Stability of Complexes of Several Carboxylic Acids Formed with Bivalent Metals[*]

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Numerous reports have been published on the stability of various complexes formed between bivalent metals and carboxylic acids; however, no extensive study regarding these complexes has ever been performed in any one laboratory under identical experimental conditions. Experiments under identical conditions are of primary importance because the respective values of the stability of these complexes and the differences between these values are quite small; therefore, a precise comparison of these stability constants is possible only when the values determined under the same conditions are available.

In this report the stability of various complexes formed between carboxylic acids and bivalent metals having the ratio of 1 : 1 was determined by using the pH titration method. The monobasic and dibasic acids containing the COOH groups alone were studied, i. e. the acids containing the OH groups in addition to the COOH group were excluded. Thus tartaric acid or similar acids were not studied because of their rather complicated bahavior in a solution.

Experimental

Materials.—The nitrates of lead, copper, cadmium, zinc and nickel were chemicals of the analytical grade. The carboxylic acids used are listed in Table I. They were reagents of the analytical or highest grade available.

Procedure.—The pH values were measured with a pH meter having a glass electrode made by Horiba and Co. The temperature of the measurement was 25°C and the ionic strength of the solution was maintained at 0.1 by the addition of sodium perchlorate; however, in some cases where the stability of the complex was small such as in the nickel benzoate complex the ionic strength of the solution was kept at 0.1 by nickel nitrate itself without the addition of sodium perchlorate.

The concentration of the metal nitrate was kept generally higher than that of the carboxylic acid to prevent the formation of a complex having the metal to ligand ratio of 1 : 2. The concentrations used were as follows:

Monobasic acids

Lead nitrate	0.004∼0.02M	Acid	0.004∼0.009M
Copper nitrate	0.006∼0.015	〃	0.004∼0.009
Cadmium nitrate	0.03	〃	0.012
Zinc nitrate	0.034	〃	0.012
Nickel nitrate	0.026	〃	0.009∼0.012

Dibasic acids except diglycolic and thiodiglycolic acids

Lead nitrate	0.004M	Acid	0.002M
Copper nitrate	0.003	〃	0.002
Cadmium nitrate	0.006	〃	0.01
Zinc nitrate	0.007	〃	0.01
Nickel nitrate	0.01	〃	0.01

Diglycolic and thiodiglycolic acids

Lead nitrate	0.002M	Acid	0.001M
Cadmium nitrate	0.002	〃	0.001
Zinc nitrate	0.002	〃	0.001
Copper nitrate	0.0015	〃	0.001
Nickel nitrate	0.0026	〃	0.001

To convert the hydrogen ion activity into its concentration in the solution, the value 0.83 suggested by Kielland[1] was used.

Results

Acid Dissociation Constant.—If the dibasic acid is represented as H_2A, the acid dissociation constants to be determined may be expressed as

$$K_1 = \frac{[H^+]\,[HA^-]}{[H_2A]} \tag{1}$$

and

$$K_2 = \frac{[H^+]\,[A^{2-}]}{[HA^-]} \tag{2}$$

where [ ] expresses the concentration in mole per litre. The values of the dissociation constant were determined by titration with alkali and they are given in Table I[2]. For some dicarboxylic acids such as succinic, itaconic, glutaric, adipic, diglycolic and thiodiglycolic acids the first and second dissociation occurred simultaneously and the method of successive approximation was used to calculate their dissociation constants.

Stability Constant.—The values of the stability constant of the complexes formed are expressed by

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[1] J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

[2] The results for phthalic acid were taken from the report by M. Yasuda, K. Suzuki and K. Yamasaki, *J. Phys. Chem.*, **60**, 1649 (1956).

TABLE I. ACID DISSOCIATION CONSTANTS
25°C, $\mu=0.1$

	Acids	pK_1	pK_2
1	Acetic acid	4.53	
2	Benzoic acid	4.01	
3	*o*-Methoxybenzoic acid	3.90	
4	Succinic acid	4.00	5.21
5	Itaconic acid	3.68	5.14
6	Glutaric acid	4.14	5.01
7	Adipic acid	4.28	5.00
8	Phthalic acid	2.76	4.92
9	Malonic acid	2.76	5.29
10	Maleic acid	<2	5.79
11	Citraconic acid	2.2	5.60
12	Diglycolic acid	2.77	3.92
13	Thiodiglycoic acid	3.15	4.13

$$k_1=\frac{[MA]}{[M^{2+}]\,[A^{2-}]} \tag{3}$$

Under the conditions in the present experiments, the formation of complexes having a metal to ligand ratio of 1:2 is negligible. Therefore the species present in the solutions are H^+, M^{2+}, MA, A^{2-}, HA^-, H_2A and OH^- except in the case of sodium and perchlorate ions which were added in order to keep the ionic strength of the solution constant. Then the following relations exist between the total concentrations of acidic hydrogen, acid and metal for which the symbols C_H, C_A and C_M are used respectively.

The concentration of OH^- is negligible in acid solutions.

Thus

$$C_H=[H^+]+[HA^-]+2[H_2A] \tag{4}$$

$$C_A=[A^{2-}]+[HA^-]+[H_2A]+[MA] \tag{5}$$

$$C_M=[M^{2+}]+[MA] \tag{6}$$

By substituting Eqs. 1 and 2 into 4, Eq. 7 may be obtained

$$C_H-[H^+]=\frac{[H^+]\,[A^{2-}]}{K_2}+\frac{2[H^+]^2[A^{2-}]}{K_1K_2} \tag{7}$$

From the pH measurements of the solutions $[H^+]$ was calculated. By substituting $[H^+]$ into 7 $[A^{2-}]$ was found and then [MA] and $[M^{2+}]$ were obtained from 5 and 6 combined with 1 and 2 and finally $k_1=[MA]/[M^{2+}]\,[A^{2-}]$ was found. The logarithmic values of the stability constant thus obtained are given in Table II. For monobasic acids the calculations are more simple than for dibasic acids shown above.

The stability of these complexes under somewhat different experimental conditions of temperature and ionic strength have been previously determined by several other authors, as listed in Table III:

If the differences in temperature and ionic strength of the solution are taken into consideration, their results agree fairly well with the results of the present study.

From the results shown in Table II the acids studied are divided into three groups:

1) Dibasic acids forming a seven membered or a larger chelate ring and having no double bonds in the chelate ring. Monobasic acids also belong to this group.

2) Dibasic acids forming a six membered ring such as malonic acid and those having double bonds in the chelate ring such as maleic and citraconic acids.

3) Dibasic acids seeming to act as tridentate chelating agent. Diglycolic and thiodiglycolic acids belong to this group.

It is obvious from Table II that the acids of the first group form complexes whose stability constants follow the order

$$\mathrm{Pb}>\mathrm{Cu}>\mathrm{Cd}>\mathrm{Zn}>\mathrm{Ni}$$

and that lead shows the highest stability. The values for monobasic acids are nearly

TABLE II. STABILITY CONSTANTS ($\log k_1$)

	Acids	Pb	Cu	Cd	Zn	Ni
1	Acetic acid	2.1	1.8	1.5	1.0	1.0
2	Benzoic acid	2.0	1.6	1.4	0.9	0.9
3	*o*-Methoxybenzoic acid	1.9	1.6	1.3	0.9	0.8
4	Succinic acid	2.8	2.6	2.1	1.6	1.6
5	Itaconic acid	3.1	2.8	2.3	1.9	1.8
6	Glutaric acid	2.8	2.4	2.0	1.6	1.6
7	Adipic acid	2.8	2.3	2.1	1.8	1.6
8	Phthalic acid[2)]	ppt.	3.1	2.5	2.2	2.1
9	Malonic acid	3.1	5.0	2.3	2.7	3.2
10	Maleic acid	3.2	3.4	2.4	2.0	2.0
11	Citraconic acid	3.3	3.4	2.2	1.8	1.8
12	Diglycolic acid	4.4	3.9	3.3	3.6	2.6
13	Thiodiglycolic acid	3.6	4.3	2.6	2.9	4.0

TABLE III

Acids	References
Acetic	Cannan and Kibrick[3]
	Lloyd, Wycherley and Monk[4]
	Edmonds and Birnbaum[5]
	Fronaeus[6]
	Tanaka et al.[7]
Succinic	Cannan and Kibrick[3]
	Peacock and James[8]
Glutaric	Cannan and Kibrick[3]
	Peacock and James[8]
Adipic, phthalic and maleic	Peacock and James[8]
Malonic	Riley[9]
	Stock and Davies[10]
	Money and Davies[11]
Diglycolic and thiodiglycolic	Tichane and Bennett[12]

the same and show only small differences between them. The dibasic acids show higher values than monobasic acids. Both succinic and itaconic acids form seven membered rings, but the stability constants are a little larger for the latter, which has a double bond in the side chain.

The empirical stability order for bivalent metals was proposed by various authors and the order

$$\mathrm{Cu} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Co},\ \mathrm{Zn}$$

found by Mellor and Maley[13] holds with some variations for many O and N type ligands. Irving and Williams[14] pointed out that the order

$$\mathrm{Zn} < \mathrm{Cu} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Fe} > \mathrm{Mn}$$

for the metals of the first transition series held irrespective of the nature of the ligands involved. However, generally the order of stability depends on the nature of ligands, especially when metals of non-transition series are concerned.

The stability constants of more than five hundred ligands have so far been determined, but no example of a ligand showing a high stability for lead has been found except in the case of β-(*S*-ethyl)mercaptopropionic acid as determined by Irving and Fernelius[15] in a water-dioxane mixture. The order of stability found by them is the same as the present one, i. e. lead showed the highest stability. The highest stability found in the lead complexes of carboxylic acids is, therefore, quite remarkable. The exact reason for the large stability of lead is rather difficult to explain at present.

The above mentioned order in the first group does not hold for the acids in the second group. The complexes of malonic acid which form six membered chelate rings follow the stability order

$$\mathrm{Cu} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Zn} > \mathrm{Cd}$$

However, with the other two acids, maleic and citraconic acids which form seven membered chelate rings, copper is the highest in the stability order,

$$\mathrm{Cu} > \mathrm{Pb} > \mathrm{Cd} > \mathrm{Zn} > \mathrm{Ni}$$

Citraconic acid has a methyl group and its effect seems to decrease somewhat the stability, perhaps due to steric hindrance.

If the size of the chelate ring for one metal is compared, for example, for copper, the stability is highest for malonic acid and it decreases in the following order as the size of the chelate ring increases,

malonic acid	six membered ring,
succinic acid	seven membered ring,
glutaric acid	eight membered ring,
adipic acid	nine membered ring.

If we could determine the stability of oxalic acid complexes which form a five membered ring, it might be interesting. However, under the experimental conditions of the present study, precipitation occurred instantaneously. The stability of oxalic acid complexes given in the literature are few and no data for lead are available.

For the acids in the third group the order of metals are

$\mathrm{Pb} > \mathrm{Cu} > \mathrm{Zn} > \mathrm{Cd} > \mathrm{Ni}$ for diglycolic acid

and

$\mathrm{Cu} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Zn} > \mathrm{Cd}$ for thiodiglycolic acid.

These two acids have rather small values for their acid dissociation constants. On the other hand, the values of their stability constant are large and it seems that they form tridentate complexes with O and S atoms participating in the chelation as Tichane and Bennett[12] pointed out.

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[8] J. M. Peacock and J. C. James, *J. Chem. Soc.*, **1951**, 2233.

[9] H. L. Riley, ibid., **1930**, 1642.

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[13] L. E. Maley and D. P. Mellor, *Austhal. J. Sci. Res.*, **A2**, 92, 579 (1949).

[14] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192.

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In connection with this point, *o*-methoxybenzoic acid was studied to ascertain whether the O atom of the methoxy group participates in the chelation. The values for *o*-methoxybenzoic acid complexes were nearly the same as those of the benzoic acid complexes. This appears to mean that the O atom of the methoxy group has very little relation to the chelation.

Concerning the chelating tendency of various bivalent metals for O and S atoms of similar ligands, several studies have been made on *o*-aminobenzenethiol(16), β-mercaptopropionic acid(17), β-(*S*-ethyl)mercaptopropionic acid(15) and purine derivatives(18), and zinc was found to form a stronger complex than nickel when sulfur is involved in the metal-ligand bond. However, this is not the case for thiodiglycolic acid, and a more detailed study on ligands containing sulfur is desirable to elucidate this problem.

Finally the use of these dicarboxylic acids as the eluting agent of the metal ions adsorbed on ion exchange resins was investigated. As the acid, adipic acid was chosen, as it showed suitable differences of stability for various metals.

Metal ions were adsorbed on the resin Dowex 50, H-form. Sodium adipate solution of pH 5.2 (0.1 molar solution) was poured into the column. Lead was omitted as it formed a precipitate in the 0.1 molar solution of sodium adipate. The metals in the eluted solution were determined by titration with ethylenediaminetetraacetate. The vertical axis of the graph (Fig. 1) indicates the values proportional to the metal concentration in each fraction (5 ml.) and the horizontal axis the fraction number. The separation between copper, cadmium and zinc is complete, but the separation between zinc and nickel is not. Diglycolic acid was also tested for the eluting agent, but in this case the tailing of each metal was remarkable and the complete separation was difficult.

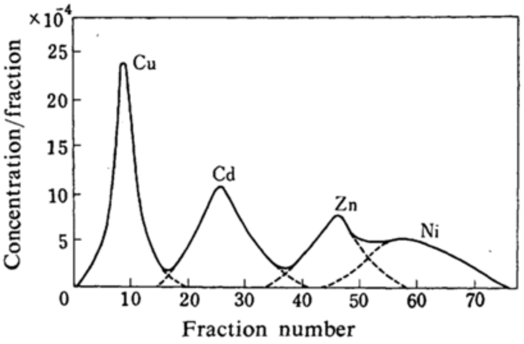

Fig. 1. Elution of Cu, Cd, Zn and Ni ions by adipic acid.

Resin : Dowex 50×−4
Column : dia. 1 cm.×5 cm.
Flow rate : 0.5 ml. per min.
Adipic acid : 0.1 M pH 5.2
One fraction : 5 ml.

Summary

Stability constants of the bivalent metal complexes formed with several mono- and dicarboxylic acids were determined at 25°C and ionic strength of 0.1. For monocarboxylic acids and several dicarboxylic acids having no double bond or forming larger chelate rings than six membered rings the following stability order held : Pb>Cu>Cd>Zn>Ni. It is very remarkable that lead showed the highest stability among bivalent metals.

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