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Complexes of Polyvalent Metal Ions (VI). Complexes of Nickel and Cadmium with Dibasic Organic Acids in Aqueous, Ethanol-Water and Acetone-Water Solutions*

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Solutions of Ni^{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 Ni^{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 : $Ni^{2+} < Cd^{2+}$ complexes. Succinate < malonate < *o*-phthalate < tartarate complexes. Aqueous < mixed solvent systems.

Introduction

In a previous paper of this series,[1] we 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 technique[2–9] was used to examine the complex formation. 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.

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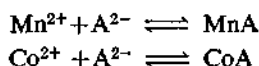
By comparing the values of formation constants of the complexes, it was concluded that the relative stabilities of both Mn^{2+} and Co^{2+} complexes in solution increased generally in the order:

Succinate$<$malonate$<$o–phthalate$<$tartarate complexes.

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.

$$Mn^{2+} \text{ complexes}<Co^{2+} \text{ complexes}$$
$$\text{Aqueous}<\text{mixed solvent systems}$$

It then appeared of interest to extend the studies further to the corresponding systems of nickel 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 Ni^{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.

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 paper.[9] 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 nickel

(^{65}Ni) and cadmium (^{115}Cd), solid samples of $Ni(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ were irradiated with neutrons in the nuclear reactor TRIGA–II*. After the irradiated samples were mixed with inactive solids of nickel nitrate and cadmium nitrate, 1.8 g of the mixed nickel nitrate and 0.9 g of the mixed cadmium nitrate were dissolved each in 10 m*l* of distilled water. The resulting solutions 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 150 mg of the cation exchange resin and 10 m*l* of the stock solution of radioactive Ni^{2+} or Cd^{2+} were placed in 125 m*l* Erlenmeyer flasks at room temperature. To one of the flasks, 40 m*l* 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 40 m*l*. An example of the compositions of sample solutions is illustrated in Table 1. The solutions in the Erlenmeyer flasks contained Ni^{2+} or Cd^{2+} of the following concentrations:

$$[Ni^{2+}]=1.2 \times 10^{-3} \text{ mole/}l$$
$$[Cd^{2+}]=0.58 \times 10^{-3} \text{ mole/}l$$

The flasks were shaked 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 (m*l*) of the solution, m the weights (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. 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.

TABLE 1: Composition of Sample Solutions of the Ni–Succinate System

Flask No.	Resin, mg	Ni^{2+}, m*l*	Acid, m*l*	NaCl, m*l*	Solvent, m*l*
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

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Results

Ni^{2+} *Complexes.* The experimental studies were carried out on the systems of Ni^{2+} with succinate (Suc^{2-}), malonate (Mal^{2-}), o-phthalate (Pth^{2-}) or tartarate (Tar^{2-}) anion. The results are summarized in Table 2.

If it was assumed that the Ni^{2+} formed the one-to-one complexes with the acid anions 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]

$$\frac{1}{K_d} = \frac{1}{K_d{}^\circ} + \frac{k_f}{K_d{}^\circ}[Acid],$$

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

TABLE 2: Distribution Ratios of Ni^{2+} between Resin and Solution at Room Temperature

Acid	Conc., 10^{-3} mole/l	$1/K_d$, mg/ml		
		Aqueous	20% Ethanol–H_2O	20% Acetone–H_2O
Succinic	0.417	0.85	1.01	1.68
	1.67	1.06	1.19	1.76
	2.92		1.45	1.84
	4.17	1.12	1.56	1.98
	5.42	1.23	1.52	2.27
	6.67	1.23	1.71	1.87
	7.92	1.27	1.94	
Malonic	0.417	1.29		
	1.67	2.10		
	2.92	3.41		
	4.17	3.94		
	5.42	5.59		
	6.67	5.73		
	7.92	6.77		
	0.0417		1.89	1.54
	0.167		2.15	1.78
	0.292		2.24	1.95
	0.417		2.39	2.47
	0.542		2.75	2.69
	0.667		2.86	2.84
	0.792		3.15	3.07
o-Phthalic	0.417	1.05	1.19	1.57
	1.67	0.85	1.55	2.37
	2.92	1.18	1.95	2.77
	4.17	1.34	2.36	3.99
	5.42	1.63	3.21	4.63
	6.67	1.90	3.57	4.94
	7.92	2.14		
Tartaric	0.417	0.94	1.76	1.84
	1.67	1.48	2.09	3.23
	2.92	1.60	2.76	3.94
	4.17	1.92	3.89	6.55
	5.42	2.41	4.18	8.19
	6.67	2.58		7.99
	7.92	3.26	5.25	

Experimental data indicate reasonably good linearities between the values of $1/K_d$ and the acid concentrations, as shown graphically in Figures 1-3. This fact shows therefore that the assumption of the one-to-one complex formation between Ni^{2+} and the dibasic organic acids in solution is correct.
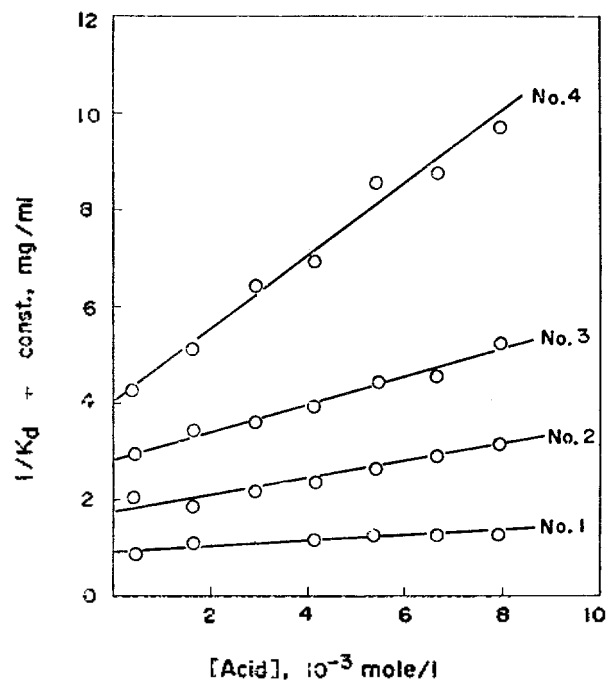

[Acid], 10^{-3} mole/l

Figure 1. Plots of $1/K_d$ versus [Acid] for Ni–acid complexes in aqueous solution. No.1: Ni–succinate (const.=0), No.2: Ni–o–phthalate (const.=1.0). No.3: Ni–tartarate (const.=2.0), and No.4: Ni–malonate (const.=3.0).
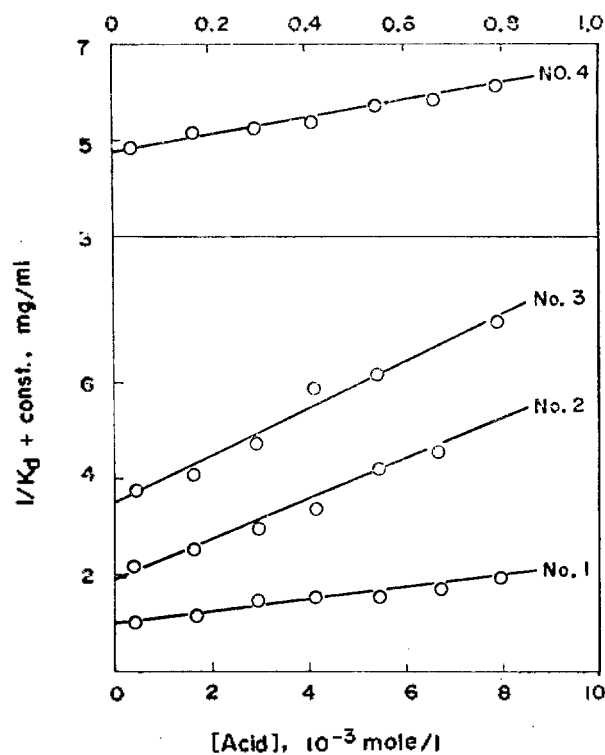

[Acid], 10^{-3} mole/l

Figure 2. Plots of $1/K_d$ versus [Acid] for Ni–acid complexes in ethanol–water solution. No.1: Ni–succinate (const.=0), No.2: Ni–o–phthalate (const.=1.0), No.3: Ni–tartarate (const. =2.0), and No.4: Ni–malonate (const.=3.0).

Figure 3. Plots of $1/K_d$ versus [Acid] for Ni–acid complexes in acetone–water solution. No.1: Ni–succinate (const.=0). No.2: Ni–*o*–phthalate (const.=1.0), No.3: Ni–tartarate (const.=2.0), and No.4: Ni–malonate (const.=3.0).
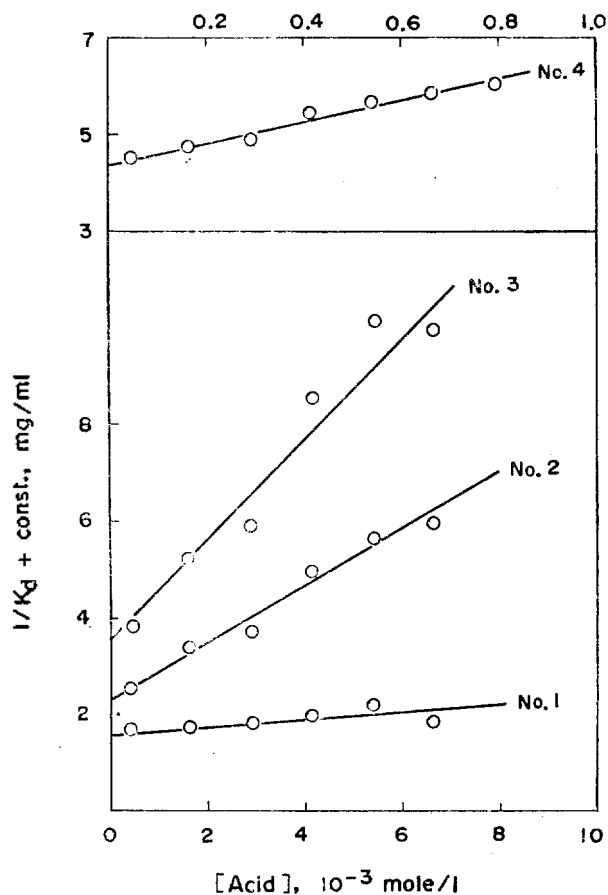
TABLE 3: Formation Constants of Ni²⁺ Complexes with Dibasic Organic Acids in Solution at Room Temperature

Complex	Solvent	$1/K_d{}^o$, mg/ml	K_f, 10^3 l/mole
NiSuc	H₂O	0.89	0.061
	20% Ethanol–H₂O	1.0	0.11
	20% Acetone–H₂O	1.6	0.059
NiMal	H₂O	1.0	0.74
	20% Ethanol–H₂O	1.8	0.91
	20% Acetone–H₂O	1.4	1.5
NiPth	H₂O	0.72	0.24
	20% Ethanol–H₂O	0.90	0.45
	20% Acetone–H₂O	1.3	0.43
NiTar	H₂O	0.83	0.35
	20% Ethanol–H₂O	1.5	0.34
	20% Acetone–H₂O	1.3	0.90

The values of K_f and $K_d{}^o$ for the formation of the Ni–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 $K_d{}^o$ are summarized in Table 3.

Cd²⁺ Complexes. Studies were extended to the systems of Cd²⁺ 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

TABLE 4: Distribution Ratios of Cd²⁺ between Resin and Solution at Room Temperature

| Acid | Conc., 10^{-4} mole/l | $1/K_d$, mg/ml | | |
		Aqueous	20% Ethanol–H₂O	20% Acetone–H₂O
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	2.08
	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	2.35
	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	1.90
	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		

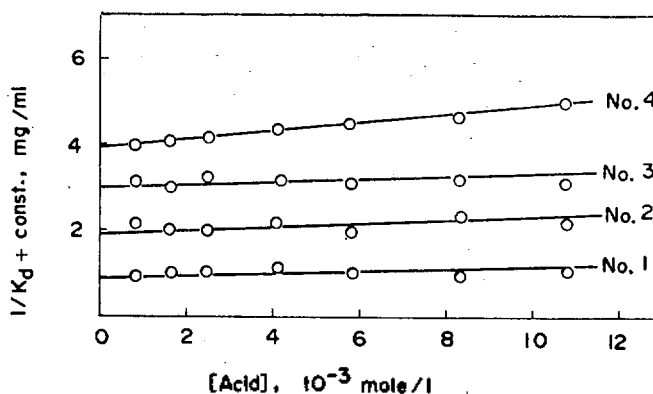**Figure 4.** Plots of $1/K_d$ versus [Acid] for Cd–acid complexes in aqueous solution. No.1: Cd–succinate (const.=0), No.2: Cd–malonate (const.=1.0), No.3: Cd–*o*–phthalate (const.=2.0), and No.4: Cd–tartarate (const.=3.0).
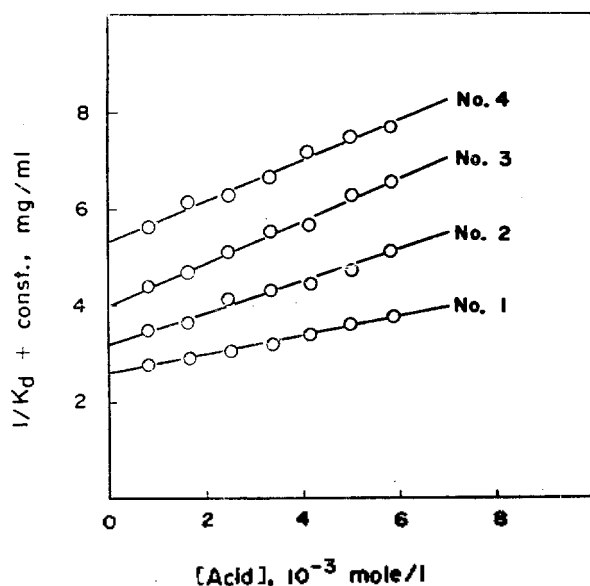
Figure 5. Plots of $1/K_d$ versus [Acid] for Cd–acid complexes in ethanol–water solution. No.1: Cd–succinate (const.=0), No. 2: malonate (const.=1.0), No.3: Cd–*o*–phthalate (const. =2.0) ,and No.4: Cd–tratarate (const.=3.0).
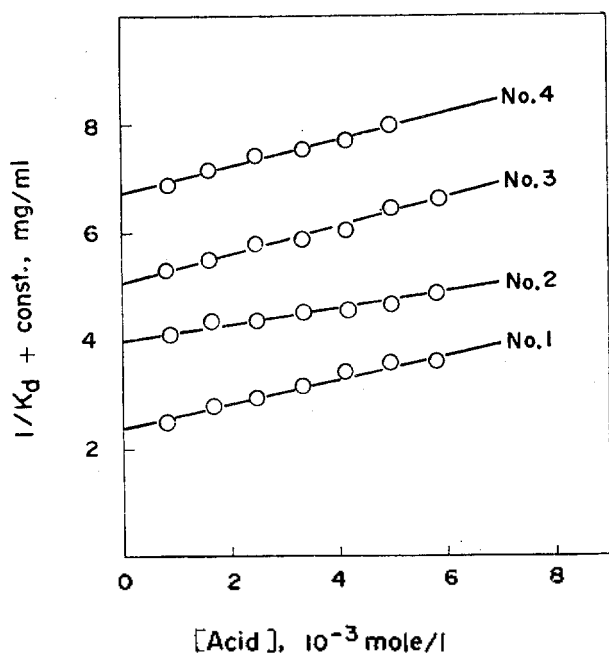

Figure 6. Plots of $1/K_d$ versus [Acid] for Cd–acid complexes in acetone–water solution. No.1: Cd–succinate (const.=0), No.2: Cd–malonate (const.=2.0), No.3: Cd–*o*–phthalate (const. =3.0), and No.4: Cd–tartarate (const.=5.0).

in all the solvent systems examined(Table 4 and Figures 4–6).

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 $1/K_f$ versus the acid anion concentrations, the values of K_d° 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 5: Formation Constants of Cd^{2+} Complexes with Dibasic Organic Acids in Solution at Room Temperature

Complex	Solvent	$1/K_d^\circ$ mg/ml	K_f, 10^3 l/mole
CdSuc	H_2O	0.91	0.28
	20% Ethanol–H_2O	2.6	0.80
	20% Acetone–H_2O	2.4	0.98
CdMal	H_2O	0.87	0.55
	20% Ethanol–H_2O	2.2	1.4
	20% Acetone–H_2O	2.0	0.70
CdPth	H_2O	0.87	0.65
	20% Ethanol–H_2O	2.0	2.2
	20% Acetone–H_2O	2.1	1.2
CdTar	H_2O	0.90	1.1
	20% Ethanol–H_2O	2.3	1.9
	20% Acetone–H_2O	1.7	1.4

Discussion

The results of the present study indicate that Ni^{2+} and and Cd^{2+} 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 Mn^{2+}, Co^{2+} and Zn^{2+} ions formed one-to-one complexes with the above-mentioned organic acids in solution. It is concluded therefore that Ni^{2+} and Cd^{2+} ions have similar nature to Mn^{2+}, Co^{2+} and Zn^{2+} 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 an exception of Ni–malonate complex:

Succinate<malonate<*o*-phthalate<tartarate complexes.

This order of increasing stabilities of Ni^{2+}- 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 of 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,[13] 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 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 an exception of Ni–malonate complex:

Ni^{2+}<Mn^{2+}<Cd^{2+}<Co^{2+}<Zn^{2+} complexes.

It was mentioned previously[1] that the crystal radii of the

TABLE 6: Formation Constants of the One–to–One Complexes of Various Metal Ions with Organic Acids in Solution at Room Temperature

Acid	Sovent	K_f, 10^3 l/mole				
		Ni^{2+}	Mn^{2+}	Cd^{2+}	Co^{2+}	Zn^{2+}
Succinic	H$_2$O	0.061	0.11	0.28	0.50	0.88
	20 % Etanol–H$_2$O	0.11	0.18	0.80	0.87	1.5
	20 % Acetone–H$_2$O	0.059	0.20	0.98	1.3	1.7
Malonic	H O	0.74	0.29	0.55	0.59	1.8
	20 % Ethanol–H$_2$O	0.91	0.64	1.4	1.1	2.3
	20 % Acetone–H$_2$O	1.5	0.76	0.70	1.7	2.3
o–Phthalic	H O	0.24	0.49	0.65	1.1	2.0
	20 % Ethanol–H$_2$O	0.45	0.79	2.2	1.3	2.3
	20 % Acetone–H$_2$O	0.43	0.80	1.2	1.8	2.0
Tartaric	H O	0.35	1.0	1.1	1.5	2.2
	20 % Ethanol–H$_2$O	0.34	1.3	1.9	1.8	2.4
	20 % Acetone–H$_2$O	0.90	1.5	1.4	2.0	2.6
Reference		*	1	*	1	1

*The present study.

"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 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.

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Study of Oganophosphorus Compound (I). Synthesis of Heterocyclic Compounds Containing Phosphorus Atom

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Trichloromethylphosphonyl dichloride was prepared by the aluminium chloride method. We synthesized several heterocyclic compounds containing phosphorus atom by the stepwise esterification of trichloromethylphosphonyl dichloride with ethylene glycol, 2–mercaptoethanol, ethylene diamine, and 2–aminoethanol and the resulting heterocyclic compounds are 2–trichloromethyl–1,3,2–dioxa–, 2–trichloromethyl–1,3,2–thioxa–, 2–trichloromethyl–1,3,2–diaza–, and 2–trichloromethyl–1,3,2–oxazaphospholane–2–oxide. The best results were obtained in the solution of triethylamine as hydrochloric acid trapping agent. The structure of five-mebered heterocyclic phosphonates were characterized by their IR, NMR, and elementary analysis and the mass spectra of the compounds were analyzed.