Study of Metal–Polycarboxylate Complexes Employing Ion-Selective Electrodes. Cu(II) and Cd(II) Complexes with Poly(acrylic acid) and Poly(itaconic acid)

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The complex formation of bivalent metal ions, Cu(II) and Cd(II), with poly(acrylic acid) and poly(itaconic acid) in aqueous solutions was studied by pH titration at 25 °C and at an ionic strength of 0.1, and at the same time the concentration of free metal ions was measured using ion-selective electrodes. In order to calculate the equilibrium constants of metal–polycarboxylate complex formation, a modified Gregor method is proposed and a more reasonable method for the determination of the formation constants of the complexes is also presented. The equilibrium constant of the metal–polycarboxylate complex formation involving two carboxylate groups was calculated from this method. The value for the Cu(II)–poly(itaconic acid) complex formation was $10^{-2.9}$, and was constant in the lower neutralization region. But constant values for the Cd(II) complexes were not obtained over the entire neutralization range.

In order to calculate the stability constants or the equilibrium constants of the complex formation of bivalent metal ions with polyelectrolytes by pH titration, the modified Bjerrum[1] method has been established by Gregor and co-workers,[2] and the reference plot method has been proposed by Mandel and Leyte.[3] In the scheme of Gregor and that of Mandel and Leyte, several hypotheses had to be taken into account, since the concentrations of ionic species for equilibrium in the complex formation cannot be determined at each stage of neutralization using only the equation of stoichiometric material balance.

Recently, ion-selective electrodes which are responsive to specific ions have been available for the investigation of ion activity. Rechnitz[4,5] has shown that the complex formation constants of Cu(II) with low molecular organic acids can be easily and precisely estimated using these electrodes.

In the present study, the equilibrium constants of metal–polycarboxylate complex formations were investigated using the pH titration method using ion-selective electrodes, and the data obtained were analyzed by the newly-proposed method.

Experimental

Material. The poly(itaconic acid)(PIA) sample used was material prepared by Dr. Muto[6] of this laboratory, and its molecular weight was estimated to be about 10^5. The sodium polyacrylate(PAA-Na) obtained commercially was manufactured by the Kishida Chem. Co. The acid form PAA solution was obtained from an aqueous solution of PAA-Na with the addition of hydrochloric acid and was purified by dialysis using cellophane tubing. Its molecular weight was estimated to be 7.6×10^5 by viscometric measurement. These solutions of polyacids were standardized by pH titration and stored in polyethylene containers at 5 °C.

All the chemicals used were of guaranteed reagent grade. The concentrations of the stock solutions of the bivalent metal ion salts, $Cu(NO_3)_2$ and $Cd(NO_3)_2$, were determined by the spectrophotometric chelatometric titration method. A carbonate-free NaOH solution was used as the titrant. The aqueous solutions were prepared using deionized water.

Potentiometric Titration. The pH measurements were carried out using a Yokogawa Model KPH-51A pH meter equipped with Toadenpa Model HG-4005 glass and HC-2005 calomel electrodes, and also with a Denkikagakukeiki Model HG-2 Digital pH meter equipped with Denkikagakukeiki Model MC-511 glass and Horiba Model 2050-05T calomel electrodes connected by a saturated KNO_3-agar salt bridge.

The concentrations of bivalent metal ions were measured with the pH meter equipped either with a Beckman Model 39612 cupric electrode or with a Toadenpa Model CD-125 cadmium electrode.

The titration, namely the measurements of the pH and the concentrations of the bivalent metal ions were carried out in a titration vessel with a water jacket maintained at 25.0 ± 0.05 °C in a nitrogen atmosphere.

Results and Discussion

Potentiometry Using Cu(II) and Cd(II) Ion-Selective Electrodes. The response of the cupric or cadmium electrode, the emf of the cell, was plotted linearly against the logarithm of the concentration for each ion and the corresponding slopes were 30.5 mV and 28.0 mV, respectively, in the concentration range from 10^{-6} to 10^{-2} mol/l at an ionic strength of 0.1 (KNO_3). These values of the slopes are very near to those expected from the Nernstian equation, and, according to their high reproducibility, the measurement of the concentrations of the ions was carried out with calibration at two points. The effect of pH on the response of the metal ions has to be taken into account because metal hydroxides are formed at values of pH more than 6. In the present work, however, the concentrations of the metal ions are much lower than those of the polyacids, therefore, all metal ions exist essentially as chelates in the pH region where the metal hydroxides are formed in the absence of chelating agents. It was shown by Rechnitz[4,5] that the activity measurement of the metal ion by the ion-selective electrode yields a reliable estimation of formation constants for a number of soluble copper complexes. In other words, the value of the electrode response is only due to the free metal ions, and their results suggest that metal ion chelates with polyacids have no effect on the response of the electrodes. Consequently, the activity values obtained for the present measurements were used without any special correction, except that of the activity coefficient of the concentrations.

Theory and Method of Calculation of the Equilibrium Constants of Complexation. Gregor and co-workers[2] have shown that the method of Bjerrum[1] for the evaluation of formation constants of metal complexes

may be adopted to elucidate the specific characteristics of polyelectrolytes.

By defining a reaction which does not cause any change in the charge of the polyacid, an equilibrium constant which can be expected to be independent of the charge on the polyacid was used by Gregor. Thus, the equilibrium exchange reaction between a proton and a metal ion is described as the equilibrium of the complex formation reaction.

A modification by Gregor of the calculation of the average coordination number $\bar{n}$ is as follows. Consider a solution in which the total acid concentration (dissociated, undissociated and chelated) is $[A_t]$ and the metal ion concentration is $[M_t]$. Using HA and A^- to designate a carboxylic group and a nonchelating carboxylate groups, respectively, $\bar{n}$ is given as follows:

$$\bar{n} = \frac{[A_t]-[HA]-[A^-]}{[M_t]}$$

Thus, if a relationship between $\bar{n}$ and $p([H^+]/[HA])$ can be obtained, the values of log B_2 is determined by the following equation:

$$p\left(\frac{[HA]}{[H^+]}\right)_{\bar{n}=1} = \frac{1}{2}\log\left(\frac{[MA_2][H^+]^2[M^{2+}]}{[M^{2+}][HA]^2[MA_2]}\right)_{\bar{n}=1}$$

$$= \frac{1}{2}\log B_2, \quad B_2 = \frac{[MA_2][H^+]^2}{[M^{2+}][HA]^2}$$

where $[M^{2+}]/[MA_2]$ is equal to 1 at $\bar{n}=1$. But for any $\bar{n}$, the values of $[M^{2+}]/[MA_2]$ cannot be estimated, because there is, in general, no direct method for separately determining the values of $[M^{2+}]$ or $[MA_2]$.

Furthermore, in the case of polyacids, there is a difficulty in the determination of $[A^-]$. In order to estimate $[A^-]$, Mandel and Leyte[3] have devised the reference plot method instead of that of Gregor. The essential assumption of Mandel is based on the idea that in the Henderson-Hasselbach equation the α-dependent part of pK is only a function of the charge density on the polyacid. Thus,

$$pK = G + \zeta_\alpha$$

where G is a constant and ζ_α a function depending on α. Further,

$$p\left(\frac{[H^+]}{[HA]}\right) = G - p[A^-] + \zeta_\alpha.$$

On the basis of this equation Mandel and Leyte have suggested the reference plot method. A relationship between $p([H^+]/[HA])$ and $p[A^-]$ without metal ions is first plotted on a graph, and then, assuming that the metal ions added have no influence on this relationship, the values of $[A^-]$ can be obtained on the graph from the values of $p([H^+]/[HA])$ which can always be calculated.

In the present study, on the other hand, in addition to the pH values, the concentrations of free metal ions $[M^{2+}]$ can be determined simultaneously using ion-selective electrodes. Then, considering the relationship between the total metal ion concentration $[M_t]$ and the concentration of free metal ions $[M^{2+}]$, it can be easily seen that the difference between these two values is equal to the concentration of the truly complexed metal ions. Now, it is proposed that a real average coordination number $\bar{n}_r$ is introduced instead of $\bar{n}$ of Gregor (or Bjerrum), from which it can be shown how to calculate the equilibrium constant of the exchange reaction between protons and metal ions. The $\bar{n}_r$ is defined by the following equation:

$$\bar{n}_r = \frac{[A_t]-[HA]-[A^-]}{[M_t]-[M^{2+}]}$$

In contrast to the $\bar{n}$ of Gregor's method, $[M^{2+}]$ appears in the denominator of $\bar{n}_r$, and hence $\bar{n}_r$ is the average coordination number of the metal ions which are complexed with polyacids. Unfortunately, however, even when the value of $[M^{2+}]$ can be determined by the ion-selective electrode, the stoichiometric calculation of $[A^-]$ without any assumptions encounters difficulty. In the present study, the value of $[A^-]$

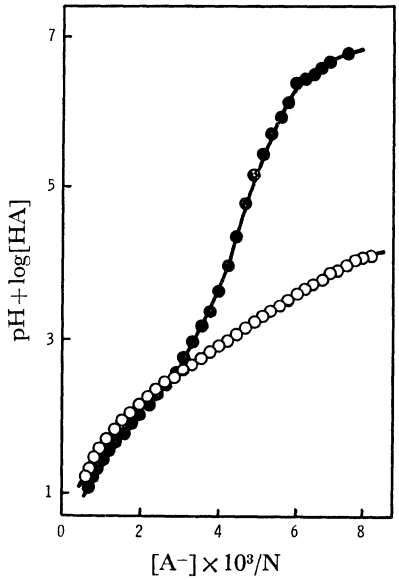

Fig. 1. The reference plots of 9.87×10^{-3} monomol/l PAA (○) and 4.75×10^{-3} monomol/l PIA ($=9.50\times10^{-3}$ N as carboxylic groups)(●) in 0.1 mol/l KNO_3.

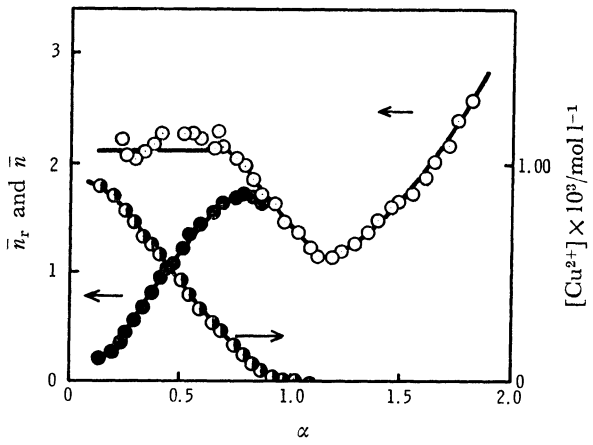

Fig. 2. The formation curves and the concentrations of Cu^{2+} at 4.75×10^{-3} monomol/l PIA and 1.09×10^{-3} mol/l $Cu(NO_3)_2$ in 0.1 mol/l KNO_3. ○: $\bar{n}_r$ by our method, ●: $\bar{n}$ by Gregor's method, and ◑: the concentration of Cu^{2+}.

is estimated by the reference plot method (Fig. 1).

In Fig. 2, not only $\bar{n}_r$ for Cu(II)-PIA, but also $\bar{n}$ and the concentrations of free Cu(II) ions [Cu^{2+}], are plotted against the degree of neutralization α. Comparing the $\bar{n}_r$ with $\bar{n}$, these average coordination numbers agree with each other at the point of zero [M^{2+}]. Consider a system where half of the [M_t] involves two ligands and the other half are free from complexation. Then, $\bar{n}$ is equal to 1, but $\bar{n}_r$ is 2. It is clear that the real coordination number of the metal ion is, in this case, two. This fact shows that $\bar{n}_r$ is more useful than $\bar{n}$. From $\bar{n}$ in Fig. 2, it can only be seen that some complexes whose "true" average coordination numbers are unknown are formed. On the other hand, from $\bar{n}_r$ the "true" average coordination number, and moreover, from the denominator of $\bar{n}_r$, the concentration of the complexes formed can be determined. As is shown in Fig. 2, at the low value of α, $\bar{n}_r$ shows clearly that the complex formed involves two carboxylate groups as ligands. Their equilibrium can be described by the following equation:

$$M^{2+} + 2HA \rightleftharpoons MA_2 + 2H^+;\ B_2 = \frac{[MA_2][H^+]^2}{[M^{2+}][HA]^2}$$

Then, in the region of α where the $\bar{n}_r$ is constant and equal to 2, the equilibrium constant B_2 can be stoichiometrically calculated with the assumption that only complexes involving two carboxylate groups are formed. In such a region of α, all the calculated values of log B_2 are constant, and are equal to -2.9. In comparison with the fact that the apparent acid-dissociation constants for polyacids are not constant, this result is interesting from the view point of chelation in polymeric systems.

Formation Curves and Stability of Complexes. In Figs. 3—5, the formation curves obtained using the present method for the Cd(II)–PIA, Cu(II)–PAA, and Cd(II)–PAA systems are shown. These curves are obtained under approximately the same conditions, and the concentration of polyacids is represented in the following way. Considering that all the carboxylic groups on the PAA and PIA chains are equivalent, concentrations of these groups are expressed in molarity,

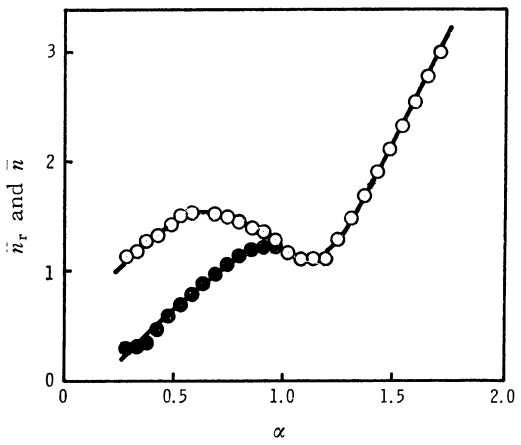

Fig. 3. The formation curves at 4.75×10^{-3} monomol/l PIA and 9.88×10^{-4} mol/l $Cd(NO_3)_2$ in 0.1 mol/l KNO_3. ○: $\bar{n}_r$ and ●: $\bar{n}$.

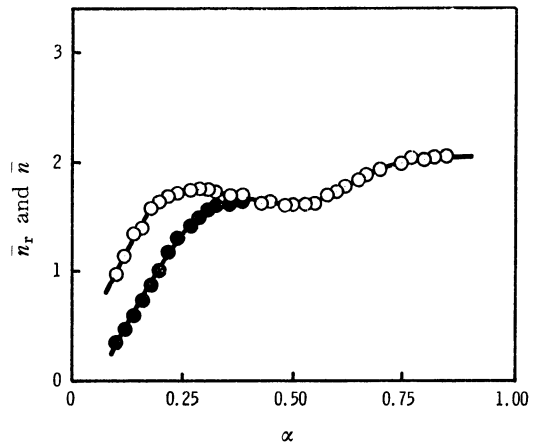

Fig. 4. The formation curves at 9.87×10^{-3} monomol/l PAA and 1.05×10^{-3} mol/l $Cu(NO_3)_2$ in 0.1 mol/l KNO_3. ○: $\bar{n}_r$ and ●: $\bar{n}$.

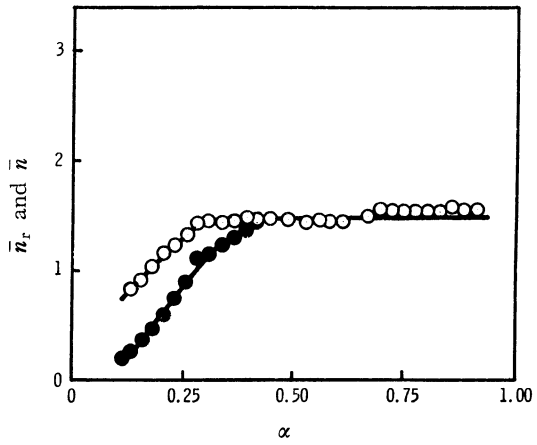

Fig. 5. The formation curves at 9.87×10^{-3} monomol/l PAA and 9.88×10^{-4} mol/l $Cd(NO_3)_2$ in 0.1 mol/l KNO_3. ○: $\bar{n}_r$ and ●: $\bar{n}$.

and hence the concentration of monomer units of PIA is equal to one half of the value of the present concentration of carboxylic groups.

From Fig. 3, it may be seen that no stable Cd(II)–PIA complex involving two carboxylate groups is formed, in contrast to the Cu(II)–PIA complex, and no constant value of log B_2 is obtained. Furthermore, for PIA complexes, Figs. 2 and 3 demonstrate that $\bar{n}_r$ begins to decrease at $\alpha=0.7$ and that for an increase in α, $\bar{n}_r$ increases passing through a minimum.

Figures 4 and 5 show $\bar{n}_r$ plots of PAA complexes of Cu(II) and Cd(II), which are similar in shape to those for $\bar{n}$ found by other workers, except that $\bar{n}_r$ begins from the value of 1. In spite of the existence of a flat region of $\bar{n}_r$ for the Cd(II)–PAA system, no constant value of log B_2 is obtained. For the Cu(II)–PAA system, there is a region $\bar{n}_r$ is equal to 2, but in this region no measurable free Cu(II) ions were present in the system, and therefore, a calculation of the equilibrium constant B_2 is impossible.

It is an interesting result that the stable Cu(II)–PIA complexes involving two carboxylate groups are formed but that no stable Cd(II)–PIA complexes are formed

at low values of α.

This fact can be explained by the fact that PIA is a polymer of dicarboxylic acid. Muto[6] has interpreted the specific counterion binding of alkali metal ions by taking into account the formation of a ring structure involving cooperative hydrogen bonding by two carboxylate groups. Now, we consider that the ring structure reacts with a free bivalent metal ion. If this bivalent ion must break this structure before forming the complex by entering between these two carboxylate groups and replacing a hydrogen ion. The difference in $\bar{n}_r$ between Cu(II)–PIA and Cd(II)–PIA in the region of α below 0.7 may be due to the difference of this ring-breaking ability for the Cu(II) and Cd(II) ions. This concept of hydrogen-bonded ring structure, however, seems not to be necessary, if we attribute the difference in the complexing ability of the Cu(II) and Cd(II) ions, irrespective of the structure of ligand groups.

The curves of $\bar{n}_r$ (and, of course, of $\bar{n}$) of PIA complexes in the region of α above 0.7 show strange behavior that the values of $\bar{n}_r$ increase more and more after a minimum has been reached. This tendency of the curves of the degree of binding for alkali metal ions was also shown by Muto. Therefore, this tendency need not result only from complex formation by bivalent metal ions. In connection with this fact several reasons are presented, for example, conformation change, the formation of metal hydroxides, and/or the formation of more complicated complexes, *etc.* It must be pointed out here that the method of calculation of $\bar{n}_r$ is more important. Thus, in the calculation of $\bar{n}_r$ (or of $\bar{n}$), the primary carboxylic groups are regarded as equivalent to secondary groups in the PIA monomer units and the concentrations of free carboxylate groups are estimated from the reference plot. Therefore, $\bar{n}_r$ shows some deviation due to uncertainty around the first neutralization step.

Calculating the formation constants by the present method, only the result of Cu(II)–PIA was obtained over a wide range of α, but other complexes, for example, Cd(II)–PAA, in spite of the existence of a flat region of $\bar{n}_r$, no constant value of the equilibrium constant is obtained for each value of α. In connection with this fact, in spite of taking into account 1–1 complex formation, the test was not successful. Some reasons may be given, such as unevaluated errors in the potentiometric measurements or the uncertainty in the estimation of the concentration of each ion which participates in the complex formation equilibrium (for example, employing the Mandel reference plot). In some cases, however, a series of values of equilibrium constants which vary monotonously with α has been obtained. This behavior as a function of the difference in the stability of the complexes is as follows. If the complexes formed, whose ligands are two carboxylate groups in a monomer unit, are very stable, the equilibrium of complex formation may not be influenced by, for example, the change of the polymer conformation, and this is the case of the Cu(II)–PIA system. On the other hand, when the complexes are not as stable, the equilibrium constants for complex formation must be influenced, if the conformation of the polymer chain is changed with α. Thus, it can be seen that the Cu(II)–PIA complexes involving two carboxylate groups in the low pH region are more stable than others and that both Cd(II) complexes with PAA and PIA are not so stable. These results are summarized in Table 1.

TABLE 1. $\log B_1$ AND $\log B_2$ VALUES OBTAINED FROM OUR METHOD IN Figs. 3—5

	Cu^{2+}	Cd^{2+}	
PAA complexes			
$\log B_1$	—	—	$(\bar{n}_r=1.5)$
$\log B_2$	-3.4 $(0.55<\alpha)$	—	$(\bar{n}_r=1.5)$
PIA complexes			
$\log B_1$	—	—	
$\log B_2$	-2.9 $(\alpha<0.66)$	—	

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