

알칼리토류 금속의 유기산 착물

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Complexes of Alkaline Earth Metals with Organic Acids*

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요 약 방사성의 Ba^{++} , Sr^{++} , Ca^{++} 이온과 양이온 교환수지를 이용한 평형교환법에 의하여 알칼리토류 금속이온과 2염기 유기산 이온사이에 어떤 착물이 형성되는가를 실온에서 조사하였다. 유기산으로서 썩신산과 타르타르산을 사용하였고, 용매로서는 H_2O , 20% 아세톤- H_2O 및 20% 에탄올- H_2O 를 사용하였다. 용액의 pH는 7.2~7.4로 조절하였고 용액의 이온 강도는 약 0.1로 조절하였다. 본 연구결과 알칼리토류 금속 이온과 썩신산 또는 타르타르산 사이에 1:1 착물이 용액내에서 형성됨을 알았고 또 착물의 상대적 안정도가 다음 순으로 증가함을 알았다.

$Ba^{++} < Sr^{++} < Ca^{++}$; 썩신산 < 타르타르산; 수용액 < 혼합용매

Abstract. Formation of the complexes of barium, strontium and calcium ions with dibasic organic acid ions in dilute solution was studied at room temperature, utilizing the equilibrium exchange technique which involved the uses of radioactive alkaline earth metal ions and cation exchange resin. The organic acids used in this study were succinic and tartaric acids, and the solvents used were water, 20% acetone-water and 20% ethanol-water. The pH of the solutions was controlled to 7.2~7.4, and the ionic strength of the solutions was kept at approximately 0.1. The experimental results indicated that the alkaline earths formed one-to-one complexes in solution with the dibasic acids examined, and that the relative stabilities of the complexes increased in the order:

$Ba^{++} < Sr^{++} < Ca^{++}$; succinic < tartaric acid; aqueous < mixed solvent system.

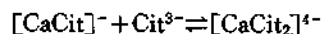
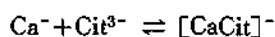
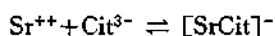
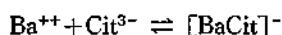
Introduction

In a previous paper of this series,¹ we reported that Ba^{++} and Sr^{++} formed one-to-one citrate complexes, $[M Cit]^-$, in aqueous, acetone-water and ethanol-water solutions. We also reported that Ca^{++} formed one-to-one citrate complex, $[CaCit]^-$, in aqueous solution, and both 1:1

and 1:2 citrate complexes, $[CaCit]^-$ and $[CaCit_2]^{4-}$, in acetone-water and ethanol-water solutions. These studies were carried out by the equilibrium ion exchange technique which involved the measurements of distribution of radioactivity between a cation exchange resin and solution phase after the radioactive metal ions were equilibrated with the cation exchange

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resin in the presence of citrate ions (Cit^{3-}) of varying concentrations.



By comparing the formation constants of these citrate complexes, we examined the relative stabilities of the complexes, and concluded that the relative stabilities increased in the order: $\text{Ba}^{++} < \text{Sr}^{++} < \text{Ca}^{++}$. It then appeared of interest to extend the studies to similar system with other organic acids, such as dibasic organic acids. The present study was undertaken on the complexes of Ba^{++} , Sr^{++} and Ca^{++} with succinic and tartaric acids. The solvents chosen in the present study were water, acetone-water (20 % by volume) and ethanol-water (20 % by volume) mixed solvents.

Experimental

Materials. Acetone and ethanol were purified by the method reported in the previous paper.¹ The purity of the materials was found satisfactory by measuring refractive indices and IR spectra. Acetone-water and ethanol-water mixed solvents (both 20 % by volume) were prepared by mixing appropriate amount of acetone and ethanol with triply distilled water. Cation exchange resin (Dowex 50W-X8, 100~200 mesh) was treated with 6N-HCl and washed with 10 % NaCl solution to convert the resin to the sodium form. The pH of the solution above the resin was adjusted to 7.2~7.4 by adding a small quantity of dil. NaOH solution. The resin was then filtered and dried in the air.

Stock solutions of radioactive barium (^{139}Ba), strontium (^{89}Sr) and calcium (^{45}Ca) were prepared by the method mentioned in the previous

paper.¹ Solid samples of barium nitrate (about 0.1 g), strontium nitrate (about 1 g) and calcium nitrate (about 1 g) were irradiated with neutrons in the nuclear reactor TRIGA-II (neutron flux of about 10^{12} neutrons/cm²/sec) for 15 minutes, 70 hours and 140 hours, respectively, and the resulting solid samples were dissolved in 100 ml, 20 ml and 20 ml of each solvent system, respectively. One ml of each solution was further diluted to 100 ml in the cases of Sr^{++} and Ca^{++} .

Stock solution of sodium chloride (0.125 mole/l) was prepared by dissolving appropriate amount (1.827 g) in each solvent system and diluting to 250 ml. Stock solutions of sodium succinate and sodium tartarate (both 0.0417 mole/l) were also prepared by dissolving appropriate quantities (4.924 g and 6.259 g, respectively) in each solvent system and diluting to 100 ml.

The pH values of all the stock solutions were adjusted to 7.2~7.4. A Beckman Zeromatic SS-3 pH-meter was used to measure the pH values.

Procedure. Experimental procedures were described in the previous paper.¹ Into 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 solution of sodium succinate or sodium tartarate, the stock solution of sodium chloride, and the solvent were added to the Erlenmeyer flasks according to Table I. Thus, the final solution in each flask had the ionic strength of 0.1, and contained the radioactive metal ions of the following concentrations:

$$[\text{Ba}^{++}] = 8.0 \times 10^{-4} \text{ mole/l}$$

$$[\text{Sr}^{++}] = 5.0 \times 10^{-4} \text{ mole/l}$$

$$[\text{Ca}^{++}] = 4.0 \times 10^{-4} \text{ mole/l}$$

Table I. Composition of Sample Solutions

Flask No.	Resin, mg.	M ⁺⁺ , ml	Acid, ml	NaCl, ml	Solvent, ml
1	150	10.0	0	0	40.0
2	150	10.0	1.0	39.0	0
3	150	10.0	2.5	37.5	0
4	150	10.0	5.0	35.0	0
5	150	10.0	10.0	30.0	0
6	150	10.0	25.0	15.0	0

Table II. Distribution Ratios of Ca⁺⁺ between Resin and Solution (Room Temperature)

Acid	Conc., 10 ⁻³ mole/l	1/K _d , mg/ml		
		Aqueous	20 % Acetone	20 % Ethanol
Succinic	0.83	0.42	0.75	1.04
"	2.09	0.45	0.80	1.05
"	4.17	0.46	0.94	1.23
"	8.34	0.50	1.23	1.40
"	20.9	0.60	2.00	1.96
Tartaric	0.83	0.85	0.68	1.20
"	2.09	0.87	0.78	1.51
"	4.17	1.01	1.15	1.92
"	8.34	1.22	1.72	2.77
"	20.9	1.80	3.13	4.80

Each flask was shaken for 5~6 hours to equilibrate radioactivity between the resin and solution phases. The resin was filtered by pouring into a porous steel disc in chimney funnel, and dried in the air. The radioactivity remained in the resin particles was counted with G-M tube (Nuclear Radiation Detector, Medel 108) and scaler (Nuclear Chicago, Model 8770). A correction was made for decay of the radioisotopes during each run of the experiment, if necessary.

The distribution ratios, K_d , of the metal ions between the resin and solution phases were calculated by

$$K_d = \frac{V}{m} \frac{A(\text{resin})}{A(\text{total}) - A(\text{resin})},$$

where $A(\text{resin})$ denotes the radioactivity of

the resin phase, $A(\text{total})$ the total activity of the metal ions present in the resin and solution phases, V the volume (in ml) of the solution, and m the weight (in mg) of the resin.

Results

Ca⁺⁺ Complexes. The distribution ratios of Ca⁺⁺ between the resin and solution phase were determined in aqueous, 20 % acetone-water, and 20% ethanol-water solutions in the presence of succinate or tartarate ions of varying concentrations. The results obtained at room temperature are summarized in Table II.

The values of $1/K_d$ listed in Table II were plotted against the acid ion concentrations. The

results revealed good linearity in each case. An example of the plots is shown graphically in Fig. 1. The linearities observed between $1/K_d$ and acid ion concentrations indicate that the assumption of one-to-one complex formation is correct, as discussed in the previous paper.¹

$$\frac{1}{K_d} = \frac{1}{K_d^0} + \frac{K_f}{K_d^0} [A^{--}],$$

where K_d^0 denotes the K_d value at infinite

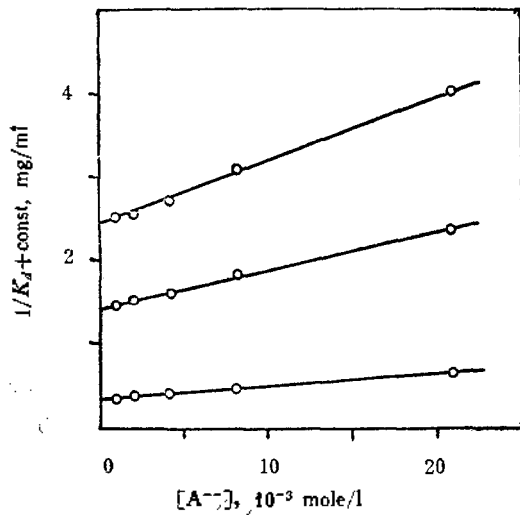


Fig. 1. Plots of $1/K_d$ versus $[A^{--}]$ for Ca^{++} -succinic acid system. Bottom: aqueous (const. = 0); middle: 20 % acetone-water (const. = 1.0); top: 20 % ethanol-water (const. = 2.0).

dilution, K_f the formation constant of the complex species, and $[A^{--}]$ the acid ion concentration.

From the slopes and intercepts of the linear plots, the formation constants of the one-to-one Ca^{++} -complexes were obtained to be as follows:

- [Ca Suc] 0.25×10^2 /mole in H_2O
- 0.86×10^2 " in acetone- H_2O
- 0.46×10^2 " in ethanol- H_2O
- [Ca Tar] 0.59×10^2 " in H_2O
- 2.0×10^2 " in acetone- H_2O
- 1.7×10^2 " in ethanol- H_2O

Sr⁺⁺ and Ba⁺⁺ Complexes. Studies were extended to the systems with Sr^{++} and Ba^{++} . The results are summarized in Tables III and IV. Again, we observed linear relations between $1/K_d$ and the acid ion concentration in all the systems investigated. It was concluded therefore that the assumption of one-to-one complex formation was correct also in these cases. From the slopes and intercepts of the plots, the formation constants of the one-to-one Sr^{++} -complexes were obtained to be as follows:

- [Sr Suc] 0.11×10^2 1/mole in H_2O
- 0.71×10^2 " in acetone- H_2O
- 0.94×10^2 " in ethanol- H_2O

Table III. Distribution Ratios of Sr^{++} between Resin and Solution (Room Temperature)

Acid.	Conc., 10^{-3} mole/l	$1/K_d$, mg/ml		
		Aqueous	20 % Acetone	20 % Ethanol
Succinic	0.83	0.35	0.38	0.43
"	2.09	0.36	0.39	0.44
"	4.17	0.38	0.41	0.55
"	8.34	0.39	0.50	0.67
"	20.9	0.43	0.83	1.15
Tartaric	0.83	0.34	0.45	0.53
"	2.09	0.36	0.53	0.55
"	4.17	0.40	0.60	0.74
"	8.34	0.45	0.83	1.08
"	20.9	0.65	1.37	2.02

Table IV. Distribution Ratios of Ba⁺⁺ between Resin and Solution (Room Temperature)

Acid	Conc., 10 ⁻³ mole/l	1/K _d , mg/ml		
		Aqueous	20 % Acetone	20 % Ethanol
Succinic	2.09	0.10	0.10	0.10
"	4.17	0.10	0.10	0.12
"	8.34	0.11	0.17	0.12
"	20.9	0.13	0.17	0.17
Tartairic	0.83	0.16	—	—
"	2.09	0.16	0.26	0.21
"	4.17	0.17	0.28	0.25
"	8.34	0.19	0.40	0.38
"	20.9	0.25	0.51	0.52

[Sr Tar]	0.45 × 10 ²	1/mole in H ₂ O
	1.3 × 10 ²	" in acetone-H ₂ O
	1.6 × 10 ²	" in ethanol-H ₂ O
[Ba Suc]	0.18 × 10 ²	" in H ₂ O
	0.36 × 10 ²	" in acetone-H ₂ O
	0.36 × 10 ²	" in ethanol-H ₂ O
[Ba Tar]	0.30 × 10 ²	" in H ₂ O
	0.58 × 10 ²	" in acetone-H ₂ O
	0.87 × 10 ²	" in ethanol-H ₂ O

Discussion

From the results of the present investigation, it is concluded that the alkaline earth metals form the one-to-one complex with succinate or tartarate ions in aqueous, acetone-water (20 % by volume) and ethanol-water (20 % by volume) solutions. By comparing the formation constants, it is possible to establish the relative stabilities of the complexes.

In the case of succinate complexes, the experimental results do not indicate gradual change in the relative stabilities among the three alkaline earth complexes. It is true, however, that experimental error is usually magnified greater for the calculation of the formation constants of less stable complexes than more stable complexes. This could be

considered as a reason why we have rather irregular trend of the relative stabilities among the succinate complexes of the three alkaline earths. Nevertheless, it still could be said that Ca⁺⁺ forms a little more stable succinate complex and Ba⁺⁺ forms a little less stable succinate complex. In the case of tartarate complexes, it is concluded from the experimental results that Ca⁺⁺ forms more stable tartarate complex than Sr⁺⁺, which in turn forms more stable tartarate complex than Ba⁺⁺. The same trend was observed for the citrate complexes of the alkaline earths.¹

It is also concluded from the results of the present study that tartarate ions form more stable alkaline earth complexes than succinate ions, and that all the complexes observed are more stable in acetone-water or ethanol-water mixed solvents than in water.

The results of the present study are compared with those of the previous investigation of this series¹ (Table V). It is seen from Table V that the relative stabilities of the complexes of alkaline earths with organic acids increase generally in the following order:

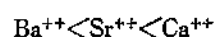


Table V. Formation Constants of Complexes of Alkaline Earths with Organic Acids (Room Temperature).

Acid	Solvents	$K_1, 10^3$ 1/mole			$K_2, 10^3$ 1/mole		
		Ca ⁺⁺	Sr ⁺⁺	Ba ⁺⁺	Ca ⁺⁺	Sr ⁺⁺	Ba ⁺⁺
Succinic*	H ₂ O	0.25	0.11	0.18	—	—	—
"	20 % Acetone-H ₂ O	0.86	0.71	0.36	—	—	—
"	20 % Ethanol-H ₂ O	0.46	0.94	0.36	—	—	—
Tartaric*	H ₂ O	0.59	0.45	0.30	—	—	—
"	20 % Acetone-H ₂ O	2.0	1.3	0.58	—	—	—
"	20 % Ethanol-H ₂ O	1.7	1.6	0.87	—	—	—
Citric**	H ₂ O	6.9	4.1	3.9	—	—	—
"	20 % Acetone-H ₂ O	9.0	13	7.3	2.0	—	—
"	20 % Ethanol-H ₂ O	12	13	7.3	2.2	—	—

*Present study. **Ref. 1.

Aqueous < mixed solvent systems.

It appears reasonable to conclude that metal ions with smaller naked radii form more stable complexes with organic acid ions. This agrees with the results reported by Schubert and his coworkers on the one-to-one citrate complexes of alkaline earth metals in aqueous system.²⁻⁶ When we compare the relative electrostatic attraction between the cationic and anionic species in solution, the solvation of metal ions must be considered. If so, the results of the present investigation are contrary to what we expect for the solvated cations.⁷ Therefore, it seems that mere size of solvated cations may not be the only factor to affect the relative stabilities of the complexes of alkaline earths with organic ions in solution.

It is concluded that succinate ions form less stable alkaline earth complexes than tartarate ions, which in turn form less stable alkaline earth complexes than citrate ions, in all the solvent systems examined. This may indicate that the number of groups, such as OH and COOH in the anionic species might also affect the formation constants of alkaline earth complexes.³

It is also concluded that the complexes are

more stable in acetone-water and ethanol-water solutions than in aqueous solution. This may be explained by the dielectric constants of the solvent systems. Smaller values of dielectric constant may result in stronger Coulombic attractions between the metal cations and the anionic species to form more stable complexes in solution. This agrees with the results reported previously on citrate complexes of alkaline earths.¹

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