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Study of Metal–Polycarboxylate Complexes Employing Ion-selective Electrodes. III. Complex Formation between Maleic Acid Copolymers and Bivalent Transition Metal Ions

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The complex formation of bivalent transition metal ions, Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), with copoly(maleic acid–ethylene) and copoly(maleic acid–styrene) in aqueous solution was studied by potentiometric titration at 25 °C and the ionic strength of 0.1. The systems containing copper(II) ions were investigated by potentiometry employing the copper(II) ion-selective electrode. The titration curves of the bivalent metal–copoly(maleic acid–ethylene) systems were situated in a lower pH region than in the absence of the metal ions. The complex formed involves two carboxylate groups: primary and secondary. The equilibrium constant of the copper(II) complex was estimated to be $10^{-2.6}$. In copoly(maleic acid–styrene) systems, however, the titration curves in the absence and presence of bivalent metal ions overlapped partly in the first neutralization step. From the potentiometric results employing the ion-selective electrode, it was observed that the concentrations of copper(II) ions decrease slightly in the region of overlap. This anomalous behavior is due to the acid dissociation influenced by the conformational transition, including the effect of the side groups of the polymers.

The study of solution properties of the aqueous polyelectrolytes containing various counterions has been well established, especially in the cases of poly(acrylic acid) and poly(methacrylic acid), from the viewpoints of the counterion binding and the conformational transition of polyelectrolytes. Since the various hydrophobic residues of maleic acid copolymers can be relatively easily introduced in polymer chains as comonomers, they are of interest in connection with the short range interaction of the side groups and have been extensively studied.

In addition, the succinic acid residues derived from maleic anhydride units are also of interest as a polymeric ligand consisting of carboxyl pairs, because the acid dissociation constants of these carboxyl groups are found to be quite different. The interaction and complex formation with metal ions, especially with bivalent ones, are important and have been studied by some workers.[1–5)]

In our previous papers,[6,7)] the systems consisting of copper(II) ions and poly(itaconic acid), whose monomer unit has two carboxyl groups, have been studied by potentiometric titration employing the copper(II) ion-selective electrode. It was concluded that bis(carboxylato)copper(II) complexes are formed and that one of chelating carboxylate groups is the secondary carboxyl group, even in the first neutralization step. In a recent paper,[8)] the systems of maleic acid–styrene copolymer were studied and the anomalous overlap of the titration curves in the absence and presence of the bivalent metal ions was observed.

In the present paper, the overlap in maleic acid–styrene copolymer systems was investigated by potentiometry employing an ion-selective electrode, and the maleic acid–ethylene copolymer, in which the hydrophobic side groups are absent, was studied for comparison.

Experimental

Materials. Copoly(maleic acid–ethylene), MAEt, was obtained by hydrolysis of the alternating 1 : 1 copolymer of maleic anhydride with ethylene; this was Monsanto Chemical Co.'s Grade 31. Its characterization was outlined in Technical Bulletin I-261 of the company.

Copoly(maleicanhydride–styrene) was prepared and reprecipitated by the procedures of Ohno and coworkers,[9)] and the copolymer was hydrolyzed to obtain copoly(maleic acid–styrene), MASt, in water at 60 °C for 24 h. The aqueous solution of MASt was purified by dialysis using cellophane tubing. The 1 : 1 composition of comonomers was confirmed by elemental analysis, and the molecular weight was found to be 10^5 by viscometry.[9)]

The other chemicals and bivalent metal nitrate salts used were guaranteed reagent grade.

Potentiometric Titration. The pH measurements were performed by use of a Yokogawa Model KPH-51A pH meter equipped with Toadenpa Model HG-4005 galss and Model HC-2005 calomel electrodes. The titrations were carried out with about 0.1 mol/l aqueous solution of carbonate-free NaOH at 25±0.05 °C and ionic strength of 0.1(KNO_3) under nitrogen atmosphere.

The activity measurements of free copper(II) ions were carried out by use of an Orion Model 801A digital ion meter equipped with Beckman Model 39612 Cupric and Horiba Model 2010-05T calomel electrodes. The corrections and determination of the concentrations of copper(II) ions were carried out with the calibration curve obtained by potentiometric measurements of the systems free from polymeric ligands.

Each system measured consists of about 5×10^{-3} monomol/l polyacid, 1×10^{-1} mol/l KNO_3, and about 1×10^{-3} mol/l bivalent metal ions.

All the potentiometric measurements were operated in the pH region less than 6.00 because of the precision of pH titration of this weak polyacid and the formation of bivalent metal hydroxides.

Results and Discussion

Titration Behaviors of Copolymers without Complexing Metal Ions. The apparent dissociation constant $pK_{1,app}$ of the primary carboxyl groups is given as

$$pK_{1,app} = pH - \log \alpha_1/(1-\alpha_1),$$

where α_1 is the degree of dissociation of the primary carboxyl groups. The α_1 dependences of $pK_{1,app}$ of MAEt and MASt are shown in Fig. 1. The shapes

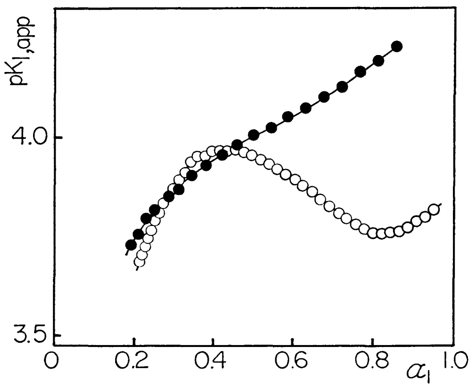

Fig. 1. Apparent dissociation constant, $pK_{1,app}$, as a function of α_1 for MAEt and MASt at the ionic strength of 0.1(KNO_3): (●) MAEt(0.00498 monomol/l); (○) MASt(0.00432 monomol/l).

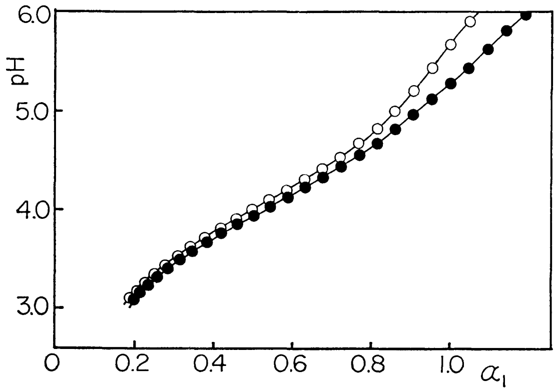

Fig. 2. Titration curves of MAEt(0.00498 monomol/l) in (○) the absence and (●) the presence of zinc(II) ions(1×10^{-3} mol/l $Zn(NO_3)_2$) at the ionic strength of 0.1(KNO_3).

of these curves are similar to those of the same samples observed by some other authors,[9,10] and small dis crepancies of $pK_{1,app}$ values may correspond to the difference of concentrations of neutral salts added.

The values of $pK_{1,app}$ of MAEt are linearly dependent on α_1, which shows that the acid dissociation is influenced only by the change of charge density on polyions and that interaction of side groups is absent, as can be concluded from its chemical structure. And the fact that the slope of the $pK_{1,app}$ curve is smaller than that of other homopolymers confirms the dependence on charge density.

In the case of MASt, an anomalous dependence of $pK_{1,app}$ on α_1, the so-called pH-induced conformational transition, is observed. This anomaly was discussed in detail by Ohno and coworkers,[9,11,12] who interpret this anomalous behavior as due to the conformational transition from the compact form, which is stabilized by the hydrophobic interaction between the phenyl groups, to the extended coil form of the copolymer chain. This interpretation is probably reasonable, but it is strange that the decrease of $pK_{1,app}$ with increasing in α_1 is apparently observed in the range from 0.4 to 0.8. This behavior is also observed in the case of poly(methacrylic acid). Such a tendency implies that there occurs some promotion of dissociation with α_1, which is generally improbable. In this dissociation range, the fact that the polymer chain extends suddenly was observed in the viscometric data by Ohno. In such a case, the hydrophobic interaction may decrease, and the local effective dielectric constant may vary; its effect may be reflected in the decrease of the acid dissociation constant, although this point must be confirmed by other experiments.

Titration Behaviors of Systems Containing Bivalent Metal Ions. The titration curves of MAEt in the absence and presence of zinc(II) ions are shown in Fig. 2; the cases of the other bivalent metal ions are similar to this. When complex formation occurs, it is generally observed that the titration curves in the presence of transition metal ions are situated in a lower pH region than in the case of such simple salts as the alkali metal salts. It can be seen from Fig. 2 that a complex is formed between the carboxylate groups of MAEt and zinc(II) ions. In the cases of the other metal ions, the same result was obtained.

Furthermore, the first equivalence point of the titration curve in the presence of the metal ions is observed a little beyond 1.0 of α_1. As is discussed in the previous papers,[7,8] the point at $\alpha_1=1$ corresponds to the end of the titration of the primary carboxyl groups. It is considered that the deviation of the equivalence point from $\alpha_1=1.0$ results from the complex formation including the secondary carboxyl groups.

Thus, it can be concluded that the complex formed involves two carboxylate groups in the same succinic unit : one is a primary carboxylate group and the other a secondary one, even in the first neutralization step; this conclusion agrees with those of Felber[2,3] and Delben.[4,5]

The titration curves of MASt in the absence and presence of zinc(II) ions are shown in Fig. 3. The curves for the other metal ions are similar to this figure, except those of copper(II) ions. Around at $\alpha_1=1.0$, behaviors like those of MAEt systems are observed: there is an apparent shift of the first equivalence point. Thus it can be concluded that bis(carboxylato)zinc(II) complexes which have both the primary and secondary

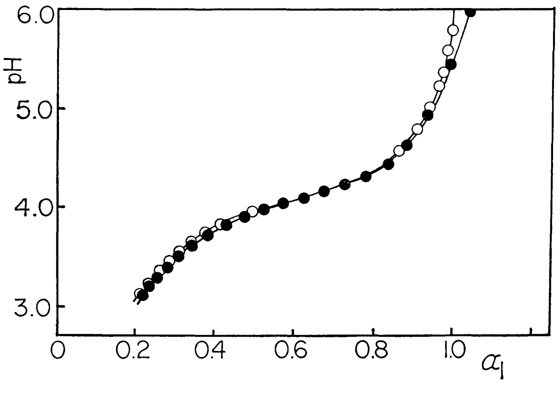

Fig. 3. Titration curves of MASt(0.00432 monomol/l) in (○) the absence and (●) the presence of zinc(II) ions (1×10^{-3} mol/l $Zn(NO_3)_2$) at the ionic strength of 0.1(KNO_3).

carboxylate groups are formed.

In the neighborhood of $\alpha_1=0.7$, a behavior quite different from the case of MAEt is observed; this is shown in Fig. 3. In this region of α_1, the titration curves of MASt in the absence and presence of the metal ions overlap partly, which suggests that the carboxylate groups are released from the metal ions by some effect. However, it is well known that the carboxylate groups produce relatively stable complexes with bivalent transition metal ions. In order to elucidate this point, the results of potentiometry employing the ion-selective electrode were examined.

Titrations Employing a Copper(II) Ion-selective Electrode. Since there is some complexity in the response of this electrode,[6,13] the reproducibility and stability of the response were confirmed again in the present study by measurements of the solutions containing copper(II) ions of known concentrations under similar conditions without the added copolymer.

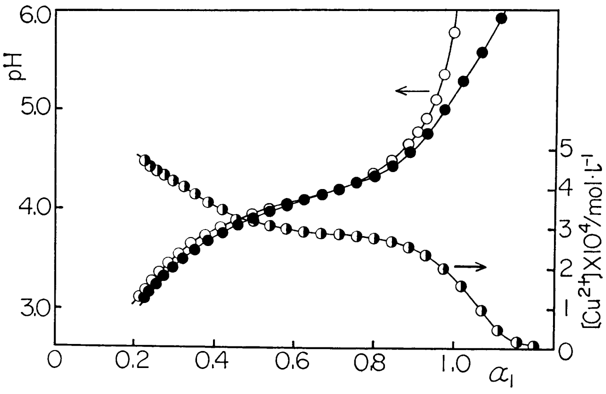

Fig. 5. Dependence of concentration of free copper(II) ions on α_1 (◑), and titration curves of MASt (0.00432 monomol/l) in (○) the absence and (●) the presence of copper(II) ions (5×10^{-4} mol/l $Cu(NO_3)_2$) at the ionic strength of $0.1(KNO_3)$.

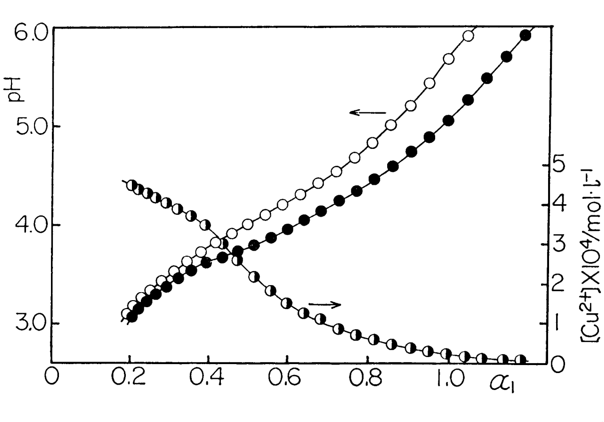

Fig. 4. Dependence of concentration of free copper(II) ions on α_1 (◑), and titration curves of MAEt (0.00498 monomol/l) in (○) the absence and (●) the presence of copper(II) ions (5×10^{-4} mol/l $Cu(NO_3)_2$) at the ionic strength of $0.1(KNO_3)$.

In Fig. 4, the titration curves of MAEt in the absence and presence of copper(II) ions and the dependence of the concentrations of free copper(II) ions, $[Cu^{2+}]$, on α_1 are shown. In this figure, the initial concentration of copper(II) ions is 5.00×10^{-4} mol/l. The α_1 dependence of the pH difference, ΔpH, between the values in the absence and presence of copper(II) ions at the same value of α_1 corresponds well to the dependence of $[Cu^{2+}]$. This fact shows that the complex formation proceeds along with the increase in α_1. Relatively stable complexes are formed in the α_1 range above 0.35. But when the total concentration of copper(II) ions added is relatively high: more than 10^{-3} mol/l, it was confirmed that the complexes are formed from the first titration step.

Just as in MAEt–zinc(II) systems or poly(itaconic acid)–copper(II) systems,[6] it can be concluded that relatively stable complexes are formed between MAEt and copper(II) ions and that the complex involves both the primary and secondary carboxylate groups in the same succinic acid unit.

In Fig. 5, the dependences of pH and concentrations of free copper(II) ions on α_1 in the case of MASt are shown. The anomalous overlap of the titration curves, as in MASt–zinc(II) systems, is observed in the α_1 ranging from 0.6 to 0.8, which shows that the complexes once formed are broken. In the same α_1 range, on the other hand, the concentration of free copper(II) ions decreases slightly, which shows that the complexes are not broken and do not change to free copper(II) ions. These two results are incompatible with each other. Considering that rather stable complexes are generally formed between the carboxylate groups of the other polyelectrolytes and copper(II) ions, and that the concentration of carboxylate groups as a ligand increases with α_1, it is difficult to conclude that the complexes once formed may break up.

Thus, one of causes of the anomalous overlap may lie in the character of the dissociation equilibrium of MASt, because this overlap corresponds to the α_1 range where the values of $pK_{1,\mathrm{app}}$ are decreasing. The equilibrium constant of the complex formation can be described as the products of the acid dissociation constant, K_a, and the stability constant, β, of the complex; for example:

$$B_2 = \frac{[MA_2][H^+]^2}{[M^{2+}][HA]^2} = \frac{[MA_2]}{[M^{2+}][A^-]^2}\,\frac{[A^-]^2[H^+]^2}{[HA]^2}$$
$$= \beta_2 \times (K_a)^2.$$

If the equilibrium constant is only slightly dependent on α_1, the value of β decreases with the decrease in pK_a. In the neighborhood of $\alpha_1=0.7$, where the overlap occurs, such a relation of each constant can be assumed, and the concentration of the complexes scarcely increases, because of the cancelling between the decrease of β and the increase of the concentration of the free carboxylate groups. Such a discussion interprets the variation of the concentration of free copper(II) ions. In order to explain the anomalous overlap of the titration curves sufficiently, it is necessary to have more detailed knowledge of the conformational transition not only of the MASt chain itself but also of the chain which contains the complexing metal ions.

Stability of Complexes. The stability of the metal complex can be compared by use of the pH difference, ΔpH, between the values in the absence and presence of the bivalent metal ions at the same metal concentration and at the same degree of dissociation. In Table 1, ΔpH of MAEt systems where the initial concentration of each metal ion added is about 1×10^{-3} mol/l are given. The copper(II) complex is much more stable than the others, and the stabilities of each metal complex are roughly in the order of $Cu(II) \gg Zn(II) > Ni(II) \simeq Co(II) \simeq Mn(II)$. This result agrees approximately with the results for the same systems of Felber[2] and Delben[5] and those for the poly(methacrylic acid) of Sunahara.[14]

In Table 2, the values of ΔpH of MASt systems are given. The stabilities of the MASt complex are in the order of $Cu(II) \gg Zn(II) \simeq Ni(II) \simeq Co(II) > Mn(II)$. These results are reasonable, except for manganese(II).

Table 1. Effect of bivalent transition metal ions on pH titration of MAEt (polymer concentration = 0.00498 monomol/l) at the ionic strength of 0.1 (KNO_3)

α_1	Blank pH	−ΔpH Mn-(II)	Co-(II)	Ni-(II)	Zn-(II)	Cu-(II)
0.0						
0.1						
0.2						
0.3	3.50	0.04	0.03	0.04	0.04	0.17
0.4	3.77	0.05	0.04	0.06	0.06	0.33
0.5	4.02	0.06	0.04	0.06	0.07	0.47
0.6	4.24	0.06	0.05	0.07	0.08	0.54
0.7	4.49	0.08	0.07	0.08	0.10	0.62
0.8	4.79	0.10	0.11	0.11	0.14	0.70
0.9	5.19	0.18	0.20	0.20	0.24	0.84
1.0	5.6_9	0.2_9	0.3_0	0.3_0	0.4_0	1.0_0

Table 2. Effect of bivalent transition metal ions on pH titration of MASt (polymer concentration = 0.00432 monomol/l) at the ionic strength of 0.1 (KNO_3)

α_1	Blank pH	−ΔpH Mn-(II)	Co-(II)	Ni-(II)	Zn-(II)	Cu-(II)
0.0						
0.1						
0.2						
0.3	3.51	0.01	0.03	0.05	0.05	0.17
0.4	3.79	0.01	0.02	0.03	0.03	0.16
0.5	3.97	0.02	0.02	0.03	0.03	0.15
0.6	4.08	0.01	0.01	0.02	0.02	0.06
0.7	4.19	0	0	0	0	0.03
0.8	4.36	0	0	0	0.01	0.02
0.9	4.74	0	0.03	0.06	0.04	0.17
1.0	6.0_2	0.2_4	0.3_7	0.4_3	0.4_7	1.1_3

The stability or formation constant of the complex must be estimated for detailed comparison. In the case of the MAEt–copper(II) complex, since the concentration of copper(II) ions can be obtained from potentiometry employing an ion-selective electrode, and since $pK_{1,app}$ of MAEt changes relatively linearly with α_1, the formation constant B_2 can be estimated by the scheme proposed in the previous paper.[6] Here, the constant B_2 is defined as follows:

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

In the α_1 range less than 0.65, the real average coordination number $\bar{n}_r$ of the copper(II)–MAEt system is equal to about two, and each value of $\log B_2$ evaluated from titration is constant and equal to −2.6.

On the other hand, $pK_{1,app}$ of MASt shows a complicated dependence on α_1, so that the reference plot method proposed by Mandel and Leyte[15] cannot be applied. But the value of $\log B_2$ of the copper(II) complex was roughly estimated to be −4.

Thus, it is concluded that the bis(carboxylato) bivalent transition metal complex is formed, in fact, in the first neutralization step of MAEt and MASt, and that the copper(II) complex is the most stable one.

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