YOUNGSTOWN STATE UNIVERSITY

GRADUATE SCHOOL

THESIS

Submitted in Partial Fulfillment of the Requirements

For the Degree of Master of Science

TITLE The Association Constants of Strontium Ion with Pyrophosphate Ions in Aqueous Solution

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ABSTRACT

THE ASSOCIATION CONSTANTS OF STRONTIUM ION WITH PYROPHOSPHATE IONS IN AQUEOUS SOLUTION

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The determination of equilibrium free (uncomplexed) metal ion in the presence of complexing agents is critical in the evaluation of association constants. In this study equilibrium free strontium ion concentration has been evaluated by determining the strontium ion distribution between a cation exchange resin and aqueous solution with the help of radiotracer Sr^{90} in the absence and in the presence of complexing agent pyrophosphate ion. The association constants have been determined for a 1:1 Sr^{2+}-$P_2O_7^{4-}$ complex at 25°C, pH=10.0, and at various ionic strengths. The log K values at different ionic strengths studied are:

Ionic Strength	log K
0.10	5.35 ± 0.18
0.25	4.50 ± 0.05
0.50	3.97 ± 0.13
0.75	3.78 ± 0.20

The log K values indicate that strontium is strongly bonded to the pyrophosphate ion and the variation of log K with the ionic strength is as expected for this type of system.

ACKNOWLEDGEMENTS

I want to express my sincere gratitude to my adviser, Dr. Inally Mahadeviah, who made this work possible.

I also wish to thank Dr. Orlando Bravo and Dr. Harry Szmant for recommending me to Youngstown State University.

The thesis is dedicated to El Taller Constancio Umana, Professor Gilberto Lopez, Fulvia de Vargas, Argenide Tasara, Verna Lee Doheny and Mr. George Pappas for their encouragement.

Finally, I would like to express my thanks to Dr. Leon Rand, chairman of the chemistry department, and Dr. R. K. Smith and Dr. F. W. Smith for making valuable suggestions to improve the manscript.

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CHAPTER I

Introduction

Pyrophosphate is the first member of straight chain polyphosphates belonging to a large family of condensed phosphates. Condensed phosphates, particularly sodium pyrophosphate and sodium triphosphate are used extensively as "builders" in detergent mixtures. Normal salts contain the ions, $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$, respectively. The formation of relatively stable complexes of these ions with alkaline earth metals has been recognized since 1892.

Different analytical techniques such as, solubility,[1,2] ion-exchange,[3,4] pH titration[5,6] have been successfully employed in determining the formation constants of calcium ion with polyphosphate ions.

This work describes the use of strontium-90, a beta emitter ($t_{\frac{1}{2}}$=29 years), in conjunction with a highly cross-linked cation enchanger, Dowex 50-X12, to evaluate the association constant of Sr^{2+} ion with pyrophosphate ion at various ionic strengths and at pH=10.0. The log K's vary from 3.60 to 5.54 for ionic strengths 0.75 to 0.10.

CHAPTER II

Ion-Exchange Method -- Background

The ion-exchange phenomenen is very common in nature and its consequences have been seen from the time of Aristotle when sand filters were used for the purification of water. Many other natural substances such as silk, cellulose and cell membrances possess this property of ion-exchange.

One study of soils by Spence investigated the loss of ammonia from manure heaps. It was found that when a solution of ammonium sulfate was passed through a packed column of soil the effluent from the column did not contain ammonium salts but sulfate. Thompson[7] reported his findings to the Royal Agricultural Society in 1850.

A very complete investigation of ion-exchange was carried out by Way[8] and his results are said to have placed ion-exchange theory on a real foundation. The most important conclusions were that the process of exchanging ions involved equivalent quantities and that some ions are more readily exchanged than others.

Still, the ion-exchange technique was not used as sn analytical tool until after 1935 when Adams and Holmes[9] prepared synthetic organic exchangers. Since then an enormous amount of work in the field, in both pure and applied research, has enabled industry to manufacture resins of very high quality making possible new developments in chemical separation techniques.

There are many examples in which this technique is applied, one of them in the inorganic field being the separation of rare earths and actinides. A second and very important example is found in the study of fluid and electrolyte balance in the fields of Biology, Biochemistry, Biomedicine and Pharmacology. The application of ion-exchange is expanding so rapidly that in addition to several hundred publications each year many books have been written[10,11,12,13] as well as several excellent annual summaries[14,15] and reviews.[16,17,18]

Synthesis and Chemical Structure

Adams and Holmes[9] are said to be the pioneers in the field of synthetic organic resins. They based their method on the fact that polyphenols and polyamines have weak acid and base properties respectively. So if these two chemical species were to condense with formaldehyde, a fraction of the polar groups would remain uncombined and the resulting polymer would be expected to exhibit the ability to absorb acids or bases respectively. The simple phenol-formaldehyde polymer did exhibit exchange properties but only in strongly alkaline solution.

A second important step forward in the field of synthetic resins of acceptable physico-chemical properties was due to the research of D'Alelio[19] who based his invention on the idea of building up an inert, three dimensional, cross-linked hydrocarbon network structure by copolymerization of styrene with divinyl benzene obtaining a product to which inorganic groups could be attached to confer ionic properties on the resulting material. This has helped the synthesis of a variety of anionic and cationic exchangers of varying capacity, particularly in the field of sulfonic acid type cation exchangers.

Properties of Ion-Exchange Resins

Resins, synthetic organic ion-exchangers, are cross-linked, three dimensional molecular networks containing structurally bound inorganic groups. The numbers of these bound groups determines the exchange capacity, usually expressed as milliequivalents per gram of dry resin.

Ion-exchange resins immersed in water vapor of varying pressure take up a considerable amount of water. The hydration is dependent upon the number of polar groups persent in the resin and when most of them have been used up this depends on the variation of the pressure rather than an the unoccupied polar groups. The amount of water that is absorbed by the resin usually in the hydrogen form reaches a maximum. If we compare the ability of the resin to absorb water in different ionic forms we observe that the maximum absorption decreases in going from hydrogen through lithium, sodium, ammonium and potassium forms.

The same sequence is obtained with these ions in other types of measurements[20] based on the variation of the ratio of charge over radii of the ions. Volume increases in the resin due to the hydration phenomenon and further increases due to the solvent water going into the resin trying to equalize partial pressure. This is known as "swelling" and in practice it is of great importance to choose the right amount of resin according to the dimensions of the column. It is logical to think that a stage of equilibrium is reached at which the resin has expanded to a maximum. The value of this depends on: (a) the degree of cross-linking and (b) the ionic composition of the exchanger.

The point at which the resin has absorbed a maximum of water is known as water of gelation, consisting of water of hydration plus water absorbed due to osmotic pressure.

All definitions about synthetic resins agree that they are high molecular weight organic polyacids and polybases. It is not surprising to find that these species possess properties similar to the acids and bases. Studies of the pH titration are done in order to determine exchange properties.[21,22] The titration curve that is obtained with sulfanic acid cation exchange resin with sodium hydroxide is similar to the typical curve of pH in strong acid versus strong base. The shape of the curve obtained with resin with carboxylic acid is similar to those of acetic acid. Ionic conductivities for the resins have also been measured.[23]

Theory of the Method

Ion-exchange resins in conjunction with radioactive tracers have made possible the study of complexation at low concentrations. The method is particularly suitable for dealing with metal ion concentration determination which cannot be accomplished by the conventional methods. Both cationic[23,24,25,26,27] and anionic[28,29,30] have been successfully used in the determination of complexity constants of several metal ions with a variety of ligands.

Many attempts have been made to give a theoretical interpretation to the data on equilibrium partition of strong electrolytes. These attempts may be classified into three groups.

Group I: Many consider ion-exchange phenomena as analogous to an ionic adsorption reaction, capable of being described by the Langmuir adsorption isotherm for a mixture of adsorbates.[31]

Group II: Donnan[32] membrane equilibrium considerations have been applied frequently to interpret the data of ion-exchange reactions.[33]

Group III: A majority of the investigators view ion exchange reactions in terms of the law of mass action and consequently most applications are based on this view to interpret their findings.[34,35,36,37] Ion exchange resins are considered strong electrolytes and hence their reactions in aqueous solutions can be represented as heterogeneous reversible double decomposition reactions.

Schubert has shown that ion exchangers can be used in the determination of formation constants.[38,39,40] In the present work the method of Schubert as modified by MacAvoy[3] is employed for the determination of free strontium ion in pyrophosphate solutions. Some experimental details are provided here in order that mass action theory may be developed in specific form.

In all experiments the adsorbent used was the cation exchanger, Dowex 50-X12 in the tetramethylammonium form. Dowex 50 is an aromatic polymer containing nuclear sulfonic acid groups. The properties of this polymer have been discussed by Bauman and Eichorn.[41] In the present study the system consisted of a 0.0080 to 0.1000g sample resin in the TM^+ ion form in equilibrium with solution 10^{-6} to 10^{-3} M in $SrCl_2$, 10^{-5} to 10^{-3} in tetramethylammonium pyrophosphate (TMPP) at a pH of 10.0. Ionic strengths were established at 0.10, 0.25, 0.50, or 0.75 by addition of standardized tetramethylammonium chloride solution, and pH by the addition of tetramethylammonium hydroxide.

In general, the equilibrium between an ion exchanger, here TMR, and a metal ion, in this case Sr^{2+}, may be written:

$$Sr^{2+} + 2TMR_{(s)} \qquad SrR_{2(s)} + 2\,TM^+ \tag{1}$$

And according to the law of mass action, the equilibrium quotient, K is given by

$$K = \frac{A_{SrR_2} \cdot A^2{}_{TM^+}}{A_{Sr^{2+}} \cdot A^2{}_{TMR}} \tag{2}$$

Where A, is the activity of the different chemical species,

SrR_2 = Sr^{2+} ion in the resin phase

Sr^{2+} = Sr^{2+} ion in the aqueous phase

TMR = TM^+ ion in the resin phase

TM^+ = TM^+ ion in the aqueous phase

Equation (2) describes ion exchange reactions in aqueous solutions and in this form it is used by most investigators. The problem in applying equation (2) to the determination of free metal ion concentration in the aqueous complexing solutions is the lack of data regarding the activity coefficients of ions in the resin phase. This difficulty can be overcome by using "tracer" concentrations, 10^{-9} to 10^{-10} M, metal ions, and the establishment of the following conditions as shown by Schubert.[38,39,40]

(a) The system is swamped with excess neutral salt; the ionic strength remains nearly constant.

(b) The concentration of the metal ion is negligible as compared with the concentration of complexing anion.

(c) All solutions have the same pH

(d) The exchanger used has been previously saturated with the cation component of the bulk electrolyte (in this case TM^+)

(e) No adsorption of the complex forming anion or the complex ion takes place.

On substituting molar concentrations and activity coefficients for activity terms in equation (2), one gets for K:

$$K = \frac{\gamma_{SrR_2}\,[TM^+]^2}{[TMR]^2\gamma_{Sr^{2+}}} \cdot \frac{[SrR_2]\cdot\gamma_{TM^+}^{2}}{[Sr^{2+}]\cdot\gamma^2_{TMR}} \qquad (3)$$

If TM^+ ion is present in large concentration in solution, it will determine both the swelling and activity coefficient in the resin phase. Further, keeping TM^+ ion concentration and ionic strength constant with Sr^{2+} ion present in "tracer" concentration, all the activity coefficients as well as TMR and the density of the resin can be regarded as constant, and thus equation (3) with the incorporation of the above ideas becomes:

$$\frac{[SrR_2]}{[Sr^{2+}]} = K^1{}_D = \frac{[TMR]^2}{[TM^+]^2} \cdot \frac{\gamma_{Sr^{2+}} \cdot \gamma^2{}_{TMR}}{\gamma_{SrR_2} \cdot \gamma^2{}_{TM^+}} \cdot K = \text{constant} \qquad (4)$$

where $K^1{}_D$ is the distribution coefficient of Sr^{2+} ion between the resin and the aqueous phases. Introducing the following terms:

W = weight of the resin in grams

d = density of the resin in grams per milliliter

N_{SrR_2} = moles of Sr^{2+} ion in the resin phase, equation (4) becomes:

$$\frac{N_{SrR_2/W}}{[Sr^{2+}]} = K_D = \frac{1}{d} \cdot K^1{}_D = \frac{[TMR]^2}{[TM^+]^2} \cdot \frac{\gamma_{Sr^{2+}} \cdot \gamma^2{}_{TMR}}{\gamma_{SrR_2} \cdot \gamma^2{}_{TM^+}} \cdot K \cdot \frac{1}{d} = \text{constant} \qquad (5)$$

If the above assumptions are valid, K_D, which can be evaluated experimentally, is a constant independent of Sr^{2+} ion in solution equilibrated with the resin. Once determined K_D could be used to calculate $[Sr^{2+}]$ in a solution equilibrated with the resin, from $N_{SrR_2/W}$, the moles of Sr^{2+} adsorbed from the solution per unit weight of resin.

In the work of MacAvoy[3] and Mahadeviah[4], as well as in the present work, the concentrations of metal ions studied were not at <u>tracer</u> level and consequently MacAvoy modified the method for application at higher than tracer level, but still at low metal ion concentrations. At higher level, he reasoned, the factors $[TMR]$, γ_{TMR} and $\gamma^2_{SrR_2}$, in equation (5) no longer remain constant because of the extensive substitution of TM^+ ion in the resin by the adsorbed metal ion. However, the activity coefficients in the solution and the density of the resin should not vary if $[TM^+]$ ion and the ionic strengths are kept constant. But the three factors related to the activities in the resin phase vary as a function of metal ion concentration. Therefore, it is possible to obtain by experiment, for each $[TM^+]$ and ionic strength, a unique calibration curve relating $N_{SrR_2/W}$ to $[Sr^{2+}]$. This curve, once determined, would allow the estimation of $[Sr^{2+}]$ in a solution from $N_{SrR_2/W}$ for resin in equilibration with the solution. It should be emphasized, however, that by this method, one determines the free Sr^{2+} or metal ion concentrations, <u>not</u> <u>activities</u>, in unknown solutions.

CHAPTER III

Experimental Procedure

In this investigation ion-exchange resin in conjunction with radioactive tracer was used to measure the association constants of Sr^{2+} ion with pyrophosphate ion in aqueous solutions. This method is excellent for metal ions at low concentrations whose determination is hampered by conventional methods. The method consists of the determination of the adsorption of strontium ion on the tetramethylammonium (TM^+) form of the cation exchange resin, Dowex 50-12X, as a function of strontium ion concentration in presence and absence of tetramethylammonium pyrophosphate (TMPP). With tetramethylammonium chloride (TMCl) added to establish the appropriate ionic strength and tetramethylammonium hydroxide (TMOH) to adjust the pH to 10.0. The distribution of strontium ion between resin and solution was determined by use of radioactive Sr^{90} tracer.

A. Apparatus

All equilibrations were carried out in a constant temperature bath equipped with a shaking mechanism. The temperature was controlled at 25.0 ± 1.0°C. The shaking bath accommodated 50ml conical reaction flasks which were tightly stoppered with rubber stoppers.

Tracer counting was done on samples evaporated in stainless steel planchetts using a thin (1.9mg/cm^2, mica) end-window Geiger tube, mounted in a lead shield, and attached to a Nuclear Chicago scaler.

B. Materials

1. Deionized water

The dionized water used in this investigation was obtained by passing distilled water through an ion exchanger research model supplied by the Illinois water treatment company of Rockford, Illinois. The pH of the deionized water was found to be 7.5.

2. Sodium pyrophosphate

Fisher certified reagent grade was used to make solutions without further purification.

3. Tetramethylammonium chloride (TMCl)

Eastman Kodak reagent grade was used to make solutions of approximately 2M concentration in deionized water, the solutions were always filtered before their use. The exact concentration of TMCl were determined by potentiametric titration against standardized silver nitrate.

4. Strontium chloride

Baker Analysed reagent grade strontium chloride hexahydrate was used to prepare an approximately 0.1 M solution of strontium chloride in deionized water. It was then standardized with standard $AgNO_3$ by potentiometric titration. This stock standard was then used to prepare solutions of desired concentrations.

5. Tetramethylammonium hydroxide (TMOH)

A 1:1 solution was made from Eastman Kodak reagent grade tetramethylammonium hydroxide.

6. Tetramethylammoniumpyrophosphate (TMPP)

TMPP was prepared by ion-exchange on the cation exchange resin, Dowex 50W-X2, of total exchange capacity (dry basis) 5.2meq/g, Baker Analysed reagent grade. The resin originally in H^+ ion form and 100-200 mesh was equilibrated with 2M hydrochloric acid and then packed into a column of 2cm diameter until it reached a height of 30cm. This required 90g of resin (dry basis). The column of resin was then washed thoroughly and slowly with 2 liters of 2 M HCl solution in order to ensure that all the active sites were associated with H^+ ions. This was followed by 2 liters of 0.25M sodium pyrophosphate solution in order to remove ions like Ca^{2+}, Mg^{2+} from the column. The column was then washed with a liter of 2M NaCl solution. The resin in the column was then converted to NH_4^+ ion form by washing slowly (one ml per minute) and thoroughly with 2 liters of 2M NH_4Cl. The purpose of the last treatment was to remove Na^+ ions from the column and put in their place a cation that would exchange more readily than Na^+ ion with TM^+ ion. After washing with deionized water until the effluent was free from chloride, the resin was converted to TM^+ ion form by washing slowly (0.5ml per minute) with a ten-fold excess of 1M TMCl solution. The resin was washed again with deionized water until the effluent gave a negative test for chloride ions. Sodium pyrophosphate solution of suitable concentration (approximately 0.02M) was passed through the column in one 400 ml batch at a rate of about 0.5 ml per minute. There was at least a ten-fold excess of resin sites per pyrophosphate ion. The effluent collected initially until it reached a pH of 8.5 was discarded, that fraction of the effluent at pH 8.5 - 8.0 was collected and used. The phosphate concentration in this TMPP solution was determined colorimetrically as phosphate by the phosphovanadomolybdate method.[42,43] The concentration of phosphorus so determined was 0.0125 M.

7. Radioactive strontium - 90

Radiotracer Sr^{90} was purchased from New England Nuclear Company, Boston, Massachusetts, as $SrCl_2$ in 0.1 N HCl, purity of the sample $99^{+}\%$, processed from fission material. The solution was further diluted in deionized water to give an appropriate number of counts.

8. Resin

The cation exchange resin Dowex-50X12 (12% divinylbenzene cross-linking; 100-200 mesh) was selected for the adsorption of Sr^{2+} ion from test solutions. A highly cross-linked resin was chosen to avoid the undesirable effects of resin swelling.

A seventy-five gram sample of Dowex 50-X12 cation exchange resin (total capacity 5.0meq/g, dry basis) in the H^{+} ion form was packed in a column (2 cm diameter) to a height of 30 cm. The resin was washed first with 2 liters of 2M HCl and then with deionized water until the effluent gave a negative test for chloride.

The resin was then converted to the TM^{+} ion form by passing through the column four liters of 1 M TMCl, equivalent to ten-times more than what was required on a 1:1 exchange basis. The rate of flow of TMCl through the column was ten drops per minute. Excess TMCl was removed by washing thoroughly with deionized water until the effluent gave negative test for chloride. The TM^+ ion form thus prepared was taken out of the column, rinsed several times with deionized water and air dried.

C. Procedure

1. Counting of samples

All samples of Sr^{90} counting were evaporated in stainless steel or aluminum planchetts and placed in a reproducible position beneath the counter window. A minimum of 10,000 counts were collected for each sample to give an expected standard deviation of one per cent. For each reaction mixture counting was done on duplicate mixtures and the average counting rate was used for calculations. In most cases, the counting rates were sufficiently low, 2,000 cpm or less, os that coincidence corrections were not necessary. In cases where the counting rates were higher, however, necessary corrections were made. Bakcground coutning rates were determined each working day and subtracted from the rates of samples. In order to avoid corrections for self-adsorption, the necessary inert material was added where necessary. No corrections were applied for back scattering.

2. Strontium adsorption in the absence of pyrophosphate

For each experiment appropriate volumes of standardized stock solutions were transferred from burettes or Lambda pipettes into 50ml conical flasks; $SrCl_2$, salt (TMCl) to give the desired ionic strength, 0.100 - 0.200 ml of highly dilutes $Sr^{90}Cl_2$ tracer, base (TMOH) to adjust the pH of 10.0, and finally deionized water to bring the total volume to a definite value, usually 25.0 ml. The contents of each flask was thoroughly mixed, and duplicate aliquots of 0.100 ml (100) were taken for Sr^{90} measurement, counting each aliquot twice, the counting rates being averaged. A sample of resin in the TM^+ ion form was then carefully weighed into the flask. The flask was placed securely in the constant temperature bath at 25°C and equilibrated by shaking for 12 to 24 hours.

At the end of equilibration, the flask was removed from the bath, the resin was allowed to settle, and duplicate aliquots of 0.500 ml were transferred, evaporated for Sr^{90} measurement; counting rates of the aliquots were averaged. A check on the pH was made at this point, in case the value was below 10.0.

3. Strontium adsorption in the presence of pyrophosphate

The experimental procedure for measuring strontium adsorption in the presence of phosphate was the same as that described for no phosphate, except for the addition of standardized TMPP solution to the other reagents in the reaction flask.

4. The "Calibration Curve" - relating moles of strontium

ion adsorbed per gram of resin and the equilibrium free strontium ion concentration in solution

The data accumulated from the equilibrations of resin with solutions free of pyrophosphate were used to establish the relationship between the amount of Sr^{2+} ion adsorbed on the resin and the free Sr^{2+} ion concentration in this heterogeneous equilibrium system. This is as follows:

(a) From the counting rate of the solution and its known Sr^{2+} ion concentration before equilibration with the resin, the ratio of counting rate to Sr^{2+} ion concentration was established.

(b) After equilibration with the resin, the counting rate of the solution was used to measure the concentration of Sr^{2+} ion remaining in the aqueous phase. From the known volume of solution, the concentrations of strontium ion before, ${Sr^{2+}}_I$, and after equilibration, $[Sr^{2+}]_E$, and the weight (W) of the resin, the number of moles of Sr^{2+} adsorbed per gram of resin and $\frac{N_{SrR_2}}{W}$, was determined.

(c) By choosing different initial Sr^{2+} ion concentration, ${Sr^{2+}}_I$, and different weights of resin for separate equilibrations, many values of the relationship between $\frac{N_{SrR_2}}{W}$ and $[Sr^{2+}]_E$ were obtained, and a plot of $-\log \frac{N_{SrR_2}}{W}$ vs $-\log [Sr^{2+}]_E$ was made. This is the "calibration curve." This curve is unique for each ionic strength. In this investigation four ionic strengths were studied and thus there are four calibration curves. (Pages 25, 26, 27 and 28)

5. The free, uncomplexed, strontium ion concentration in

solutions containing pyrophosphate

The data from equilibrations of resin with solutions containing pyrophosphate were processed similarly. Here, however, the total strontium ion, $[Sr^{2+}]_T$, found in the solution after equilibration includes both free Sr^{2+} ion, $[Sr^{2+}]_E$, and complexed Sr^{2+} ion, $[SrP_2O_7{}^{2-}]$. Nevertheless, $\frac{N_{SrR_2}}{W}$, as calculated from such an equilibration, when applied to the appropriate "calibration curve," gives the corresponding value for $[Sr^{2+}]_E$, the free (uncomplexed) Sr^{2+} ion concentration in the phosphate solution.

6. The association constant of the strontium-pyrophosphate complex

The evaluation of the association constant is based on one assumption, namely there is a 1:1 complex formed in all the compositions studied. The association constant, K, of the strontium-pyrophosphate was taken as

$$K = \frac{[SrP_2O_7{}^{2-}]}{[Sr^{2+}][P_2O_7{}^{4-}]}$$

For calculation of this constant for each equilibration in presence of pyrophosphate, the following procedure was used:

(a) $Sr^{2+}{}_E$ was determined as described before.

(b) The equilibrium concentration of the complexion, $[SrP_2O_7{}^{2-}]$, was derived by subtracting $[Sr^{2+}]_E$ from the total Sr^{2+} ion concentration, $[Sr^{2+}]_T$, found in the solution after equilibration with the resin.

(c) The concentration of uncomplexed pyrophosphate ion at equilibrium, $[P_2O_7{}^{4-}]_E$, was calculated by subtracting

$[SrP_2O_7^{2-}]$ from total pyrophosphate ion concentration, $[P_2O_7^{4-}]_T$.

Chapter IV

Results and Conclusions

A. Adsorption in the absence of phosphate: TMR-TMCl-$SrCl_2$ system

Many experiments were done with carefully weighed samples of resin in the tetramethylammonium ion form (TMR) equilibrated with solutions containing strontium chloride, tetramethylammonium chloride (TMCl), tetramethylammonium hydroxide, and strontium-90 chloride. Tetramethylammonium chloride was added to adjust the ionic strength to 0.10, 0.25, 0.50, and 0.75, tetramethylammonium hydroxide to bring the pH of the solutions to 10.0, and strontium-90 chloride tracer in order to facilitate the determination of strontium ion at low concentration. The equilibrium strontium ion concentrations in solution range from 10^{-6} to 10^{-4} M. The results are shown in tables I (μ=0.10), II (μ=0.25), III (μ=0.50), and IV (μ=0.75).

A plot of the negative logarithum of the equilibrium concentration of free strontium ion, $-\log [Sr^{2+}]_E$, versus the negative logarithum of moles of strontium adsorbed per gram of resin, $-\log \frac{N_{SrR_2}}{W}$ is shown in figures I (μ=0.10), II (μ=0.25), III (μ=0.50), and IV (μ=0.75). These are the <u>calibration curves</u>.

Test of the theoretical relations

The data accumulated from resin equilibration experi-

Table I

Relative Adsorption of Sr^{2+} ion from Solutions by Dowex 50-12x in TM^{+} ion form

Pyrophosphate absent (PH = 10; $\mu = 0.10$; T = 25.0 ± 1° C)

Total Initial $[Sr^{2+}]_I$ x10^4 (Molar) "I"	Weight of Resin (g)	Total Volume (ml)	Equilibrium $[Sr^{2+}]_E$ x10^6 (Molar)	-log $[Sr^{2+}]_E$	$\frac{N_{SrR_2}}{W}$ x10^6 (moles/g)	-log $\frac{N_{srR_2}}{W}$	$\frac{[Sr^{2+}]_E}{N_{SrR_2}/W}$ (g/liter)
39.60	0.1050	25.0	112.0	3.96	914.0	3.04	0.123
39.60	0.0518	25.0	728.0	3.14	1560.0	2.81	0.467
19.80	0.0729	25.0	121.0	3.92	678.0	3.17	0.178
9.90	0.0599	25.0	5.11	5.29	410.0	3.39	0.012
1.19	0.0169	25.0	0.578	6.24	175.0	3.76	0.003 *
0.0198	0.0143	25.0	0.005	8.30	3.45 *	5.46	0.001
0.0198	0.0048	25.0	0.014	7.87	10.2 *	5.00	0.001 *
0.396	0.0120	25.0	0.188	6.73	82.1 *	4.10	0.002 *

Table II

Relative Adsorption of Sr^{2+} ion from Solutions by Dowex 50-12x in TM^+ ion form

Pyrophosphate absent (pH = 10; $\mu = 0.25$; T = 25.0 ± 1° C)

Total Initial $[Sr^{2+}]_I$ x10^4 (Molar)	Weight of Resin (g)	Total Volume (ml)	Equilibrium $[Sr^{2+}]_E$ x10^6 (Molar)	-log $[Sr^{2+}]_E$	$\frac{N_{SrR_2}}{W}$ x10^6 (moles/g)	-log $\frac{N_{srR_2}}{W}$	$\frac{[Sr^{2+}]_E}{N_{SrR_2}/W}$ (g/liter)
39.6	0.1040	25.0	269.0	3.57	887.0	3.05	0.303
19.8	0.0714	25.0	72.7	4.14	667.0*	3.18	0.109
9.9	0.0479	25.0	19.9	4.70	506.0*	3.30	0.039
3.96	0.0232	25.0	9.67	5.0	416.0*	3.38	0.023*
1.19	0.0184	25.0	1.27	5.9	160.0	3.80	0.008*
0.022	0.0158	25.0	0.011	7.98	3.5	5.46	0.003*

Table III

Relative Adsorption of Sr^{2+} ion from Solutions by Dowex 50-12x in TM^{+} ion form

Pyrophosphate absent (pH = 10; $\mu = 0.50$; T = 25.0 ± 1° C)

Total Initial $[Sr^{2+}]_I$ $\times 10^4$ (Molar)	Weight of Resin (g)	Total Volume (ml)	Equilibrium $[Sr^{2+}]_E$ $\times 10^6$ (Molar)	$-\log [Sr^{2+}]_E$	$\frac{N_{SrR_2}}{W}$ $\times 10^6$ (moles/g)	$-\log \frac{N_{SrR_2}}{W}$	$\frac{[Sr^{2+}]_E}{N_{SrR_2}/W}$ (g/liter)
39.6	0.1083	25.0	424.0	3.37	817.0	3.09	0.519
39.6	0.0535	25.0	1000.0	3.00	1380.0	2.86	0.725
19.8	0.0732	25.0	156.0	3.81	621.0	3.21	0.251
9.9	0.0507	25.0	55.40	4.26	461.0*	3.34	0.120*
1.19	0.0100	25.0	21.50	4.67	244.0*	3.61	0.088*
0.0396	0.0141	25.0	0.055	7.26	6.93	5.16	0.008*
0.0396	0.0066	25.0	0.179	6.75	14.3	4.84	0.013
0.396	0.0141	25.0	2.12	5.67	66.5*	4.18	0.032

Table IV

Relative Adsorption of Sr^{2+} ion from Solutions by Dowex 50-12x in TM^+ ion form

Pyrophosphate absent (pH = 10; $\mu = 0.75$; T = 25.0 ± 1° C)

Total Initial $[Sr^{2+}]_I$ x10^4 (Molar)	Weight of Resin (g)	Total Volume (ml)	Equilibrium $[Sr^{2+}]_E$ x10^6 (Molar)	$-\log [Sr^{2+}]_E$	$\frac{N_{SrR_2}}{W}$ x10^6 (moles/g)	$-\log \frac{N_{SrR_2}}{W}$	$\frac{[Sr^{2+}]_E}{N_{SrR_2}/W}$ (g/liter)
19.80	0.0505	25.0	353.0	3.45	805.0	3.09	0.438
7.92	0.0309	25.0	101.0	4.00	557.0 *	3.25	0.181*
1.98	0.0215	25.0	12.9	4.89	215.0 *	3.67	0.060*
0.396	0.0116	25.0	2.7	5.57	79.5 *	4.10	0.034*
0.0396	0.0174	25.0	0.074	7.13	5.59	5.25	0.013
0.0396	0.0087	25.0	0.184	6.74	10.80	4.97	0.017

Figure I (μ=0.10)

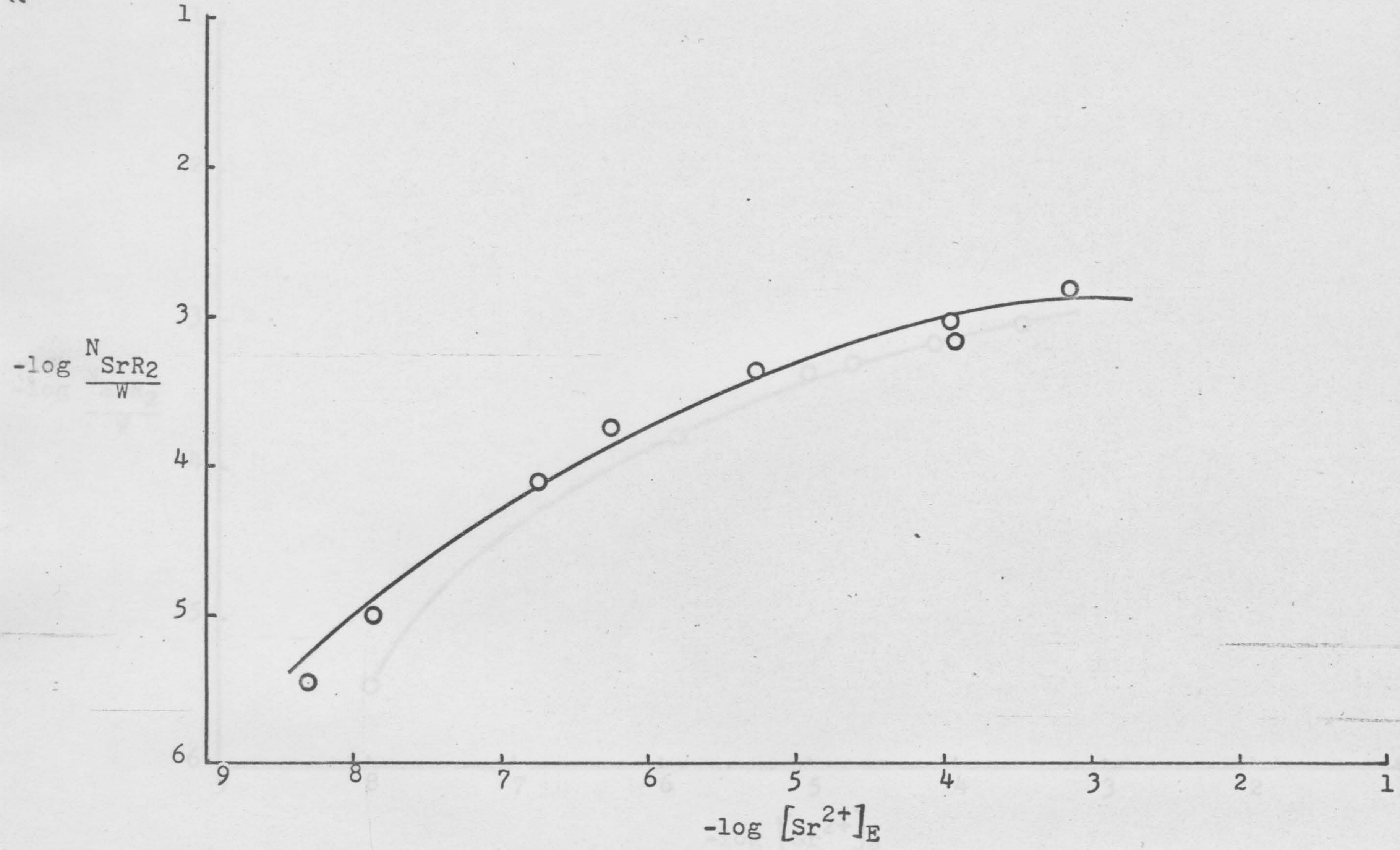


Figure II (μ=0.25)

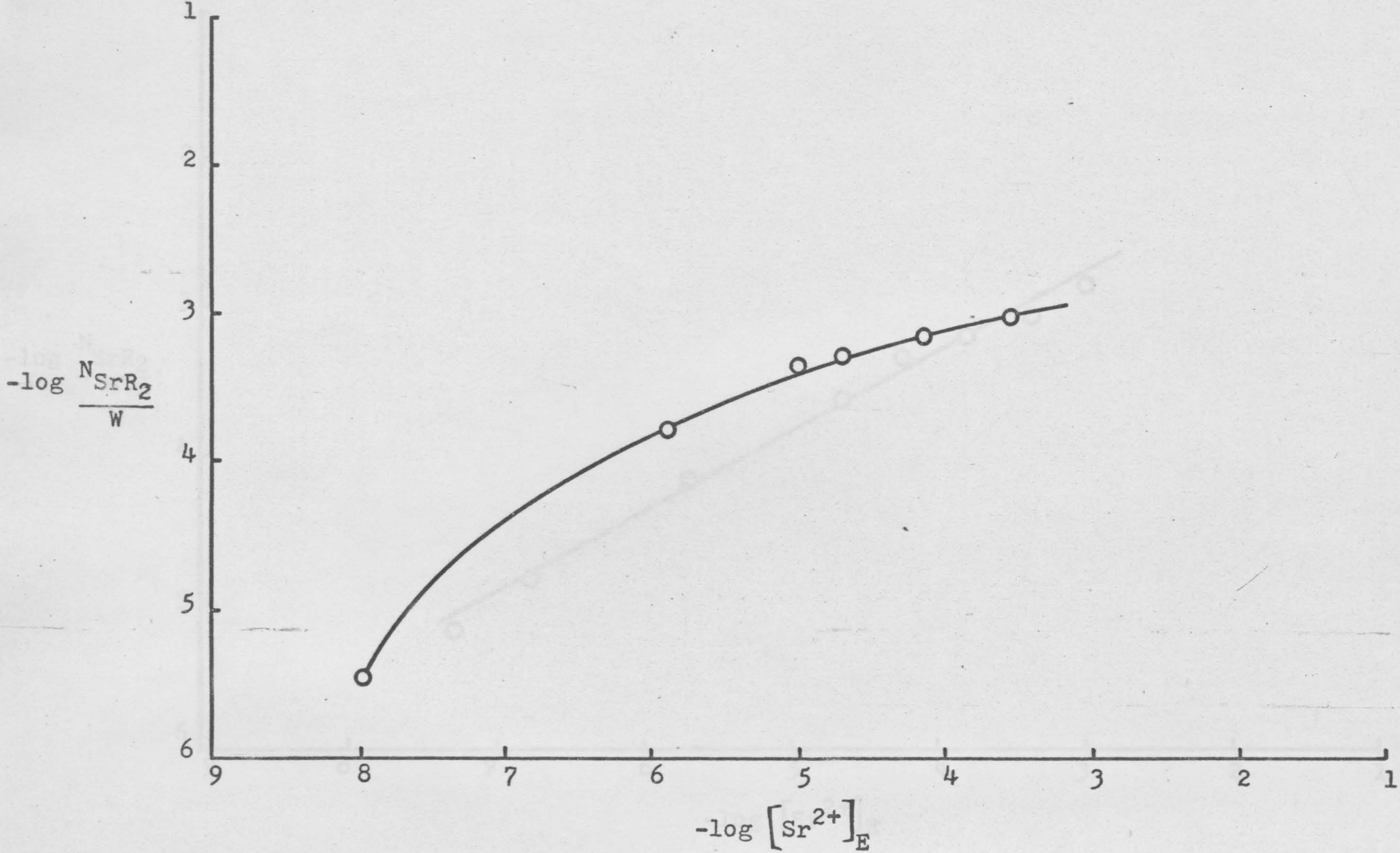


Figure III (μ=0.50)

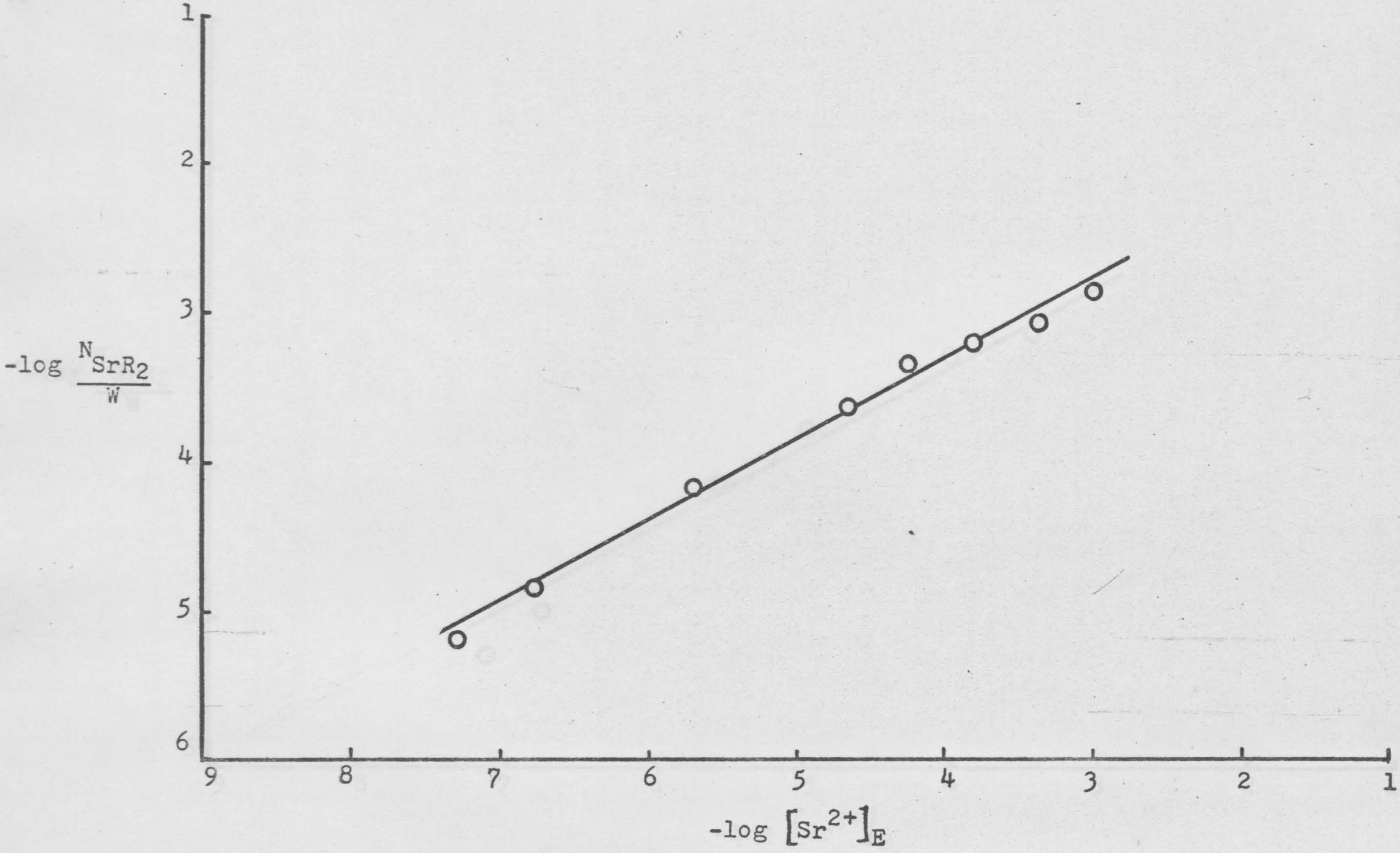
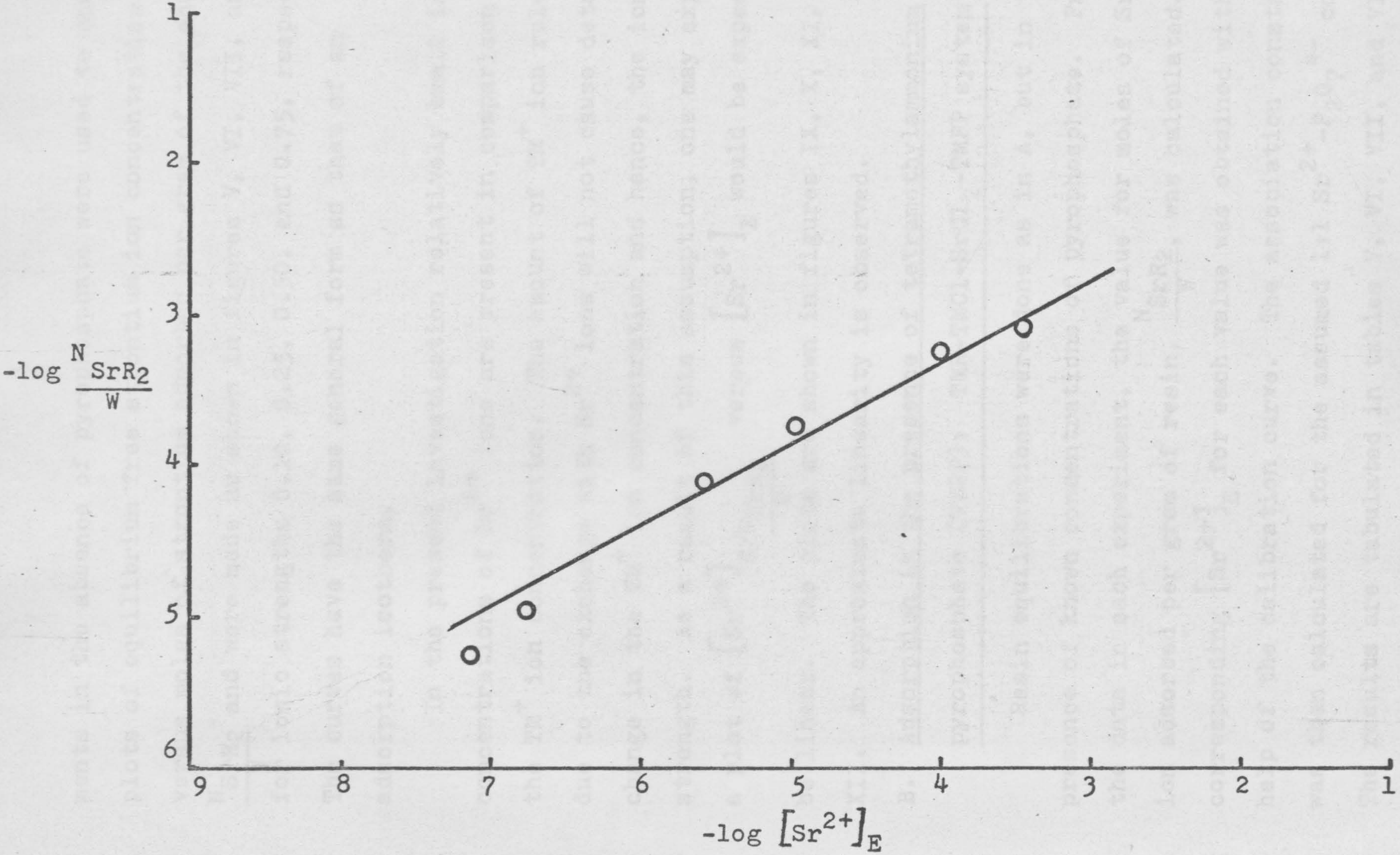


Figure IV (μ=0.75)



ments in the absence of pyrophosphate were used to construct plots of equilibrium free strontium ion concentration $Sr^{2+}{}_E$ versus moles of strontium adsorbed per gram of the adsorbent, $\frac{N_{SrR_2}}{W}$ and were made as shown in figures V, VI, VII, and VIII for ionic strengths 0.10, 0.25, 0.50, and 0.75, respectively. The curves have the same general form as that of an adsorption isotherm.

In the present investigation relatively small initial concentrations of Sr^{2+} ions are present in comparison with the TM^+ ion concentration. The amount of TM^+ ion released due to the exchange with Sr^{2+} ions will not cause detectable change in the TM^+ ion concentration and hence, the ionic strength. As a result of this assumption, one may expect a plot of $[Sr^{2+}]_{E/\frac{N_{SrR_2}}{W}}$ versus $[Sr^{2+}]_E$ would be expected to be linear. The plots are shown in figures IX, X, XI, and XII. An approximate linearity is observed.

B. Adsorption in the presence of tetramethylammonium pyrophosphate (TMPP): TMR-TMCl-$SrCl_2$-TMPP system

Resin equilibrations were done as in A, but in the presence of known concentrations of pyrophosphate. From the data in each experiment, the value for moles of Sr^{2+} ion adsorbed per gram of resin, $\frac{N_{SrR_2}}{W}$, was calculated. The corresponding $[Sr^{2+}]_E$ for each value was obtained with the help of the calibration curve. The association constant, K, was then calculated for the assumed 1:1 Sr^{2+}-$P_2O_7{}^{4-}$ complex. The results are tabulated in tables V, VI, VII, and VIII at

Figure V (μ=0.10)

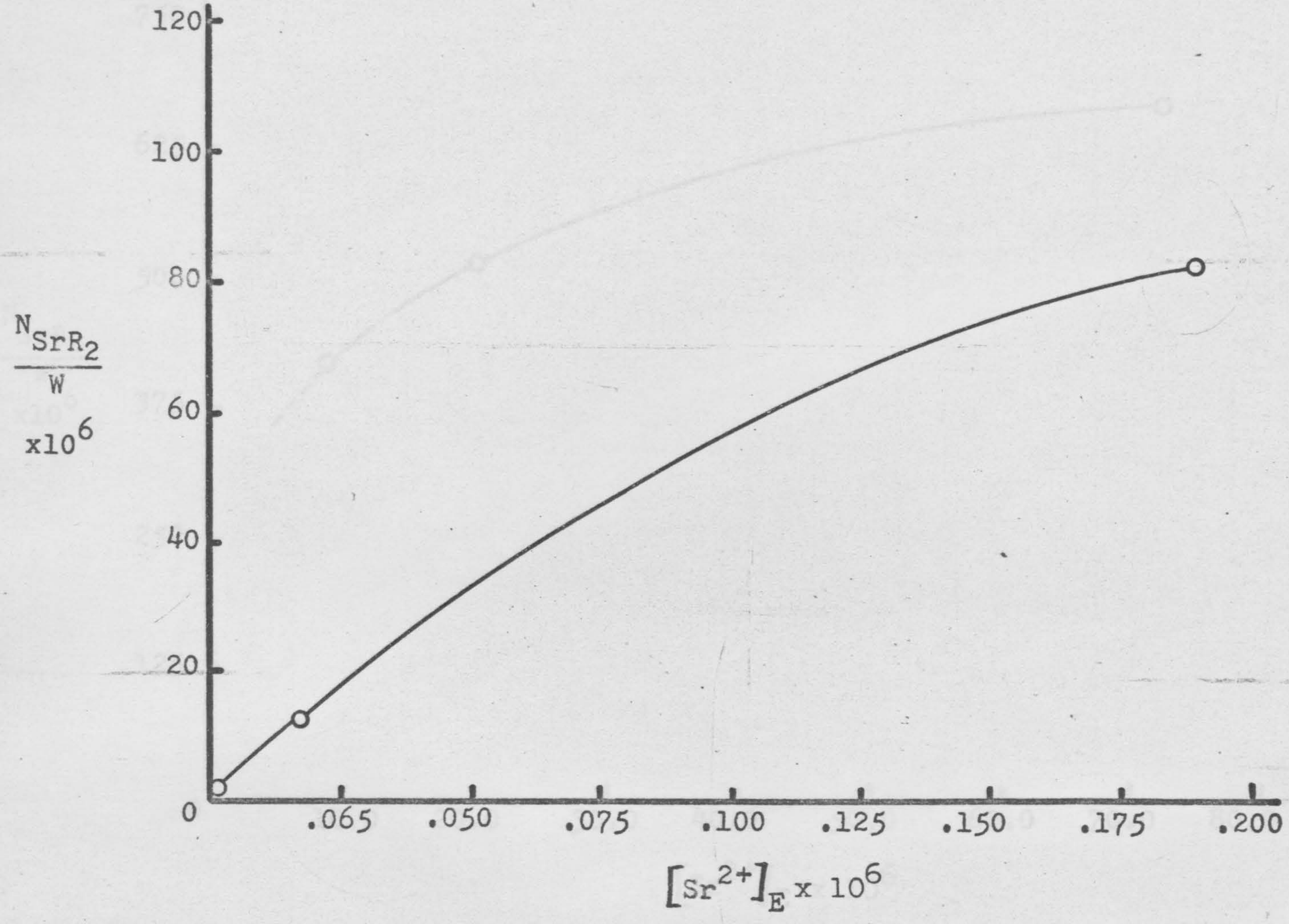


Figure VI (μ=0.25)

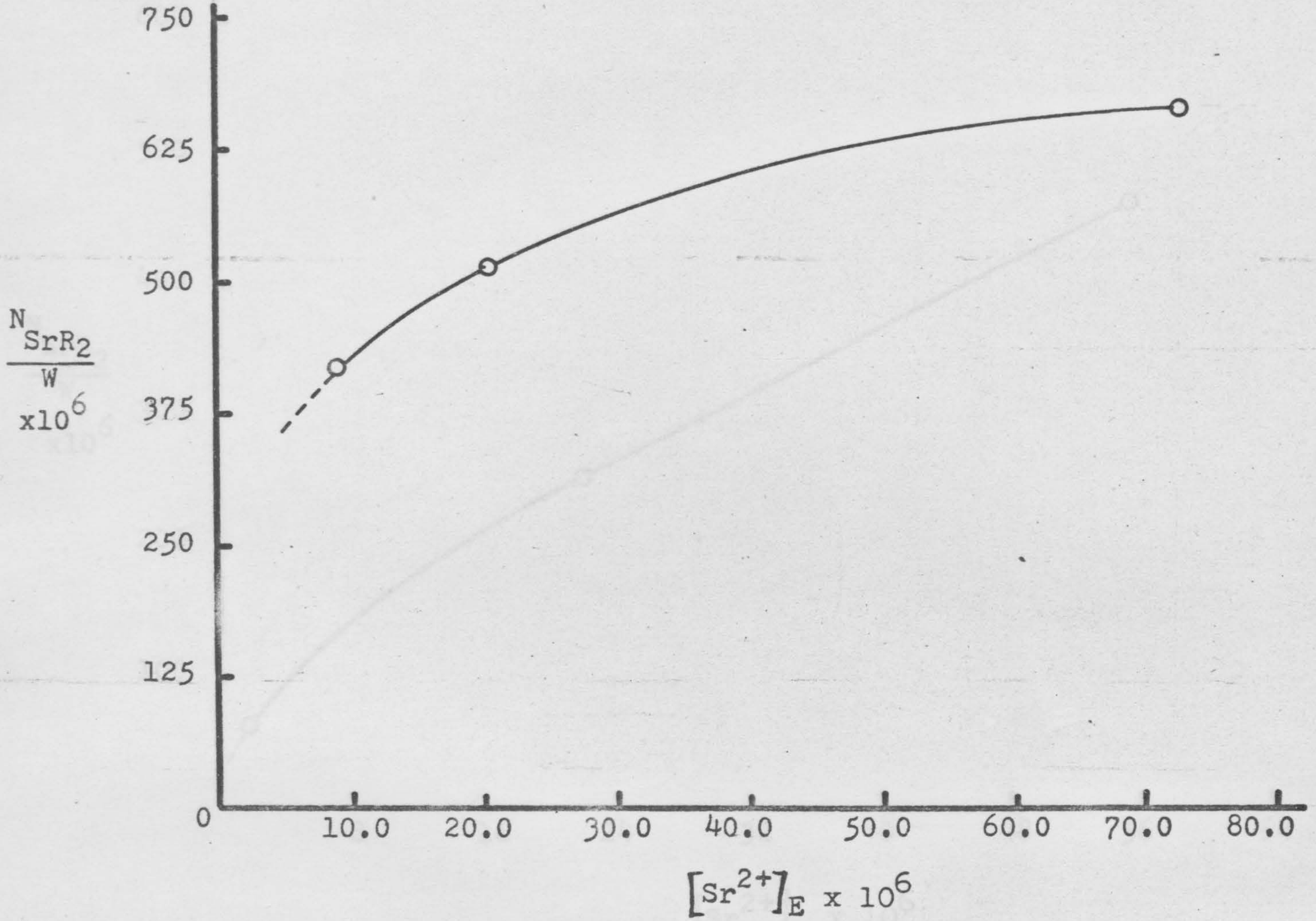


Figure VII (μ=0.50)

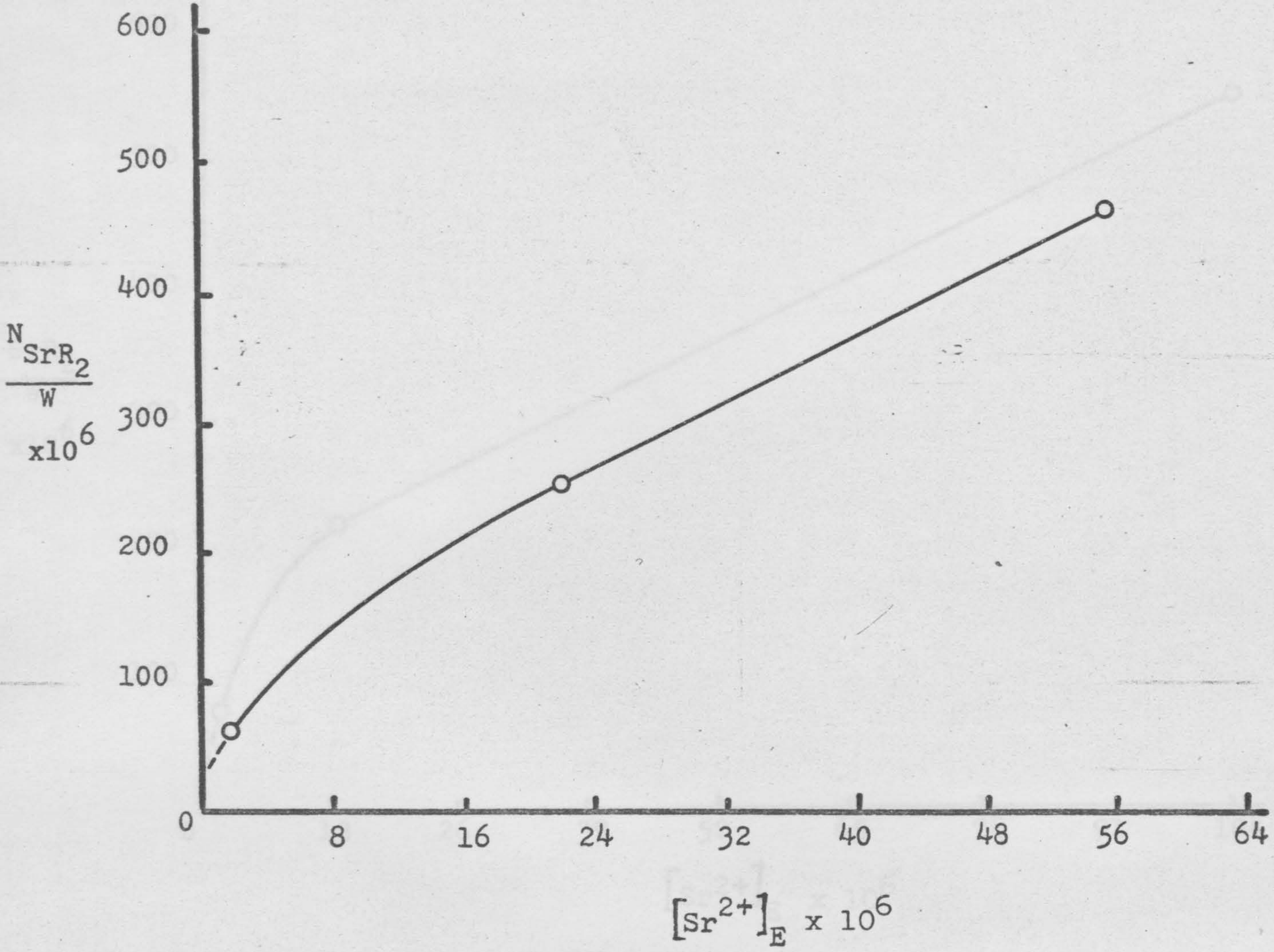


Figure VIII (μ=0.75)

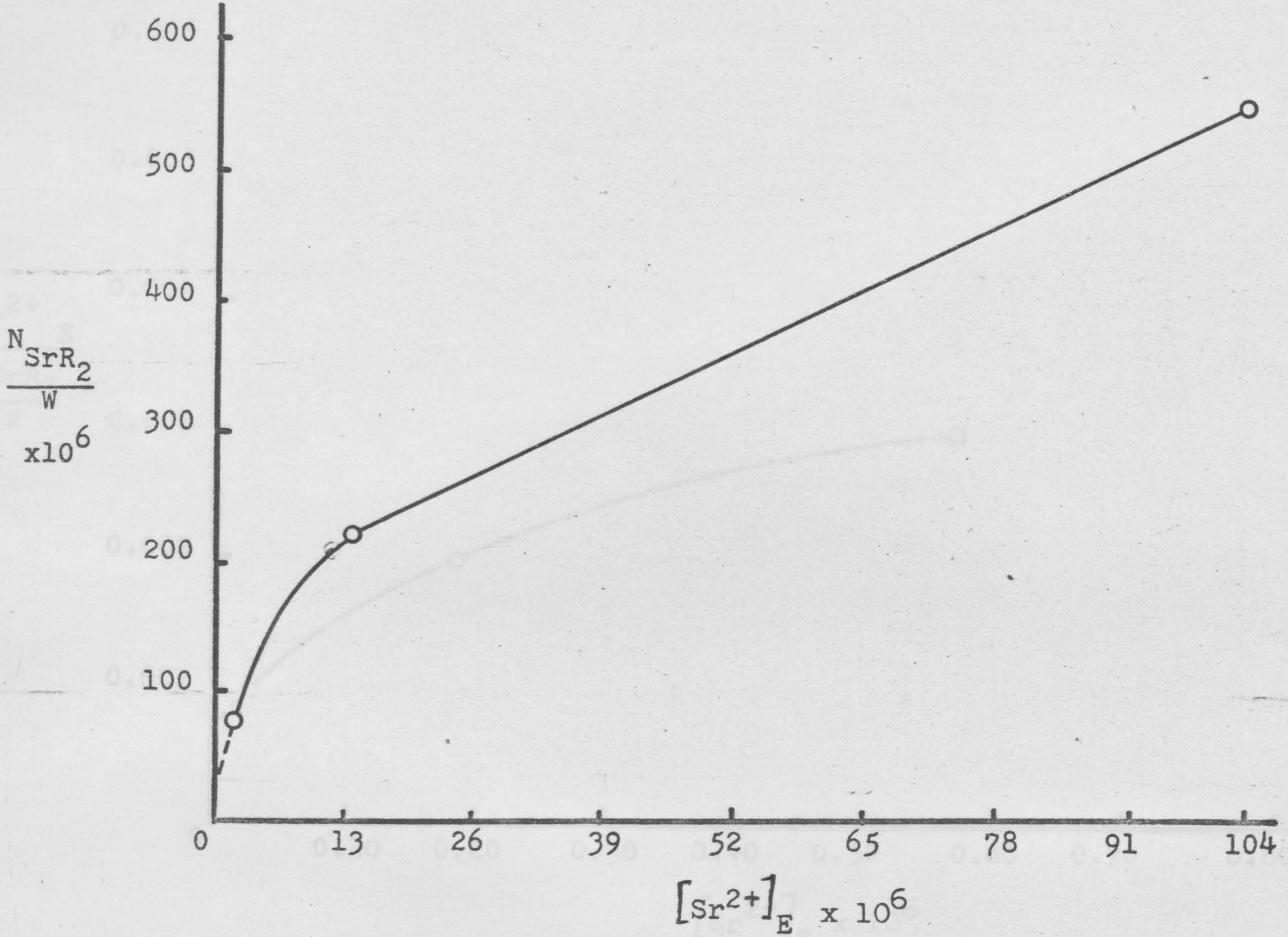


Figure IX (μ=0.10)

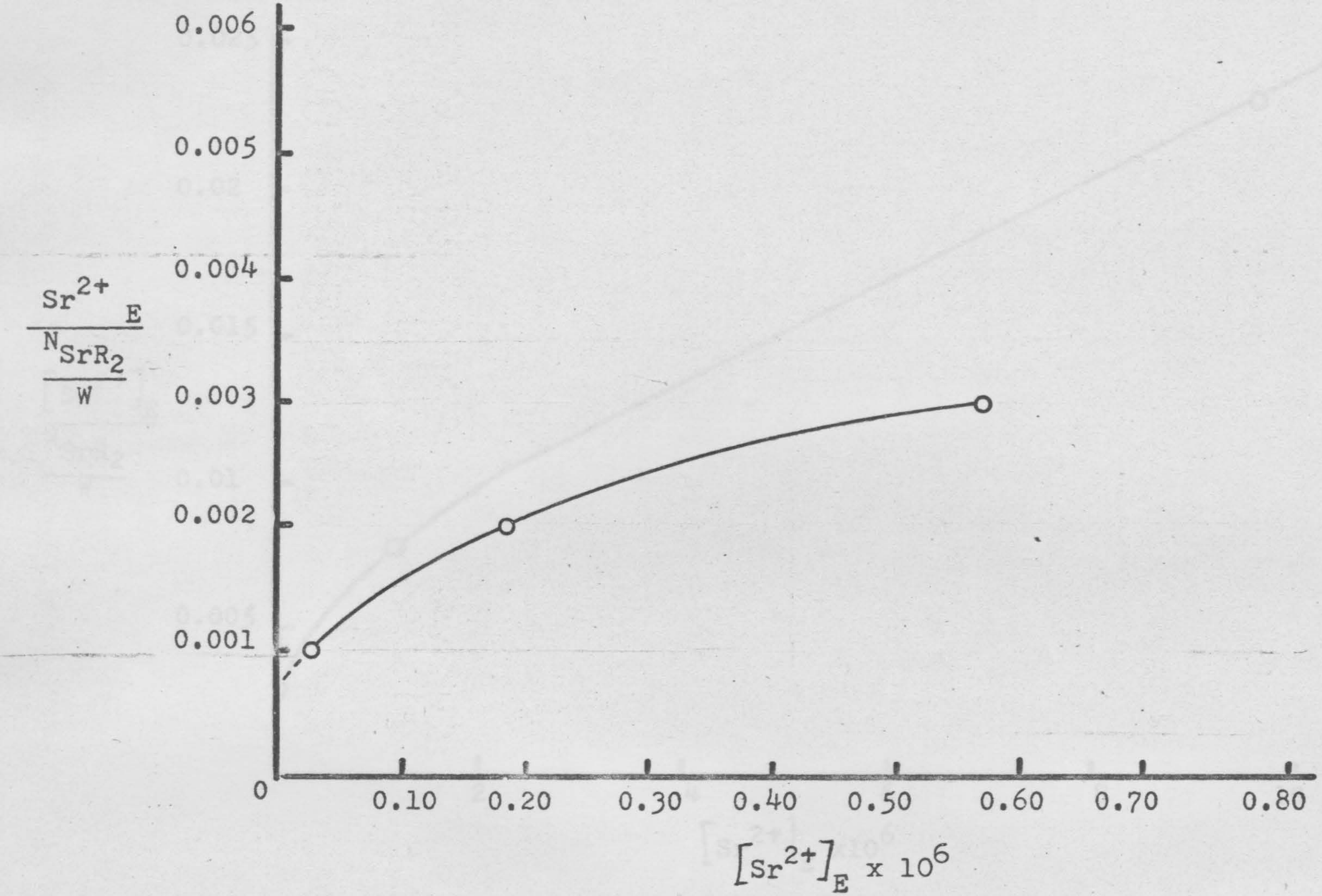


Figure X (μ=0.25)

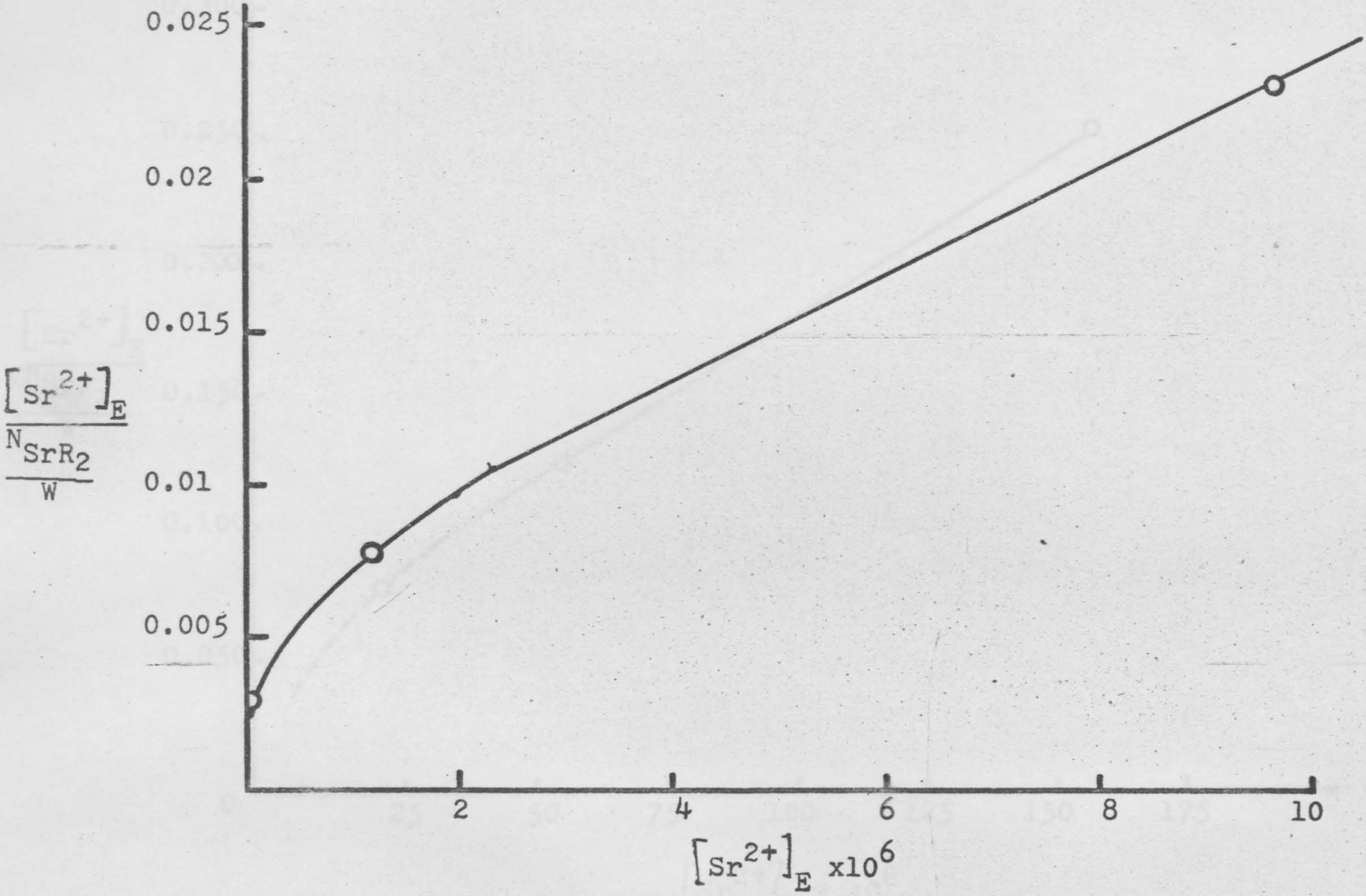


Figure XI (μ=0.50)

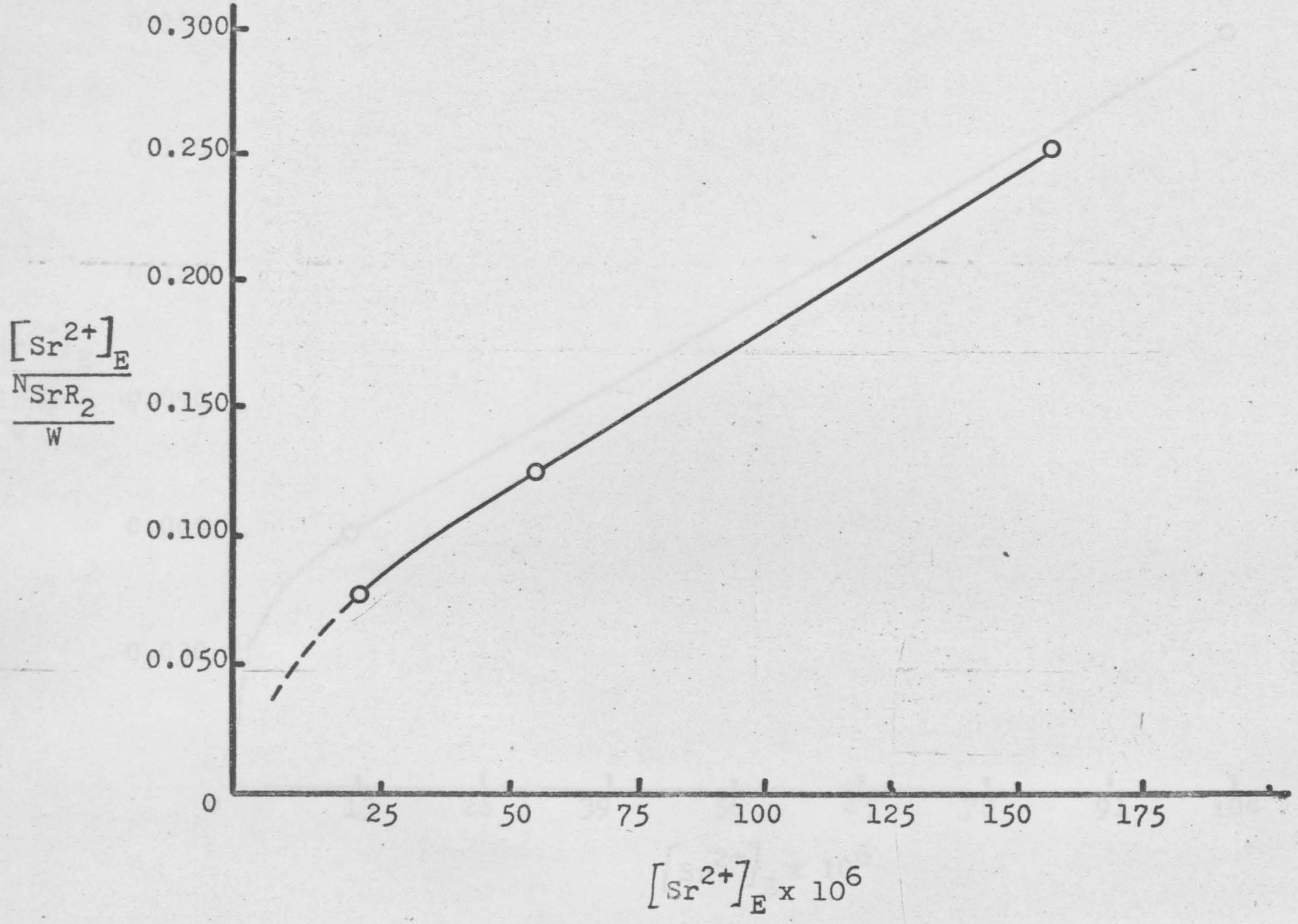
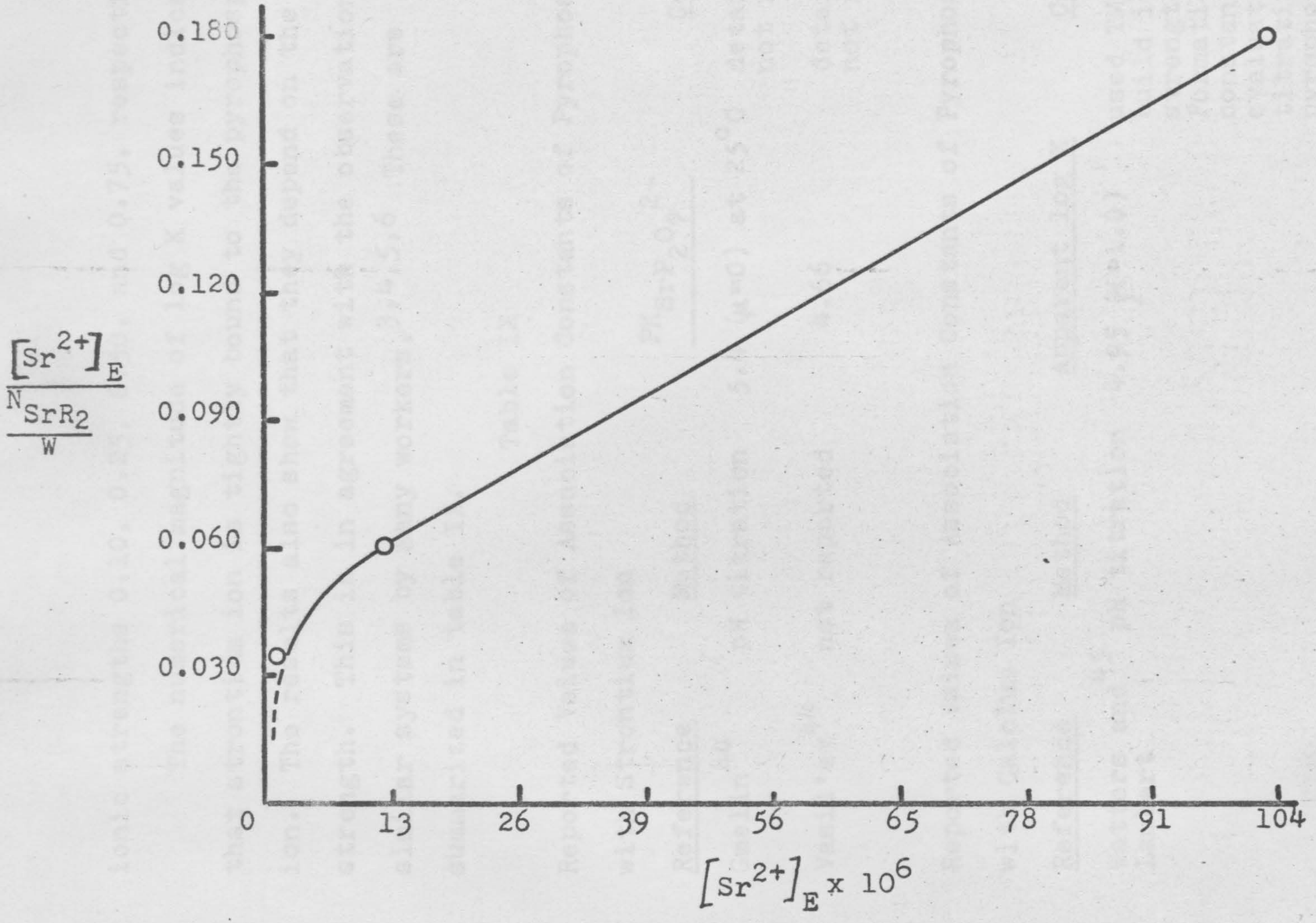


Figure XII (μ=0.75)



ionic strengths 0.10, 0.25, 0.50, and 0.75, respectively.

The numerical magnitude of log K values indicates that strontium ion is tightly bound to the pyrophosphate ion. The results also show that they depend on the ionic strength. This is in agreement with the observations on similar systems by many workers.[3,4,5,6] These are summarized in table IX.

Table IX

Reported Values of Association Constants of Pyrophosphate with Strontium Ion

Reference	Method	$PK_{SrP_2O_7^{2-}}$	Comment
Gmelin[44]	pH titration	5.4 (μ=0) at 25°C	details are not reported
Vasil'ev[44]	not reported	4.66	details are not reported

Reported Values of Association Constants of Pyrophosphate with Calcium Ion

Reference	Method	Apparent log K	Comment
Watters and Lambert[45]	pH titration	4.95 (μ=1.0)	used TMCl to build ionic strength to 1.0. Formation constants were evaluated by titrating pyrophosphate ion in the form of TMPP with H^+ ion at 25°C.

Irani and[46] Callis	Nephelometric titration	4.89 (μ=1.0)	used TMBr to build ionic strength. Studied the effect of pH, temperature, ionic strength, and chain length on the formation constant.
Mahadeviah[4]	ion exchange	4.72 (μ=1.0)	used TMCl to build ionic strength and TMOH to adjust the pH. Tracer calcium-45 was used to measure the calcium ion concentration in complex mixtures.

Table V

Relative Adsorption of Sr^{2+} ion from Solution by Dowex 50-x12 Resin in TM^+ ion form: Pyrophosphate present. (PH = 10.0; μ = 0.10; T = 25.0° C)

Total Initial $[Sr^{2+}]_I$ x10^4 (Molar)	Total $[P_2O_7{}^{4-}]_T$ x10^4 (Molar)	Weight of Resin (g)	Total Volume (ml)	Total Equil. $[Sr^{2+}]_T$ x10^6 (Molar)	$\frac{N_{SrR_2}}{W}$ x10^4 (Molar)	Equil. free $[Sr^{2+}]_E$ x10^6 (Molar)	log K
5.94	0.75	0.0217	25.0	19.10	6.62	3.16	5.12
5.94	0.75	0.0221	25.0	18.90	6.62	3.20	5.11
0.792	0.75	0.0117	25.0	9.35	1.49	0.50	5.42
1.98	1.25	0.0139	25.0	32.9	2.97	1.01	5.53
0.75	0.75	0.0138	25.0	32.2	3.0	1.01	5.54
0.792	0.75	0.0118	25.0	8.64	1.51	0.50	5.37

Table VI

Relative Adsorption of Sr^{2+} from Solutions by Dowex 50-x12 in TM^+ ion form: Pyrophosphate Present. (PH = 10.0; $\mu = 0.25$; T = 25.0° C)

Total Initial $[Sr^{2+}]_I$ x10^4 (Molar)	Total $[P_2O_7^{4-}]_T$ x10^4 (Molar)	Weight of Resin (g)	Total Volume (ml)	Total Equil. $[Sr^{2+}]_T$ x10^6 (Molar)	$\frac{N_{SrR_2}}{W}$ x10^4 (Molar)	Equil. free $[Sr^{2+}]_E$ x10^6 (Molar)	log K
1.19	0.50	0.0103	25.0	9.24	2.66	3.55	4.56
1.19	0.50	0.0137	25.0	5.89	2.08	2.44	4.54
0.729	1.25	0.0146	25.0	4.54	1.20	1.00	4.46
0.413	1.30	0.0094	25.0	2.53	1.03	0.63	4.43
0.413	1.30	0.0120	25.0	2.48	0.81	0.56	4.49

Table VII

Relative Adsorption Sr^{2+} ion from Solutions by Dowex 50-x12 in TM^{+} ion form: Pyrophosphate Present. (PH = 10.0; $\mu = 0.50$; T = 25.0° C)

Total Initial $[Sr^{2+}]_I$ x10^4 (Molar)	Total $[P_2O_7^{4-}]_T$ x10^4 (Molar)	Weight of Resin (g)	Total Volume (ml)	Total Equil. $[Sr^{2+}]_T$ x10^6 (Molar)	$\frac{N_{SrR_2}}{W}$ x10^4 (Molar)	Equil. free $[Sr^{2+}]_E$ x10^6 (Molar)	log K
0.396	2.5	0.1005	25.0	0.22	0.098	0.063	4.00
0.0396	2.5	0.0517	25.0	0.78	0.189	0.251	3.84
0.198	1.25	0.0248	25.0	0.49	0.195	0.251	3.89
0.079	0.38	0.0384	25.0	0.07	0.05	0.018	3.87
0.079	5.0	0.0228	25.0	0.134	0.087	0.016	4.17
0.039	5.0	0.0229	25.0	0.067	0.043	0.014	3.87
0.039	2.5	0.0240	25.0	0.055	0.041	0.013	4.13

Table VIII

Relative Adsorption of Sr^{2+} ion from Solutions by Dowex 50-x12 in TM^{+} ion form: Pyrophosphate Present. (PH = 10.0; $\mu = 0.75$; T = 25.0° C)

Total Initial $[Sr^{2+}]_I$ $\times 10^4$ (Molar)	Total $[P_2O_7^{4-}]_T$ $\times 10^4$ (Molar)	Weight of Resin (g)	Total Volume (ml)	Total Equil. $[Sr^{2+}]_T$ $\times 10^6$ (Molar)	$\frac{N_{SrR_2}}{W}$ $\times 10^4$ (Molar)	Equil. free $[Sr^{2+}]_E$ $\times 10^6$ (Molar)	log K
4.16	1.25	0.0588	25.0	10.90	1.72	11.30	3.84
1.98	0.50	0.0236	25.0	15.0	1.94	12.60	3.70
1.98	0.25	0.0200	25.0	17.5	2.31	17.12	3.91
0.792	0.50	0.0234	25.0	4.5	0.81	2.82	3.60
0.792	2.50	0.0233	25.0	7.1	0.77	2.51	3.92
0.396	2.50	0.0100	25.0	5.98	0.84	2.82	3.71

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