

Complexes of Divalent Metal Ions with Dibasic Organic Acids in Aqueous, Ethanol-Water and Acetone-Water Solutions.

Pae, Young Il *Pak, Sang Youn

Dept. of Industrial Chemistry

(Received April 10, 1981)

<Abstract>

Solutions of Cu^{2+} and Cd^{2+} were mixed with the solutions of 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 Cu^{2+} and Cd^{2+} formed one-to-one complexes with succinate, malonate, o-phthalate and tartarate ions in aqueous, 20% ethanol-water and 20% acetone-water solutions. The results of the present study indicated that the relative stabilities of the complexes in solution increased generally in the order: $\text{Cu}^{2+} > \text{Cd}^{2+}$ complexes. Succinate < malonate < o-phthalate < tartarate complexes. Aqueous < mixed solvent systems.

2가 금속이온과 2가 유기산 사이의 착물형성에 관한연구

배 영 일 · 박 상 윤

工業化學科

(1981. 4. 10 접수)

<요 약>

2가유기산(말론산, 타르타르산, 프탈산, 숙신산)용액에서 방사성 동위원소 구리 및 카드뮴 이온이 양이온 교환수지와 용액 사이에 어떻게 분배되는가를 실온에서 조사하여 유기산과의 착물형성에 관한 연구를 하였다.

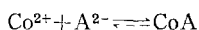
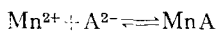
용매로는 물, 에탄올-물(20%)과 아세톤-물(20%)을 사용하였고 용액의 pH는 7.0-7.5 그리고 이온강도는 0.10으로 고정하였다. 연구결과 금속이온들은 유기산과 1:1 착물을 형성하였고 착물의 안정도는 다음 순으로 증가하였다. (1) $\text{Cd}^{2+} < \text{Cu}^{2+}$ (2) 숙신산 < 말론산 < 프탈산 < 타르타르산 (3) 수용액 < 혼합용액.

I. Introduction

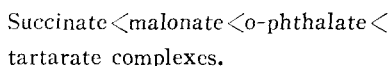
In a previous paper of this series¹, they reported the results of the studies on the formation of the complexes of transition metals such as manganese and cobalt with some of the

dibasic organic acids in aqueous, ethanol-water and acetone-water solutions. The organic acids used were succinic, malonic, o-phthalic, and tartaric acids. The solvents used were water, 20% ethanol-water and 20% acetone-water mixtures. The equilibrium ion exchange technique²⁻⁹ was used to examine the complex for-

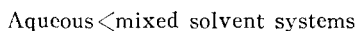
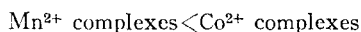
mation. It was concluded from the experimental results that the Mn^{2+} and Co^{2+} ions formed the one-to-one complexes, MnA and CoA, with the dibasic organic acids, H_2A , in all the solvent systems used.



By comparing the values of formation constants of the complexes, it was concluded that the relative stabilities of both Mn^{2+} and Co^{2+} complexes in solution increased generally in the order:



It was also observed that the Mn^{2+} and Co^{2+} complexes were more stable in the mixed solvent systems than in water, and that the Mn^{2+} complexes were less stable than the Co^{2+} complexes in each solvent system.



It then appeared of interest to extend the studies further to the corresponding systems of copper and cadmium, in order to compare the behaviors of various metal ions towards the complex formation with the dibasic organic acids in solution. Thus, the present study was undertaken on the formation of the Cu^{2+} and Cd^{2+} complexes with succinic, malonic, o-phthalic, and tartaric acids in aqueous, 20% (by volume) ethanol-water and 20% (by volume) acetone-water solutions at room temperature, utilizing the equilibrium ion exchange technique.

II. Experimental

Materials. Ethanol (C. P., Eastman Organic Chemical Co.) and acetone (A. R., Eastman Organic Chemical Co.) were purified by the method described in the previous paper⁹. Ethanol-water and acetone-water mixed solvents were prepared by mixing appropriate amounts of ethanol and acetone with triply distilled water.¹⁰ Cation exchange resin (Ion Exchange

Resin CGC 241, 200-400 mesh, ionic form, J. T. Baker Chemical Co.) was treated with a small quantity of dil. NaOH solution and/or dil. HCl solution in order to adjust the pH of the solution above the resin to 7.2-7.4.

Stock Solutions. Stock solution of sodium chloride (0.0834 mole/l) and stock solutions of sodium succinate, malonate, o-phthalate and tartarate (0.0417 mole/l) were prepared by dissolving appropriate amounts in each solvent system.¹⁰

In order to prepare the stock solutions of radioactive copper (^{64}Cu) and cadmium (^{115}Cd) solid samples of $Cu(NO_3)_2 \cdot 2H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ were irradiated with neutrons in the nuclear reactor TRIGA-II. (The Korea Atomic Energy Research Institute, Seoul, Korea). After the irradiated samples were mixed with inactive solids of cupric nitrate and cadmium nitrate, 1.5g of the mixed cupric nitrate and 0.9g of the mixed cadmium nitrate were dissolved each in 10ml. of distilled water. The resulting solution were diluted by a factor of 100, using either water or the mixed solvents.

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 the ones described in the previous papers of this series.^{1,9,11-13} About 150mg of the cation exchange resin and 10ml of the stock solution of radioactive Cu^{2+} or Cd^{2+} were placed in 125ml Erlenmeyer flasks at room temperature. To one of the flasks, 40ml of the solvent were added. To the other flasks, no solvent was added, but the stock solutions of the organic acids and the stock solution of sodium chloride were added, the sum of the two solutions being 40ml. An example of the compositions of sample solutions is illustrated in Table 1. The solutions in the Erlenmeyer flasks contained Cu^{2+} or Cd^{2+} of the following concentrations:

**Table 1: Composition of Sample Solutions
of the Cu-Succinate System**

Flask No.	Resin, mg	Cu ²⁺ , ml	Acid, ml	NaCl, ml	Solvent, ml
1	150	10.0	0	0	40.0
2	150	10.0	0.5	39.5	0
3	150	10.0	2.0	38.0	0
4	150	10.0	3.5	36.5	0
5	150	10.0	5.0	35.0	0
6	150	10.0	6.5	33.5	0
7	150	10.0	8.0	32.0	0
8	150	10.0	9.5	30.5	0

$$[Cu^{2+}] = 1.2 \times 10^{-3} \text{ mole/l}$$

$$[Cd^{2+}] = 0.58 \times 10^{-3} \text{ mole/l}$$

The flasks were shaken for 1–3 hours, and the resin was filtered 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 the resin and solution phases were calculated by the following equation:

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

where v denotes the volume(ml) of the solution, m the weights(mg) of the resin, $A(\text{resin})$ the radioactivity of the resin phase, and $A(\text{total})$ the total radioactivity of the metal ions in the resin and solution phases. The observed values of the K_d 's were used to obtain the formation constants of the metal-acid complexes in solution, as was mentioned in the previous papers of this series.

III. Results

Cu²⁺ Complexes. The experimental studies were carried out on the systems of Cu²⁺ with succinate (Suc²⁻), malonate (Mal²⁻), o-phthalate (Pth²⁻) or tartarate (Tar²⁻) anion. The results are summarized in Table 2.

If it was assumed that the Cu²⁺ formed the one-to-one complexes with the acid anions

**Table 2: Distribution Ratios of Cu²⁺ between
Resin and Solution at Room Temperature**

Acid	Conc, 10 ⁻⁴ mde/l	1/kd, mg/ml			
		Aqueous	20% Ethand-H ₂ O	20% Acetone-H ₂ O	
Succinic	0.834	0.50	0.92	0.75	
	1.67	0.38	1.09	0.93	
	2.50	0.54	1.11	0.86	
	3.34	0.51	0.95	0.73	
	4.17	0.70	1.21	1.10	
	5.00	0.45	1.00	0.76	
	5.84	0.60	1.25	1.03	
	0.834	1.40	5.03	4.21	
Malonic	1.67	1.96	7.05	7.19	
	2.50	3.17	10.20	9.00	
	3.34	4.30	13.03	10.90	
	4.17	4.83	15.23	14.47	
	5.00	6.00	—	17.48	
	5.84	7.51	—	19.01	
	o-Phthalic	0.834	0.50	1.55	0.89
		1.67	0.83	1.90	1.00
2.50		0.92	1.79	1.03	
3.34		0.73	2.24	1.18	
4.17		1.16	2.25	1.58	
5.00		0.91	2.31	1.62	
5.84		1.16	2.86	1.72	
Tartaric		0.834	1.10	7.02	5.94
	1.67	2.27	10.71	8.42	
	2.50	3.18	14.16	9.91	
	3.34	4.40	17.00	12.72	
	4.17	5.29	20.53	14.23	
	5.00	6.45	—	16.24	
	5.84	7.01	—	18.69	

in solution, good linearities should have been observed between the values of $1/K_d$ and the acid anion concentrations, as was discussed in the previous papers of this series.^{9,10}

$$\frac{1}{K_d} = \frac{1}{K_d^0} + \frac{K_f}{K_d^0} [\text{Acid}],$$

where K_d^0 denotes the K_d value at infinite dilution, K_f the formation constant of the complexes in solution, and [Acid] the acid concentration.

Experimental data indicate reasonably good linearities between the values of $1/K_d$ and the acid concentrations. This fact shows therefore that the assumption of the one-to-one complex formation between Cu^{2+} and the dibasic organic acids in solution is correct.

The values of K_f and K_d^0 for the formation of the Cu-acid complexes in solution were calculated from the slopes and intercepts of the linear plots of the values of $1/K_d$ versus the acid concentrations. The results of the calculation of K_f and K_d^0 are summarized in Table 3.

Table 3: Formation Constants of Cu^{2+} Complexes with Dibasic Organic Acids in Solution at Room Temperature

Complex	Solvent	$1/K_a^0$, mg/ml	K_f , 103 /mole
CuSuc.	H ₂ O	0.27	2.8
	20% Ethanol-H ₂ O	0.80	1.0
	20% Acetone-H ₂ O	0.48	2.5
CuMal.	H ₂ O	0.13	90
	20% Ethanol-H ₂ O	2.18	15
	20% Acetone-H ₂ O	1.64	18
CuPth.	H ₂ O	0.44	3.0
	20% Ethanol-H ₂ O	1.34	1.8
	20% Acetone-H ₂ O	0.66	2.9
CuTar.	H ₂ O	0.20	60
	20% Ethanol-H ₂ O	3.88	10
	20% Acetone-H ₂ O	3.98	6.3

Cd^{2+} Complexes. Studies were extended to the systems of Cd^{2+} with succinate, malonate, o-phthalate or tartarate ion. The experimental data indicated fairly good linearities between the values of $1/K_d$ and the acid anion concentrations in all the solvent systems examined (Table 4).

It was concluded therefore that the one-to-one complexes were formed also between Cd^{2+} and organic acid anions in solution. From the values of the slopes and intercepts of the linear plots of the values of $1/K_d$ versus the acid anion concentrations, the values of K_d^0 and K_f

for the formation of one-to-one complexes of Cd^{2+} with the organic acids in solution were calculated (Table 5).

Table 4: Distribution Ratios of Cd^{2+} between Resin and Solution at Room Temperature

Acid	Conc, 10^{-4} mole/l	$1/K_d$, mg/ml		
		Aqu- eous	20% Ethanol -H ₂ O	20% Acetone -H ₂ O
Succinic	0.834	0.94	2.79	2.51
	1.67	1.01	2.91	2.78
	2.50	1.03	3.06	2.96
	3.34	—	3.20	3.15
	4.17	1.15	3.40	3.40
	5.00	—	3.64	3.59
	5.84	1.04	3.78	3.61
	8.34	1.00	—	—
	10.8	1.10	—	—
	Malonic	0.834	1.11	2.49
1.67		1.00	2.70	2.38
2.50		0.93	3.11	2.36
3.34		—	3.32	2.52
4.17		1.16	3.49	2.58
5.00		—	3.75	2.68
5.84		0.94	4.12	2.88
8.34		1.34	—	—
10.8		1.19	—	—
o-Phthalic		0.834	1.11	2.41
	1.67	0.99	2.69	2.52
	2.50	1.29	3.15	2.81
	3.34	—	3.52	2.90
	4.17	1.13	3.64	3.08
	5.00	—	4.26	3.44
	5.84	1.10	4.55	3.60
	8.34	1.20	—	—
	10.8	1.15	—	—
	Tartaric	0.834	0.97	2.61
1.67		1.07	3.12	2.19
2.50		1.14	3.29	2.40
3.34		—	3.65	2.52
4.17		1.32	4.15	2.74
5.00		—	4.50	3.00
5.84		1.48	4.70	—
8.34		1.68	—	—
10.8		1.98	—	—

Table 5: Formation Constants of Cd²⁺ Complexes with Dibasic Organic Acids in Solution at Room Temperature

Complex	Solvent	1/K _{d0} mg/ml	K _f , 10 ³ l/mole
CdSuc	H ₂ O	0.91	0.28
	20% Ethanol-H ₂ O	2.6	0.80
	20% Acetone-H ₂ O	2.4	0.98
CdMal	H ₂ O	0.87	0.55
	20% Ethanol-H ₂ O	2.2	1.4
	20% Acetone-H ₂ O	2.0	0.70
CdPth	H ₂ O	0.87	0.65
	20% Ethanol-H ₂ O	2.0	2.2
	20% Acetone-H ₂ O	2.1	1.2
CdTar	H ₂ O	0.90	1.1
	20% Ethanol-H ₂ O	2.3	1.9
	20% Acetone-H ₂ O	1.7	1.4

IV. Discussion

The results of the present study indicate that Cu²⁺ and Cd²⁺ form one-to-one complexes

with succinate, malonate, o-phthalate and tartarate ions in aqueous, 20% ethanol-water and 20% acetone-water solutions. In a previous paper of this series,¹ it was reported that Mn²⁺, Co²⁺ and Zn²⁺ ions formed one-to-one complexes with the above-mentioned organic acids in solution. It is concluded therefore that Cu²⁺ and Cd²⁺ ions have similar nature to Mn²⁺, Co²⁺ and Zn²⁺ ions towards the complex formation with the dibasic organic acids in solution.

In order to compare the relative stabilities of the various metal-acid complexes, the formation constants of the complexes in solution are summarized in Table 6. It is noted that the relative stabilities of the complexes of each metal with various acids in solution increase generally in the following order, with exceptions of Ni-malonate and Cu-malonate complexes.

Succinate < malonate < o-phthalate < tartarate complexes.

This order of increasing stabilities of Cu²⁺-

Table 6: Formation Constants of the one-to-one Complexes of Various Metal Ions with Acids in Solution at Room Temperature

Acid	Solvent	K _f , 10 ³ 1/mole					
		Ni ²⁺	Mn ²⁺	Cd ²⁺	Co ²⁺	Zn ²⁺	Cu ²⁺
Succinic	H ₂ O	0.061	0.11	0.28	0.50	0.88	2.8
	20% Etanol-H ₂ O	0.11	0.18	0.80	0.87	1.5	1.0
	20% Acetone-H ₂ O	0.059	0.20	0.98	1.3	1.7	2.5
Malonic	H ₂ O	0.74	0.29	0.55	0.59	1.8	90
	20% Ethanol-H ₂ O	0.91	0.64	1.4	1.1	2.3	15
	20% Acetone-H ₂ O	1.5	0.76	0.70	1.7	2.3	18
o-Phthalic	H ₂ O	0.24	0.49	0.65	1.1	2.0	3.0
	20% Ethanol-H ₂ O	0.45	0.79	2.2	1.3	2.3	1.8
	20% Acetone-H ₂ O	0.43	0.80	1.2	1.8	2.0	2.9
Tartaric	H ₂ O	0.35	1.0	1.1	1.5	2.2	60
	20% Ethanol-H ₂ O	0.34	1.3	1.9	1.8	2.4	10
	20% Acetone-H ₂ O	0.90	1.5	1.4	2.0	2.6	6.3
Reference		(10)	(1)	*	(1)	(1)	*

* The present study

and Cd^{2+} -acid complexes agrees with what was observed on similar one-to-one complexes of alkaline earth metals with the organic acids in solution.¹³⁾ It seems therefore that the order or increasing stabilities written above might be a general trend for the formation of complexes of the metal ions with dibasic organic acids in solution. This fact might be explained in a similar way to the one mentioned in the previous paper,¹⁵⁾ saying that the K_f values of the metal-acid complexes decrease generally with increasing separation of the carboxylic groups in the dibasic acid molecules, and that the existence of aromatic ring or OH group in the acid anions increases the stabilities of the metal-acid complexes. The reasons for the high stability of the Ni-malonate complex and Cu-malonate complex in each solvent system are not known.

It can be also said from Table 6 that the relative stabilities of the one-to-one complexes of various metal ions with a given organic acid in solution increase generally in the following order, with exceptions of Ni-malonate and Cu-malonate complexes.

$\text{Ni}^{2+} < \text{Mn}^{2+} < \text{Cd}^{2+} < \text{Co}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ complexes.

It was mentioned previously¹ that the crystal radii of the "naked" metal ions may play a major role on the determination of relative stabilities of the complexes of the metal ions with various organic acids in solution. If this is the the case, the smallest ion among the above-mentioned metals, Ni^{2+} , is expected to form the most stable complexes with the dibasic acids in solution. The experimental facts shown in Table 6 indicate, however, that this is not true. Hence, factors other than the crystal radii of the "naked" metal ions may also play important role on the relative stabilities of the metal-acid complexes in solution. One possible factor could be the degree of solvation of the metal ions in solution. Unfortunately, the factors to play major role on the

formation of various metal-acid complexes in solution are not completely known. It is hoped that future study should be undertaken to examine the controlling factors for the formation of complexes between various metal ions and dibasic organic acids in solution.

It is also seen from Table 6 that all the complexes examined are more stable in ethanol-water and acetone-water solutions than in aqueous solution.

Aqueous (mixed solvent) systems.

This may be attributed to the difference in dielectric constant between water and organic solvents. Smaller values of dielectric constants of ethanol and acetone may cause stronger electrostatic attraction between the metal ions and the organic acid anions in solution.

Acknowledgement. This work was supported by U.I.T-Hyundai Research Fund in 1980. This financial support is gratefully acknowledged.

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