알칼리토류 금속과 2 염기 유기산 사이의 착물*

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Complexes of Alkaline Earth Metals with Dibasic Organic Acids in Aqueous, Ethanol-Water and Acetone-Water Solutions*

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요 약. 양이온 교환수지 (Ion Exchange Resin CGC 241)와 2 염기산인 말론산 혹은 프탈산이온이 들어있는 용액에서 방사성 알칼리토류금속 이온이 수지와 용액사이에 어떻게 분배되는가를 실온에서 조사함으로써 알칼리토류금속의 유기산 착물 형성에 관한 연구를 하였다. 용매로서 H_2O, 20 % 에탄올—물 및 20 % 아세톤—물을 사용하였고, 용액의 pH 는 7.2~7.5 로 조절하였고, 이온강도는 0.10~0.11 로 유지하였다.

본 연구결과 알칼리토류금속 이온과 말론산 및 프탈산 사이에 1 : 1착 물이 모든 용매계에서 형성되었고 착물의 안정도는 다음순으로 증가됨을 알았다.

$Ba^{++} < Sr^{++} < Ca^{++}$,　　　말론산 < 프탈산,　　　수용액 < 혼합용매

Abstract. Formation of the complexes of alkaline earth metal ions with malonate and *o*-phthalate ions in aqueous, ethanol-water and acetone-water solutions (20% by volume) was studied at room temperature by the equilibrium ion exchange technique. This technique involved the measurements of distribution of radioactivity between cation exchange resin (Ion Exchange Resin CGC 241) and solution phases after the radioactive metal ions were equilibriated with the cation exchange resin in the presence of malonate or *o*-phthalate ions of varying concentrations. The pH of the solutions was controlled to 7.2~7.5, and the ionic strength of the solutions was kept at 0.10~0.11. The results of the present study indicated that the alkaline earth metal ions formed one-to-one complexes with the dibasic organic acids in all solvent systems examined. The present study showed that the relative stabilities of the complexes increased in the order: $Ba^{++} < Sr^{++} < Ca^{++}$ complexes. It was also observed that the relative tendency of the *o*-phthalate ion for the complex formation was somewhat greater than that of malonate ion in each solvent system. Furthermore, it was noted that the complexes were formed more readily in the mixed solvent than in the aqueous solution.


Introduction

Formation of the complexes of alkaline earth metal ions with various organic acids in aqueous solution was studied by Schubert and his co-workers. [1~4] 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 the solution phase after the radioactive metal ions were equilibriated with the cation exchange resin in the presence of organic acids of varying concentrations. Schubert and his coinvestigators reported the formation of one-to-one complexes between alkaline earth metal ions (M^{++}) and various organic acid ions (A^{--}) in aqueous solution.

$$M^{++} + A^{--} \rightleftharpoons MA$$
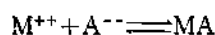
In a previous paper of this series[5], we reported that alkaline earth metal ions formed one-to-one complexes with succinate ions (Suc^{--}) and tartrate ions (Tar^{--}) not only in aqueous solution but also in ethanol-water and acetone-water mixed solvents. Although we were unable to determine the structure of the complex species present in solution, we assumed that the following equilibria might exist in solution, based on the conclusion made by Schubert and his coworkers:

$$M^{++} + Suc^{--} \rightleftharpoons MSuc$$
$$M^{++} + Tar^{--} \rightleftharpoons MTar$$
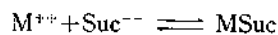
By comparing the formation constants of the alkaline earth metal complexes, we examined the relative stabilities of the complexes, and concluded that the relative stabilities increased in the order:

$$Ba^{++} < Sr^{++} < Ca^{++}.$$
Succinic < tartaric < citric acid.
Aqueous < mixed solvent system.
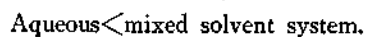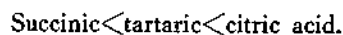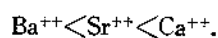
In the present study the complexes of alkaline earth metal ions with malonate (Mal^{--}) and o-phthalate (Pth^{--}) ions were examined by the equilibrium exchange technique to see if complexes would exist in aqueous and mixed solvent systems, and to find out the composition of the complexes, and to investigate the effect of the nature of metal ions, anionic species and solvent systems on the stabilities of the complexes. More specifically, it was aimed to see if the stabilities of the complexes were affected by the extent of separation of two carboxyl groups in the dibasic anions, and by the presence of aromatic ring in the anionic molecules.

Ba—139, Sr—89 and Ca—45 were used as tracers in the present investigation. The solvents chosen in the present study were water, ethanol-water (20 % by volume), and acetone-water (20% by volume) mixed solvents.

Experimental

Purification of Reagents and Preparation of Solutions. Ethanol (C. P., Eastman Organic Chemical Co.) and acetone (A. R., Eastman Organic Chemical Co.) were purified by the methods reported in the previous papers. [6,7] The purity of the materials thus purified was found satisfactory by measuring refractive indices and IR spectra. Ethanol-water and acetone-water mixed solvents (both cases, 20 % by volume) were prepared by mixing appropriate amount of ethanol and acetone with triply distilled water.

Cation exchange resin used in the present investigation was Ion Exchange Resin CGC 241 (200~400 mesh, Na-form). Appropriate quantity of the resin was placed in a 1-liter beaker, and triply distilled water was poured in. The mixture was then stirred with a magnetic stirrer. 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 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 malonate and sodium o-phthalate(both cases, 0.0625 mole/l) were also prepared by dissolving appropriate quantity of malonic acid(1.631 g) and o-phthalic acid(2.596 g) in about 240 ml of each solvent, by adding sodium hydroxide solution to bring pH of the solution to 7.2~7.5, and then diluting the solutions to 250 ml.

Stock solutions of radioactive barium(^{139}Ba), strontium(^{89}Sr) and calcium(^{45}Ca) were prepared by the methods mentioned in the previous paper of this series.[6]

The pH values of all the stock solutions were adjusted to 7.2~7.5. A Beckman Zeromatic SS-3 pH-mater was used to measure the pH values.

Procedures. Experimental procedures used in the present study were the same as those described in the previous papers.[6,7] The cation exchange resin(150 mg) and the stock solutions of radioactive Ca^{++}, Sr^{++} or Ba^{++} ions(10 ml) were placed in 125 ml Erlenmeyer flasks. The stock solutions of sodium malonate or o-phthalate, sodium chloride, and the solvents were added according to *Table* 1. The sample solution in each flask had the ionic strength of 0.10~0.11, and contained the metal ions of the following concentrations:

$$Ba^{++}=8\times 10^{-4} \text{ mole}/l$$
$$Sr^{++}=9\times 10^{-4} \text{ mole}/l$$
$$Ca^{++}=8\times 10^{-4} \text{ mole}/l.$$

After each flask was shaked for about 3 hours, the resin was filtered on a porous steel disc in a chimney funnel and dried in the air. The radioactivity remained in the resin particles was counted with a G-M tube(Nuclear Radiation Detector, Model 108, operating voltage 980 volts) and a 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 the following equation:

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

where each symbol denotes the same quantity as was described in the previous paper of this series[6].

Table 1. 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	0.1	39.9	0
3.	150	10.0	0.5	39.5	0
4.	150	10.0	1.0	39.0	0
5.	150	10.0	2.5	37.5	0
6.	150	10.0	5.0	35.0	0
7.	150	10.0	7.5	32.5	0
8.	150	10.0	10.0	30.0	0

*The concentrations of the stock solutions are as follow:
[Ba^{+}]=8×10^{-4} mole/l, [Sr^{++}]=9×10^{-4} mole/l, [Ca^{++}]=8×10^{-4} mole/l, [Acid]=0.0625 mole/l, and [NaCl]=0.125 mole/l.

Results

Ca^{++} Complexes. The stock solution of radioactive Ca^{++} ions was mixed at room temperature with the stock solution of sodium malonate or sodum o-phthalate in the presence of cation exchange resin. The distributon ratios of Ca^{++} between the resin and solution phases were then measured. The experimental results obtained in aqueous, 20 % ethanol-water and 20 % acetone-water solutions are summarized in *Table 2.*

When the values of $1/K_d$ listed in *Table* 2 were plotted against the acid anion concentrations, good linearities were observed in all cases. (The actual graphs are not shown here in this paper.) It was discussed in previous papers of this series that linearity should be observed between $1/K_d$ and acid anion concentrations if the assumption of the one-to-one complex formation between Ca^{++} and acid ions was correct.[5,6] In other words, if the one-to-one complexes were formed in solution, the following relation should be valid:

$$\frac{1}{K_d} = \frac{1}{K^\circ_d} + \frac{K_f}{K^\circ_d}[\text{Acid}],$$

where K°_d denotes the K_d value at infinite dilution, K_f the formation constant of the complex species, and [Acid] the acid concentration.

Since we actually observed good linearities between the values of $1/K_d$ and the acid anion concentrations, it was concluded that Ca^{++} formed the one-to-one complex with malonate or o-phthalate ions in aqueous, 20 % ethanol-water or 20 % acetone-water solution. From the slopes and intercepts of the linear plots of $1/K_d$ versus [Acid], the values of K_f and K°_d were calculated. The results are shown in *Table 3.*

Sr^{++} and Ba^{++} Complexes. The studies were extended to the systems of Sr^{++} and Ba^{++} with malonate ions or o-phthalate ions in water, 20 % ethanol-water or 20 % acetone-water solution. The experimental results are summarized in *Tables* 4 and 6. Again, we observed good linearities between the values of $1/K_d$ and the acid anion concentrations in all the systems

Table 2. Distribution ratios of Ca^{++} between resin and solution(room temperaure)

Acid	Conc., 10^{-3} mole/l	$1/K_d$, mg/ml		
		Aqueous	20 % Ethanol	20 % Acetone
Malonic	0.125	0.54	0.89	0.95
//	0.625	0.55	0.96	0.99
//	1.25	0.56	1.1	1.1
//	3.13	0.60	1.3	1.3
//	6.25	0.63	1.8	1.9
//	9.38	0.69	2.2	2.3
//	12.54	0.74	2.6	2.7
o-Phthalic	0.125	0.54	0.96	0.99
//	0.625	—	1.0	1.0
//	1.25	0.58	1.1	1.2
//	3.13	0.61	1.4	1.4
//	6.25	0.65	1.9	2.0
//	9.38	0.72	2.4	2.5
//	12.5	0.77	2.9	3.1

Table 3. Formation constants of complexes of Ca^{++} with malonate or o-phthalate ions(room temperature)

Complex	Solvent	$1/K^{\circ}_d$, mg/ml	K_f, 10^2 mole/l
(CaMal)	H$_2$O	0.54	0.29(0.23*)
"	20 % Ethanol	0.88	1.6
"	20 % Acetone	0.91	1.6
(CaPth)	H$_2$O	0.55	0.33
"	20 % Ethanol	0.93	1.7
"	20 % Acetone	0.93	1.8

*Ref. 1.

investigated. It was concluded therefore that the one-to-one complexes of Sr^{++} and Ba^{++} with malonate ions or o-phthalate ions were present in aqueous, 20 % ethanol-water or 20 % acetone-water solution. From the slopes and intercepts of the linear plots, the values of K_f and K°_d for the formation of one-to-ne complexes of Sr^{++} and Ba^{++} with malonate ions

Table 4. Distribution ratios of Sr^{++} between resin and solution(room temperature)

Acid	Conc., 10^{-3} mole/l	$1/K_d$, mg/ml		
		Aqueous	20 % Ethanol	20 % Acetone
Malonic	0.125	0.28	0.34	0.36
"	0.625	—	0.37	0.38
"	1.25	0.30	0.38	0.41
"	3.13	0.32	0.42	0.45
"	6.25	0.34	0.48	0.53
"	9.38	0.36	0.57	0.65
"	12.5	0.37	0.67	0.73
o-Phthalic	0.125	0.29	0.35	0.36
"	0.625	0.29	0.38	0.39
"	1.25	0.31	0.40	0.42
"	3.13	0.32	0.47	0.50
"	6.25	0.36	0.58	0.61
"	9.38	0.37	0.69	0.73
"	12.5	0.39	0.82	0.86

Table 5. Formation constants of complexes of Sr^{++} with malonate or o-phthalate ions(room temperature)

Complex	Solvent	$1/K^{\circ}_d$, mg/ml	K_f, 10^2 mole/l
(SrMal)	H$_2$O	0.29	0.26(0.19*)
"	20 % Ethanol	0.34	0.74
"	20 % Acetone	0.36	0.81
(SrPth)	H$_2$O	0.29	0.29
"	20 % Ethanol	0.37	0.87
"	20 % Acetone	0.37	1.1

*Ref. 1.

or o-phthalate ions were calculated. The results are shown in *Tables* 5 and 7.

Discussion

As the results of the present study it is concluded that Ca^{++}, Sr^{++} and Ba^{++} form the one-to-one complexes with malonate or o-phthalate ions in aqueous, 20 % ethanol-water and 20 % acetone-water solutions. This agrees with the results reported in the literature[1,8] on the malonate complexes of alkaline earths in aqueous solution(*Tables* 3, 5 and 7).

By comparing the formation constants it is possible to establish the relative stabilities of the complexes. From *Tables* 3, 5 and 7, it is concluded that Ca^{++} ions form more stable one-to-one complexes with malonate or o-phthalate ions in solution than Sr^{++} ions, which in turn form more stable complexes than Ba^{++} ions. Similar trend was also observed on other alkaline-earth complexes with succinate, tartrate and citrate ions[5,6](*Table* 8). This indicates that the relative complexing power of the three metal ions increases with decreasing crystal radii of the metal ions.
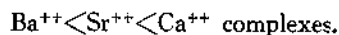
$$Ba^{++} < Sr^{++} < Ca^{++} \text{ complexes.}$$

Table 6. Distribution ratios of Ba^{++} between resin and solution(room temperature)

Acid	Conc., 10^{-3} mole/l	$1/K_d$, mg/ml		
		Aqueous	20 % Ethanol	20 % Acetone
Malonic	0.125	0.086	0.13	0.13
"	0.625	0.091	0.13	0.14
"	1.25	0.094	0.14	0.14
"	3.13	0.095	0.14	0.15
"	6.25	0.097	0.15	0.16
"	9.38	0.10	0.17	0.18
"	12.5	0.11	0.18	0.20
o-Phthalic	0.125	0.12	0.18	0.19
"	0.625	0.12	0.19	0.19
"	1.25	0.13	0.20	0.20
"	3.13	0.13	0.21	0.21
"	6.25	0.13	0.22	0.24
"	9.38	0.14	0.25	0.25
"	12.5	0.15	0.26	0.26

Table 7. Formation constants of complexes of Ba^{++} with malonate or o-phthalate ions(Room temperature)

Complex	Solvent	$1/K^{\circ}_d$, mg/ml	K_f, 10^2 mole/l
[BaMal]	H_2O	0.089	0.18(0.17*)
"	20 % Ethanol	0.13	0.34
"	20 % Acetone	0.13	0.37
[BaPth]	H_2O	0.12	0.19
"	20 % Ethanol	0.18	0.35
"	20 % Acetone	0.19	0.38

*Ref. 8.

If it is assumed that the complexes are formed merely through electrostatic attraction between the hydrated cations and the anionic species in solution, the results of the present investigation are contrary to what we expect for the solvated cations, because the relative size of the solvated alkaline-earth cations might be of the following order[9]:

$$Ba^{++}(aq) < Sr^{++}(aq) < Ca^{++}(aq).$$
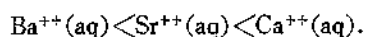
Therefore, it seems that mere electrostatic attraction between the hydrated cations and the anionic species may not be the only factor to affect the formation of the complexes. It is speculated that anionic species may penetrate into the hydration sheath surrounding the metal ions in order to form complexes with metal ions in solution. If so, the crystal size of metal ions may play more important role on the complex formation than the size of the hydrated cations in solution.

It is noticed from *Table* 8 that the relative stabilities of the malonate complexes are some-what greater than the corresponding succinate complexes. This agrees with the fact that the K_f values of the metal-acid complexes decrease generally with increasing separation of carboxyl groups in the dibasic anions.[1,8] On this basis the stabilities of the malonate complexes would be greater than the o-phthalate or tartrate complexes. This is reverse to what is observed experimentally. Thus, it seems reasonable to say that aromatic ring or OH groups in the acid molecules may play important role on the metal-acid complex formation in solution.

It can also be seen from *Table* 8 that all the complexes examined are formed more readily in ethanol-water and acetone-water solutions than in aqueous solutions. This might be attributed to the difference in dielectric constant between water and organic solvent molecules. Smaller values of dielectric constants of ethanol and acetone may result in stronger Coulombic attraction between the cationic and anionic species in solution. Therefore, it can be said that the complexes are formed more readily in

Table 8. Formation constants of complexes of alkaline earth metals with organic acids(room temperature)

Acid	Solvent	K_1, 10^2 mole/l			K_2, 10^2 l/mole		
		Ca^{++}	Sr^{++}	Ba^{++}	Ca^{++}	Sr^{++}	Ba^{++}
Succinic*	H$_2$O	0.25	0.11	0.18	—	—	—
''	20 % Ethanol-H$_2$O	0.46	0.94	0.36	—	—	—
''	20 % Acetone-H$_2$O	0.86	0.71	0.36	—	—	—
Malonic**	H$_2$O	0.29	0.26	0.18	—	—	—
''	20 % Ethanol-H$_2$O	1.6	0.74	0.34	—	—	—
''	20 % Acetone-H$_2$O	1.6	0.81	0.37	—	—	—
o-Phthalic**	H$_2$O	0.33	0.29	0.18	—	—	—
''	20 % Ethanol-H$_2$O	1.7	0.87	0.35	—	—	—
''	20 % Acetone-H$_2$O	1.8	1.1	0.38	—	—	—
Tartaric*	H$_2$O	0.59	0.45	0.30	—	—	—
''	20 % Ethanol-H$_2$O	1.7	1.6	0.87	—	—	—
''	20 % Acetone-H$_2$O	2.0	1.3	0.58	—	—	—
Citric***	H$_2$O	6.9	4.1	3.9	—	—	—
''	20 % Ethanol-H$_2$O	12	13	7.3	2.2	—	—
''	20 % Acetone-H$_2$O	9.0	13	7.3	2.0	—	—

*Ref. 5. **The present investigation. ***Ref. 6.

ethanol-water and acetone-water solutions than in aqueous solutions.

Acknowledgment

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