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POTENTIOMETRIC BEHAVIOR OF AQUEOUS SOLUTIONS OF MALEIC ACID-STYRENE COPOLYMER WITH ADDED BIVALENT METAL IONS

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The interaction of copoly(maleic acid-styrene),MASt, with bivalent metal ions, Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), was investigated by pH titration method at 25°C and the ionic strength of 0.1 mol/kg. The titration curves in the absence and presence of bivalent metal ions overlap in some dissociation region of the first neutralization step.

The potentiometric titrations of aqueous solutions of maleic acid copolymers, derived from maleic anhydride copolymers by hydrolysis, have been widely studied from the viewpoint of short range interactions between hydrophobic side groups, whereas the interactions of the copolymers with bivalent metal ions have been investigated by relatively few workers.[1-5)]

It has been reported in the previous study[6)] by potentiometry that dicarboxylato copper(II) complex was formed in the poly(itaconic acid)-copper(II) system and that one of these two carboxylate groups came from secondary carboxyl groups (which dissociate in the second neutralization step) in the same monomer unit even in the first neutralization step. Then, it is aimed to confirm whether this conclusion can be applied to other polymers consisting of dicarboxylic acid monomer units.

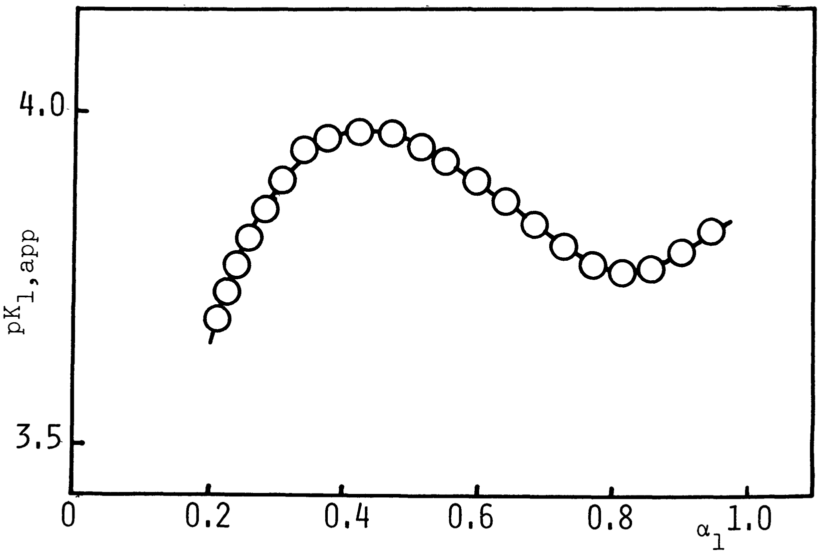

Fig. 1. Dependence of $pK_{1,app}$ of MASt(polymer concentration=0.00432 monomol/dm^3) on α_1 at the ionic strength of 0.1 mol/kg (KNO_3).

In the present paper, thus, potentiometric study of the system consisting of hydrolyzed copoly(maleic anhydride-styrene) and bivalent metal ions, Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), was carried out.

The polymerization and hydrolysis of

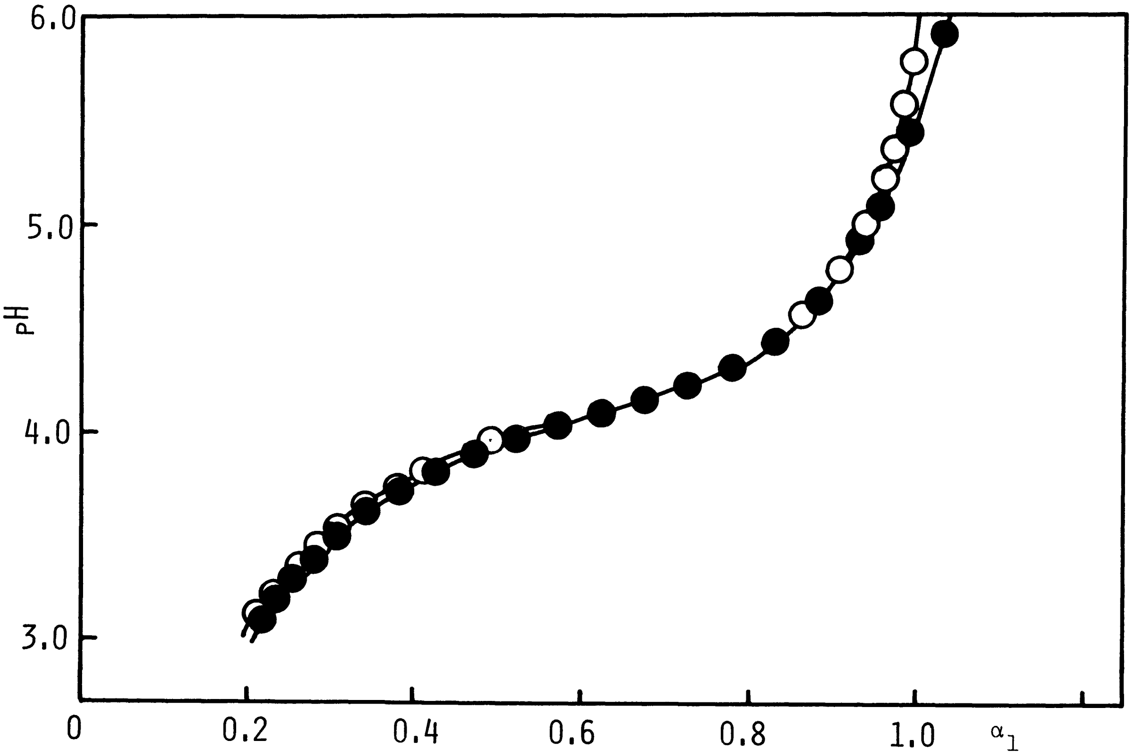

Fig. 2. Titration curves of zinc(II)-MASt(polymer concentration=0.00432 monomol/dm^3) at the ionic strength of 0.1 mol/kg (KNO_3). (●)1×10^{-3} mol/dm^3 $Zn(NO_3)_2$; (○)0 mol/dm^3 $Zn(NO_3)_2$.

copoly(maleic anhydride-styrene) was carried out by the procedures of Ohno and co-workers,[7] and the purification of the copolymer was carried out by reprecipitation and dialysis of the aqueous solution using cellophane tubing. The 1:1 composition of comonomer was confirmed by elemental analysis, and the molecular weight was found to be 10^5 from viscometry.[7] The other chemicals and bivalent metal nitrate salts used were a guaranteed reagent grade.

The pH titration was carried out with about 0.1 mol/dm^3 aqueous solution of carbonate-free NaOH at 25±0.05°C and the ionic strength of 0.1 mol/kg (KNO_3) under nitrogen atmosphere.

In Fig. 1, the dependence of apparent dissociation constant $pK_{1,app}$ of the primary carboxyl groups (which dissociate in the first neutralization step) on the degree of dissociation α_1 is demonstrated in the absence of bivalent transition metal ions. As can be seen from this anomalous dependence, it is questionable to apply the reference plot method proposed by Mandel and Leyte[8] to the analysis of MASt-bivalent metal ions systems. In the present paper, the discussion is limited to pH titration behaviors in the pH range less than 6.00 because of the precision of pH titration of polycarboxylic acids.

In Fig. 2, the titration curves of MASt systems in the absence and presence of zinc(II) ions are shown; the cases of the other bivalent metal ions are similar to this. It is generally observed in the other polycarboxylic acid systems that the titration curve in the presence of bivalent transition metal ions is situated on lower pH region than in the absence of the metal ions, which is attributed to

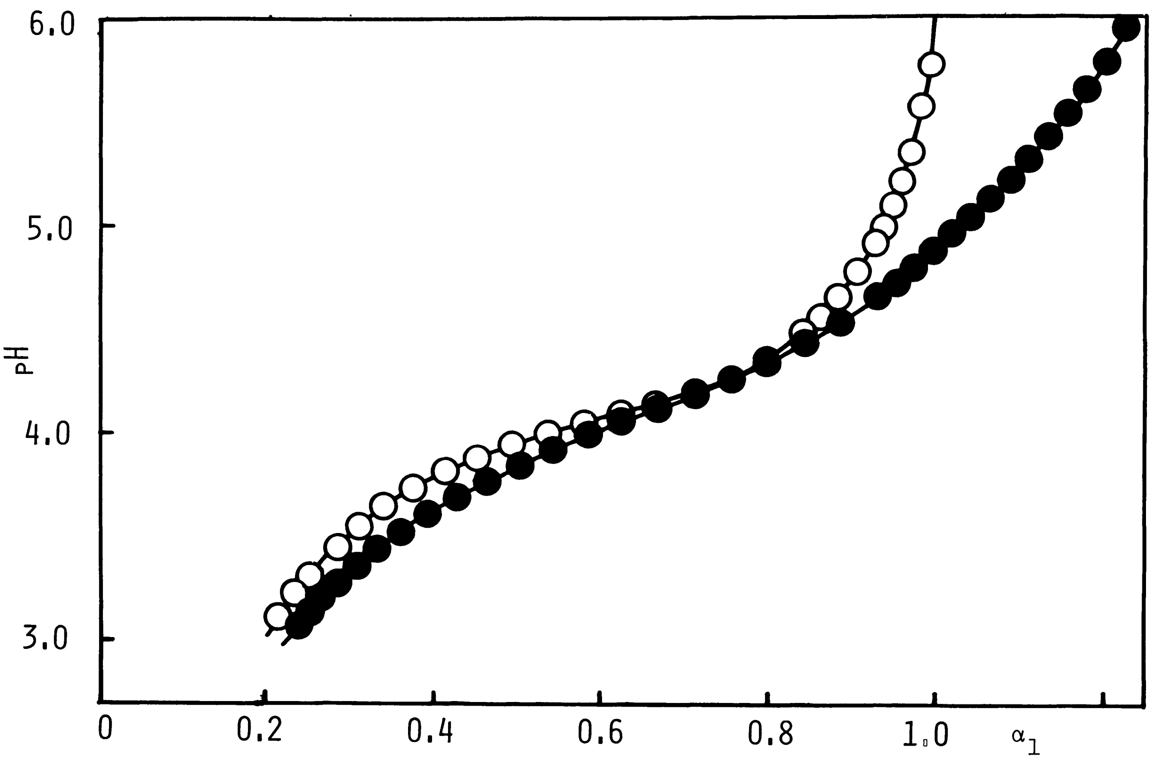

Fig. 3. Titration curves of copper(II)-MASt(polymer concentration=0.00432 monomol/dm^3) at the ionic strength of 0.1 mol/kg (KNO_3). (●)1×10^{-3} mol/dm^3 $Cu(NO_3)_2$; (○)0 mol/dm^3 $Cu(NO_3)_2$.

the complex formation. And in the case of MASt systems, this fact is more or less observed in a wide dissociation range, but in the neighborhood of α_1=0.7, the titration curves in the absence and presence of the metal ions overlap each other and the effect of complexation apparently disappears. To the best of our knowledge, this finding of overlap of the titration curves in the absence and presence of the bivalent transition metal ions is the first example in complexation of polymers. As can be seen from Fig. 1, the dissociation range where the overlap occurs corresponds to the one where the apparent pK_1 values tend to decrease (strange to say). As is pointed out by some authors,[7)] the conformational transition of polymer chains from compact to coiled form may occur in this range. Considering this fact, it is suggested that some steric effect is reflected on the titration curves, whereas the complexation itself is not considerably affected.

The characteristics of each bivalent metal ion are estimated in terms of the values of ΔpH, the difference between the pH values in the absence and presence of metal ions at the apparently same α_1 value, and these results are given in Table. The values of ΔpH, which are related to the stability of the bivalent metal complex formed, are found to be in the order Cu(II)$\gg$Zn(II)$\simeq$Ni(II)$\simeq$Co(II)>Mn(II).

In Fig. 3, the titration curves in the absence and presence of copper(II) ions are shown. This curve differs remarkably from the cases of the other metal ions. In the range of lower α_1, the pH values in the presence of copper(II) ions are considerably small, which suggests that some relatively stable complex is formed.

The titration behavior beyond α_1=1.0 is interesting. The equivalent point for

Table Effect of bivalent transition metal ions on the pH titration of MASt (polymer conc.=0.00432 monomol/dm^3) at the ionic strength of 0.1 mol/kg (KNO$_3$).

α_1	Blank pH	ΔpH				
		Mn(II)	Co(II)	Ni(II)	Zn(II)	Cu(II)
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 primary carboxyl groups of copper(II)-MASt system seems to be apparently shifted to the neutralization range of the secondary carboxyl groups, which is confirmed in various concentrations of copper(II) ion, although the results are not shown in the figure. Thus, it is considered that the complexes formed involve the primary and secondary carboxylate groups of the same succinic residues in the copolymers. Such a result is similar to that in the case of poly(itaconic acid) and copper(II) system reported previously.[6,9]

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