

Complexes of Polyvalent Metal Ions (VII). Complexes of Cadmium, Cobalt and Nickel with Hydroxycarboxylic Acids in Aqueous, Ethanol-Water and Acetone-Water Solutions*

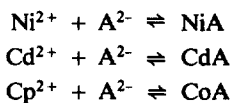
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Solutions of Cd^{2+} , Co^{2+} and Ni^{2+} were mixed with the solutions of hydroxycarboxylic acids such as salicylic, lactic and mandelic acids in the presence of cation exchange resin at room temperature. The distribution ratios of the metal ions between resin and solution were measured, using radioactive metal ions as tracer. From the observed variation of the distribution ratios with the acid anion concentrations, it was concluded that Cd^{2+} , Co^{2+} and Ni^{2+} formed the one-to-one complexes with salicylate, lactate and mandelate ions in aqueous, 20% ethanol-water and 20% acetone-water solutions. The results of the present study indicated that the relative stabilities of the metal-acid complexes in solution increased in the order: $\text{Cd}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+}$ complexes. Salicylate < lactate < mandelate complexes. Aqueous < mixed solvent systems.

Introduction

It was previously reported that Ni^{2+} , Cd^{2+} and Co^{2+} ions formed one-to-one complexes with dibasic organic acids (H_2A) such as succinic, malonic, *o*-phthalic and tartaric acids in aqueous, 20% ethanol-water and 20% acetone-water solutions.^{1,2}



The equilibrium ion exchange technique was used to examine the complex formation and to evaluate the formation constants, K_f , of the complexes.³⁻⁹ By comparing the K_f values of the complexes, it was concluded that the relative stabilities of the complexes in solution increased generally in the order:

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

Thus, the tartarate complexes indicated greater stabilities than the similar complexes of other organic acids examined. It was speculated that the existence of OH group in the acid molecule increased the stabilities of the metal-acid complexes in solution.^{1,10}

It appeared interesting to extend the studies further to the systems of cadmium, cobalt and nickel with hydroxycarboxylic acids, in order to examine the possible effect of OH group in the acid molecules on the complex formation. Thus, the present study was undertaken on the complex formation of Cd^{2+} , Co^{2+} and Ni^{2+} ions with salicylic, lactic and mandelic acids in aqueous, 20% (by volume) ethanol-water and 20% (by volume) acetone-water solutions, using the equilibrium ion exchange technique.

Experimental

Materials. Ethanol and acetone were purified, and cation ex-

change resin was treated with dil. NaOH and dil. HCl, by the methods described in the previous papers of this series.^{1,9} The stock solution of sodium chloride (0.125 mole/l) and the stock solutions of sodium salicylate, lactate and mandelate (0.125 mole/l) were prepared by dissolving appropriate amounts in each solvent system.¹¹ The stock solutions of radioactive cadmium (^{115}Cd), cobalt (^{60}Co) and nickel (^{65}Ni) were prepared by the processes reported previously.¹

Procedure. The experimental procedures used in the present study were described in the previous papers.^{1,2,9} The cation exchange resin was placed in Erlenmeyer flasks, and then the stock solutions of radio-active metal ions, the stock solutions of organic acids and the solvent were added, according to Table 1. The solution in the flasks contained Cd^{2+} , Co^{2+} or Ni^{2+} of the following concentrations:

$$\begin{aligned}\text{Cd}^{2+} &= 0.59 \times 10^{-3} \text{ mole/l} \\ \text{Co}^{2+} &= 1.2 \times 10^{-3} \text{ mole/l} \\ \text{Ni}^{2+} &= 1.2 \times 10^{-3} \text{ mole/l}\end{aligned}$$

TABLE 1: Composition of Sample Solution

Flask No.	Resin, mg	M ²⁺ m/	Acid, m/	NaCl, m/	Solvent, m/
1	150	10.0	0	0	40.0
2	150	10.0	0.5 (0.5)	39.5 (39.5)	0
3	150	10.0	2.0 (1.0)	38.0 (39.0)	0
4	150	10.0	3.5 (3.0)	36.5 (37.0)	0
5	150	10.0	5.0 (5.0)	35.0 (35.0)	0
6	150	10.0	6.5 (9.0)	33.5 (31.0)	0
7	150	10.0	8.0 (11.0)	32.0 (29.0)	0
8	150	10.0	9.5 (13.0)	30.5 (27.0)	0

(): Amount used in the system of Cd^{2+} with mandelic acid in aqueous solution.

* Abstracted, in part, from M.S. Thesis of Joon Kil Kang, Sogang University, Seoul 121, Korea, 1978.

After the flasks were shaken for 1-3 hours, 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 resin and solution 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 weight (mg) of the resin, $A(\text{resin})$ the radioactivity of the resin phase, $A(\text{total})$ the total radioactivity of the metal ions in the resin and solution phases.

Results

Cd^{2+} Complexes. The results obtained on the systems of Cd^{2+} with salicylate (Sal^{2-}), lactate (Lac^{2-}) and mandelate (Man^{2-}) anions in aqueous, 20% ethanol-water and 20% acetone-water solutions are summarized in Table 2.

If it was assumed that Cd^{2+} formed the one-to-one complexes with the acid anions, good linearity should have been obtained between the values of $1/K_d$ and the acid concentra-

tions, as was described previously.¹

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

where K_d^0 denotes the K_d value at infinite dilution, K_f the formation constant of the complexes in solution, and $[\text{Acid}]$ the acid concentrations.

The data summarized in Table 2 indicate fairly good linearities between the values of $1/K_d$ and the acid concentrations. This indicates therefore that the assumption of the one-to-one complex formation between Cd^{2+} and acid anions is correct. To illustrate the linearities between $1/K_d$ and acid concentrations, an example of the plots is shown in Figure 1.

The formation constants of the Cd-acid complexes were calculated from slopes and intercepts of the linear plots of $1/K_d$ versus acid concentrations. The results are summarized in Table 3.

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

Acid	Conc., 10 ⁻³ mole/l	1/ K_d , mg/ml		
		Aqueous	Ethanol-H ₂ O	Acetone-H ₂ O
Salicylic	1.25	1.45	1.74	3.81
	5.00	1.50	1.78	4.17
	8.75	1.49	1.76	4.30
	12.5	1.48	—	4.37
	16.3	1.49	1.88	4.43
	20.0	1.49	1.88	4.53
Lactic	1.25	0.96	—	—
	5.00	0.95	2.19	3.27
	8.75	0.97	2.31	3.64
	12.5	—	2.37	3.66
	16.3	0.97	2.42	3.96
	20.0	0.97	2.53	4.35
Mandelic	23.8	0.98	2.61	4.57
	1.25	1.29	2.97	5.88
	2.50	1.32	—	—
	5.00	—	3.27	6.75
	7.50	1.29	—	—
	8.75	—	3.72	7.41
12.5	1.44	3.87	8.24	
16.3	—	4.12	9.04	
20.0	—	—	10.1	
22.5	1.65	—	—	
23.8	—	4.82	11.7	
27.5	1.70	—	—	
32.5	1.76	—	—	

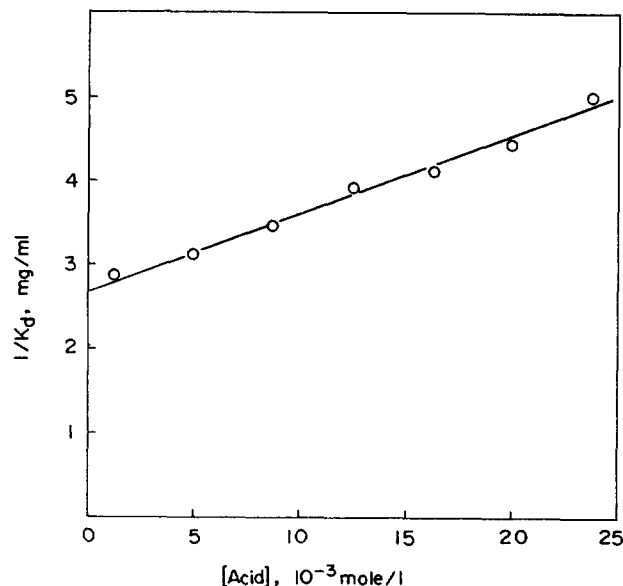


Figure 1. Plots of $1/K_d$ versus Acid for Ni-mandelate complex in aqueous solution.

TABLE 3: Formation Constants of Cd^{2+} with Hydroxycarboxylic Acids in Solution at Room Temperatures

Complex	Solvent	1/ K_d^0 , mg/ml	K_f , l/mole
CdSal	H ₂ O	1.4	2.6
	20% Ethanol-H ₂ O	1.7	4.2
	20% Acetone-H ₂ O	3.9	7.8
CdLac	H ₂ O	0.95	1.3
	20% Ethanol-H ₂ O	2.1	10
	20% Acetone-H ₂ O	2.9	24
CdMan	H ₂ O	1.2	13
	20% Ethanol-H ₂ O	2.9	28
	20% Acetone-H ₂ O	5.4	46

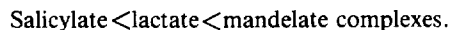
Co²⁺ Complexes. Studies were extended to the systems of Co²⁺ with salicylate, lactate and mandelate ions. The results (Table 4) indicated fairly good linearities between $1/K_d$ and acid concentrations. It was concluded therefore that the one-to-one complexes were formed also between Co²⁺ and the acid anions in solution. The formation constants of the Co-acid complexes were calculated (Table 5).

Ni²⁺ Complexes. Studies were further extended to the systems with Ni²⁺. From the experimental results (Table 6), it was concluded that Ni²⁺ also formed the one-to-one complexes with the acid anions. The formation constants of the

Ni-acid complexes were also calculated (Table 7).

Discussion

The results of the present study are summarized in Table 8. It is noted that the relative stabilities of the complexes of each metal ion with the hydroxymonocarboxylic acids increase in the following order:



Based on this trend of increasing stabilities, it may be said that the K_f values decrease with increasing separation between

TABLE 4: Distribution Ratios of Co²⁺ between Resin and Solution at Room Temperatures

Acid	Conc., 10 ⁻³ mole/l	1/K _d , mg/ml		
		Aqueous	Ethanol-H ₂ O	Acetone-H ₂ O
Salicylic	1.25	0.76	1.64	1.53
	5.00	0.81	1.71	1.56
	8.75	0.83	1.68	1.62
	12.5	0.84	1.75	1.62
	16.3	0.86	1.72	1.67
	20.0	0.88	1.74	1.68
	23.8	0.91	1.82	1.70
Lactic	1.25	0.80	1.78	1.44
	5.00	0.82	1.97	1.62
	8.75	0.95	2.30	1.82
	12.5	1.01	2.37	2.06
	16.3	1.07	2.62	2.19
	20.0	1.14	2.80	2.43
	23.8	1.19	2.99	2.56
Mandelic	1.25	0.83	1.70	1.51
	5.00	0.88	1.95	1.71
	8.75	0.95	2.07	1.90
	12.5	1.03	2.36	2.09
	16.3	1.11	2.38	2.36
	20.0	1.17	2.85	2.62
	23.8	—	3.12	2.86

TABLE 5: Formation Constants of Co²⁺ with Hydroxycarboxylic Acids in Solution at Room Temperatures

Complex	Solvent	1/K _d ^o	K _f
		mg/ml	l/mole
CoSal	H ₂ O	0.77	7.9
	20% Ethanol-H ₂ O	1.6	4.3
	20% Acetone-H ₂ O	1.5	5.2
CoLac	H ₂ O	0.76	24
	20% Ethanol-H ₂ O	1.7	31
	20% Acetone-H ₂ O	1.4	37
CoMan	H ₂ O	0.79	24
	20% Ethanol-H ₂ O	1.6	39
	20% Acetone-H ₂ O	1.4	43

TABLE 6: Distribution Ratios of Ni²⁺ between Resin and Solution at Room Temperatures

Acid	Conc., 10 ⁻³ mole/l	1/K _d , mg/ml		
		Aqueous	Ethanol-H ₂ O	Acetone-H ₂ O
Salicylic	1.25	1.60	2.01	1.17
	5.00	1.64	2.11	1.24
	8.75	1.67	2.24	1.21
	12.5	—	1.97	1.30
	16.3	1.75	2.26	1.32
	20.0	1.83	2.32	—
	23.8	1.89	2.40	1.37
Lactic	1.25	2.73	1.58	1.75
	5.00	3.01	—	2.00
	8.75	3.21	2.07	2.27
	12.5	3.51	2.34	2.61
	16.3	3.61	2.59	3.13
	20.0	4.11	2.80	3.30
	23.8	4.23	3.09	3.22
Mandelic	1.25	2.87	1.76	3.17
	5.00	3.12	2.04	3.95
	8.75	3.46	2.30	4.39
	12.5	3.92	2.49	5.03
	16.3	4.12	3.04	5.59
	20.0	4.45	3.22	6.33
	23.8	4.99	3.50	—

TABLE 7: Formation Constants of Ni²⁺ with Hydroxycarboxylic Acids in Solution at Room Temperatures

Complex	Solvent	1/K _d ^o	K _f
		mg/ml	l/mole
NiSal	H ₂ O	1.6	8.1
	20% Ethanol-H ₂ O	1.9	11
	20% Acetone-H ₂ O	1.2	7.9
NiLac	H ₂ O	2.6	26
	20% Ethanol-H ₂ O	1.5	44
	20% Acetone-H ₂ O	1.6	47
NiMan	H ₂ O	2.7	35
	20% Ethanol-H ₂ O	1.6	49
	20% Acetone-H ₂ O	3.0	54

hydroxy and carboxylic groups in the acid molecules, and that the presence of phenyl group in acid molecules increases the stabilities of the complexes.

It is also concluded that the relative stabilities of the complexes increase in the following order:

TABLE 8: Formation Constants of the One-to-One Complexes of Metal Ions with Hydroxycarboxylic Acids in Solution at Room Temperature

Acid	Solvent	K_f , //mole		
		Cd ²⁺	Co ²⁺	Ni ²⁺
Salicylic	H ₂ O	2.6	7.9	8.1
	20 % Ethanol-H ₂ O	4.2	4.3	11
	20 % Acetone-H ₂ O	7.8	5.2	7.9
Lactic	H ₂ O	1.3	24	26
	20 % Ethanol-H ₂ O	10	31	44
	20 % Acetone-H ₂ O	24	37	47
Mandelic	H ₂ O	13	24	35
	20 % Ethanol-H ₂ O	28	39	49
	20 % Acetone-H ₂ O	46	43	54

TABLE 9: Ionic Radii of Metal Ions

Ion	Coordination number	Ionic radius, A
Ni ²⁺	4	0.69
	6	0.83
Co ²⁺	4 (HS*)	0.72
	6 (LS*)	0.79
	6 (HS*)	0.885
Cd ²⁺	4	0.92
	6	1.09

* LS: low spin, HS: high spin.

TABLE 10: Formation Constants of the One-to-One Complexes of Metal Ions with Dibasic Organic Acids in Solution at Room Temperature^{1,2}

Acid	Solvent	K_f , 10 ³ //mole		
		Ni ²⁺	Cd ²⁺	Co ²⁺
Succinic	H ₂ O	0.061	0.28	0.50
	20 % Ethanol-H ₂ O	0.11	0.80	0.87
	20 % Acetone-H ₂ O	0.059	0.98	1.3
Malonic	H ₂ O	0.74	0.55	0.59
	20 % Ethanol-H ₂ O	0.91	1.4	1.1
	20 % Acetone-H ₂ O	1.5	0.70	1.7
<i>o</i> -Phthalic	H ₂ O	0.24	0.65	1.1
	20 % Ethanol-H ₂ O	0.45	2.2	1.3
	20 % Acetone-H ₂ O	0.43	1.2	1.8
Tartaric	H ₂ O	0.35	1.1	1.5
	20 % Ethanol-H ₂ O	0.34	1.9	1.8
	20 % Acetone-H ₂ O	0.90	1.4	2.0



If it is speculated that the relative stabilities of the complexes are determined primarily by the magnitude of electrostatic attraction between metal ions and acid anions, smaller metal ions of same positive charges should form more stable complexes. If it is assumed that the "naked" ionic radii¹² (Table 9) are the major factor to determine the relative sizes of the metal ions in solution, the Ni²⁺ ion must be the smallest among the divalent metal ions examined, and hence Ni²⁺ may form the most stable complexes. This agrees with the experimental observations.

It is also noted from Table 8 that the complexes seem to be more stable in the mixed solvent systems than in aqueous solution.

Aqueous < mixed solvent systems.

This may be explained in a similar way to the one described in the previous papers.^{1,2} Smaller values of dielectric constants of ethanol and acetone may cause stronger electrostatic attraction between the metal ions and the organic anions in solution.

In order to compare the relative stabilities of the complexes listed in Table 8 with those of similar complexes with dibasic organic acids, the results of the previous studies on the systems of Cd²⁺, Co²⁺ and Ni²⁺ with succinic, malonic, *o*-phthalic and tartaric acids are summarized in Table 10. It was mentioned previously that the existence of OH group in the acid molecules led to greater stabilities of the metal-acid complexes in solution.^{1,10} By comparing Table 8 with Table 10, however, it is concluded that Cd²⁺, Co²⁺ and Ni²⁺ form more stable complexes with dibasic organic acids than with hydroxymonocarboxylic acids. Hence, it could be said that the magnitude of the charges of acid anions may play more important role than the existence of OH group in the acid molecules for the formation of the metal-acid complexes.

As it was mentioned above, the present study revealed that the relative stabilities of the metal-acid complexes increased in the order:



for relatively unstable complexes with monocarboxylic acids. In the previous investigations, however, a different order of increasing stabilities was observed:



for relatively stable complexes with monocarboxylic acids the size of the "naked" metal ions could be a major factor to affect the relative stabilities of the metal-acid complexes, whereas in the case of more stable complexes other factors besides the size of the "naked" metal ions should affect also the relative stabilities of the complexes in solution.

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Determination of Reactivity by MO Theory (XVIII). An Intermolecular Perturbation Study of the Acid-Catalyzed Hydrolysis of Difformamide *

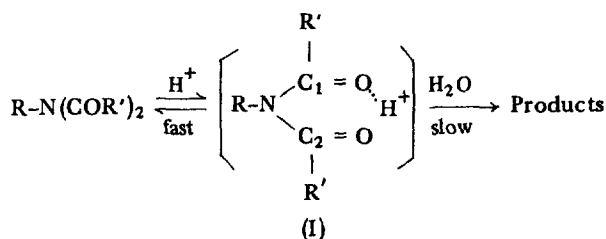
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The Murrell-Fueno type of the intermolecular perturbation approach was applied to the acid-catalyzed hydrolysis of difformamide. The results show that: (1) the attack of a water molecule on the protonated carbonyl carbon is favored over that on the unprotonated carbonyl carbon; (2) the σ -approach model of water is preferred to the π -approach model; (3) the major contributing term to the total energy is the Coulomb energy, E_q , especially in the σ -approach, while the contribution of E_{ct} (and E_k) increases moderately in the π -approach; (4) the reaction is a charge-controlled one, a hard-hard type in the language of the HSAB principle.

Introduction

Recently it has been shown that the mechanism for the acid-catalyzed hydrolysis of diacylamines, $RN(COR')_2$, involves the attack by a water molecule on one of the carbonyl carbon of the conjugate acid (I) as the rate determining step.¹



The protonation was found to occur on a carbonyl oxygen,^{1b,2} the *trans-trans* form of diacylamine (I) being preferred when protonated.^{2,3} Laurent and coworkers suggested that the attack by a water occurred on the carbon atom of the unprotonated carbonyl group, C_2 . However, based on a simple interpretation of MO properties we have argued that the attack should occur on the carbon atom of the protonated carbonyl group, C_1 ,³ since protonation caused an increase in the positive charge as well as in the AO coefficient of the π -LUMO (lowest unoccupied MO) of C_1 enhancing both charge-controlled and orbital-controlled S_N reactivities of C_1 .

In this work we will pursue further this problem of deciding which carbonyl carbon that is attacked by a water molecule in

the acid-catalyzed hydrolysis of diacylamines adopting the intermolecular interaction approach developed by Murrell^{4a} and Fueno.^{4b} In this type of intermolecular perturbation method, various interaction energies, *i.e.*, the Coulomb E_q , exchange-repulsion E_k , induction E_p , dispersion E_d , and charge-transfer E_{ct} , energies, are evaluated separately for assumed geometries of the reacting systems and their relative contributions to the orienting effect are assessed.

In this work we have chosen the simplest form of diacylamine, difformamide $HN(COH)_2$, and the interaction energies between protonated difformamide and water were calculated at various distances and orientations of approach.

Calculations

In the intermolecular perturbation theory of Murrell *et al.*,^{4a} the ground-state configuration (AB) of the two interacting system A and B are mixed with the locally excited (A^*B and AB^*), doubly excited (A^*B^*) and charge-transfer (A^+B^- and A^-B^+) configurations, and the stabilization energy of the ground-state due to the configuration interaction is calculated by a double perturbation expansion with respect to the intermolecular potential U and overlap S up to the order of U^2S^2 . Thus expressions for the Coulombic (U^1S^0), exchange-repulsion (U^1S^2), induction-dispersion (U^2S^0) and charge-transfer (U^2S^2) energies are derived. These expressions are then expanded into terms associated with atomic orbitals. Actual

* This paper is dedicated to the memory of the late Professor Suk-kee Lee of the Busan National University, who was a respected teacher, colleague and scientist. On his suggestion this work was originally initiated.