Study of Metal-Polycarboxylate Complexes Employing Ion-selective Electrodes. II.[1] Stability Constants of Copper(II) Complexes with Poly(acrylic acid) and Poly(methacrylic acid)

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(Received May 26, 1978)

The copper(II) complex formation with poly(acrylic acid) and poly(methacrylic acid) in aqueous solution was studied by potentiometric titration employing glass and copper(II) ion-selective electrodes. The values of the equilibrium constants of the complex formation and the stability constants were estimated in various degree of neutralization. Since the concentration of free copper(II) ions could be determined by employing the copper(II) ion-selective electrode, the concentrations of two complex species, involving one and two carboxylato groups, were determined from stoichiometric equations. The equilibrium and stability constants of the complexes obtained were observed to pass through peaks with increase in the degree of neutralization. The order of magnitude of the equilibrium constant of the polyacrylate complex was larger than that of the polymethacrylate complex.

Studies of bivalent metal–polyelectrolyte complex formations by potentiometry have been reported by Gregor and coworkers,[2] as well as by Mandel and Leyte.[3] The formation curves, namely the average coordination numbers, of the bivalent metal–polyelectrolyte systems have a flat region in the range of higher degrees of neutralization and the value of the average coordination number is equal to 2. This result suggests that the predominant complex in the system is the bivalent metal ions chelated by two carboxylato groups.

Marinsky and coworkers[4–6] have investigated the complex formation of bivalent metal ions with polycarboxylic acid. It is concluded, though their systems are composed of gels, that two carboxylato groups of poly(methacrylic acid) coordinate to copper(II) ions in the range of higher degrees of neutralization. The stability constants of some bivalent metal complexes were also calculated.

On the other hand, it seems that the results of spectrophotometric studies have been satisfactorily interpreted. When the degree of neutralization is varied, the absorbance of copper(II) complexes with polycarboxylate passes through a maximum in the course of neutralization. This fact shows that the copper(II) complexes partially change in favor of some other form of binding, and as pointed out by Mandel and Leyte,[7] the spectrophotometric and potentiometric results show a breakdown of the chelate in the higher neutralization region.

In our previous paper,[1] it was shown that the potentiometric titration employing ion-selective electrodes was available for the investigation of complex formation of the bivalent metal ions with polycarboxylic acid, especially with poly(itaconic acid). But poly(acrylic acid) systems were studied for comparison purposes and the discussion was carried out mainly on the basis of the formation curves of complexes. In this study, then, poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) were investigated by pH titration and potentiometry employing the ion-selective electrode, and the concentrations of the complexes formed and the formation constants were evaluated from the potentiometric data.

Experimental

Materials. The preparation of all materials used was described previously.[1,8]

Potentiometric Titration. The pH measurements were carried out in nitrogen atmosphere at 25±0.05 °C by use of a Yokogawa Model KPH-51A pH meter equipped with Toadenpa Model HG-4005 glass and HC-2005 calomel electrodes.

The activities of copper(II) ions were measured with an Orion Model 801A digital ion meter equipped with Beckman Model 39612 Cupric and Horiba Model 2010-05T calomel electrodes, and the concentrations of copper(II) ions were estimated with the calibration curve which is obtained by measurements of the systems without only polyligands. The other conditions and techniques of potentiometry were described previously.[1]

Results and Discussion

Potentiometry Employing Copper(II) Ion-Selective Electrode. In our previous paper,[1] the potentiometry employing a copper(II) ion-selective electrode applied to the copper(II) ion-polycarboxylic acid systems was discussed. In this case it was not necessary to consider the effect of pH, because the concentration of the bivalent metal ions compared with that of the polyacid is so low that all the metal ions exist essentially as chelates in the pH region where the metal hydroxides are formed in the absence of polyacid.

In the case of the present study, however, nonchelated copper(II) ions exist in the pH region where the metal hydroxides are to be formed in the absence of polyacid. Thus, all the potentiometric measurements were carried out in the pH region less than 6.00.

Concentrations of Complexes as Functions of Degree of Neutralization. Assuming that both monocarboxylato and dicarboxylato complexes are formed, and that the concentrations of the other complexes are negligible even if they are formed, the following equations hold:

$$[\mathrm{Cu_t}] = [\mathrm{Cu^{2+}}] + [\mathrm{CuA^+}] + [\mathrm{CuA_2}],$$

$$[\mathrm{A_t}] = [\mathrm{A^-}] + [\mathrm{HA}] + [\mathrm{CuA^+}] + 2[\mathrm{CuA_2}],$$

where $[\mathrm{Cu_t}]$ is the total concentration of copper(II) ions and $[A_t]$ is that of carboxylato groups. In these equations, the values of $[CuA^+]$ (designating the concentration of monocarboxylato copper(II) complex), of $[CuA_2]$ (that of dicarboxylato complex), and of $[A^-]$ (that of nonchelating carboxylato groups) are unknown. In the present paper, the concentration of free copper(II) ions, $[Cu^{2+}]$, can be determined by potentiometric measurements employing the copper(II) ion-selective electrode. But these equations cannot be solved stoichiometrically without the estimation of $[A^-]$ based on some assumption.

By use of the reference plot method proposed by Mandel and Leyte,[3] the concentrations of nonchelating carboxylato groups, $[A^-]$, can be estimated. When the concentrations of free copper(II) ions have been determined by employing the copper(II) ion-selective electrode, these two stoichiometric equations make it possible to know the concentrations of the two complex species, $[CuA^+]$ and $[CuA_2]$.

In Figs. 1 and 2, the values of $[CuA^+]$ and $[CuA_2]$ obtained by the above method are plotted against the apparent degree of neutralization α'. In Fig. 1, the results for the copper(II)–PAA system (9.9×10^{-3} monomol/l PAA, 1.0×10^{-3} mol/l $Cu(NO_3)_2$, and 1.0×10^{-1} mol/l KNO_3), and in Fig. 2 those for the copper(II)–PMA system (1.0×10^{-2} monomol/l PMA, 1.0×10^{-3} mol/l $Cu(NO_3)_2$, and 1.0×10^{-1} mol/l KNO_3) are presented. As shown in these figures, the concentrations of the monocarboxylato complex are found to be significantly high, though the values of $[CuA^+]$ are relatively small compared with $[CuA_2]$. As the degree of neutralization increases, the concentrations of the two complex species, $[CuA^+]$ and $[CuA_2]$, increase and reach maxima in both systems, PAA and PMA. The values of the degree of neutralization of PAA at which the complex concentrations reach a maximum are 0.35 for $[CuA_2]$ and 0.45 for $[CuA^+]$. In the case of PMA two maxima are observed; their degree of neutralization values are 0.27 and 0.43 for $[CuA_2]$, and 0.35 and 0.60 for $[CuA^+]$.

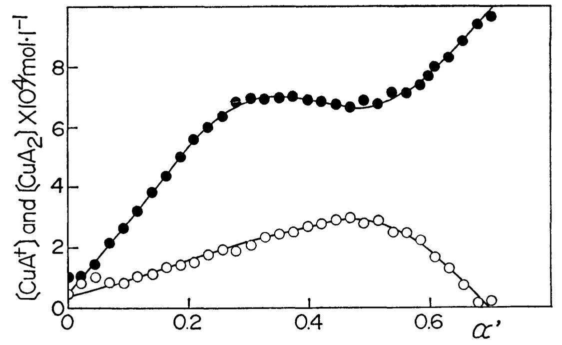

Fig. 1. Dependence of the concentrations of monocarboxylato and dicarboxylato copper(II) complexes, $[CuA^+]$ (○) and $[CuA_2]$ (●), on the apparent degree of neutralization α' for PAA system.

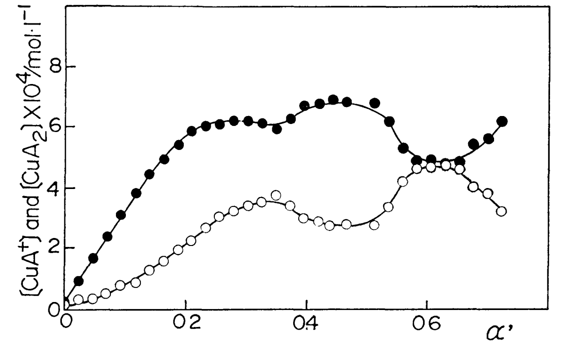

Fig. 2. Dependence of the concentrations of monocarboxylato and dicarboxylato copper(II) complexes, $[CuA^+]$ (○) and $[CuA_2]$ (●), on the apparent degree of neutralization α' for PMA system.

It is very interesting that maxima are obtained in the potentiometric measurements. In most studies[6,7,9,10] of spectrophotometric measurement it has been observed that the absorbance due to the copper(II) complex with carboxylato groups increases and passes through a maximum with increase in the degree of neutralization, and that the value of the degree of neutralization at the maximum of the absorption is about 0.3 to 0.4 for systems composed of similar concentration ratios. In the study of Mandel and Leyte,[7] it is shown that the disagreement between the spectrophotometric and the potentiometric results appears in the region of higher degree of neutralization. In such a neutralization region, the absorbance due to the complex formation begins to decrease, whereas the formation curve by potentiometry shows constant or increasing values. In the present study, however, the variations of $[CuA^+]$ and $[CuA_2]$ against the degree of neutralization show a decreasing tendency; this fact is similar to the spectrophotometric results. Therefore, potentiometric data also show that the monocarboxylato and dicarboxylato copper(II) complexes are partially broken or change in favor of some other form of binding with increase in the degree of neutralization. Since the concentration of hydroxide ions as ligands increases in the high neutralization region, some carboxylato ligands may be released and the concentrations of the complexes may decrease.

In Fig. 2, where the copper(II)–PMA system is treated, two maxima are observed. The maximum in the region of lower neutralization may be due to the conformational transition of PMA which appears in the course of potentiometric titration. Here, it is interesting that the value of the degree of neutralization at the maximum agrees with that found by the spectrophotometric measurement of the similar conditions. But it is not clear whether this maximum came from the reference plot method or the figure actually reflects the fact.

In Figs. 1 and 2, moreover, in the region of higher degree of neutralization the concentrations of dicarboxylato complex show an increasing tendency again. In such a region, the concentrations of nonchelating carboxylato groups are very high, whereas the concentrations of free bivalent metal ions are negligibly low; such an equilibrium is difficult to treat precisely. On the other hand, the estimation of the concentration of nonchelating carboxylato groups by Mandel's reference plot method may become inapplicable because of the higher charge density on the polyions. Thus, a precise discussion is impossible in the region of such a degree of neutralization.

Stability and Equilibrium Constants of Complexes. The stability and equilibrium constants of the copper(II) complex with PAA calculated from the concentrations of the complexes obtained by the above mentioned method are shown in Table 1.

TABLE 1. STABILITY AND EQUILIBRIUM CONSTANTS OF Cu(II)-PAA COMPLEXES

α'	β_1	β_2	B_2	B_2'
0.00	9.3×10^{1}	3.8×10^{5}	6.5×10^{-4}	1.3×10^{-5}
0.05	2.0×10^{2}	3.7×10^{5}	5.1×10^{-4}	9.9×10^{-6}
0.10	1.9×10^{2}	7.2×10^{5}	7.8×10^{-4}	1.4×10^{-5}
0.15	3.0×10^{2}	9.5×10^{5}	9.5×10^{-4}	1.5×10^{-5}
0.20	4.1×10^{2}	1.4×10^{6}	1.4×10^{-3}	1.8×10^{-5}
0.25	8.2×10^{2}	2.0×10^{6}	1.3×10^{-3}	1.9×10^{-5}
0.30	1.3×10^{3}	2.8×10^{6}	1.3×10^{-3}	1.8×10^{-5}
0.35	2.5×10^{3}	3.7×10^{6}	1.1×10^{-3}	1.6×10^{-5}
0.40	4.4×10^{3}	4.7×10^{6}	9.6×10^{-4}	1.2×10^{-5}
0.45	7.3×10^{3}	5.9×10^{6}	7.9×10^{-4}	8.3×10^{-6}
0.50	1.1×10^{4}	8.0×10^{6}	7.2×10^{-4}	7.4×10^{-6}
0.55	1.5×10^{4}	1.2×10^{7}	6.7×10^{-4}	6.7×10^{-6}
0.60	1.7×10^{4}	1.7×10^{7}	6.6×10^{-4}	5.2×10^{-6}
0.65	9.7×10^{3}	2.5×10^{7}	7.0×10^{-4}	4.8×10^{-6}
0.70	3.5×10^{3}	4.0×10^{7}	7.3×10^{-4}	4.3×10^{-6}

The parameters β_1, β_2, B_2, and B_2' in the table will be discussed in some detail. When the concentration of nonchelating carboxylato groups is estimated, the effect of the change in the electrostatic potential on the polyion is considered in the reference plot method. The stability constants of the momocarboxylato and dicarboxylato complexes, β_1 and β_2, apparently vary with increase in the degree of neutralization. In the estimation of such a constant of polymer systems, therefore, it seems that the variation of the charge density on the polyion must be taken into account, as is shown in the series of these constants.

Then, consider the following equilibrium equation and constant:

$$\mathrm{Cu^{2+}} + 2\mathrm{HA} \rightleftharpoons \mathrm{CuA_2} + 2\mathrm{H^+},\quad B_2 = \frac{[\mathrm{CuA_2}][\mathrm{H^+}]^2}{[\mathrm{Cu^{2+}}][\mathrm{HA}]^2}.$$

Since the complex formation on the polyion is described as an exchange of copper(II) ion with two hydrogen ions, the total charge on the polyion remains unchanged by the chelate formation. Then, the B_2 without the effect of the change in the charge density may be constant. As is shown in Table 1, the sufficiently constant values of B_2 were not obtained.

TABLE 2. STABILITY AND EQUILIBRIUM CONSTANTS OF Cu(II)-PMA COMPLEXES

α'	β_1	β_2	B_2	B_2'
0.00	1.0×10^{1}	4.9×10^{5}	4.8×10^{-5}	1.0×10^{-6}
0.05	1.9×10^{2}	1.6×10^{6}	1.1×10^{-4}	2.2×10^{-6}
0.10	2.9×10^{2}	2.6×10^{6}	1.3×10^{-4}	2.5×10^{-6}
0.15	6.4×10^{2}	3.3×10^{6}	1.2×10^{-4}	2.5×10^{-6}
0.20	1.2×10^{3}	4.0×10^{6}	1.0×10^{-4}	1.6×10^{-6}
0.25	3.4×10^{3}	5.3×10^{6}	8.3×10^{-5}	1.3×10^{-6}
0.30	8.0×10^{3}	9.3×10^{6}	6.6×10^{-5}	9.5×10^{-7}
0.35	1.5×10^{4}	1.2×10^{6}	5.5×10^{-5}	7.3×10^{-7}
0.40	1.8×10^{4}	1.6×10^{7}	5.4×10^{-5}	7.0×10^{-7}
0.45	2.1×10^{4}	1.8×10^{7}	5.3×10^{-5}	6.0×10^{-7}
0.50	2.4×10^{4}	1.8×10^{7}	5.0×10^{-5}	4.8×10^{-7}
0.55	4.0×10^{4}	1.5×10^{7}	4.0×10^{-5}	3.3×10^{-7}
0.60	6.0×10^{4}	1.3×10^{7}	3.2×10^{-5}	2.8×10^{-7}
0.65	7.5×10^{4}	1.5×10^{7}	1.8×10^{-5}	1.8×10^{-7}
0.70	7.3×10^{4}	2.2×10^{7}	2.8×10^{-5}	1.7×10^{-7}

On the other hand, the following equilibrium equation and constant have been proposed by Wall and Gill:[11)]

$$\mathrm{Cu^{2+}} + \mathrm{H_2A_2} \rightleftharpoons \mathrm{CuA_2} + 2\mathrm{H^+},\quad B_2' = \frac{[\mathrm{CuA_2}][\mathrm{H^+}]^2}{[\mathrm{Cu^{2+}}][\mathrm{H_2A_2}]}.$$

The results by this scheme with the relation of $[\mathrm{H_2A_2}] = 1/2[\mathrm{HA}]$ are shown in Table 1, and the values of B_2' still failed to be constant.

In all ways of evaluating the constants, no constant values independent of the degree of neutralization were obtained, but orders of magnitude of the constants may be estimated as 10^6 for β_2 and 10^{-3} for B_2 in the copper(II)-PAA system.

In Table 2, the results with the copper(II)-PMA system obtained by the same scheme of estimation are shown. Since the values of the stability and equilibrium constants of the copper(II) complex with PMA vary over a wider range, it is rather difficult to determine the order of magnitude of these constants, and the values are roughly 10^{-5} for B_2.

Comparing the values of these constants and their dependence on the degree of neutralization, it is seen that the PAA complex is relatively more stable than the PMA complex. But it is also suggested that the effect of the charge density on the polyion is not the only predominant factor in such a complicated complex formation as polyelectrolytes, and the conformational transition must be considered not only by acid dis-

TABLE 3. COMPARISON OF STABILITY AND EQUILIBRIUM CONSTANTS WITH VALUES OBTAINED BY SOME AUTHORS

	$[\mathrm{A_t}]$	$[\mathrm{Cu_t}]$	μ	Constant	Ref.
Cu(II)-PAA	1×10^{-2}	1×10^{-3}	$0.1(\mathrm{KNO_3})$	$B_2=7\times10^{-4}$	by present analysis
	1×10^{-2}	1×10^{-3}	$0.2(\mathrm{NaNO_3})$	$B_2=4.6\times10^{-3}$	2
	2.5×10^{-3}	2×10^{-4}	$0.25(\mathrm{NaNO_3})$	$B_2=1.5\times10^{-4}$	12
	2×10^{-3}	2×10^{-4}	$0.1(\mathrm{NaNO_3})$	$B_2=4\times10^{-2}$	13
Cu(II)-PMA	1×10^{-2}	1×10^{-3}	$0.1(\mathrm{KNO_3})$	$B_2\simeq10^{-4}$	by present analysis
	2×10^{-2}	2×10^{-3}	$0.1(\mathrm{NaNO_3})$	$B_2=2.5\times10^{-4}$	3
	5.5×10^{-3}	4.4×10^{-4}	$0.1(\mathrm{NaNO_3})$	$B_2=2.5\times10^{-4}$	14

sociation but also by chelation and the other steric factors.

In Table 3, the stability and equilibrium constants reported previously and estimated by the present analysis are summarized. Although it is meaningless to compare the absolute values of these constants, as was stated above, the agreement of the order of magnitude of these constants is apparent.

Thus, the conclusion is as follows. The stability and equilibrium constants of the copper(II) complexes with PAA and PMA (apparently) change with increase in the degree of neutralization; the order of magnitude of these constants can be estimated; and the B_2 values of the dicarboxylato copper(II) complex are of the order 10^{-3} for PAA and 10^{-4} for PMA, respectively.

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