

Citrate Complexes of Alkaline Earth Metals in Aqueous, Acetone-Water and Ethanol-Water Solutions*

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수용액, 물-아세톤 및 물-에탄올 혼합 용매내에서 형성되는 알칼리토류금속의 시트르산 착물

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諸元穆

요 약

양이온 교환수지와 시트르산 이온(Cit^{3-})이 들어 있는 용액에서 방사성 알칼리 토류 금속 이온이 수지와 용액 사이에 어떻게 분배되는가를 실온에서 조사함으로써 이들 금속 이온의 시트르산 착물형성에 관한 연구를 하였다. 용매로서 H_2O , 아세톤- H_2O 및 에탄올- H_2O 를 사용하였다. 용액의 pH는 7.2-7.5로 조절하였고 이온 강도는 0.10-0.12로 유지 하였다.

본 연구의 결과 Ba^{++} 과 Sr^{++} 은 어떤 용매계에서도 1:1착물(M Cit^-)을 형성하는 것을 알았다. 그리고 Ca^{++} 은 수용액에서는 1:1착물을 형성하지만 혼합 용매계에서는 1:1착물(Ca Cit^-)과 1:2착물(Ca Cit_2^{4-})을 형성함을 알았다. 그리고 이들 착물의 안정도는 $\text{Ba}^{++} < \text{Sr}^{++} < \text{Ca}^{++}$ 의 순으로 커지며 또 혼합용매의 유기 성분의 농도 증가순으로 커짐을 알았다.

ABSTRACT

Formation of the complexes of alkaline earths with citrate ions in aqueous, acetone-water and ethanol-water solutions was studied at room temperature by the equilibrium exchange technique. This technique involved the measurements of distribution of radioactivity between cation exchange resin and solution phase after the radioactive metal ions were equilibrated with the cation exchange resin in the presence of citrate ions (Cit^{3-}) of varying concentrations. The pH of the solutions was controlled

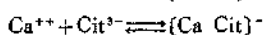
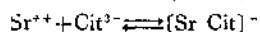
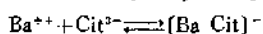
*Complexes of Polyvalent Metal Ions. 1.

to 7.2-7.5, and the ionic strength of the solutions was kept at 0.10-0.12.

The present study revealed that both barium and strontium ions formed the one to one citrate complexes, $(M \text{ Cit})^-$ in all solvent systems examined. It was also observed that calcium ions formed the one to one citrate complex in aqueous solution. In acetone-water and ethanol-water solutions, however, calcium ions were observed to form both one to one and one to two complexes, $(Ca \text{ Cit})^-$ and $(Ca \text{ Cit})_2^{4-}$. The results of the present study indicated also that relative stabilities of the complexes increased in the order: $Ba^{++} < Sr^{++} < Ca^{++}$, and in the order of increasing concentration of the organic components in the mixed solvent systems.

INTRODUCTION

Formation of the complexes of alkaline earth metal ions with various organic acids in aqueous solution was studied by Schubert and co-investigators.⁽¹⁻⁵⁾ These studies were carried out by equilibrium exchange technique which involved measurements of distribution of radioactivity between aqueous solution and cation exchange resin after the radioactive metal ions were equilibrated with ion exchange resin in the presence of organic acids of varying concentrations. Schubert and co-investigators reported formation of the one to one complexes of alkaline earths with citrate ions (Cit^{3-}) in aqueous solution.



It appeared interesting to see if the one to one complexes would exist in the solvents other than water, and, if so, to find out the effect of solvents on stabilities of the complexes. The solvents chosen in the present study were acetone-water and ethanol-water mixed solvents, the concentrations of the organic components being 10, 20 and 30% by volume. Thus, we undertook the present study on the citrate complexes of barium, strontium and calcium in aqueous, acetone-water and ethanol-water solutions.

EXPERIMENTAL PART

Materials.

Ethanol (Reagent grade, Baker) was refluxed for several hours after calcium oxide was added.⁽⁶⁾ It

was fractionated in a 100-cm. Todd column packed with glass helices. Acetone (C. P., Eastman Organic Chemical Co.) was treated with potassium permanganate, and refluxed with potassium carbonate for 1 hour.⁽⁶⁾ It was then fractionated in a Todd column. Triply distilled water was used in the present study. Acetone-water and ethanol-water mixed solvents of 10, 20 and 30% by volume were prepared by mixing appropriate quantities of the components, and used in the present study.

Cation exchange resins (Dowex 50W-X8, 100-200 mesh) were washed alternately with 6N HCl and 10% NaCl solution. The washing was continued with 0.125 mole/l. NaCl solution to convert the resin into sodium form. A small amount of dil. NaOH solution was added until pH of the solution above the resin indicated 7.2-7.5. (A Corning pH meter, model 12, was used.) The resin was filtered and dried in the air.

Stock Solutions of Sodium Chloride and Sodium Citrate.

A solution of sodium chloride of 0.125 mole/l. was prepared by dissolving 1.827 g. of sodium chloride in each solvent system and diluting to the mark in a 250-ml. volumetric flask. Sodium citrate solution of 0.0417 mole/l. was prepared by dissolving 2.191 g. of citric acid monohydrate in each solvent system of approximately 250 ml., adding appropriate amount of sodium hydroxide to adjust pH to 7.2-7.5, and diluting to the mark in a 250-ml. volumetric flask.

Stock Solutions of Radioactive Barium, Strontium and Calcium.

Solid samples of radioactive strontium (^{89}Sr) and

calcium(^{45}Ca) were prepared by irradiating appropriate amount of solids, strontium nitrate (about 1 g.) and calcium nitrate (about 1 g.), with neutrons in the nuclear reactor TRIGA-II (neutron flux = 10^{12} neutrons/cm 2 /sec.) for 70 hrs., and 140 hrs., respectively.* The resulting nitrate salts of radioactive strontium and calcium were dissolved in about 10 ml. of distilled water. One ml. of each of these solutions was pipetted into and diluted with water or mixed solvent to the mark in a 100-ml. volumetric flask.

Radioactive barium (^{139}Ba) was prepared also by the irradiation of solid barium nitrate (about 0.1g.) with neutrons in the nuclear reactor TRIGA-II for 10 min. The resulting solid of radioactive barium nitrate was dissolved in each solvent system, water or mixed solvent, and diluted to the mark in a 100-ml. volumetric flask. Thus, stock solutions of radioactive barium, strontium and calcium in each solvent system were prepared.

Procedure

Into each of seven 125-ml. Erlenmeyer flasks 150 mg. of the cation exchange resin were weighed, and 10 ml. of the stock solution of radioactive metal ions were added. The stock solutions of sodium citrate, sodium chloride and solvent were added to the Erlenmeyer flasks according to Table 1. The ionic strength of each sample solution was kept in the range of 0.10-0.12.

TABLE 1. Composition of Sample Solutions

Flask No.	Resin, mg.	M $^{2+}$, ml*.	Cit $^{3-}$, ml.	NaCl, ml.	Solvent, ml.
1	150	10	0	0	40
2	150	10	0.5	39.5	0
3	150	10	1.0	39.0	0
4	150	10	2.5	37.5	0
5	150	10	5.0	35.0	0
6	150	10	7.5	32.5	0
7	150	10	10.0	30.0	0

* $[\text{Ba}^{2+}] = 7.7 \times 10^{-4}$ mole/l, $[\text{Sr}^{2+}] = 9.4 \times 10^{-4}$ mole/l, $[\text{Ca}^{2+}] = 8.5 \times 10^{-4}$ mole/l.

*This assistance given by Atomic Energy Research Institute, Seoul, is gratefully acknowledged.

Each flask was stoppered and shaken for about 3 hours to equilibrate radioactivity between the resin and solution phases. Although a period of about one hour was found to be sufficient for the equilibration, samples were shaken for about 3 hours in this experiment in order to insure the complete equilibration. The resin was filtered onto a porous metal disc in chimney funnel (Fig. 1) and the radioactivity in the resin particles was counted in the following manner.

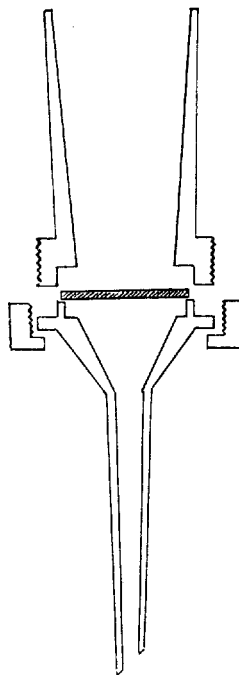


Fig. 1. Chimney funnel.

A steel planchet was placed in the chimney funnel and about 5 ml. of Celite suspension (1 mg./ml.) was poured. After waiting 5-10 seconds for the Celite to settle, vacuum was applied to the filter flask until water was drawn off. The resin suspension was poured into the funnel. Several rinses of water helped complete transfer of resin and sufficient washing of the chimney funnel, flask and resin.

After the suction was turned off, the flask was rinsed with 20 ml. of methanol which was then poured into the chimney funnel, and the suction was resumed. The upper part of the chimney was removed. The planchet was removed carefully and dried in the air for at least 20 minutes.

The planchet was inserted into the G-M counter slide and the β -activity was counted. A G-M tube (Nuclear Radiation Detector, Model 108, Serial No. 152, operating voltage 980 volts) and a scaler (Nuclear Chicago, Model 8770) were utilized. A correction was made for decay of the radioisotopes during each run of the experiment, if necessary.

Determination of Distribution Ratio of Metal Ions.

From the observed counting rate of each sample, the distribution ratio, K_d , of the metal ions between resin phase and solution phase in the following manner. The concentration of metal ions in the resin must be proportional to the radioactivity of the resin phase, $A(\text{resin})$.

$$\text{Moles of } M^{2+} \text{ in resin} = k \cdot A(\text{resin})$$

Likewise, the concentration of metal ions in solution must be proportional to the radioactivity of the solution phase, $A(\text{soln.})$.

$$\text{Moles of } M^{2+} \text{ in solution} = k \cdot A(\text{soln.})$$

The total radioactivity, $A(\text{total})$, of metal ions in the resin and solution phases was determined by measuring the radioactivity of the resin after equilibration under conditions such that essentially all of the metal ions went into the resin (flask No. 1).

$$A(\text{total}) = A(\text{resin}) + A(\text{soln.})$$

If the concentrations of metal ions in the resin and solution phases are expressed in units of moles per unit weight of the resin, and moles per unit volume of the solution, respectively, the above equations become:

$$[M^{2+}R_2^-] (\text{resin}) = k \cdot A(\text{resin})/m,$$

$$[M^{2+}] (\text{soln.}) = k \{A(\text{total}) - A(\text{resin})\}/v,$$

where m and v denote milligrams of resin and ml. of solution, respectively. If K_d is defined as the ratio of metal ion concentration in resin to that in solution, the values of K_d can be obtained experimentally by the following equation:

$$K_d = \frac{v}{m} \cdot \frac{A(\text{resin})}{A(\text{total}) - A(\text{resin})} \quad \dots \dots \dots (1)$$

RESULTS

Citrate Complexes in Aqueous Solution.

The distribution ratios of barium, strontium and calcium metal ions between the resin and solution phases were determined in aqueous solution containing citrate ions of various concentrations. The results obtained at room temperature are summarized in Table II. The plots of the values of $1/K_d$ versus molar concentrations of citrate ions are shown in Fig. 2. A good linearity can be seen in all cases in Fig. 2

TABLE II. Distribution Ratios of Metal Ions between Resin and Aqueous Solution (Room Temperature)

Flask No.	Citrate, 10^{-4} mole l^{-1}	$1/K_d$, mg./ml.		
		Ba ⁺⁺	Sr ⁺⁺	Ca ⁺⁺
2	4.17	0.055	0.85	1.8
3	8.34	0.070	0.94	2.4
4	20.9	0.090	1.3	3.4
5	41.7	0.14	1.9	5.8
6	62.6	0.18	2.6	8.1
7	83.4	0.22	3.1	10

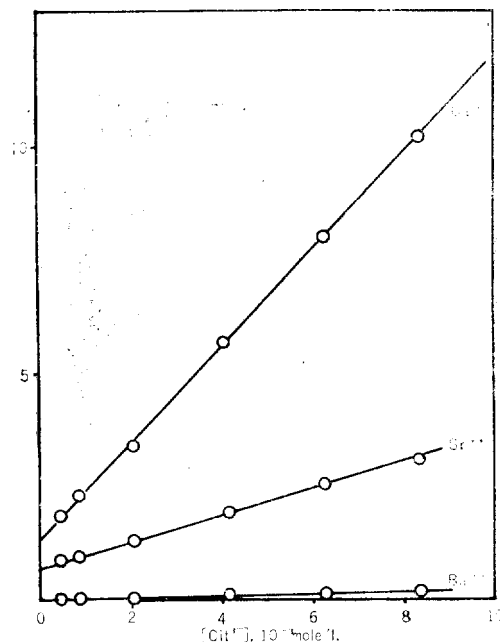
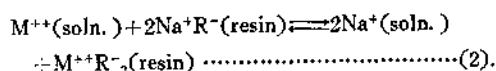


Fig. 2. Plots of $1/K_d$ versus $[Cit^{3-}]$ for $[MCit^-]$ in aqueous solution. Bottom: Ba⁺⁺, middle: Sr⁺⁺, top: Ca⁺⁺.

From the experimental data the formation constants, K_f , for the complexes were calculated in the following manner. If the sodium form of the cation exchange resin is represented by Na^+R^- , the exchange reaction with divalent metal ions may be written:



The following equilibrium expression for reaction (2) may be valid over a fairly wide range of experimental conditions.

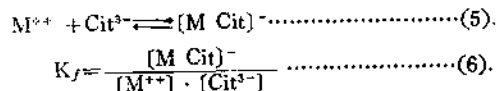
$$K_{eq} = \frac{[\text{Na}^+]^2(\text{soln.})[\text{M}^{++}\text{R}_2^-(\text{resin})]}{[\text{M}^{++}(\text{soln.})][\text{Na}^+\text{R}^-]^2(\text{resin})}$$

$$\therefore \frac{[\text{M}^{++}\text{R}_2^-(\text{resin})]}{[\text{M}^{++}(\text{soln.})]} = K_{eq} \cdot \frac{[\text{Na}^+\text{R}^-]^2(\text{resin})}{[\text{Na}^+]^2(\text{soln.})} \quad (3)$$

If it is assumed that the resin is completely in the sodium ion form, reaction (2) will not result in any appreciable change in concentrations of sodium ions in the resin and solution phases, since a large excess of NaCl is present in solution. Thus, equation (3) can be expressed by another constant, K^0_d .

$$\frac{[\text{M}^{++}\text{R}_2^-]}{[\text{M}^{++}]} = K^0_d \quad (4)$$

If it is assumed also that the metal ions form one to one complexes with citrate ions in solution, the formation constant, K_f , of the complexes can be expressed by equation (6).



Under this assumption of one to one complex formation, the distribution ratio, K_d , of the metal ions between the resin and solution phases can be written as

$$K_d = \frac{[\text{M}^{++}\text{R}_2^-]}{[\text{M}^{++}] + [\text{M Cit}]^-} \quad (7)$$

Combining equations (4), (6) and (7), the following relation is obtained:

$$\frac{1}{K_d} = \frac{1}{K^0_d} + \frac{K_f}{K^0_d} [\text{Cit}^{3-}] \quad (8)$$

Therefore, the values of intercept and slope of the linear relations between $1/K_d$ and citrate ion concentration will give the values of K^0_d and K_f .

Since we observed very good linearity between $1/K_d$ and citrate ion concentration (Fig. 1), it was concluded that the assumption of formation of the one to one complexes, $[\text{M Cit}]^-$, was correct in

aqueous solution. The values of intercepts and slopes of the straight lines were determined by the least square method, and hence, the values of K^0_d and K_f were obtained in each case studied. The results are shown in Table III.

TABLE III. Formation Constants of One to One Complexes in Aqueous Solution (Room Temperature)

Complex	K^0_d	$K_f, 10^3 \text{ l. mole}^{-1}$
$[\text{Ba Cit}]^-$	19	3.9
$[\text{Sr Cit}]^-$	1.4	4.1
$[\text{Ca Cit}]^-$	0.67	6.9

As a result of the present study, it was concluded that barium, strontium and calcium ions formed one to one complexes with citrate ions in aqueous solution (equation 5). By comparing relative values of the formation constants of the one to one complexes, it was also concluded that relative stability of the complexes in aqueous solution increased in the order,



Barium- and Strontium-Complexes in Acetone-Water Solution.

The distribution ratios of barium and strontium metal ions between the resin and solution phases were determined also in acetone-water (10, 20 and 30% by volume) solutions containing citrate ions of various concentrations. The results obtained at room temperature are summarized in Tables IV and V.

TABLE IV. Distribution Ratios of Barium Metal Ions between Resin and Acetone-Water Solution (Room Temperature)

Flask No.	Citrate, $10^{-3} \text{ mole l.}^{-1}$	10%	$1/K_d, \text{ mg./ml.}$	20%	30%
2	4.17	0.28	0.31	0.42	
3	8.34	0.31	0.37	0.61	
4	20.9	0.48	0.69	0.99	
5	41.7	0.74	1.0	1.6	
6	62.6	0.98	1.4	2.2	
7	83.4	1.2	1.7	2.9	

Good linearity was observed between $1/K_d$ and citrate ion concentration in all cases shown in Figs. 3 and 4. Based on similar consideration to the aqueous

TABLE V. Distribution Ratios of Strontium Metal Ions between Resin and Acetone-Water Solution (Room Temperature)

Flask No.	Citrate, 10^{-4} mole l^{-1}	$1/K_d$, mg./ml.		
		10%	20%	30%
2	4.17	0.85	0.92	1.0
3	8.34	1.1	1.1	1.5
4	20.9	1.5	2.1	2.8
5	41.7	2.6	3.6	6.0
6	62.6	2.7	5.3	8.6
7	83.4	4.6	6.8	12

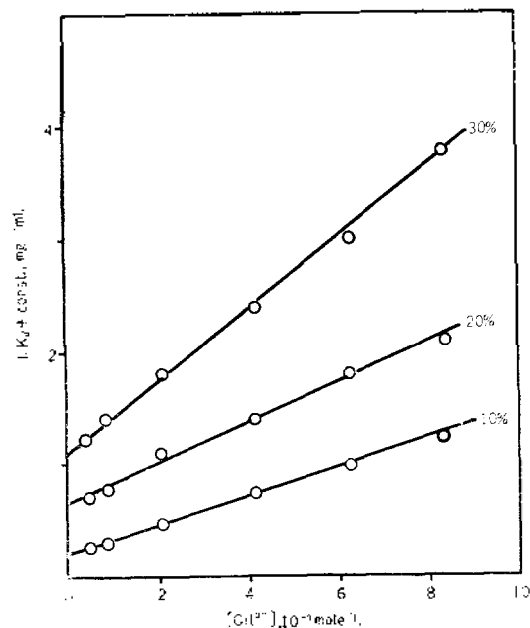


Fig. 3. Plots of $1/K_d$ versus $[Cit^{3-}]$ for $[BaCit]^-$ in acetone-water solution. Bottom: 10% (const. = 0), middle: 20% (const. = 0.4), top: 30% (const. = 0.8).

system mentioned above, it was concluded that the assumption of formation of the one to one complexes, $[M Cit]^-$, was correct also in acetone-water solution. The values of intercepts and slopes of the straight lines were determined by the least square method, and hence, the values of K_d^0 and K_f were obtained (Table VI).

From relative values of the formation constants of the one to one complexes (Table VI), it was concluded that the strontium complex was more stable

than the barium complex in each solvent system. It was also concluded that relative stability of the complexes of each alkaline earth metal increased with increasing concentration of acetone in the acetone

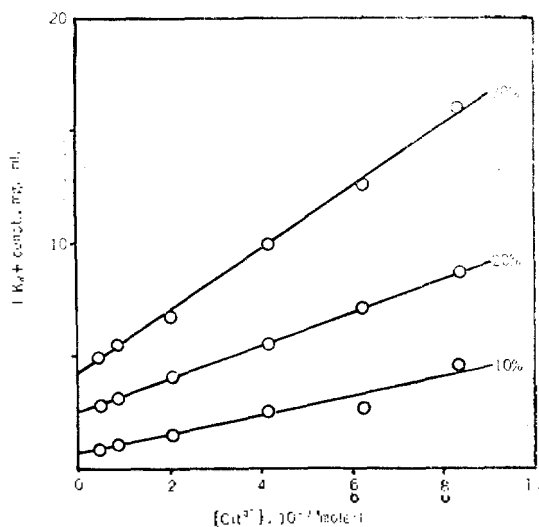


Fig. 4. Plots of $1/K_d$ versus $[Cit^{3-}]$ for $[SrCit]^-$ in acetone-water solution. Bottom: 10% (const. = 0), middle: 20% (const. = 2), top: 30% (const. = 4).

TABLE VI. Formation Constants of One to One Citrate Complexes of Barium and Strontium in Acetone-Water Solution (Room Temperature)

Complex	% Acetone in Solution	K_d^0	K_f , 10^4 $l.$ mole $^{-1}$
$[BaCit]^-$	10	4.5	5.5
	20	4.2	7.3
	30	2.9	8.8
$[SrCit]^-$	10	1.6	7.0
	20	1.8	13
	30	4.3	60

water solution.

$$0\% < 10\% < 20\% < 30\% \text{ acetone.}$$

Barium- and Strontium-Complexes in Ethanol-Water Solution.

Studies were extended to the case of ethanol-water solution. The results obtained at room temperature are summarized in Tables VII and VIII.

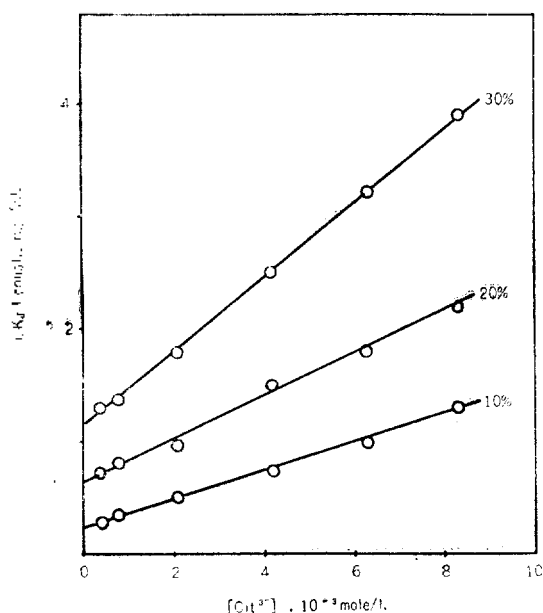
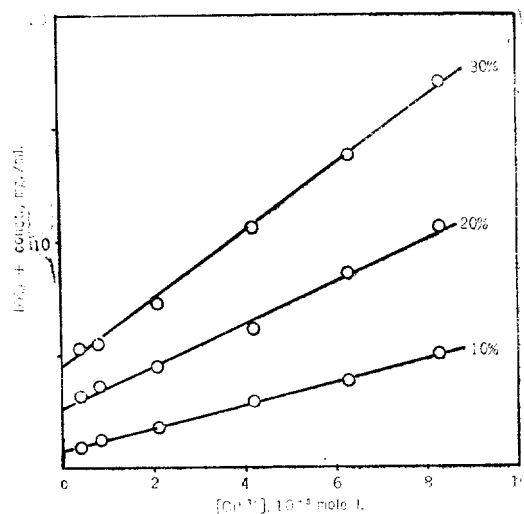
Since good linearity was observed again in all cases shown in Figs. 5 and 6, it was concluded that the

TABLE VII. Distribution Ratios of Barium Metal Ions between Resin and Ethanol-Water Solution (Room Temperature)

Flask No.	Citrate, 10^{-4} mole l^{-1}	$1/K_d$, mg./ml.		
		10%	20%	30%
2	4.17	0.27	0.32	0.50
3	8.34	0.35	0.41	0.59
4	20.9	0.51	0.58	1.0
5	41.7	0.73	1.1	1.7
6	62.6	1.0	1.4	2.4
7	83.4	1.3	1.8	3.1

TABLE VIII. Distribution Ratios of Strontium Metal Ions between Resin and Ethanol-Water Solution (Room Temperature)

Flask No.	Citrate, 10^{-4} mole l^{-1}	$1/K_d$, mg./ml.		
		10%	20%	30%
2	4.17	0.95	1.2	1.3
3	8.34	1.3	1.6	1.5
4	20.9	1.8	2.5	3.3
5	41.7	3.0	4.2	6.6
6	62.6	3.9	6.6	9.8
7	83.4	5.0	8.6	13


Fig. 5. Plots of $1/K_d$ versus $[Cit^{3-}]$ for $[BaCit]^-$ in ethanol-water solution. Bottom: 10% (const. = 0), middle: 20% (const. = 0.4), top: 30% (const. = 0.8).

Fig. 6. Plots of $1/K_d$ versus $[Cit^{3-}]$ for $[SrCit]^-$ in ethanol-water solution. Bottom: 10% (const. = 0), middle: 20% (const. = 2), top: 30% (const. = 4).

assumption of formation of the one to one complexes, $[M Cit]^-$, was correct also in ethanol-water solution. The values of intercepts and slopes of the straight lines were determined, and the values of K_d^0 and K_f were obtained (Table IX).

TABLE IX. Formation Constants of One to One Citrate Complexes of Barium and Strontium in Ethanol-Water Solution (Room Temperature)

Complex	% Ethanol in Solution	K_d^0	K_f , 10^3 $l. mole^{-1}$
$[BaCit]^-$	10	4.3	5.4
	20	4.2	7.9
	30	3.0	10
$[SrCit]^-$	10	1.2	6.2
	20	1.4	13
	30	3.3	50

By comparing relative values of the formation constants of the one to one complexes (Table IX), it was concluded that the strontium complex was more stable than the barium complex in each solvent system. It was also concluded that relative stability of the complexes of each metal ions increased with increasing concentration of ethanol in the ethanol-water solution.

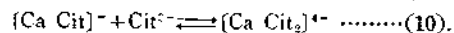
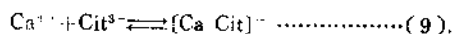
$$0\% < 10\% < 20\% < 30\% \text{ ethanol.}$$

Calcium Complex in Acetone-Water and Ethanol-Water Solutions.

Studies were extended further to the system of calcium metal ions with citrate ions in acetone-water and ethanol-water solutions. The experimental results obtained at room temperature are summarized in Tables X and XI.

Linearity was not observed between $1/K_d$ and citrate ion concentration in the cases shown in Figs. 7 and 8. It was therefore concluded that the assumption of formation of the one to one citrate complex of calcium, $[\text{Ca Cit}]^-$, was not correct in acetone-water and ethanol-water solutions.

It was then assumed that calcium ions formed both one to one complex, $[\text{Ca Cit}]^-$, and one to two complex, $[\text{Ca Cit}_2]^{4-}$, according to the following stepwise reactions:



The formation constants, K_1 and K_2 , of the two

TABLE X. Distribution Ratios of Calcium Metal Ions between Resin and Acetone-Water Solution (Room Temperature)

Flask No.	Citrate, 10^{-4} mole l^{-1}	$1/K_d$, mg./ml.		
		10%	20%	30%
2	4.17	2.0	2.3	2.5
3	8.34	2.6	2.9	3.3
4	20.9	4.3	6.7	8.8
5	41.7	8.7	16	20
6	62.6	14	24	38
7	83.4	20	34	61

TABLE XI. Distribution Ratios of Calcium Metal Ions between Resin and Ethanol-Water Solution (Room Temperature)

Flask No.	Citrate, 10^{-4} mole l^{-1}	$1/K_d$, mg./ml.		
		10%	20%	30%
2	4.17	1.4	1.7	2.7
3	8.34	1.7	2.8	3.0
4	20.9	3.9	6.4	8.5
5	41.7	7.4	14	26
6	62.6	12	23	46
7	83.4	16	34	73

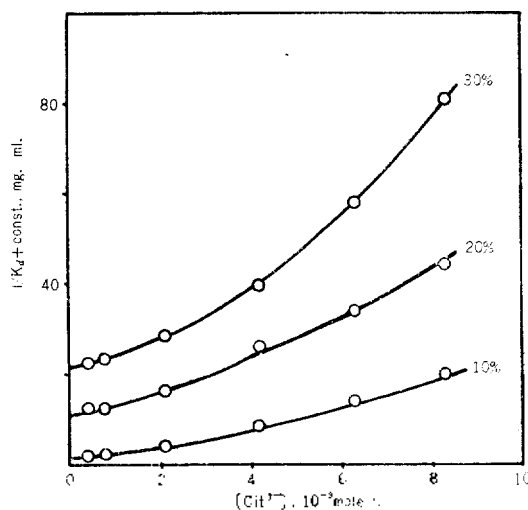


Fig. 7. Plots of $1/K_d$ versus $[\text{Cit}^{3-}]$ for the $\text{Ca}^{++}-\text{Cit}^{3-}$ system in acetone-water solution. Bottom: 10% (const. = 0), middle: 20% (const. = 10), top: 30% (const. = 20).

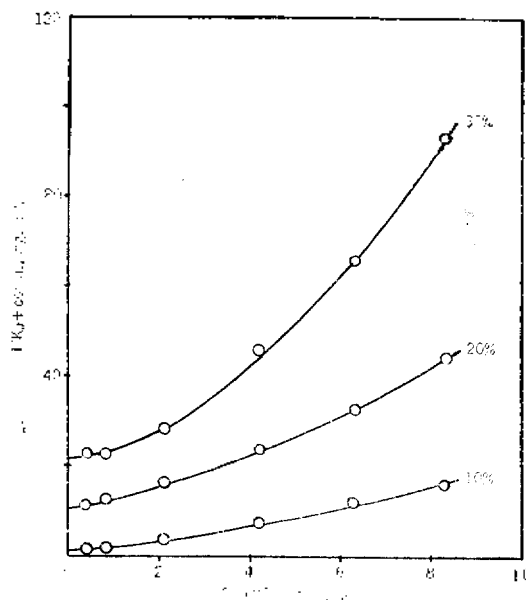


Fig. 8. Plots of $1/K_d$ versus $[\text{Cit}^{3-}]$ for the $\text{Ca}^{++}-\text{Cit}^{3-}$ system in ethanol-water solution. Bottom: 10% (const. = 0), middle: 20% (const. = 10), top: 30% (const. = 20).

complexes could be expressed by equations

$$K_1 = \frac{[\text{Ca Cit}]^-}{[\text{Ca}^{++}] \cdot [\text{Cit}^{3-}]} \quad \dots\dots\dots(11).$$

$$K_2 = \frac{[\text{Ca Cit}_2]^{4-}}{[\text{Ca Cit}]^- \cdot [\text{Cit}^{3-}]} \quad \dots\dots\dots(12).$$

Under the assumption of formation of both one to one and one to two complexes, the following equation could be obtained

$$K_d = \frac{[Ca^{++}R_2]}{[Ca^{++}] + [CaCit]^{-} + [CaCit_2]^{4-}} \dots\dots(13).$$

Equation (4) could be re-written as

$$K_d^0 = \frac{[Ca^{++}R_2]}{[Ca^{++}]} \dots\dots\dots(14).$$

From equations (11)-(14), the following equation was obtained:

$$\frac{1}{K_d} = \frac{1}{K_d^0} + \frac{K_1}{K_d^0} [Cit^{3-}] + \frac{K_1K_2}{K_d^0} [Cit^{3-}]^2 \dots\dots\dots(15).$$

$$\therefore \frac{(K_d^0/K_d) - 1}{[Cit^{3-}]} = K_1 + K_1K_2[Cit^{3-}] \dots\dots\dots(16).$$

After the K_d^0 values were estimated by the extrapolation to the zero $[Cit^{3-}]$ of the curves shown in Figs. 7 and 8, the values of $\{(K_d^0/K_d) - 1\} / [Cit^{3-}]$ were plotted against $[Cit^{3-}]$. Since large uncertainty of the values of $\{(K_d^0/K_d) - 1\} / [Cit^{3-}]$ must be considered due to long extrapolation, it could be said that the plots shown in Figs. 9 and 10 indicate fairly good linearity. It was therefore concluded that the assumption of formation of the one to one and one to two complexes of calcium ions, $[CaCit]^{-}$ and $[CaCit_2]^{4-}$, was reasonable in acetone-water and ethanol-water solutions. From the values of intercepts and slopes of the straight lines in Figs. 9 and 10, the values of K_1 and K_2 were obtained (Table XII).

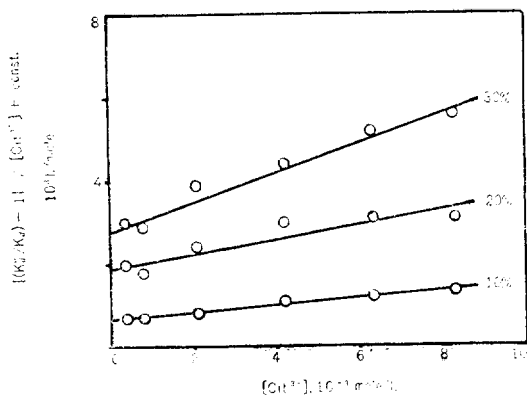


Fig. 9. Plots of $\{(K_d^0/K_d)-1\} / [Cit^{3-}]$ versus $[Cit^{3-}]$ for the $Ca^{++}-Cit^{3-}$ system in acetone-water solution. Bottom: 10% (const.=0), middle: 20% (const.=1), top: 30% (const.=2).

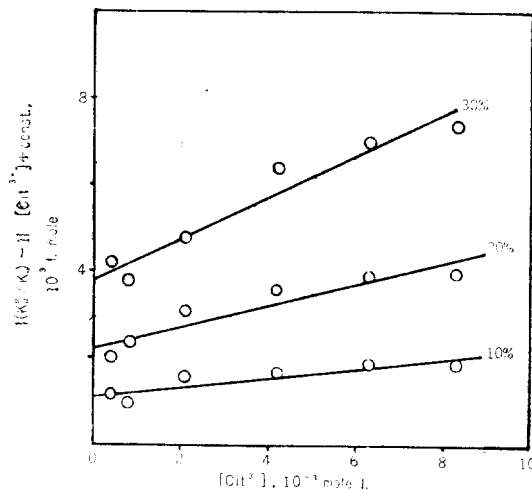


Fig. 10. Plots of $\{(K_d^0/K_d)-1\} / [Cit^{3-}]$ versus $[Cit^{3-}]$ for the $Ca^{++}-Cit^{3-}$ system in ethanol-water solution. Bottom: 10% (const.=0), middle: 20% (const.=1), top: 30% (const.=2).

TABLE XII. Formation Constants of One to One and One to Two Citrate Complexes of Calcium in Acetone-Water and Ethanol-Water Solutions (Room Temperature).

Solvent	K_d^0	$K_1, 10^3 \text{ l. mole}^{-1} (\text{CaCit}^-)$	$K_2, 10^3 \text{ l. mole}^{-1} (\text{CaCit}_2^{4-})$
10% Aceton-H ₂ O	0.63	6.7	1.2
20% "	0.59	9.0	2.0
30% "	0.56	8.7	4.0
10% Ethanol-H ₂ O	1.1	11	1.1
20% "	0.83	12	2.2
30% "	0.56	8.2	5.9

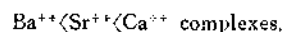
It was concluded from the data shown in Table XII that the values of K_1 for the one to one complex were greater than the values of K_2 for the one to two complex in each solvent system examined, and that the K_2 values increased with increasing concentration of acetone or ethanol in the mixed solvent systems.

DISCUSSION

Relative Stabilities of the Citrate Complexes.

As the results of the present investigation, it is

concluded that relative stabilities of the one to one and one to two citrate complexes generally increase in the following order in each solvent system examined:



This agrees well with the results reported by Schubert and his coworkers on the one to one complexes in aqueous systems.⁽¹⁾

It appears reasonable that smaller cations form more stable complexes with anionic species. On this basis, greater "hydrated" calcium ions must form less stable citrate complex than strontium or barium ions. This is contrary to the results of the present study. Therefore, some factors other than solvation must also be taken into consideration for the relative stabilities of citrate complexes of the alkaline earths in aqueous, acetone-water and ethanol-water solutions.

Effect of Solvents on Stabilities of the Citrate Complexes.

The present study reveals that nature of solvent affects greatly the stability of the citrate complexes of alkaline earths. The complexes are more stable in acetone-water and ethanol-water solutions than in aqueous solution. The relative stability of the complexes increases with increasing concentration of acetone or ethanol in the mixed solvent systems. This may

TABLE XIII. Dielectric Constants¹

Solvent	Temp., °C	Dielectric const.
H ₂ O	25	78.54
Acetone	25	20.7
Ethanol	25	24.3

¹ Ref. 7.

be attributed to the dielectric constants of the solvent systems (Table XIII).

Dielectric constant of the mixed solvent systems decreases with increasing concentration of organic component in the solvent systems. It appears that a smaller value of dielectric constant may result in a stronger Coulombic attraction between the central metal ions and the anionic ligands, citrate ions, which may lead to a greater stability of the complexes.

The present study indicates also that calcium ions form not only the one to one citrate complex but the one to two complex in acetone-water and ethanol-water solutions. This may be explained by greater capability of calcium ions to form complexes with organic acid anions than the other metal ions, and by stronger Coulombic attraction between the central cations and the ligand anions in the mixed solvent systems than in aqueous solution.

REFERENCES

- (1) J. Schubert, E. R. Russel and L. S. Myers, Jr., *J. Bio. Chem.*, **135**, 387 (1950).
- (2) J. Schubert and A. Lindenbaum, *J. Amer. Chem. Soc.*, **74**, 3529 (1952).
- (3) J. Schubert, *J. Phys. Chem.*, **56**, 113 (1952).
- (4) P. Kruger and J. Schubert, *J. Chem. Ed.*, **30**, 196 (1953).
- (5) J. Schubert, *J. Amer. Chem. Soc.*, **76**, 3442 (1954).
- (6) L. F. Fieser, *Experiments in Organic Chemistry* (D. C. Heath and Co., Boston, 1957)
- (7) R. C. Weast, *Handbook of Chemistry and Physics* (Chemical Rubber Co., 1967).