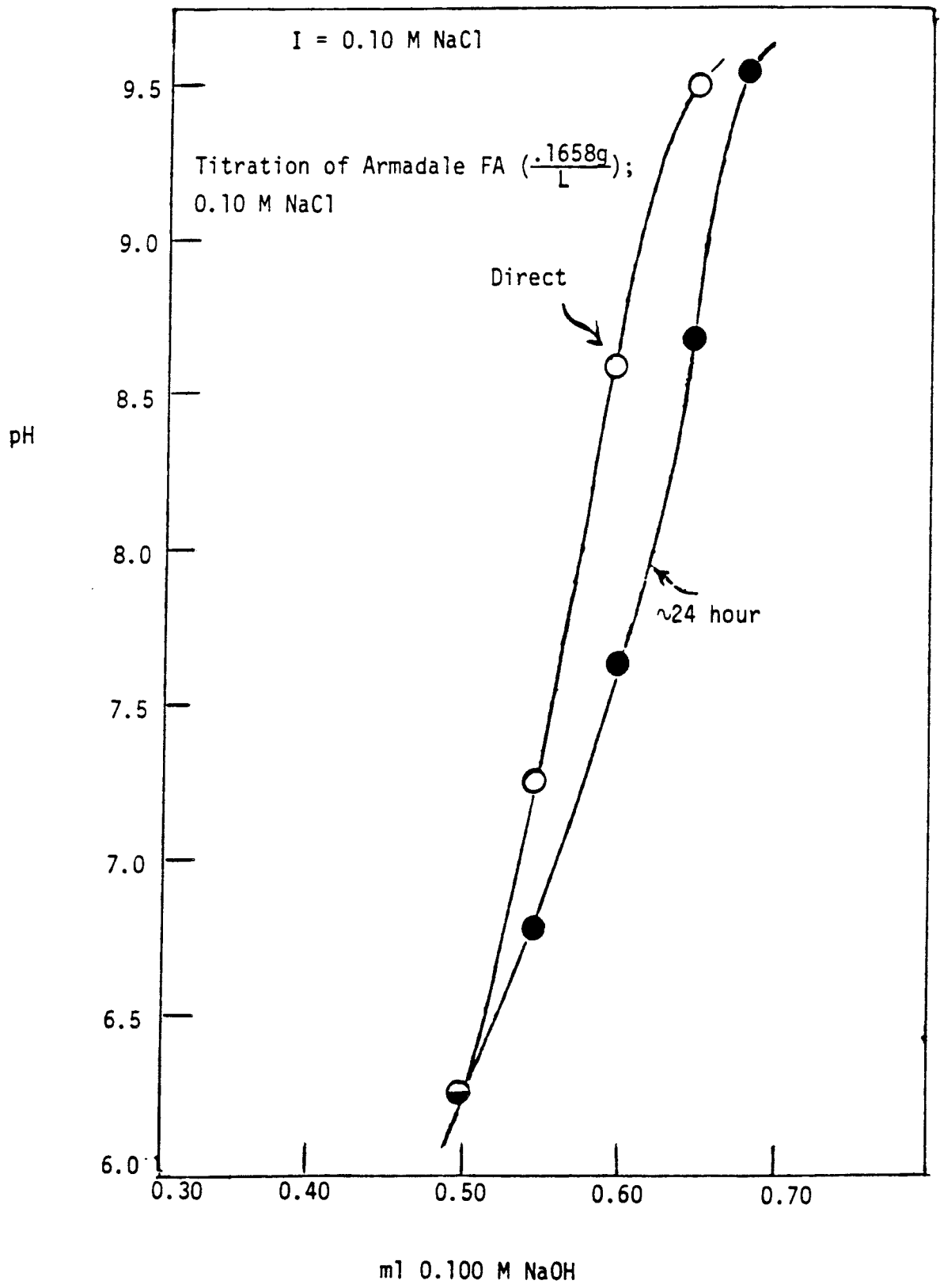


Figure 10. Titration of Armadale FA (.1658g/L) in 0.10 M NaCl (pH Measurements, Stepwise and after 24-hour Batch Equilibration).

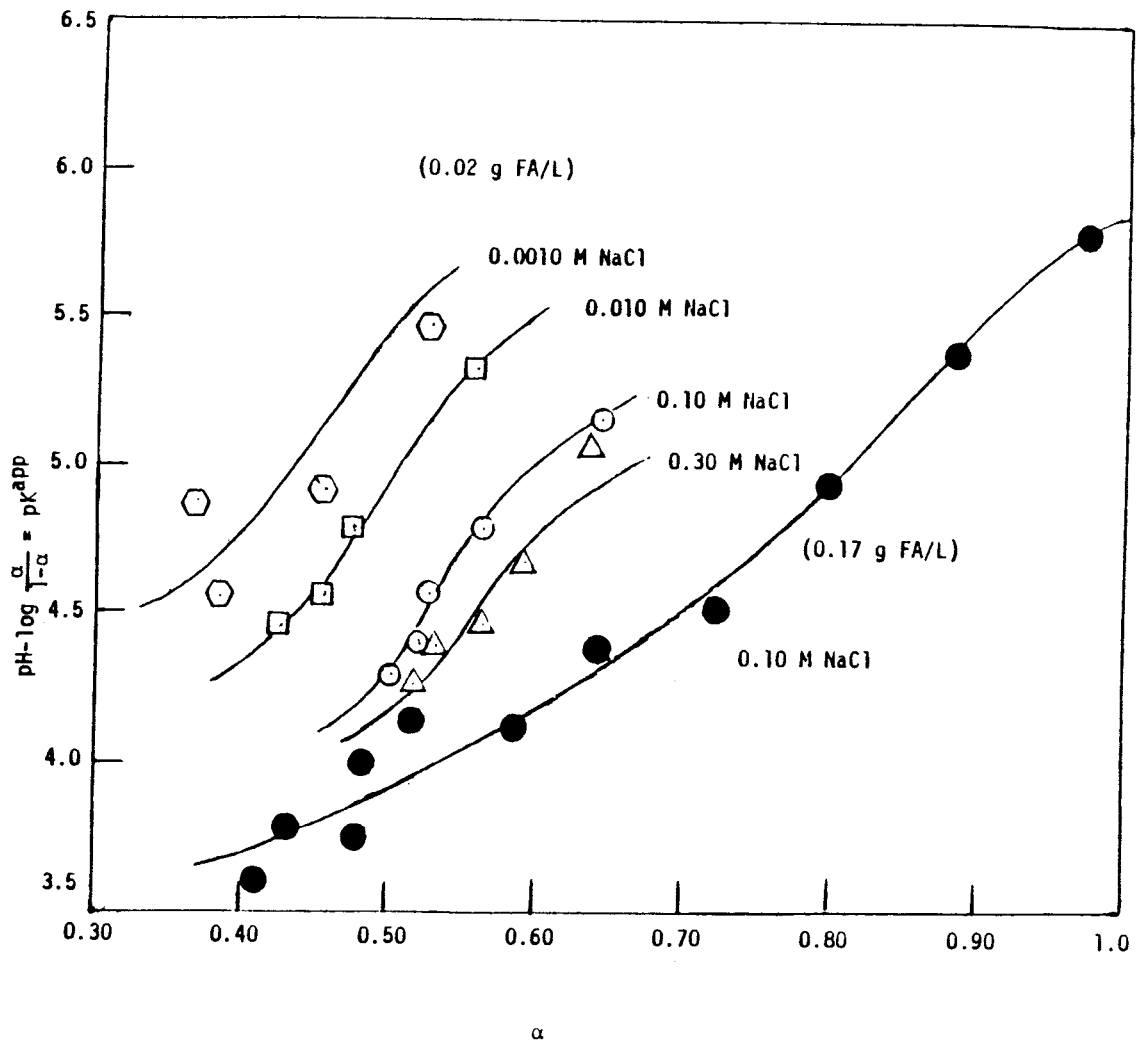


Figure 11. Potentiometric Titration Curves for Armadale FA (Eq. 6).

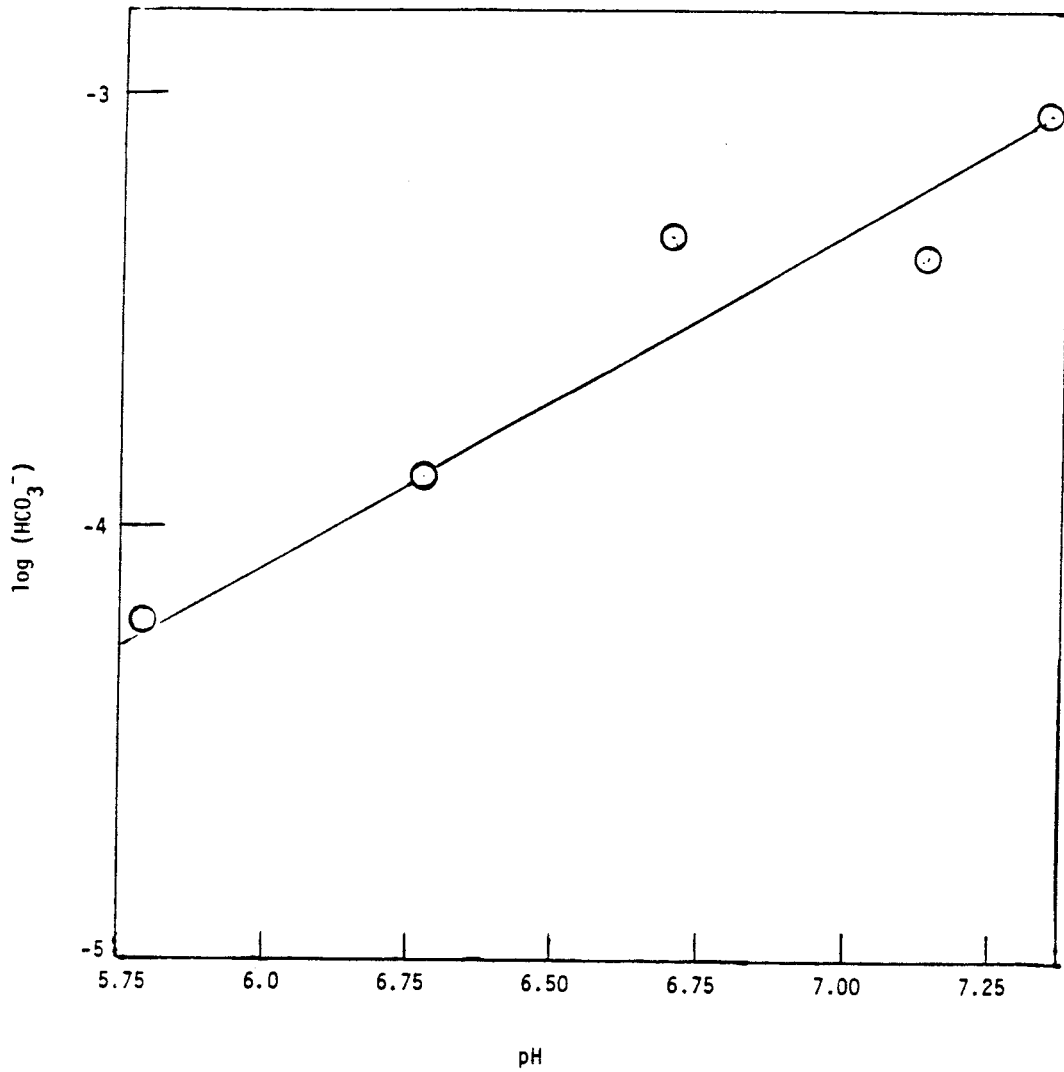


Figure 12. Bicarbonate Uptake by Dilute Acetic Acid as a Function of pH During a Typical Potentiometric Study.

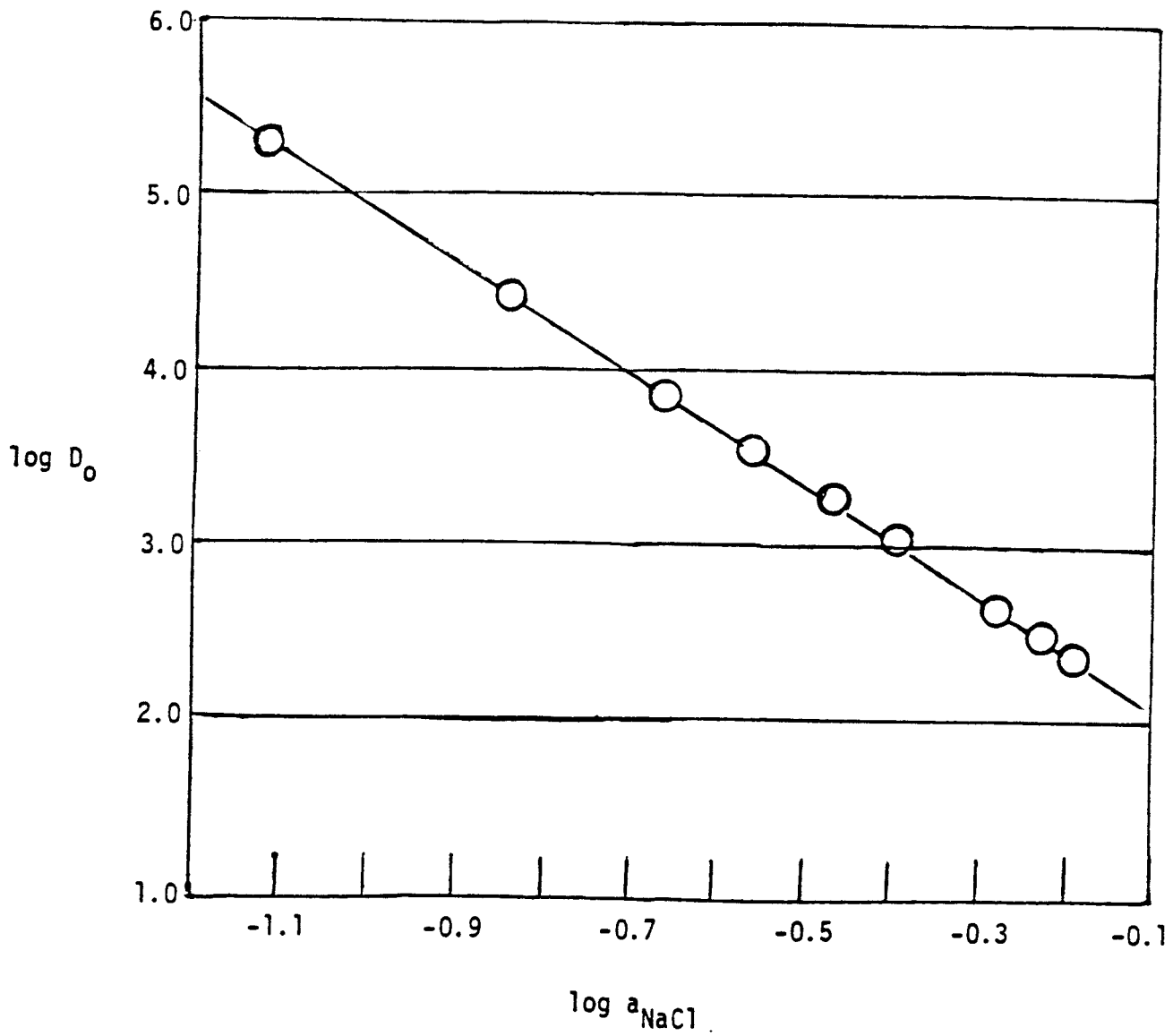


Figure 13. The Distribution of $\text{Eu}^{154}(\text{III})$ Between Na^+ -ion Form Resin and Different Concentrations of NaCl .

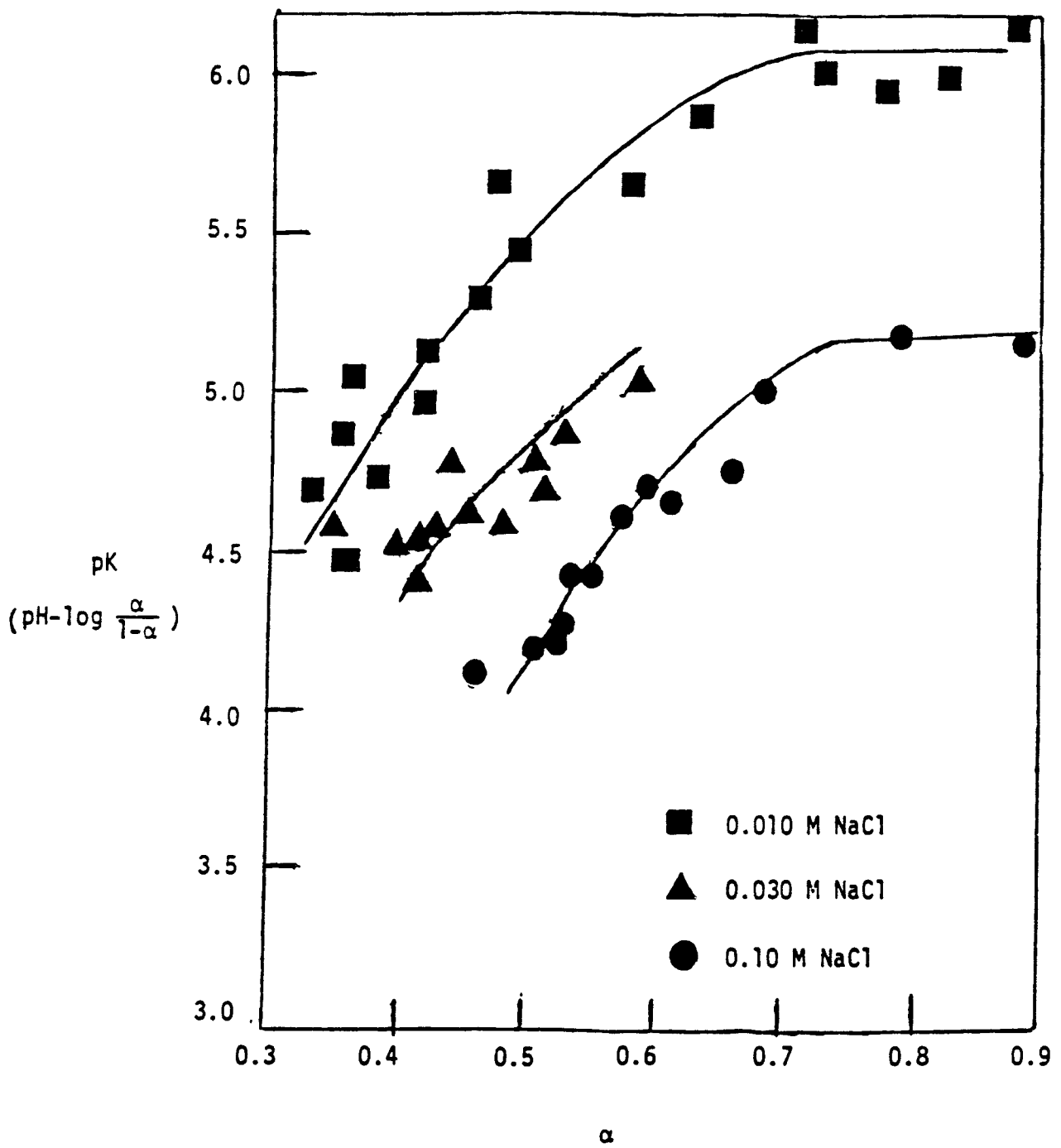


Figure 14. An Earlier Potentiometric Study of Armadale FA (Eq. 6).

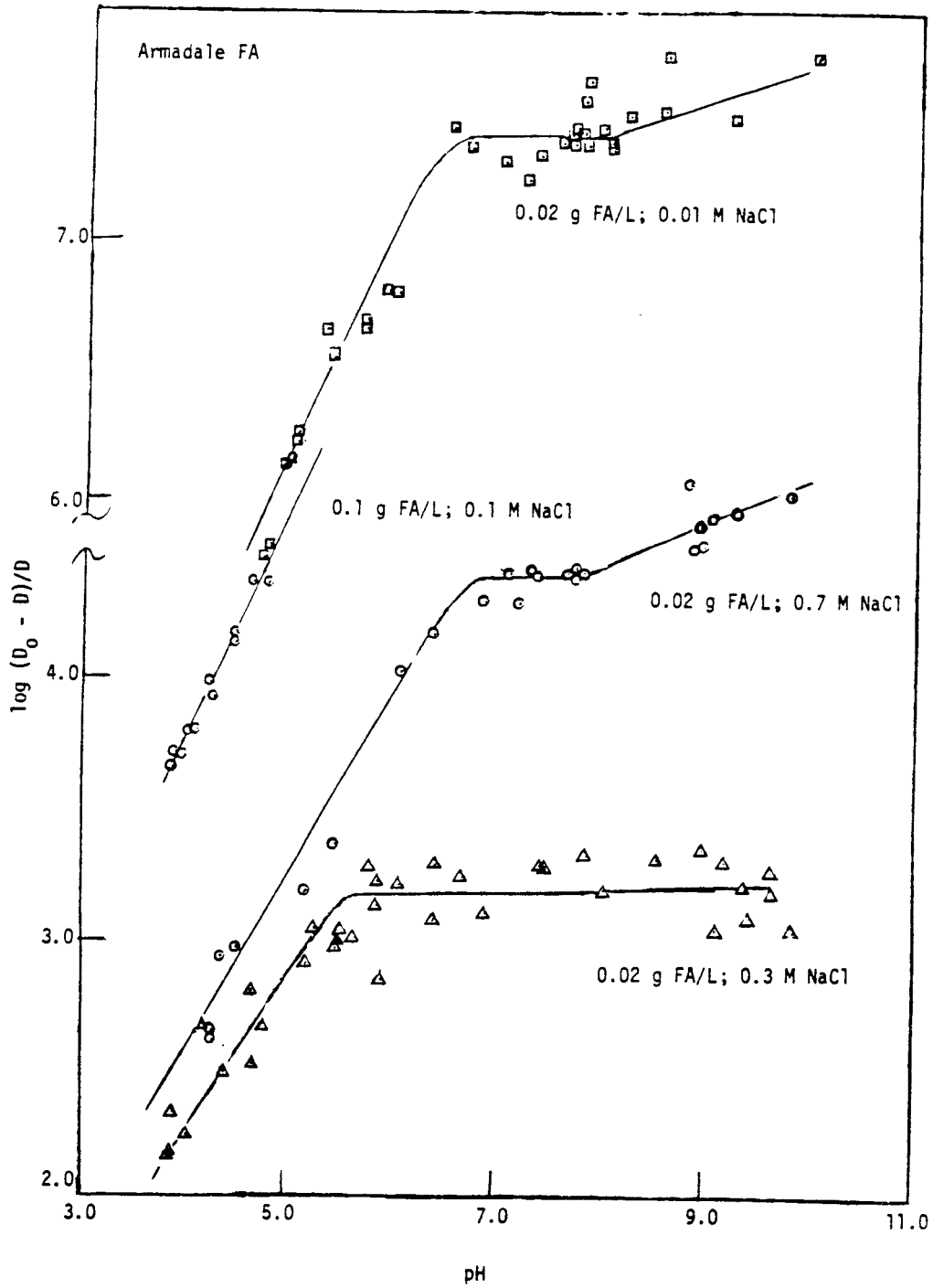


Figure 15. Plots of the Logarithmic Dependence of the Ratio of Bound to Free $\text{Eu}^{154}(\text{III})$ on pH (Other Variables: FA conc.; Ionic Strength).

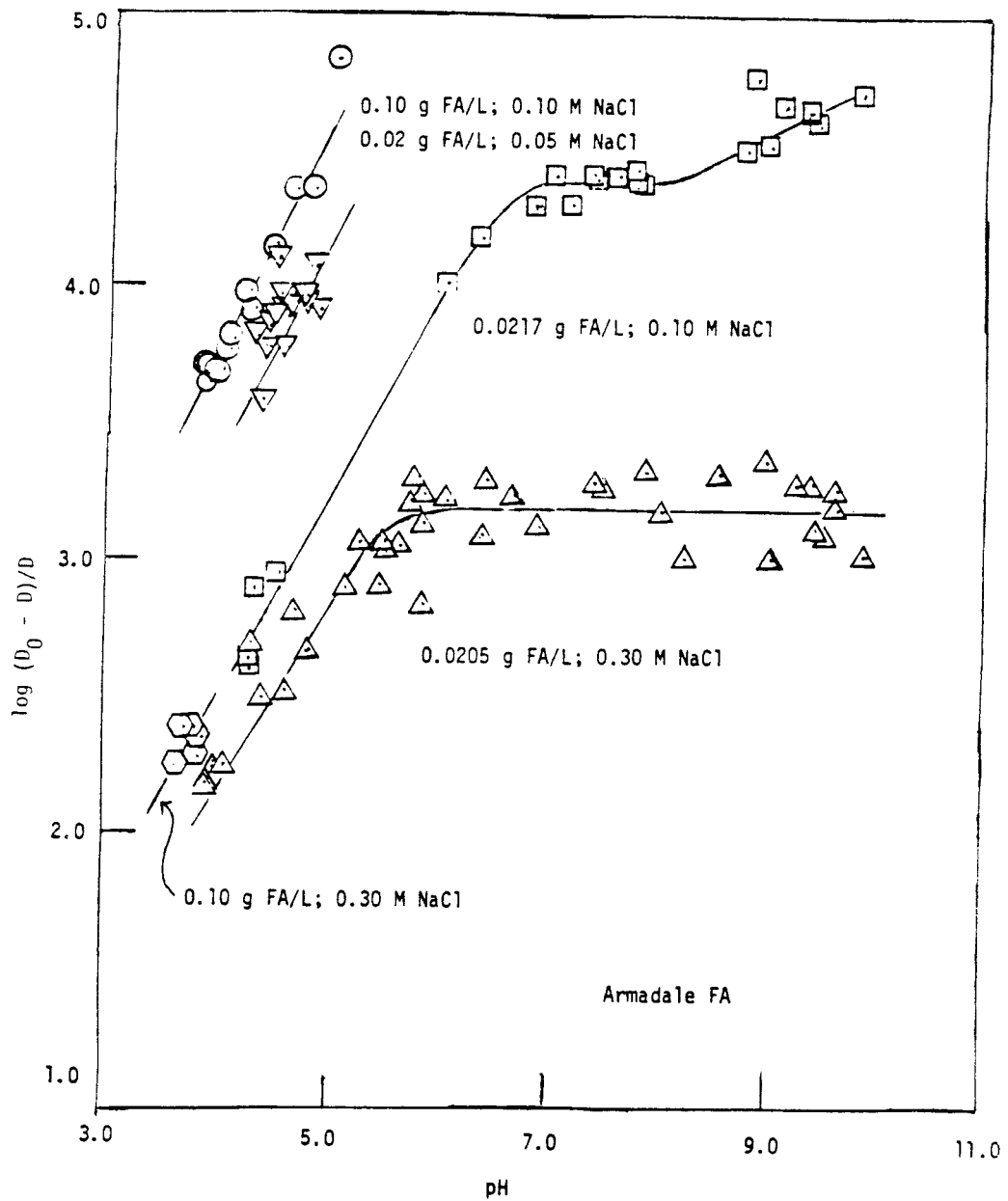


Figure 16. Plots of the Dependence of the Logarithmic Ratio of Bound to Free $\text{Eu}^{154}(\text{III})$ on pH (Other Variables: FA conc.; Ionic Strength).

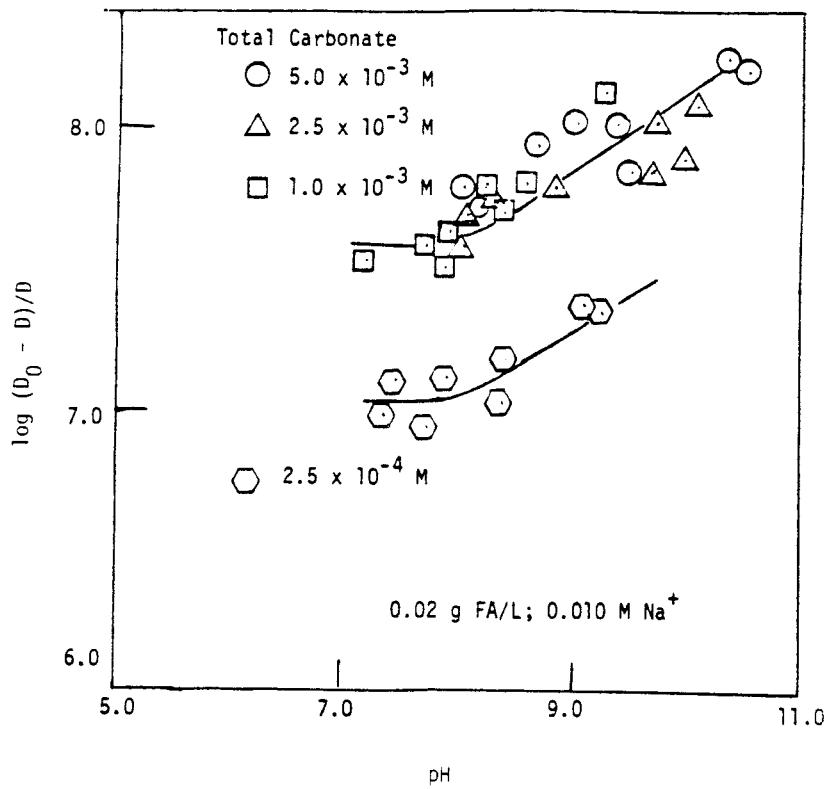


Figure 17. Plots of the Dependence of the Logarithmic Ratio of Bound to free $\text{Eu}^{154}(\text{III})$ on pH (Other Variable: Total Carbonate Concentration).

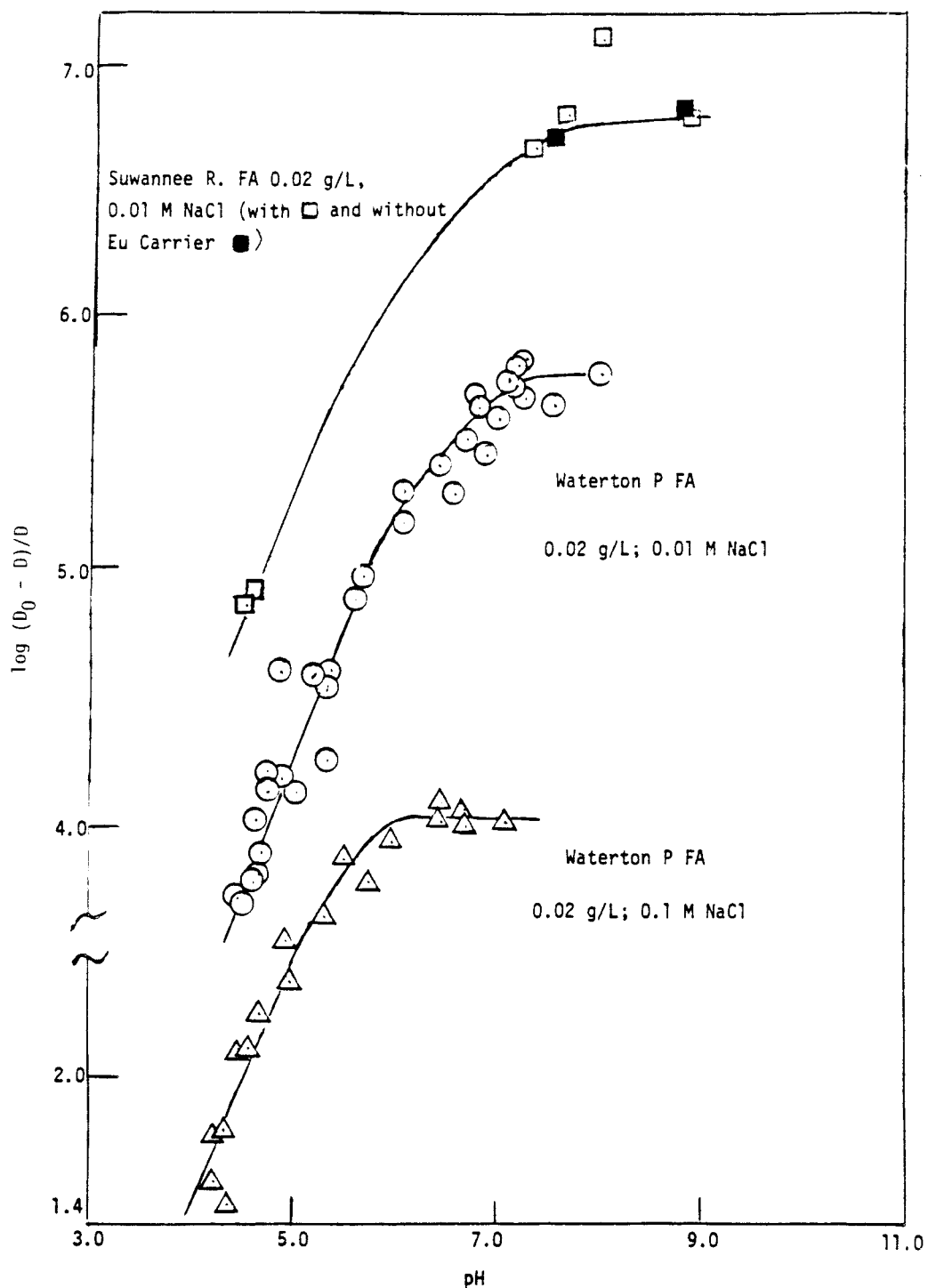


Figure 18. Plots of the Dependence of the Logarithmic Ratio of Bound to free $\text{Eu}^{154}(\text{III})$ on pH (Other Variables: FA source; Ionic Strength).

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