The Cation Exchange Adsorption of Calcium and Strontium from an Ammonium Formate or Ammonium Acetate Solution in Mixtures of Organic Solvents and Water*

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Several methods for separating calcium and strontium by cation exchange resin have been reported.[1-5] Most of them, however, have difficulty in handling a large sample. Although EDTA has been used for separating strontium from a large quantity of calcium,[6] it is not suitable for usual purposes because of the difficulty of the after-treatment of the effluent.

There are other possibilities for overcoming these difficulties, for example, the use of non-aqueous or mixed solvents as elutriants.[7-15] The results of studies of the anion exchange adsorption of anionic metal complexes have shown that the addition of an organic solvent to the system has a large effect on the exchange equilibrium when an ion exchange reaction is accompanied by a complex formation.[10-14] For a cation exchange system, Ionescou et al.[15] measured the distribution coefficients of some transition metals between a phenol - sulfonic acid - type cation exchange resin and an acetone-hydrochloric acid mixture, and used the results for the separation of these metals. Thus, a study of cation exchange equilibria when an organic solvent is added to a calcium or strontium solution containing a complexing agent would be of interest and would be useful for the separation of these metals. In this report, the selectivity coefficients of calcium-ammonium and strontium-ammonium exchange reactions have been measured in methanol-water, acetone-water and dioxane-water mixtures containing formate or acetate as a complexing agent. In addition, by using these complexing agents, the treatment of effluents is greatly simplified. Experiments by column operation have been also carried out to learn whether the expectation from the selectivity coefficient measurements can be actually applied to the separation of calcium and strontium.

Experimental

Chemicals.—Air-dried Amberlite IR-120 (a sulfonated polystylene divinylbenzene cation exchange resin, 100—120 mesh) in ammonium form was used for batch measurement after thorough conditioning. The exchange capacity was 3.5 meq. for 1 g. of the air-dried resin. The organic solvents were used after purification, and calcium and strontium salts were purified by the ion exchange method.

A column of cation exchange resin, Amberlite IR-120, 100—200 mesh in hydrogen form, 10 cm. long and 1.1 cm. in diameter, was used for the column operation.

Measurements.—The adsorption of metal ions by the resin was measured by the equilibrium method, and the results were described in terms of the selectivity coefficients of the ion against the ammonium ion, $K_{\mathrm{NH_4}}^{\mathrm{M}}$, as defined by the following equation :

$$K_{\mathrm{NH_4}}^{\mathrm{M}}=\frac{[\mathrm{M}^{2+}]_{\mathrm{r}}[\mathrm{NH_4}^+]_{\mathrm{s}}}{[\mathrm{M}^{2+}]_{\mathrm{s}}[\mathrm{NH_4}^+]_{\mathrm{r}}}$$

where parentheses denote molarities, the suffixes r and s denote the resin phase and the outer solution phase respectively, and M^{2+} denotes calcium or strontium ions, including their cationic complex ions.

Solutions with the following composition were prepared :

NH_4A :	$(1-2a)$ mol./l.
MA_2 :	a mol./l.
Organic liquid :	b % (v/v)

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where A denotes a formate or acetate ion. The value of a ranged from 1×10^{-3} to 40×10^{-3}, but it was kept constant in each series of experiments. The percentage of the organic solvent, b, was in the 0—80 range for methanol and the 0—60 range for acetone and dioxane. Fifty milliliters of the calcium solution was shaken with 1.000 g. of the dried resin for 24 hr. in a constant temperature bath at 25°C. After an exchange equilibrium had been reached, the outer solution was rapidly separated from the resin with a glass filter, and the calcium concentration in the solution was measured by EDTA titration, using Eriochrome Black T as an indicator. The ammonium ion concentration in the outer solution was determined from the difference between the total concentration and the calcium concentration measured above, the former being measured by alkalimetry after the solution had been converted to acid with a hydrogen-form cation exchange column. The quantities of calcium and ammonium ions in the outer solution and the quantities of the ions in the resin phase were then calculated, with a correction for the swelling of the ion exchanger. The relative volume decrease in the solution caused by the swelling was determined by the quotient between the initial and the equilibrium total ion concentrations of the outer solution.

Since the selectivity coefficients will vary with the fraction of exchangeable sites occupied by calcium ions, they were measured at various loading-values, and the selectivity coefficients were normalized at a certain loading-value by interpolation or extrapolation. The selectivity coefficient of strontium was obtained in the same manner as calcium.

In the column operation, the calcium and strontium adsorbed on the column were eluted with various elutriants. The concentration of ammonium ions in the elutriants was kept at 1 mol./l. throughout the experiments. The effluents from the column were divided into 5 ml. fractions and the amount of calcium or strontium in each fraction was determined by EDTA titration.

Results and Discussion

The Selectivity Coefficients of Calcium and Strontium.—In Figs. 1—6, the selectivity coefficients in an acetate solution containing methanol, acetone or dioxane are plotted against the percent concentration (v/v) of the organic solvent. Curves 1 and 2 in each figure show the selectivity coefficients of calcium and strontium against ammonium, $K_{\mathrm{NH_4}}^{\mathrm{Ca}}$ and $K_{\mathrm{NH_4}}^{\mathrm{Sr}}$, respectively, while curve 3 shows the ratio of the two coefficients, i. e., the selectivity coefficients of strontium against calcium, $K_{\mathrm{Ca}}^{\mathrm{Sr}}$, or the separation factor of these two ions.

In Figs. 7—10, the selectivity coefficients in a formate solution containing acetone or dioxane are plotted. The results are not shown for the solution containing methanol, because methyl formate was formed during 24 hr. shaking in the presence of the resin.*

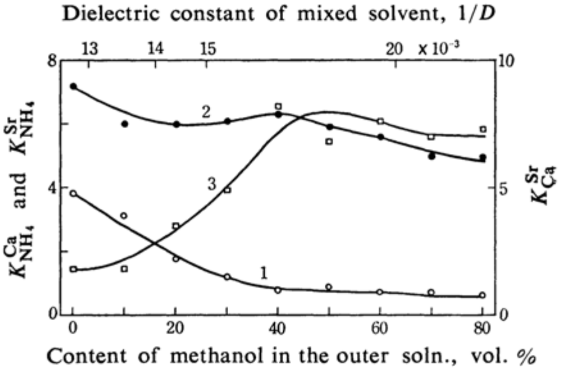

Fig. 1. Selectivity coefficients of calcium and strontium in 1 M ammonium acetate-methanol-water mixture.
(loading: 0.5%)
Curve 1 (○): $K_{\mathrm{NH_4}}^{\mathrm{Ca}}$ Curve 3 (□): $K_{\mathrm{Ca}}^{\mathrm{Sr}}$
Curve 2 (●): $K_{\mathrm{NH_4}}^{\mathrm{Sr}}$

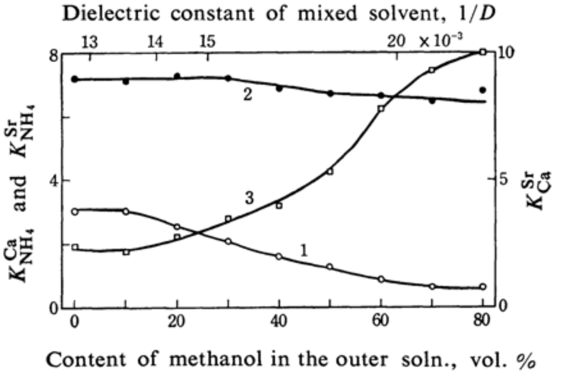

Fig. 2. Selectivity coefficients of calcium and strontium in 1 M ammonium acetate-methanol-water mixture.
(loading: 10%)
Curve 1 (○): $K_{\mathrm{NH_4}}^{\mathrm{Ca}}$ Curve 3 (□): $K_{\mathrm{Ca}}^{\mathrm{Sr}}$
Curve 2 (●): $K_{\mathrm{NH_4}}^{\mathrm{Sr}}$

The same tendencies are found in all figures, irrespective of the loading values and of the organic solvents. The selectivity coefficients of both calcium and strontium against ammonium decrease with an increasing concentration of the organic solvent. The decrease is greater for calcium than for strontium, and the separation factor between strontium and calcium increases with an increasing concentration of the organic solvent.

The causes for the variation in the selectivity coefficients with the concentration of organic

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[*] The formation of the ester was estimated by its odor, the pH rise, and the decrease in the ammonium ion concentration. The phenomenon was not found in a mixture of methanol and an ammonium formate aqueous solution without the resin.

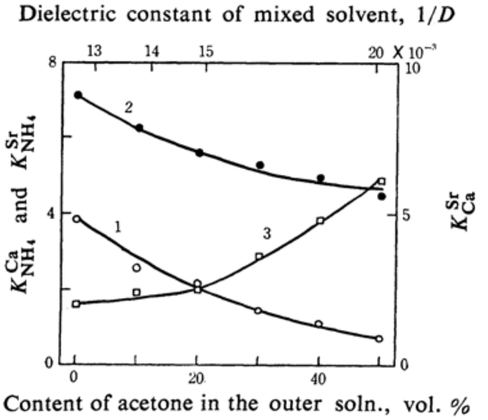

Fig. 3. Selectivity coefficients of calcium and strontium in 1 M ammonium acetate-acetone-water mixture.
(loading: 0.5%)
Curve 1 (○) : $K^{\mathrm{Ca}}_{\mathrm{NH_4}}$ Curve 3 (□) : $K^{\mathrm{Sr}}_{\mathrm{Ca}}$
Curve 2 (●) : $K^{\mathrm{Sr}}_{\mathrm{NH_4}}$

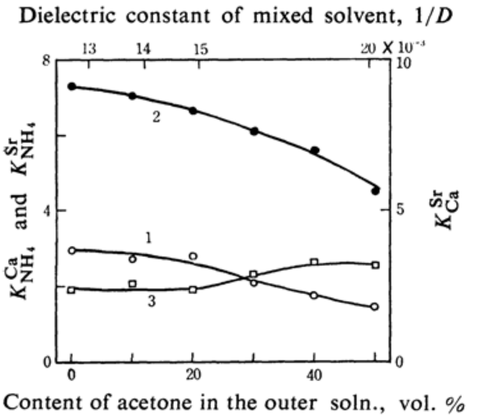

Fig. 4. Selectivity coefficients of calcium and strontium in 1 M ammonium acetate-acetone-water mixture.
(loading: 10%)
Curve 1 (○) : $K^{\mathrm{Ca}}_{\mathrm{NH_4}}$ Curve 3 (□) : $K^{\mathrm{Sr}}_{\mathrm{Ca}}$
Curve 2 (●) : $K^{\mathrm{Sr}}_{\mathrm{NH_4}}$

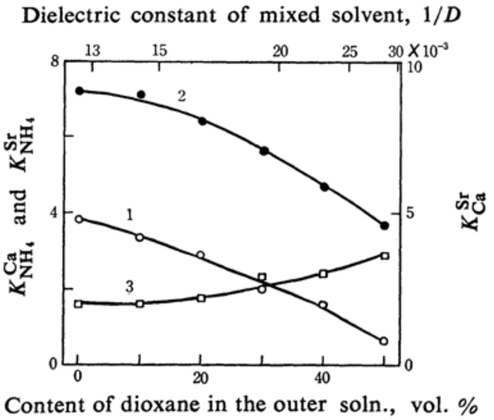

Fig. 5. Selectivity coefficients of calcium and strontium in 1 M ammonium acetate-dioxane-water mixture.
(loading: 10%)
Curve 1 (○) : $K^{\mathrm{Ca}}_{\mathrm{NH_4}}$ Curve 3 (□) : $K^{\mathrm{Sr}}_{\mathrm{Ca}}$
Curve 2 (●) : $K^{\mathrm{Sr}}_{\mathrm{NH_4}}$

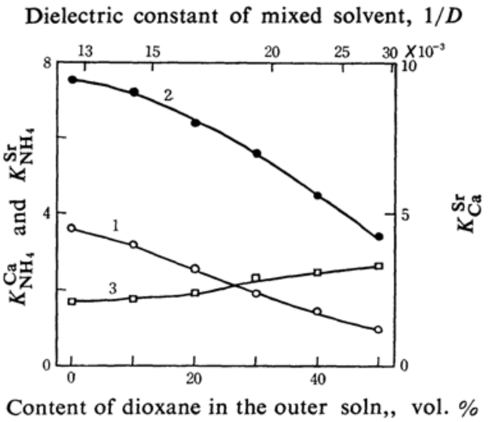

Fig. 6. Selectivity coefficients of calcium and strontium in 1 M ammonium acetate-dioxane-water mixture.
(loading: 5%)
Curve 1 (○) : $K^{\mathrm{Ca}}_{\mathrm{NH_4}}$ Curve 3 (□) : $K^{\mathrm{Sr}}_{\mathrm{Ca}}$
Curve 2 (●) : $K^{\mathrm{Sr}}_{\mathrm{NH_4}}$

solvents can not be explained clearly. We can, however, say that the change in the selectivity coefficients in these systems depends on the following three factors: 1) *The variation in the formation constant of complex ions with the dielectric constant of the outer solution.* It is known that ion association generally increases with a decrease in the dielectric constant of the solution caused by the addition of an organic solvent. 2) *The variation in the affinities of metal and complex ions for the resin with the dielectric constants of the outer solution phase and the resin phase.* It is known that the distribution coefficients for a 1-1 exchange in a mixed solvent varies with the 1/*D* (*D*: dielectric constant) of the solution phase.[8,11] In the present work, however, we can not discover any clear relationship between $K^{\mathrm{Ca}}_{\mathrm{NH_4}}$ or $K^{\mathrm{Sr}}_{\mathrm{NH_4}}$ and 1/*D*, and the correlation between $K^{\mathrm{Sr}}_{\mathrm{Ca}}$ and 1/*D*[16] is rather uncertain, as is shown in Figs. 1—10. Ohtaki and his coworkers[17] explained their experimental results concerning the distribution coefficients for a 1-1 exchange in mixed solvents, in which an electrolyte existed, on the basis of the

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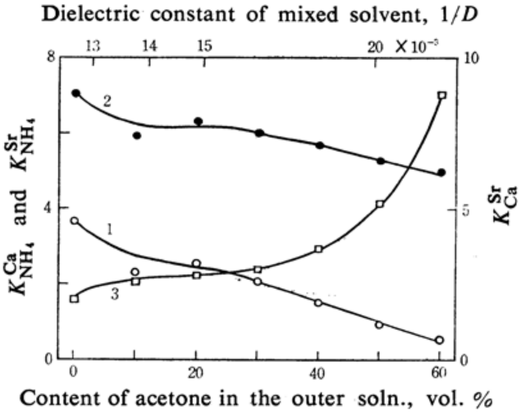

Fig. 7. Selectivity coefficients of calcium and strontium in 1 M ammonium formate-acetone-water mixture.
(loading: 1%)
Curve 1 (○) : $K_{NH_4}^{Ca}$ Curve 3 (□) : K_{Ca}^{Sr}
Curve 2 (●) : $K_{NH_4}^{Sr}$

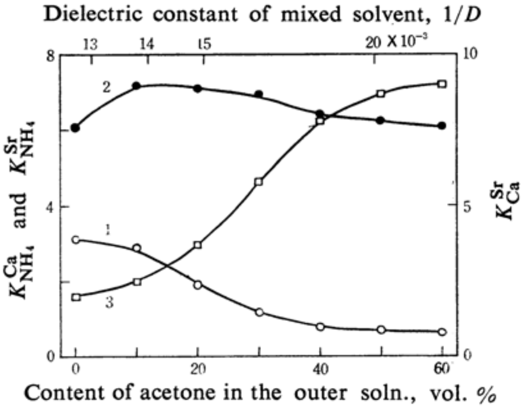

Fig. 8. Selectivity coefficients of calcium and strontium in 1 M ammonium formate-acetone-water mixture.
(loading: 10%)
Curve 1 (○) : $K_{NH_4}^{Ca}$ Curve 3 (□) : K_{Ca}^{Sr}
Curve 2 (●) : $K_{NH_4}^{Sr}$

calculated dielectric constants of the solution phase (D_s) and that of the resin phase (D_r). However, the method cannot be applied to such complicated cases as are discussed here, because D_s and D_r, the formation constants of the complex ions, and the affinities of complex and metal ions to the exchanger are not yet known for the systems studied. 3) *The specific solvation effect on the metal and complex ions.* The variation in the selectivity coefficients with an organic solvent may be caused also by the solvation effect. The finding that dioxane, unlike cellosolves,[18] is not

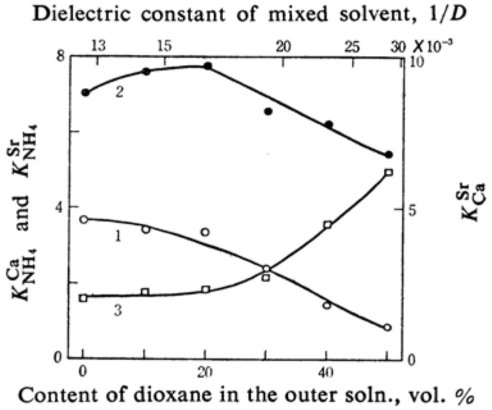

Fig. 9. Selectivity coefficients of calcium and strontium in 1 M ammonium formate-dioxane-water mixture.
(loading: 1%)
Curve 1 (○) : $K_{NH_4}^{Ca}$ Curve 3 (□) : K_{Ca}^{Sr}
Curve 2 (●) : $K_{NH_4}^{Sr}$

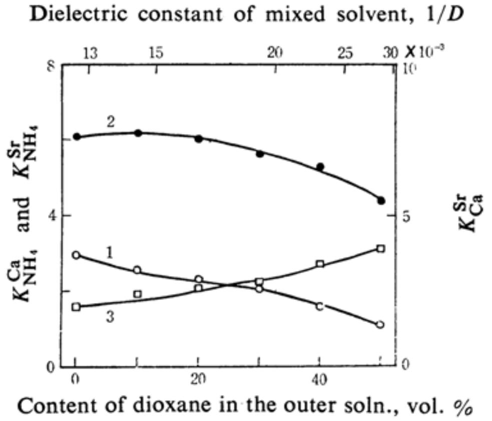

Fig. 10. Selectivity coefficients of calcium and strontium in 1 M ammonium formate-dioxane-water mixture.
(loading: 10%)
Curve 1 (○) : $K_{NH_4}^{Ca}$ Curve 3 (□) : K_{Ca}^{Sr}
Curve 2 (●) : $K_{NH_4}^{Sr}$

effective in separating calcium and strontium seems to correspond to the fact that dioxane shows no evident solvation effects[19] on these ions. When the cellosolves are used in the column operation, the separation of calcium and strontium is as excellent as can be expected, as is shown in Fig. 11. Thus, the solvation effect may be considered to be one of the factors strongly affecting the selectivity coefficients.

From these results, it may be expected that strontium can be easily separated from calcium by the column operation when an elutriant with a high separation factor, and, at the same time, a low selectivity coefficient

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[18] M. Izawa, H. Tsubota and A. Kasai, *Japan Analyst* (*Bunseki Kagaku*), **10**, 1230 (1961).

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TABLE I. COLUMN DIMENSION AND VOLUME OF ELUTRIANTS TO SEPARATE CALCIUM AND STRONTIUM

Amount of sample mg.		Column dimension	Volume of elutriant,* ml.			
			I		II	
Ca	Sr		for Ca	for Sr	for Ca	for Sr
20	20	1.1φ×10 cm.	50	40	60	50
100	20	1.1φ×12 cm.	60(**)	50	75	60
200	20	1.1φ×15 cm.	75**	60	90(**)	75
50	30	1.5φ×10 cm.	95	75	110	95
200	30	1.5φ×12 cm.	100(**)	95	130	110
400	30	1.5φ×15 cm.	140**	110	170(**)	140
100	50	2.0φ×10 cm.	170	130	200	150
300	50	2.0φ×12 cm.	200(**)	165	240	180
600	50	2.0φ×15 cm.	250**	200	300(**)	225

* Elutriant : I-Ca : Mixture of 2 M ammonium formate aqueous solution and acetone in equal volume
I-Sr : 2 M ammonium formate aqueous solution
II-Ca : Mixture of 2 M ammonium acetate aqueous solution and methanol in equal volume
II-Sr : 2 M ammonium acetate aqueous solution

** White precipitate is found in the column.

(**) White precipitate is sometimes found in the column.

of calcium against ammonium is used. A 1 M acetate solution containing over 40% methanol and a 1 M ammonium formate solution containing about 60% acetone will meet this purpose. It is, however, very difficult to ascertain the most suitable concentration of the organic solvent, because the variation in selectivity coefficients with the percentage of organic solvents is different for different loading-values. The best can be found only by experiments in the future.

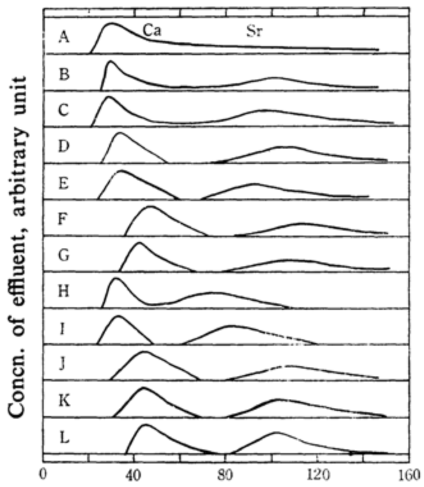

Fig. 11. Elution curves of calcium and strontium with various elutriants.
Column : Amberlite IR-120, 1.1φ×10 cm.
Elutriants : Concentration of ammonium salts was kept 1 mol./l.
A: Ammonium acetate - 80% methanol
B: Ammonium acetate - 70% methanol
C: Ammonium acetate - 60% methanol
D: Ammonium acetate - 50% methanol
E: Ammonium acetate - 40% methanol
F: Ammonium acetate - water
G: Ammonium formate - water
H: Ammonium formate - 50% dioxane
I: Ammonium formate - 50% acetone
J: Ammonium formate - 50% methanol
K: Ammonium formate - 50% methanol cellosolve
L: Ammonium formate - 25% ethyl cellosolve

The Separation of Calcium and Strontium.—Figure 11 shows the elution curves of calcium and strontium (10 mg. each) with various elutriants, using a 10 cm. column of Amberlite IR-120. The most suitable elutriant is a 1 M ammonium formate solution containing 50% acetone, as is shown by curve I in the figure; the next was a 1 M ammonium acetate solution containing 50% methanol, shown by curve D, as has been expected from the results of the batch operation.

The elution curves by the same column with various amounts of calcium and strontium are shown in Fig. 12. A 1 : 1 mixture of a 2 M ammonium formate aqueous solution and acetone and a 1 : 1 mixture of a 2 M ammonium acetate aqueous solution and methanol were used as elutriants.* When the strontium and calcium added to the column were less than 25 mg. and 50 mg. respectively, the elution front of strontium remained unchanged and well separated from the calcium fraction.

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* The results with these elutriants were essentially the same as those with the elutriants used for batch operation.

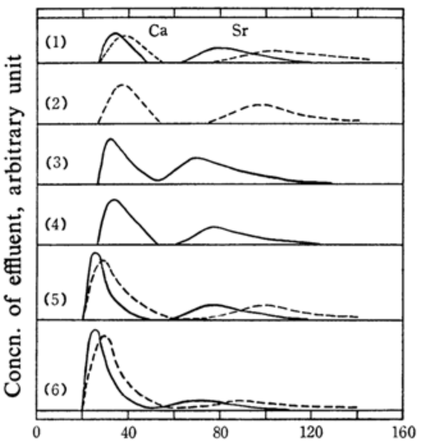

Fig. 12. Elution curves of various amounts of calcium and strontium.
Column: Amberlite IR-120, 1.1$\phi \times 10$ cm.
Elutriants:
——: mixture of 2 M ammonium formate aqueous solution and acetone in equal volume
----: mixture of 2 M ammonium acetate aqueous solution and methanol in equal volume
(1) Ca 9.7 mg., Sr 10.0 mg.
(2) Ca 19.4 mg., Sr 20.0 mg.
(3) Ca 19.4 mg., Sr 50.0 mg.
(4) Ca 19.4 mg., Sr 25.0 mg.
(5) Ca 48.5 mg., Sr 25.0 mg.
(6) Ca 67.8 mg., Sr 25.0 mg.

When the amounts of calcium and of strontium increased further, however, strontium came to be soon eluted from the column, and the elution curves of calcium and of strontium overlapped to some extent.

The column dimensions and the volume of the elutriants necessary to treat various amounts of calcium and strontium were determined; they are shown in Table I. Allowance was made for small changes in column dimensions and in the concentration of elutriants. When a large quantity of calcium existed and an ammonium formate solution in acetone-water was used, a white precipitate was formed in the column, preventing the downward flow of the solution and the clear-cut separation of the two cations. The elution curves of strontium show a considerable tailing when the elutriant used to elute calcium is used, as is shown by the dotted curves in Fig. 13. Strontium can be completely eluted with a 2 M ammonium acetate or formate aqueous solution (without organic solvents). The volume of the elutriant necessary to elute strontium is shown in the same table, while the elution curves are shown in Fig. 13 by solid curves.

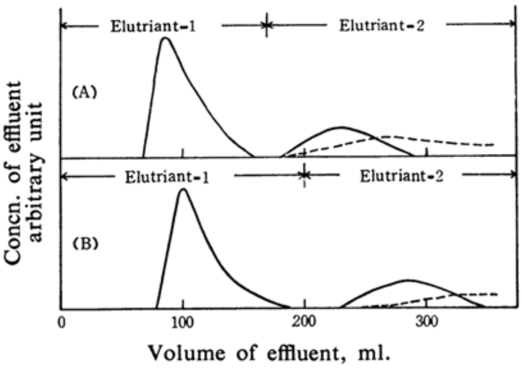

Fig. 13. Elution curves of calcium and strontium.
Column: Amberlite IR-120, 2.0×10 cm.
Elutriant:
(A) 1: mixture of 2 M ammonium formate aqueous solution and acetone in equal volume
2: 2 M ammonium formate aqueous solution
(B) 1: mixture of 2 M ammonium acetate aqueous solution and methanol in equal volume
2: 2 M ammonium acetate aqueous solution
Dotted lines show the elution curves of strontium using elutriant-1.

Summary

Ion exchange equilibria of calcium- and strontium-ammonium exchange systems have been studied in methanol-water, acetone-water and dioxane-water mixtures in which acetate or formate ions co-exist as a complexing anion. The selectivity coefficients of calcium against ammonium and those of strontium against ammonium decrease, while the separation factor between strontium and calcium increases, with an increase in the organic solvent concentration. Therefore, by the column operation, calcium can easily be eluted from the column, and strontium can be well separated from calcium when a suitable elutriant with a high separation factor between strontium and calcium and with a low selectivity coefficient of calcium against ammonium is selected. A 1:1 mixture of a 2 M ammonium formate aqueous solution and acetone or a 1:1 mixture of a 2 M ammonium acetate aqueous solution and methanol is recommended. When strontium in a large amount of calcium is to be analyzed, the latter elutriant is the most suitable.

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