

Citrate Complexes of Manganese, Zinc and Cobalt in Aqueous, Ethanol-Water and Acetone-Water Solutions*

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수용액, 에탄올-물 및 아세톤-물 혼합용매 내에서의 망간, 아연 및 코발트의 시트르산 착물

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요 약

양 이온 교환수지와 시트르산 이온(Cit^{3-})이 들어 있는 용액에서 방사성 Mn^{++} , Zn^{++} 및 Co^{++} 이 수지와 용액 사이에 어떻게 분배되는가를 실온에서 조사함으로써 이들 금속 이온의 시트르산 착물 형성에 관한 연구를 하였다. 용매로서 H_2O , 20% 에탄올- H_2O 및 20% 아세톤- H_2O 를 사용하였다. 용액의 pH는 7.0-7.4로 조절하였고 이온 강도는 약 0.10으로 유지하였다. 본 연구의 결과 Mn^{++} 과 Zn^{++} 은 어떤 용매계에서도 1:1 시트르산 착물 $[\text{M Cit}]^-$ 을 형성하는 것을 알았다. 한편 Co^{++} 은 수용액에서는 1:1 착물만을 형성하지만 위에 말한 혼합용매에서는 1:1 착물 $[\text{Co Cit}]^-$ 과 1:2 착물 $[\text{Co Cit}_2]^{4-}$ 을 형성하는 것을 알았다. 그리고 이들 시트르산 착물이 수용액에서 보다 혼합용매 내에서 더욱 안정함을 알았다.

ABSTRACT

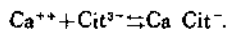
Formation of the complexes of manganese, zinc and cobaltous ions with citrate ions in aqueous, ethanol-water (20% by volume) and acetone-water (20% by volume) solutions was studied at room temperature by the equilibrium exchange technique. The pH of the solutions was controlled to 7.0-7.4, and the ionic strength of the solutions was kept at approximately 0.10. The results of the present study indicated that both Mn^{++} and Zn^{++} formed one to one citrate-complexes, $[\text{M Cit}]^-$, in all the solvent systems examined, and that Co^{++} formed one to one citrate-complex in aqueous solution but formed both one to one citrate-complex, $[\text{Co Cit}]^-$, and one to two citrate-complex, $[\text{Co Cit}_2]^{4-}$, in the mixed solvent systems mentioned above. It was also observed that the citrate-complexes of the transition metals examined were more stable in the mixed solvent systems than in water.

INTRODUCTION

Formation of the complexes of various metal ions with organic acids in aqueous solution was extensively studied by Schubert and his coworkers, using the

equilibrium exchange technique⁽¹⁻⁵⁾. They reported the formation of various one to one metal-citrate complexes in aqueous solution. For example,

*Complexes of Polyvalent Metal Ions. 1.



In previous study of this series, we observed the formation of both one to one and one to two citrate-complexes of calcium ions, $[\text{Ca Cit}]^{-}$ and $[\text{Ca Cit}_2]^{4-}$, in ethanol-water and acetone-water solutions. ⁽⁶⁾



Thus, fairly large solvent effect was observed on the nature of the complexes formed between calcium and citrate ions.

It then appeared important to extend the studies to the systems with manganese, zinc and cobaltous ions, since these ions were observed to form one to one citrate-complexes in aqueous solutions. ^(7,8) The solvents chosen in the present study were water, ethanol-water (20% by volume) and acetone-water (20% by volume) mixed solvents. Thus, the present study was undertaken on the citrate-complexes of manganese, zinc and cobaltous ions in aqueous, ethanol-water and acetone-water solutions.

EXPERIMENTAL PART

Materials.

Ethanol and acetone were purified by the method reported in the previous paper. ⁽⁶⁾ Ethanol-water and acetone-water mixed solvents were prepared by mixing appropriate amount of ethanol and acetone with triply distilled water. Cation exchange resin (Dowex 50 W-X8, 200-400 meshes) was treated with sodium chloride solution by the method mentioned in the previous paper. ⁽⁶⁾

Stock Solutions.

Stock solutions of sodium chloride (0.125 mole/l.) and sodium citrate (0.0417 mole/l.) were prepared by dissolving appropriate amount of sodium chloride (1.827 g.) and sodium citrate dihydrate (3.066 g.) in each solvent system, and diluting to 250 ml.

Stock solutions of radioactive manganese (⁵⁶Mn), zinc (⁶⁵Zn) and cobalt (⁶⁰Co) were prepared in the following manner. Solid samples of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (about 0.1 g.), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (about 0.5 g.) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (about 0.5 g.) were irradiated with neutrons in the nuclear reactor TRIGA-II (neutron flux = 10^{11} neutrons/cm²./sec.) for 12 min., 30 hrs, and 12 hrs., respectively. The resulting solid samples were dissolved in 20 ml. of distilled water. One ml.

of each of these solutions was pipetted and diluted with water or mixed solvents to 100 ml.

The pH values of all the stock solutions were adjusted to 7.0-7.4 before the final dilutions were made in volumetric flasks.

Procedure.

Experimental procedures were described in our previous paper. ⁽⁶⁾ 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 solutions of sodium citrate and sodium chloride and the solvent were added to the Erlenmeyer flasks according to Table I. Thus, the ionic strength of each sample solution was kept at approximately 0.10.

TABLE I. Composition of Sample Solutions*

Flask No.	M ⁺⁺ , ml. **	Cit ³⁻ , ml.	NaCl, ml.	Solvent, ml.
1	10	0	0	40
2	10	0.10	39.9	0
3	10	0.20	39.8	0
4	10	0.30	39.7	0
5	10	0.40	39.6	0
6	10	0.50	39.5	0
7	10	0.60	39.4	0
8	10	0.70	39.3	0
9	10	0.80	39.2	0
10	10	0.90	39.1	0
11	10	1.00	39.0	0
12	10	1.10	38.9	0
13	10	1.20	38.8	0
14	10	1.30	38.7	0
15	10	1.50	38.5	0

* Each flask contains 150 mg. of resin.

** Metal ion concentrations in each flask:

$[\text{Mn}^{++}] = 0.35 \times 10^{-4}$ mole/l.

$[\text{Co}^{++}] = 1.7 \times 10^{-4}$ mole/l.

$[\text{Zn}^{++}] = 1.7 \times 10^{-4}$ mole/l.

The flasks were shaken for about 5 hrs. or more to equilibrate radioactivity between the resin and solution phases. The resin was filtered by a chimney funnel, and dried in the air for at least 20 min. The radioactivity in the resin particles was counted by a

G-M counter. A correction due to the decay of radio-isotopes during each run of the experiment was made to the measured counting rate, if necessary.

The distribution ratios, K_d , of the metal ions between resin phase and solution phase were determined experimentally by the following equation:

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

where $A(\text{resin})$ denotes the radioactivity of the resin phase, $A(\text{total})$ the total activity of the metal ions in the resin and solution phases, v the volume (in ml.) of the solution, and m the weight (in mg.) of the cation exchange resin.

RESULTS

Citrate Complexes of Manganese and Zinc Ions.

The distribution ratios of Mn^{++} and Zn^{++} between the resin and solution phases were determined in aqueous, 20% ethanol-water and 20% acetone-water solutions in the presence of citrate ions of varying concentrations. The results obtained at room temperature are summarized in Tables II and III.

TABLE II. Distribution Ratios of Mn^{++} between Resin and Solution (Room Temperature).

Flask No.	Citrate, 10^{-4} mole l. ⁻¹	1/ K_d , mg./ml.*		
		Aqueous	20% Ethanol	20% Acetone
2	0.834	1.1	1.3	1.3
3	1.67			1.7
4	2.50	1.2	1.4	2.2
5	3.34		2.2	2.3
6	4.17	1.5	2.7	3.0
7	5.00			3.4
8	5.84		3.5	3.9
9	6.67		3.6	5.0
10	7.51	2.7	4.0	
11	8.34	2.9		
13	10.0	3.4		
15	12.5	4.6		

* 1/ K_d^0 = 1.1.

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

Flask No.	Citrate, 10^{-4} mole l. ⁻¹	1/ K_d , mg./ml.*		
		Aqueous	20% Ethanol	20% Acetone
4	2.50	7.2	26	26
6	4.17	13	28	43
8	5.84	20	42	64
10	7.51	28	48	73
12	9.17	36	61	76
14	10.8	45	71	90
15	12.5	50	86	112

* 1/ K_d^0 = 1.4.

The values of 1/ K_d were plotted against citrate concentrations in order to see if these metal ions formed one to one complexes with citrate ions in solution. The plots are shown in Figs. 1 and 2, which indicate fairly good linearity.

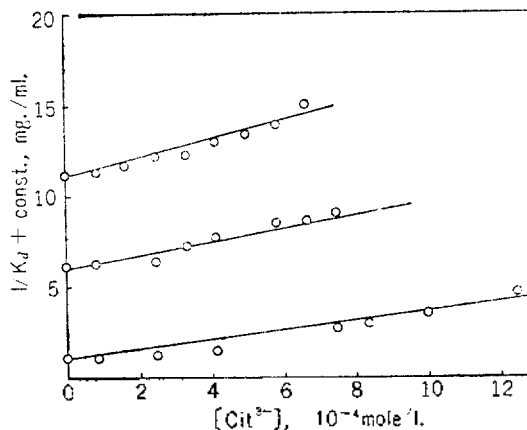
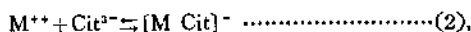


Fig. 1. Plots of 1/ k_d versus $[Cit^{3-}]$ for $[Mn Cit]^-$ in aqueous (lower plots, const. = 0), 20% ethanol-water (middle plots, const. = 5) and 20% acetone-water (upper plots, const. = 10) solutions.

If the formation of one to one citrate-complex of manganese or zinc ions was assumed,



the following equation could be obtained, as was explained in the previous paper⁽⁶⁾:

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

Here, K_1 denotes the formation constant of the one

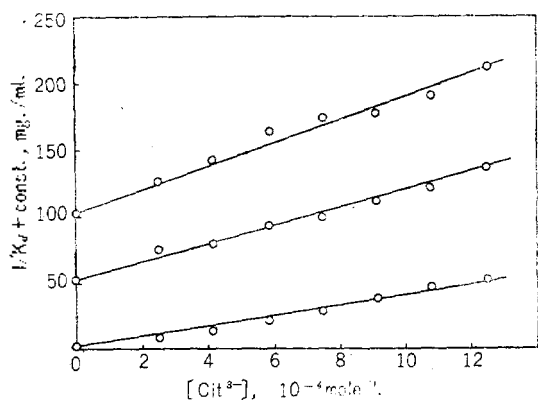


Fig. 2. Plots of $1/K_d$ versus $[Cit^{3-}]$ for $[Zn Cit]^-$ in aqueous (lower plots, const. = 0), 20% ethanol-water (middle plots, const. = 50) and 20% acetone-water (upper plots, const. = 100) solutions.

to one complex, and K_d^0 denotes the K_d value at infinite dilution.

Since linear relations were observed between $1/K_d$ and $[Cit^{3-}]$, it was concluded that the assumption of formation of the one to one complexes, $M Cit^-$, was correct in these cases. The values of intercepts and slopes of the straight lines had to be determined in order to obtain the values of K_d^0 and K_1 . Unfortunately, however, determination of the intercepts required long extrapolation of the straight lines to the zero $[Cit^{3-}]$ value.

In order to minimize error due to the long extrapolation, the determination of K_d values was repeated at very low citrate concentrations, where $[M^{++}] \gg [Cit^{3-}]$, and hence, essentially all the citrate ions were considered to exist in the complexed form in solution. The average K_d values obtained at very low citrate concentrations were taken as K_d^0 values. The values of $1/K_d^0$ obtained experimentally are included in Tables II and III.

The formation constants of the one to one complexes, K_1 , were evaluated from the values of the intercepts and slopes of the straight lines shown in Figs. 1 and 2. The results are summarized in Table IV.

TABLE IV. Formation Constant of One to One Complexes of Mn^{++} and Zn^{++} with Citrate Ions (Room Temperature).

Complex	Solvent	K_1 , l. mole ⁻¹
$Mn Cit^-$	H_2O	$0.23 \times 10^4 (0.28 \times 10^4)^*$
	20% Ethanol- H_2O	0.31×10^4
	20% Acetone- H_2O	0.47×10^4
$Zn Cit^-$	H_2O	$2.8 \times 10^4 (5.1 \times 10^4)^*$
	20% Ethanol- H_2O	4.4×10^4
	20% Acetone- H_2O	6.4×10^4

* Literature value (refs. 7 and 8).

Citrate Complexes of Cobaltous Ions.

Studies were extended to the system of cobaltous ions with citrate ions in aqueous, ethanol-water (20% by volume) and acetone-water (20% by volume) solutions. The experimental results obtained at room temperature are summarized in Table V. Again, the values of $1/K_d$ were plotted against $[Cit^{3-}]$ (Fig. 3).

TABLE V. Distribution Ratios of Co^{++} between Resin and Solution (Room Temperature).

Flask No.	Citrate, 10^{-4} mole l. ⁻¹	$1/K_d$, mg./ml.*		
		Aqueous	20% Ethanol	20% Acetone
2	0.834	1.0	3.7	
3	1.67	2.7		
4	2.50	4.3	24	17
5	3.34	6.0		
6	4.17		39	39
8	5.84	14	84	67
10	7.51	31	97	
11	8.34			1.0×10^2
13	10.0	34	1.5×10^2	1.4×10^2

* $1/K_d^0 = 1.4$.

Since fairly good linearity was observed between $1/K_d$ and $[Cit^{3-}]$ in the case of aqueous solution, it appeared reasonable to conclude that Co^{++} also formed one to one citrate-complex in aqueous solution. In the ethanol-water and acetone-water solutions, however, the plots of $1/K_d$ versus $[Cit^{3-}]$ did not yield linearity. Thus, it was assumed that Co^{++} formed both one to one and one to two citrate-complexes

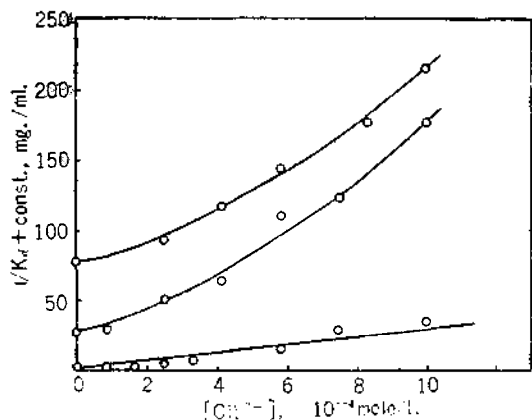
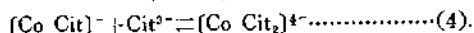
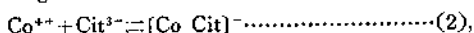


Fig. 3. Plots of $1/K_d$ versus $[Cit^{3-}]$ for the $Co^{++}-Cit^{3-}$ system in aqueous (lower plots, const. = 0), 20% ethanol-water (middle plots, const. = 25) and 20% acetone-water (upper plots, const. = 75) solutions.

in the organic-water mixed solvents,



Under this assumption, the following equation was obtained, as described in the previous paper.⁽⁶⁾

$$\frac{1}{K_d} = \frac{1}{K_d^0} + \frac{K_1}{K_d^0} [Cit^{3-}] + \frac{K_1 K_2}{K_d^0} [Cit^{3-}]^2 \dots\dots\dots(5).$$

Here, K_1 and K_2 denote the formation constants of the complexes by reactions (2) and (4), respectively.

Equation (5) can be rewritten as

$$\frac{(K_d^0/K_d) - 1}{[Cit^{3-}]} = K_1 + K_1 K_2 [Cit^{3-}] \dots\dots\dots(6).$$

The K_d^0 value was determined experimentally in this case also by taking average K_d values measured at very low citrate concentrations. The values of $\{(K_d^0/K_d) - 1\}/[Cit^{3-}]$ were then plotted against $[Cit^{3-}]$.

The results are shown in Fig. 4.

Since large experimental error might exist in the determination of K_d^0 values due to low concentrations of citrate ions, it could be said that Fig. 4 indicates fairly good linear relations between $\{(K_d^0/K_d) - 1\}/[Cit^{3-}]$ and $[Cit^{3-}]$. It was therefore concluded that the assumption of formation of the one to one and one to two complexes, $[Co Cit]^{-}$ and $[Co Cit_2]^{4-}$, was correct in the mixed solvent system. The values of intercepts and slopes of the straight

lines were determined, and hence, the values of K_1 and K_2 were obtained (Table VI).

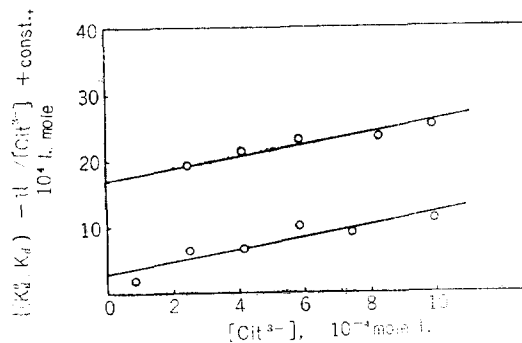


Fig. 4. Plots of $\{(K_d^0/K_d) - 1\}/[Cit^{3-}]$ versus $[Cit^{3-}]$ for the $Co^{++}-Cit^{3-}$ system in 20% ethanol-water (lower plots, const. = 0) and 20% acetone-water (upper plots, const. = 15) solutions.

TABLE VI. Formation Constants of One to One and One to Two Complexes of Co^{++} with Citrate Ions (Room Temperature).

Solvent	$K_1, \text{ l. mole}^{-1}$ ($Co Cit^{-}$)	$K_2, \text{ l. mole}^{-1}$ ($Co Cit_2^{4-}$)
H ₂ O	$2.4 \times 10^4 (4.1 \times 10^4)^*$	—
20% Ethanol-H ₂ O	3×10^4	0.3×10^4
20% Acetone-H ₂ O	2×10^4	0.5×10^4

* Literature value (ref. 8).

DISCUSSION

As the results of the present study, it is concluded that manganese and zinc ions form the one to one complexes with citrate ions, $[M Cit]^{-}$, in aqueous, ethanol-water (20% by volume) and acetone-water (20% by volume) solutions. On the other hand, the present investigation reveals that cobaltous ions form both one to one and one to two complexes with citrate ions in the mixed solvent systems but only one to one complex in aqueous solution. If K_1 values obtained for the one to one metal-citrate complexes are compared, the relative stabilities of the complexes in each solvent system increase in the order:



This agrees with the observations reported by

Schubert and his coinvestigators on the one to one complexes in aqueous system.^(7,8) If it is assumed that smaller cations form more stable complexes with anionic species, it must be concluded that the effective radii of the various metal ions in each solvent system may increase in the reverse order to that written above.

The present study reveals that the citrate-complexes of the transition metals examined are more stable in ethanol-water and acetone-water solutions than in aqueous solutions. This agrees with the results of our previous study on similar complexes of alkaline earth metals.⁽⁹⁾ The relative stabilities of the complexes in various solvent systems may be attributed to the dielectric constants of the solvent systems (Table VII). Smaller values of dielectric constant may result in stronger Coulombic attractions between the central metal cations and the anionic ligands, and hence, greater stabilities of the complexes.

TABLE VII. Dielectric Constants*

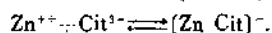
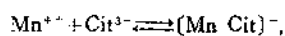
Solvent	Temp., °C	Dielectric const.
H ₂ O	25	78.54
Ethanol	25	24.3
Acetone	25	20.7

* Ref. 9.

CONCLUSIONS

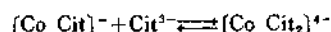
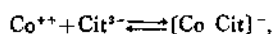
The results of the present study indicate the followings:

a) Both Mn²⁺ and Zn²⁺ form one one to one complexes with citrate ions in aqueous, ethanol-water (20% by volume) and acetone-water (20% by volume) solutions.



b) Cobaltous ions form one to one citrate-complex

in aqueous solution, but form both one to one and one to two citrate-complexes in ethanol-water and acetone-water solutions.



c) The citrate-complexes of the transition metals examined are more stable in ethanol-water and acetone-water solutions than in aqueous solution. This may be attributed to the dielectric constants of the solvent systems.

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