망간, 코발트 및 아연과 2 염기 유기산 사이의 착물*

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Complexes of Manganese, Cobalt and Zinc with Dibasic Organic Acids in Aqueous, Ethanol-Water and Acetone-Water Solutions*

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요 약. Mn^{++}, Co^{++} 및 Zn^{++} 용액을 실온에서 양이온 교환수지와 2 염기 유기산이 들어 있는 용액에 섞어 넣었다. 방사성 금속이온을 추적자로 사용함으로써 금속이온이 수지층과 용액사이에 어떻게 분배되는가를 조사하였다. 이 분배 비율이 유기산이온 농도에 따라 어떻게 달라지는가를 보아, Mn^{++}, Co^{++} 및 Zn^{++}이 수용액, 에탄올—물 및 아세톤—물에서 썩신산, 말론산, 프타르산 및 타르타르산과 사이에 1 : 1 착물을 형성한다고 결론하였다. 또한 본 연구의 결과 이들 착물의 안정도가 다음순으로 증가함을 알았다.

Mn^{++} < Co^{++} < Zn^{++}, 썩신산 < 말론산 < 프타르산 < 타르타르산, 수용액 < 혼합용매

Abstract. Solutions of Mn^{++}, Co^{++} and Zn^{++} were mixed with various dibasic organic acids in the presence of cation exchange resin at room temperature. The distribution ratios of the metal ions between resin and solution were measured, using radioactive metal ions as tracer. From the observed variation of the distribution ratios with acid anion concentrations, it was concluded that Mn^{++}, Co^{++} and Zn^{++} formed one-to-one complexes with succinate, malonate, o-phthalate and tartrate ions in aqueous, 20 % ethanol-water and 20 % acetone-water solutions. The results of the present investigation indicated that the relative stabilities of the complexes increased in the order:

Mn^{++} < Co^{++} < Zn^{++} complexes,

Succinate < malonate < o-phthalate < tartrate complexes,

Aqueous < mixed solvent systems.

Introduction

In a previous paper of this series[1], we reported the results of the investigation on the formation of citrate complexes of manganese, zinc and cobalt in aqueous, 20 % ethanol-water and 20 % acetone-water solutions, using the equilibrium ion exchange technique. [2~8] We concluded[1] from experimental results that (1) both Mn^{++} and Zn^{++} ions formed one-to-one complexes,
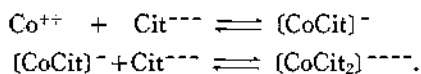

[MCit]⁻, with citrate ions (Cit⁻⁻⁻) in all the solvent system examined:

$$Mn^{++} + Cit^{---} \rightleftharpoons [MnCit]^-,$$
$$Zn^{++} + Cit^{---} \rightleftharpoons [ZnCit]^-,$$
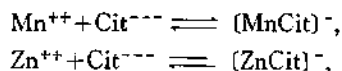
and (2) Co^{++} ions formed one-to-one citrate-complex in aqueous solution:
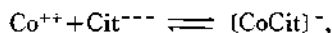
$$Co^{++} + Cit^{---} \rightleftharpoons [CoCit]^-,$$

but formed both one-to-one and one-to-two citrate-complexes in ethanol–water and acetone–water solutions:

$$Co^{++} + Cit^{---} \rightleftharpoons [CoCit]^-$$
$$[CoCit]^- + Cit^{---} \rightleftharpoons [CoCit_2]^{----}.$$

In another paper of this series,[9] we reported that(1) Ba^{++} and Sr^{++} ions also formed one-to-one complexes with citrate ions in aqueous, 20 % ethanol–water and 20 % acetone–water solutions:

$$Ba^{++} + Cit^{---} \rightleftharpoons [BaCit]^-,$$
$$Sr^{++} + Cit^{---} \rightleftharpoons [SrCit]^-,$$
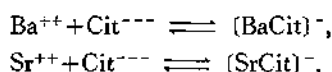
and (2) Ca^{++} ions formed one-to-one citrate-complex in aqueous solution:
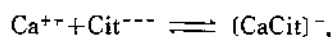
$$Ca^{++} + Cit^{---} \rightleftharpoons [CaCit]^-,$$
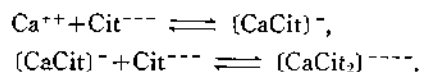
but formed both one-to-one and one-to-two citrate complexes in ethanol–water and acetone–water solution:

$$Ca^{++} + Cit^{---} \rightleftharpoons [CaCit]^-,$$
$$[CaCit]^- + Cit^{---} \rightleftharpoons [CaCit_2]^{----}.$$

By comparing the values of formation constants of the complexes in solution, it was concluded that the transition metal ions formed more stable citrate-complexes than the alkaline earth elements. Thus, we observed pronounced difference in relative stabilities of the citrate complexes between transition elements and alkaline earths. In order to examine similar effects, the studies were extended to the systems of alkaline earths with various dibasic organic acids, such as succinic, malonic, o–phthalic and tartaric acids.[10,11] The experimental rusults indicated that the relative stabilities of the alkaline–earth complexes with various dibasic organic acids in solution increased generally in the order:

Succinic < malonic < o-phthalic < tartaric acid.

It then appeared of interest to extend the studies further to the systems of manganese, cobalt and zinc ions with dibasic organic acids in solution in order to compare the transition elements with alkaline earths towards the complex formation with dibasic organic acids. Thus, the present study was undertaken on the formation of complexes of Mn^{++}, Co^{++} and Zn^{++} ions with succinic, malonic, o–phthalic and tartaric acids in aqueous, ethanol–water and acetone–water solutions, utilizing the equilibrium ion exchange technique. Mn–56, Co–60 and Zn–65 were used as tracers.

Experiment

Materials. Ethanol (C. P., Eastman Organic Chemical Co.) and acetone (A. R., Eastman Organic Chemical Co.) were purified by the methods reported in the previous paper.[11] Ethanol–water and acetone–water mixed solvents were prepared by mixing appropriate amounts of ethanol and acetone with triply distilled water. Cation exchange resin (Ion Exchange Resin CGC 241, 200~400 mesh, Na–form) was treated with a small quantity of *dil.* sodium hydroxide solution by the method described in the previous paper[11], in order to adjust the pH of the solution above the resin to 7.2~7.4. A Beckman Zeromatic SS–3 pH–meter was used to measure the pH values.

Preparation of Stock Solutions. Stock solutions of sodium chloride (0.125 mole/*l*) were prepared by dissolving appropriate amount of

sodium chloride in each solvent system.[11] Stock solutions of sodium succinate, sodium malonate, sodium o-phthalate and sodium tartrate (all cases, 0.0625 mole/l) were prepared by dissolving the appropriate quantities of the organic acids in each solvent system and adding small amount of *dil.* sodium hydroxide solution to bring the pH of the solutions to 7.2~7.4.[11]

Stock solutions of radioactive manganese (^{56}Mn), cobalt (^{60}Co) and zinc (^{65}Zn) were prepared in the following manner. Solid samples of manganese nitrate (about 0.1 g), cobaltous nitrate (about 0.5 g) and zinc nitrate (about 0.5 g) were irradiated with neutrons in the nuclear reactor TRIGA-II (neutron flux, 10^{12} neutrons/cm^2/sec) for 12 min., 12 hrs., and 30 hrs., respectively. The resulting solid samples were dissolved in 20 ml of distilled water. One ml was pipetted and diluted with water or mixed solvents to 100 ml. The pH values of all the stock solutions were adjusted to 7.2~7.4 before the final dilutions were made in volumetric flasks.

Procedure. Experimental procedures used in the present study were the same as those described in the previous papers.[1,9~12] The cation exchange resin(150 mg) and the stock solution of radioactive Mn^{++}, Co^{++} or Zn^{++} ions(10 ml) were placed in 125 ml Erlenmeyer flasks. The stock solution of sodium succinate, sodium malonate, sodium o-phthalate or sodium tartrate was added according to *Table* 1, and the stock solution of sodium chloride and the solvents were also added. The sample solution in each flask had the ionic strength of 0.10~0.11, and contained the metal ions of the following concentrations:

$$[Mn^{++}] = 2 \times 10^{-4} \text{ mole}/l$$
$$[Co^{++}] = 2 \times 10^{-4} \text{ mole}/l$$
$$[Zn^{++}] = 0.4 \times 10^{-4} \text{ mole}/l.$$

After each flask was shaked for about 3 hours, the resin was filtered on a porous metal disc in a chimney funnel and dried in the air. The radioactivity of the resin was counted with a G–M counter. The distribution ratios, K_d, of the metal ions between resin and solution were calculated by the following equation:

Table 1. Composition of sample solution.

Flask No.	Resin, mg	M^{++} ml	Acid, ml	NaCl, ml	Solvent, ml
1	150	10.0	0	0	40.0
2	150	10.0	0.05	39.95	0
3	150	10.0	0.10	39.90	0
4	150	10.0	0.15	39.85	0
5	150	10.0	0.20	39.80	0
6	150	10.0	0.25	39.75	0
7	150	10.0	0.30	39.70	0
8	150	10.0	0.35	39.65	0
9	150	10.0	0.40	39.60	0
10	150	10.0	0.50	39.50	0
11	150	10.0	0.60	39.40	0
12	150	10.0	0.70	39.30	0

The concentrations of the stock solutions are as follows:

$[Mn^{++}] = 2 \times 10^{-4}$ mole/l, $[Co^{++}] = 2 \times 10^{-4}$ mole/l, $[Zn^{++}] = 0.4 \times 10^{-4}$ mole/l, $[Acid] = 0.0625$ mole/l, and $[NaCl] = 0.125$ mole/l.

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

where V denotes the volume (in ml) of the solution, m the weight (in mg) of the resin, A(resin) the radioactivity of the resin phase, and A(total) the total radioactivity of the metal ions in the resin and solution phases.

Results

Mn^{++} Complexes. The stock solution of radioactive Mn^{++} ions was mixed at room temperature with the stock solution of sodium

succinate(Suc^{--}), sodium malonate(Mal^{--}), sodium o-phthalate(Pth^{--}) or sodium tartrate (Tar^{--}) in the presence of cation exchange resin. The distribution ratios of Mn^{++} ions between resin and solution were then measured. The experimental results obtained in aqueous, ethanol-water and 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 concentration, good linearities were observed in all cases. This fact indicates that the assumption of the one-to-one complex formation between Mn^{++} and acid ions is

Table 2. Distribution ratios of Mn^{++} between resin and solution at room temperature

Acid	Conc., 10^{-4} mole/l	$1/K_d$, mg/ml		
		Aqueous	20 % Ethanol	20 % Acetone
Succinic	0.834	0.255	1.29	0.805
〃	1.67	0.257	1.31	0.822
〃	2.50	0.260	1.32	0.831
〃	3.34	0.260	1.34	0.840
〃	4.17	0.264	1.37	—
〃	5.00	0.266	1.38	0.875
〃	5.84	0.270	1.40	0.885
Malonic	0.834	0.402	1.26	0.925
〃	1.67	0.411	1.29	0.978
〃	2.50	0.422	—	1.02
〃	3.34	—	1.42	—
〃	4.17	0.438	1.49	1.13
〃	5.00	0.453	1.55	1.20
〃	5.84	0.460	1.62	1.25
o-Phthalic	0.834	0.369	0.860	0.870
〃	1.67	0.385	—	0.950
〃	2.50	0.390	0.980	0.970
〃	3.34	0.415	1.02	—
〃	4.17	0.435	1.08	1.08
〃	5.00	0.445	1.13	1.13
〃	5.84	—	1.18	1.19
Tartaric	0.834	0.305	0.800	1.20
〃	1.67	0.327	0.855	1.31
〃	2.50	0.355	0.936	1.40
〃	3.34	0.377	0.990	1.53
〃	4.17	—	1.10	—
〃	5.00	0.424	1.18	1.88
〃	5.84	0.448	—	1.94

correct, as was discussed in previous papers of this series. [1,9]

$$\frac{1}{K_d} = \frac{1}{K^0{}_d} + \frac{K_f}{K^0{}_d}(\text{Acid}),$$

where $K_d{}^0$ denotes the K_d value at infinite dilution, K_f the formation constant of the complex species, and [Acid] the acid concentration. From the slopes and intercepts of the linear plots of $1/K_d$ versus [Acid], the values of K_f and $K^0{}_d$ were calculated. The results are shown in Table 3.

Co^{++} Complexes. Studies were extended to the systems of Co^{++} ions with succinate, malonate, o-phthalate or tartrate ions in aqueous, ethanol-water and acetone-water solution. The experimental results(Table 4) indicated good linearities between the values of $1/K_d$ and the acid anion concentrations in all the systems examined. It was concluded therefore that the one-to-one complexes were formed between Co^{++} ions and the organic acid anions in solution. From the values of slopes and intercepts of the linear plots, the values of $K_d{}^0$ and K_f for the formation of one-to-one complexes of Co^{++} ions with the organic acids were calculated(Table 5).

Zn^{++} Complexes. Studies were extended further to the systems of Zn^{++} ions with succinate, malonate, o-phthalate or tartrate ions in aqueous, ethanol-water and acetone-water. The experimental results are summarized in Table 6 and 7.

Disscussion

It is concluded from the results of the present study that Mn^{++}, Co^{++} and Zn^{++} ions form one-to-one complexes with succinate, malonate, o-phthalate or tartrate ions in aqueous, 20 % ethanol-water and 20 % acetone water solutions. Other investigators also reported the formation of one-to-one complexes of Mn^{++} with succinate and malonate ions (Table 3) and of Co^{++} with malonate ions(Table 5) in aqueous solution. [7] It is seen from Table 3 and 5 that some of the K_f values obtained in the present study agree fairly well with the values reported in the literature although the experiments were carried out under different conditions, such as ionic strengths of the solutions. But the K_f value obtained in the present study for Mn-succinate complex differs from the value reported in the literature. [7] The reason for this discrepancy is not known.

Table 3. Formation constants of Mn^{++} complexes with dibasic organic acids at room temperature

Complex	Solvent	$1/K_d{}^0$, mg/ml	K_f, 10^3 mole/l
[MnSuc]	H$_2$O	0.25	0.11(0.018)*
"	20 % Ethanol-H$_2$O	1.24	0.18
"	20 % Acetone-H$_2$O	0.79	0.20
[MnMal]	H$_2$O	0.39	0.29(0.20)*
"	20 % Ethanol-H$_2$O	1.18	0.64
"	20 % Acetone-H$_2$O	0.87	0.76
[MnPth]	H$_2$O	0.36	0.49
"	20 % Ethanol-H$_2$O	0.80	0.79
"	20 % Acetone-H$_2$O	0.81	0.80
[MnTar]	H$_2$O	0.28	1.0
"	20 % Ethanol-H$_2$O	0.71	1.3
"	20 % Acetone-H$_2$O	1.04	1.5

*Ref. 7.

Table 4. Distribution ratios of Co^{++} between resin and solution at room temperature

Acid	Conc., 10^{-4} mole/l	$1/K_d$, mg/ml		
		Aqueous	20 % Ethanol	20 % Acetone
Succinic	0.417	0.906	1.45	1.06
//	0.834	0.920	1.50	1.13
//	1.25	0.942	1.55	1.16
//	1.67	—	1.60	1.23
//	2.09	0.972	1.66	1.27
//	2.50	0.990	1.68	1.35
//	2.92	1.02	1.76	1.37
Malonic	0.417	0.912	1.45	1.32
//	0.834	0.939	1.51	1.39
//	1.25	0.960	1.60	1.47
//	1.67	0.984	1.64	1.58
//	2.09	—	1.74	1.68
//	2.50	1.02	1.79	1.72
//	2.92	1.05	1.83	1.84
o-Phthalic	0.417	0.723	1.29	—
//	0.834	0.756	1.34	1.19
//	1.25	0.778	1.41	1.27
//	1.67	0.810	1.48	1.34
//	2.09	0.846	1.54	1.41
//	2.50	0.890	—	1.48
//	2.92	0.915	1.71	1.57
Tartaric	0.417	0.700	1.13	—
//	0.834	—	—	1.27
//	1.25	0.795	1.28	1.37
//	1.67	0.820	1.37	1.46
//	2.09	0.864	1.47	1.54
//	2.50	0.895	1.53	1.63
//	2.92	0.950	1.58	1.67

Table 5. Formation constants of Co^{++} complexes with dibasic organic acids at room temperature

Complex	Solvent	$1/K_d^{\circ}$, mg/ml	K_f, 10^3 mole/l
[CoSuc]	H_2O	0.89	0.50
//	20 % Ethanol-H_2O	1.40	0.87
//	20 % Acetone-H_2O	1.01	1.3
[CoMal]	H_2O	0.89	0.59(0.71)*
//	20 % Ethanol-H_2O	1.39	1.1
//	20 % Acetone-H_2O	1.22	1.7
[CoPth]	H_2O	0.69	1.1
//	20 % Ethanol-H_2O	1.22	1.3
//	20 % Acetone-H_2O	1.05	1.8
[CoTar]	H_2O	0.66	1.5
//	20 % Ethanol-H_2O	1.06	1.8
//	20 % Acetone-H_2O	1.12	2.0

Table 6. Distribution ratios of Zn^{++} between resin and solution at room temperature

Acid	Conc., 10^{-4} mole/l	$1/K_d$, mg/ml		
		Aqueous	20 % Ethanol	20 % Acetone
Succinic	0.417	0.765	1.23	1.42
"	0.834	0.789	1.30	1.53
"	1.25	0.820	1.38	1.61
"	1.67	0.831	1.42	1.69
"	2.09	0.870	1.54	1.79
"	2.50	—	—	1.89
"	2.92	0.924	1.68	—
Malonic	0.417	0.765	1.22	1.28
"	0.834	0.810	1.31	1.36
"	1.25	0.861	1.40	1.48
"	1.67	0.910	1.58	1.56
"	2.09	0.957	1.65	1.65
"	2.50	1.01	—	1.79
"	2.92	1.08	1.84	1.93
o-Phthalic	0.417	0.755	—	1.08
"	0.834	0.827	1.19	1.16
"	1.25	0.888	1.32	1.26
"	1.67	0.937	1.40	1.35
"	2.09	—	1.49	1.40
"	2.50	1.05	1.59	1.49
"	2.92	—	—	1.58
Tartaric	0.417	—	1.14	1.14
"	0.834	0.800	1.25	—
"	1.25	0.870	1.37	1.34
"	1.67	0.933	1.45	1.46
"	2.09	1.02	1.56	1.54
"	2.50	1.05	—	1.70
"	2.92	1.11	1.76	1.80

Table 7. Formation constants of Zn^{++} complexes with dibasic organic acids at room temperature

| Complex	Solvent	$1/K_d^0$, mg/ml	K_f, 10^5 mole/l
[ZnSuc]	H$_2$O	0.72	0.88
"	20 % Ethanol-H$_2$O	1.16	1.5
"	20 % Acetone-H$_2$O	1.33	1.7
[ZnMal]	H$_2$O	0.71	1.8
"	20 % Ethanol-H$_2$O	1.11	2.3
"	20 % Acetone-H$_2$O	1.14	2.3
[ZnPth]	H$_2$O	0.69	2.0
"	20 % Ethanol-H$_2$O	1.01	2.3
"	20 % Acetone-H$_2$O	1.00	2.0
[ZnTar]	H$_2$O	0.68	2.2
"	20 % Ethanol-H$_2$O	1.04	2.4
"	20 % Acetone-H$_2$O	1.02	2.6

The results of the present investigation are now compared with those of the previous study of this series[1] (*Table* 8). It can be said from *Table* 8 that the relative stabilities of the one-to-one complexes of Mn^{++}, Co^{++} and Zn^{++} with a given organic acid increase in the following order in each solvent system examined:

$$Mn^{++} < Co^{++} < Zn^{++} \text{ complex.}$$

This order of increasing stabilities could be explained by the assumption that crystal radii of "naked" metal ions may play major role on the complex formation with various organic acids in solution. This assumption may explain also the experimental observations that the transition metal ions form more stable complexes with the dibasic organic acids than alkaline earth metals, since the transition metal ions have smaller crystal radii than alkaline-earth metal ions.

It is also noted from *Table* 8 that the relative stabilities of the one-to-one complexes of Mn^{++}, Co^{++} and Zn^{++} with various organic acids increase in the order:

Succinate <malonate <o-phthalate <tartrate <citrate-complex.
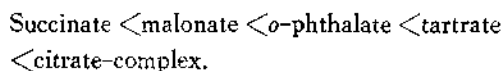
This order of increasing stabilities agrees with what we have observed on similar one-to-one complexes of alkaline earth metals with organic acids.[11] Hence, it can be said that the order of increasing stabilities written above might be expected for the formation of organic acid-metal complexes in general.

It is also seen from *Table* 8 that all the complexes examined are more stable in ethanol-water and acetone-water solutions than in aqueous solution. This could be explained by the difference in dielectric constant between water and organic solvent molecules. Smaller values of dielectric constants of ethanol and acetone may lead to stronger electrostatic attraction between the metal ions and the organic acid anions in solution.

Table 8. Formation constants of complexes of Mn^{++}, Co^{++} and Zn^{++} with organic acids at room temperature

Acid	Solvent	K_1, 10^3 mole/l			K_2, 10^3 mole/l		
		Mn^{++}	Co^{++}	Zn^{++}	Mn^{++}	Co^{++}	Zn^{++}
Succinic*	H_2O	0.11	0.50	0.88	—	—	—
"	20 % Ethanol-H_2O	0.18	0.87	1.5	—	—	—
"	20 % Acetone-H_2O	0.20	1.3	1.7	—	—	—
Malonic*	H_2O	0.29	0.59	1.8	—	—	—
"	20 % Ethanol-H_2O	0.64	1.1	2.3	—	—	—
"	20 % Acetone-H_2O	0.76	1.7	2.3	—	—	—
o-Phthalic*	H_2O	0.49	1.1	2.0	—	—	—
"	20 % Ethanol-H_2O	0.79	1.3	2.3	—	—	—
"	20 % Acetone-H_2O	0.80	1.8	2.0	—	—	—
Tartaric*	H_2O	1.0	1.5	2.2	—	—	—
"	20 % Ethanol-H_2O	1.3	1.8	2.4	—	—	—
"	20 % Acetone-H_2O	1.5	2.0	2.6	—	—	—
Citric**	H_2O	2.3	24	28	—	—	—
"	20 % Ethanol-H_2O	3.1	3×10	44	—	3	—
"	20 % Acetone-H_2O	4.7	2×10	64	—	5	—

*The present investigation.　　**Ref. 1

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