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Complex Formation of Poly(acrylic acid) with Mg, Mn, and Pb Ions in Dioxane-Water Mixed Solvents

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Equilibria between poly(acrylic acid) and Mg(II), Mn(II) and Pb(II) ions have been investigated at 25 °C by means of potentiometric and viscometric titrations in dioxane-water mixed solvents containing 0.1 mol dm^{-3} added salt to maintain a constant ionic strength. The stability constant for the complex formation reaction, $M^{2+}+iA^{-}=MA_i^{2-i}$, and the equilibrium constant for the reaction, $M^{2+}+iHA=MA_i^{2-i}+nH^{+}$ (HA denotes a carboxyl group) have been evaluated from the data of pH titration. Although the stability constants, β_1 and β_2, increased with dioxane content in the mixed solvent and depended on the kinds of added salts, the equilibrium constants, B_1 and B_2, were almost independent of both factors. The values of B_1 for Mg, Mn, and Pb monocarboxylate complexes were $10^{-3.1}$, $10^{-2.5}$, and $10^{-1.0}$ and those of B_2 for Mg, Mn, and Pb dicarboxylate complexes were $10^{-7.6}$, $10^{-5.7}$ and $10^{-2.1}$, respectively. From the data of viscometric titrations of poly(acrylic acid) solutions containing Pb(II) ion, it is considered that the contraction of polymer coil is caused by the intramolecular complex formation with two remote carboxylate groups in the range of low degree of neutralization (α'). As α' increases, the complex is transformed into another form which consists of two adjacent carboxylate groups.

The pH titration is one of the most convenient method to evaluate the stability constant of polyelectrolyte-metal complex.[1-3] But in some cases of the polyelectrolyte-metal systems, precipitation occurs and it is hard to attain the equilibrium owing to slow diffusion of metal ions.[4]

In our previous paper, complex formation of poly(acrylic acid) (abbreviated as PAA) with lead ion was investigated by potentiometric titration of aqueous solution.[5] The precipitation occurred at low degree of dissociation (α) and it could not be readily dissolved with sodium hydroxide even if α increased. Thus, the backward titration was carried out with an acid solution.

To avoid precipitation of polyelectrolyte-metal complex, hydro-organic mixed solvents have been applied to the polyelectrolyte-metal system. An uniform liquid phase enables to investigate the complex formation by means of not only pH titration but also ultraviolet spectroscopy and viscometry.[6]

In this paper, the complex formation of the PAA with Pb(II) ion was investigated in a dioxane-water mixed solvent. The solvent provides sufficient solubility of the PAA-Pb(II) complex to allow potentiometric and viscometric measurements. Furthermore, in order to know the solvent effect in systems of PAA-Mg(II) and PAA-Mn(II), solutions of various dioxane contents were used for measurements.

Experimental

Materials. The sodium polyacrylate (PAA-Na) was purchased from Nacalai Chemical Co. The acid form PAA was obtained from an aqueous solution of PAA-Na with the addition of hydrochloric acid and was purified by dialysis using a cellophane tubing. The molecular weight of PAA was found to be 5.2×10^5 by the viscometric measurement.[7] Dioxane was purified by an ordinary method.[8] The other chemicals were of guaranteed reagent grade.

Potentiometric Titration. The pH measurements were carried out under a nitrogen atmosphere at 25.0±0.1 °C and ionic strength of 0.1 M (M=mol dm^{-3}) by use of an Orion model 801A digital ion meter equipped with glass and calomel electrodes. The concentration of hydrogen ion in the dioxane-water mixed solvent was calibrated on the basis of a titration curve obtained by the titration with 0.1 M hydrogen chloride or hydrogen perchlorate solutions in the mixed solvent. Added salts used to maintain a constant ionic strength were 0.1 M KCl for Mg-PAA and Mn-PAA systems and 0.1 M $NaClO_4$, $LiClO_4$, and Et_4NClO_4 for Pb-PAA system.

Viscometric Titration. The specific viscosities of complex solutions were measured with an Ubbelohde viscometer at 25.0±0.1 °C, in the course of titration with a sodium hydroxide solution under the nitrogen atmosphere. Flow times for water and the mixed solvents containing 10 and 20% dioxane were 179, 215, and 257 s, respectively.

Results and Discussion

Potentiometric Titration of PAA-Divalent Ion Complexes in Dioxane-Water Mixed Solvents. The apparent dissociation constant (pK_a) of carboxyl groups is given as:

$$pK_a = pH - \log[\alpha/(1-\alpha)], \qquad (1)$$

where α is the degree of dissociation. Figure 1 shows the variation of pK_a of PAA with α in various dioxane-water solvents. The mixed solvents consisted of water and dioxane containing 0.1 M KCl. The dioxane contents were 0, 10, and 20% (volume %). It was observed that the pK_a exhibited a monotonous rise with α. This was attributed to the increase in negative charge density on polymer chain with α. The hydrogen ion becomes more difficult to dissociate from carboxyl group owing to the electrostatic attraction by negative charges of carboxylate groups. The curves of pK_a shifted upward with increasing dioxane content. The values at α of 0.5

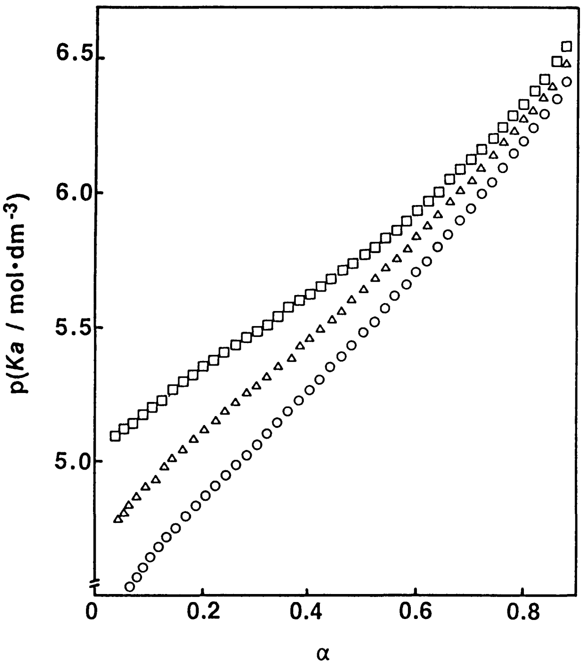

Fig. 1. Apparent dissociation constants of PAA at different dioxane contents: ○, 0%; △, 10%; □, 20%. [PAA]=1.00×10^{-2} M, I=0.1 M (KCl).

in water and mixed solvents containing 10 and 20% dioxane were 5.47, 5.62, and 5.73, respectively. The dielectric constants of water and the mixed solvents containing 10 and 20% dioxane were 78, 70, and 61, respectively, which were estimated from the literature values.[9] Since the negative electrostatic attraction energy is inversely proportional to the dielectric constant, the dissociation of carboxyl group is more restricted with increase in this, thus, PAA became a weaker acid in the mixed solvent with increase in dioxane content than in aqueous solution.

Typical pH titration curves of PAA in the mixed solvent containing 20% dioxane in the presence of either Mg(II) or Mn(II) ions and the absence of both ions are shown in Fig. 2. The degree of neutralization is defined as usual:

$$\alpha' = (C_b / C_p).$$

Here, (C_b) is the concentration of added base and (C_p) is the monomolar polyelectrolyte concentration. In the initial stage of the titration, there was almost no difference in pH between the solution containing either Mg or Mn ions and that containing neither of these, indicating that Mg and Mn ions scarcely bound to PAA at low α'. The pH lowering with Mg and Mn ion began at α' of 0.15 and 0.2, respectively. The pH lowering with Mn ion was larger than that with Mg ion in the whole range of α', suggesting that Mn–PAA complex is more stable than Mg–PAA complex.

The average coordination number ($\bar{n}$) obtained from the pH titration curve is given as follows:

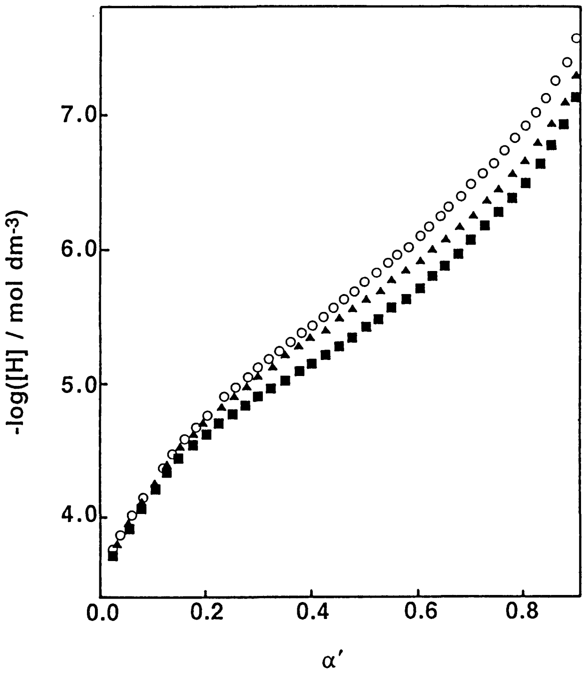

Fig. 2. Titration curves of PAA in the presence of either Mg ion(▲) or Mn ion(■) and in the absence of both ions (○) at 20% dioxane content. [PAA] =1.00×10^{-2} M, [Mg]=1.00×10^{-3} M, [Mn]=1.00×10^{-3} M, I=0.1 M (KCl).

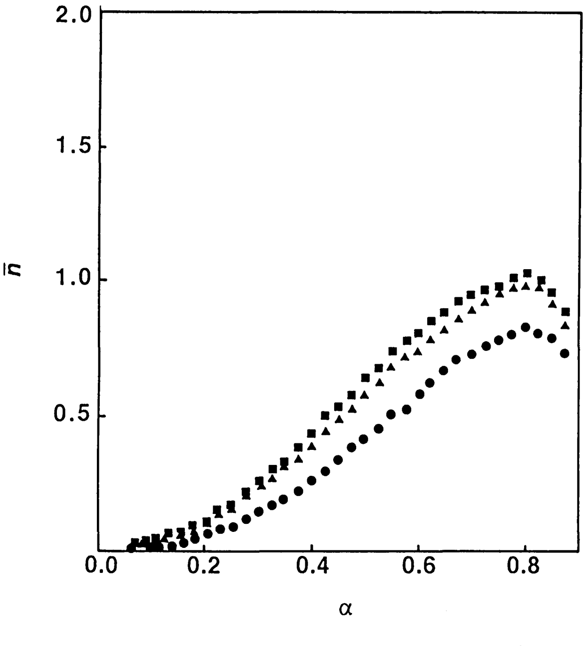

Fig. 3. Formation curves of PAA–Mg complex at different dioxane contents: ●, 0%; ▲, 10%; ■, 20%. [PAA]=1.00×10^{-2} M, [Mg]=1.00×10^{-3} M, I=0.1 M (KCl).

$$\bar{n} = \Sigma i[MA_i]/[M]_t, \tag{2}$$

where $[M]_t$ and $[MA_i]$ represent the concentration of total divalent metal ion and 1 : i divalent metal–carboxylate complex, respectively. The average coordination

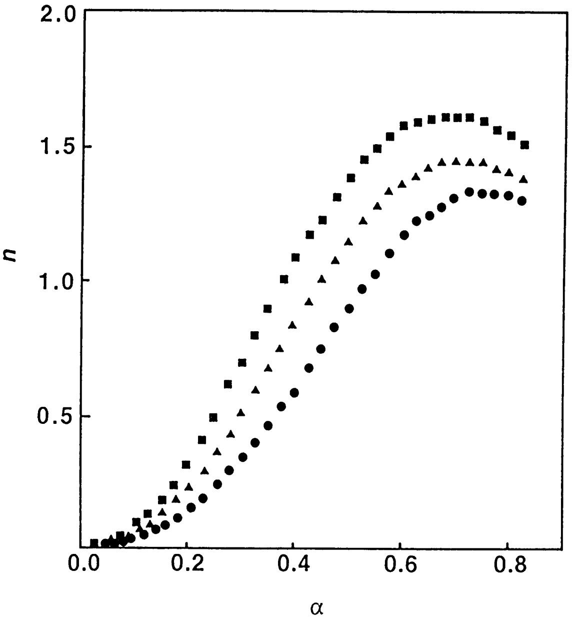

Fig. 4. Formation curves of PAA–Mn complex at different dioxane contents: ●, 0%; ▲, 10%; ■, 20%. [PAA]=1.00×10^{-2} M, [Mn]=1.00×10^{-3} M, I=0.1 M (KCl).

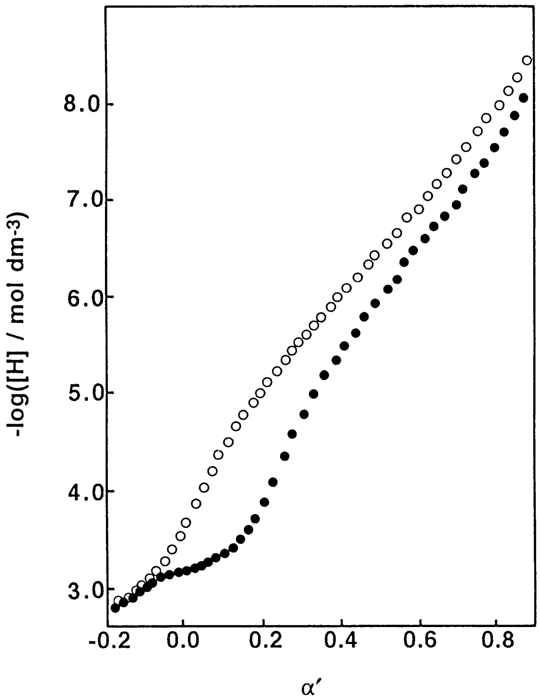

Fig. 5. Titration curves of PAA in the presence of Pb ion (●) and in the absence of Pb ion (○) at 20% dioxane content. [PAA]=1.01×10^{-2} M, [Pb]=1.01×10^{-3} M, I=0.1 M (Et$_4$NClO$_4$).

numbers ($\bar{n}$) of Mg and Mn ion for different dioxane contents are shown in Figs. 3 and 4. Calculation of $\bar{n}$ was done by using the method of reference plot contrived by Mandel et al.[1] $\bar{n}$ increased with α and dioxane content, maximum value of $\bar{n}$ were 0.85, 0.95, and 1.05 for Mg and 1.35, 1.45, and 1.6 for Mn ion when the dioxane contents were 0, 10, and 20%, respectively. As the dioxane content increases, the interaction between divalent ion and carboxylate groups becomes stronger in mixed solvents than that in aqueous solution, for negative increase in the electrostatic potential of polyelectrolyte corresponding to decrease in dielectric constant with dioxane content.

The pH titration curves of PAA in the absence and presence of Pb ion in the mixed solvent containing 20% dioxane with 0.1 M Et$_4$NClO$_4$ are shown in Fig. 5. Twenty per cent excess HClO$_4$ was added at the beginning of the titration since the pH lowering already occurred at α' of 0. A good pH titration curve was obtained without any precipitation in the mixed solvent containing 20% dioxane. The pH lowering began even at α' of -0.1 and it slowly rose with α' up to α' of 0.15, however, a rapid rise of pH was observed above this.

Plots of $\bar{n}$ against α for Pb–PAA complex in mixed solvent containing different kinds of salts, respectively, are shown in Fig. 6. All three kinds of coordination numbers increased with α up to α of 0.2 and reached a maximum value of 2.0. But, these were followed by decrease until α of 0.6 and increased again above this. Whereas these coordination numbers were approximately plotted on a single curve below α of 0.2, effect of salts on the lowering of $\bar{n}$ increased in the order: Li<Na<Et$_4$N in the range of α from 0.2 to 0.6. This anomalous behavior will be discussed later.

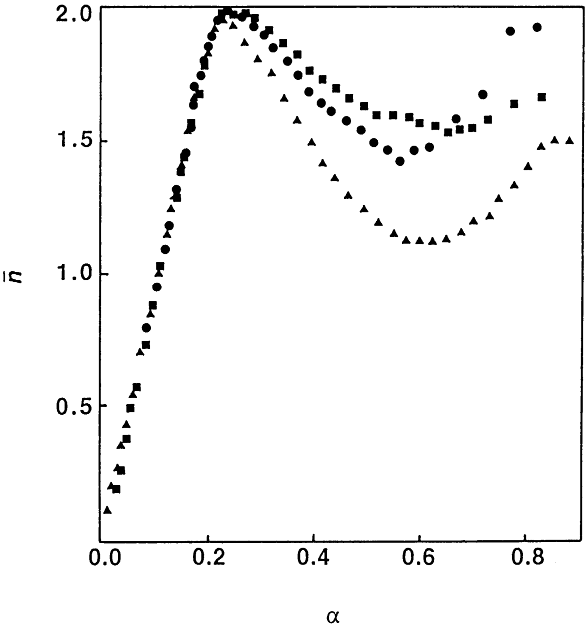

Fig. 6. Formation curves of PAA–Pb complex in 20% dioxane mixed solvent at different added salts: ■, LiClO$_4$; ●, NaClO$_4$; ▲, Et$_4$NClO$_4$. [PAA]=1.01×10^{-2} M, [Pb]=1.01×10^{-3} M.

The overall stability constants of monocarboxylate and dicarboxylate divalent metal ion complexes, β_1 and

β_2 are given by the equations:

$$\beta_1=[\mathrm{MA}]/[\mathrm{M}][\mathrm{A}], \tag{3}$$

$$\beta_2=[\mathrm{MA_2}]/[\mathrm{M}][\mathrm{A}]^2. \tag{4}$$

Here [A] represents the concentration of nonbonding carboxylate group determined by the reference plot method proposed by Mandel and Leyte.[1] β_1 and β_2 are evaluated from the plot of $\bar{n}$ against $-\log$ ([A]/M). The value of abscissa at $\bar{n}$ of 0.5 is equal to log (β_1/M) and that at $\bar{n}$ of 1.0 is equal to 0.5 log (β_2/M^2).

Gregor used exchange reactions between divalent metal ion and hydrogen ion of carboxyl group as the complex formation reactions.

$$\mathrm{M^{2+}+HA=MA^{+}+H^{+}}, \tag{5}$$

$$\mathrm{M^{2+}+2HA=MA_2+2H^{+}}. \tag{6}$$

The overall equilibrium constants of monocarboxylate and dicarboxylate divalent metal ion complexes, B_1 and B_2 are given as follows:

$$B_1=[\mathrm{MA}][\mathrm{H}]/[\mathrm{M}][\mathrm{HA}] \tag{7}$$

$$B_2=[\mathrm{MA_2}][\mathrm{H}]^2/[\mathrm{M}][\mathrm{HA}]^2. \tag{8}$$

Since the reaction (6) does not undergo any change of the charge on polyion, the equilibrium constant, B_2, is considered to be independent of the charge of the polymer. The values of B_1 and B_2 are evaluated from the plot of $\bar{n}$ against log ([HA]/[H]) in the same manner as β_1 and β_2.

The overall stability and equilibrium constants of the divalent metal ion–PAA complexes obtained from the above mentioned manner are shown in Table 1. In the case of Mg–PAA complexes, the values of β_2 and B_2 in water and the mixed solvent containing 10% dioxane could not be evaluated from the plots since the maximum values of $\bar{n}$ were less than 1.

In the cases of PAA–Mg and PAA–Mn complexes, B_1 and B_2 were independent of the dioxane content and the deviation of each value was within ±0.1 whereas β_1 and β_2 increased with this. The equilibrium constant, B_i, is described as the product of the power of acid dissociation constant, K_a, and the stability constant, β_i. Equilibrium constants were independent of the dioxane content of the mixed solvent because of compensation between the increase in β_i and the decrease in K_a.

In the case of PAA–Pb complex, β_1 and β_2 depend on the kinds of monovalent cations of added salts, however, B_1 and B_2 were almost independent of these, whereas the values of pK_a at α of 0.5 in the mixed solvent containing 0.1 M $\mathrm{NaClO_4}$, $\mathrm{LiClO_4}$, and $\mathrm{Et_4NClO_4}$ as added salts were 5.71, 5.80, and 6.45, respectively. The kinds of added salts affect the dissociation of PAA as shielding effect of counter ion. The effect of $\mathrm{Li^+}$ or $\mathrm{Na^+}$ ion is stronger than that of $\mathrm{Et_4N^+}$ ion, so the dissociation of PAA is promoted in the presence of the former ions. The equilibrium constants were independent of the kinds of added salts from the similar reason in the case of variation in the dioxane content of mixed solvent.

In this case, monovalent ions scarcely interfered with the complex formation of Pb–PAA for the affinity of the Pb ion was much stronger than that of the monovalent ions whereas the concentration of monovalent ion was higher than that of Pb ion by a factor of about 10^2.

Since the equilibrium constants, B_1 and B_2, were independent of the dioxane content in mixed solvent and the kinds of added salts, they can be compared even they are impossible to evaluate under same experimental conditions. The values of B_1 for Mg, Mn, and Pb monocarboxylate complexes were $10^{-3.1}$, $10^{-2.5}$, and $10^{-1.0}$ and those of B_2 for Mg, Mn, and Pb dicarboxylate complexes were $10^{-7.6}$, $10^{-5.7}$ and $10^{-2.1}$, respectively. The equilibrium constants of the complexes were in the order of Mg(II)<Mn(II)≪Pb(II). The crystal ion radii of Mg(II), Mn(II), and Pb(II) ions are 0.065, 0.080, and 0.132 nm, respectively. The logarithmic values of B_1 and B_2 are roughly proportional to the crystal ion radius.

Viscometric Titration of PAA-Divalent Metal Ion Complexes Solution in Dioxane-Water Mixed Solvents. Viscometric titration curves in the presence of Mg or Mn ion and in the absence of both of these in water and the mixed solvents containing 10 and 20% dioxane are shown in Figs. 7(a), (b), (c). The contribution of macromolecules to the viscosity of their solution is generally expressed by the specific viscosity as follows:

Table 1. Overall Stability and Equilibrium Constants of PAA Complexes[a)]

Metal ion	Dioxane content/%	Added salt	log(β_1/M)	log(β_2/M^2)	log B_1	log B_2
	0		2.32		−3.11	
Mg	10	KCl	2.40		−3.00	
	20		2.42	4.40	−3.08	−7.57
	0		2.51	4.75	−2.52	−5.80
Mn	10	KCl	2.61	4.94	−2.54	−5.68
	20		2.70	5.14	−2.57	−5.61
		$\mathrm{LiClO_4}$	3.57	7.32	−0.93	−2.01
Pb	20	$\mathrm{NaClO_4}$	3.98	7.86	−1.00	−2.16
		$\mathrm{Et_4NClO_4}$	4.18	8.12	−0.98	−2.08

a) Conditions: 25 °C, I=0.1 M (M=mol dm^{-3}).

$$\eta_{sp}=(\eta-\eta_0)/\eta_0.$$

Here, η and η_0 stand for the viscosities of solution and solvent. The large increment of the viscosity with α' is related to the uncoiling of the polymer chains being due to the mutual repulsion between charges of adjacent carboxylate groups. The observed decrease in the viscosity with increase in dioxane content of the solutions can be considered as an indication that dissociation of PAA salts are more difficult in mixed solvents than in aqueous solution.[10,11]

The difference in viscosities between the solution containing divalent ion and that free from it appears at low α', which increase with dioxane content. The viscosity monotonously increased with α' without any minimum point, though flat region observed in the range of α' from 0.2 to 0.5 in the case of PAA–Mn complex solution of 20% dioxane content. The values at α' of 0.9 in the presence of Mg ion for the dioxane contents of 0, 10, 20% were 78, 73, and 57% of those in the absence of Mg ion, respectively, and those in the presence of Mn ion were 56, 56, and 47% of those in the absence of Mn ion, respectively.

Binding of divalent ion to PAA causes a remarkable decrease in the viscosity of solution owing to chelate formation with two carboxylate groups. As is shown in Figs. 3 and 4, value of $\bar{n}$ for Mg–PAA complex reached unity at high α and that of Mn–PAA complex went across unity above α of 0.5 indicating that 1:2 complexes were formed when adjacent carboxyl groups

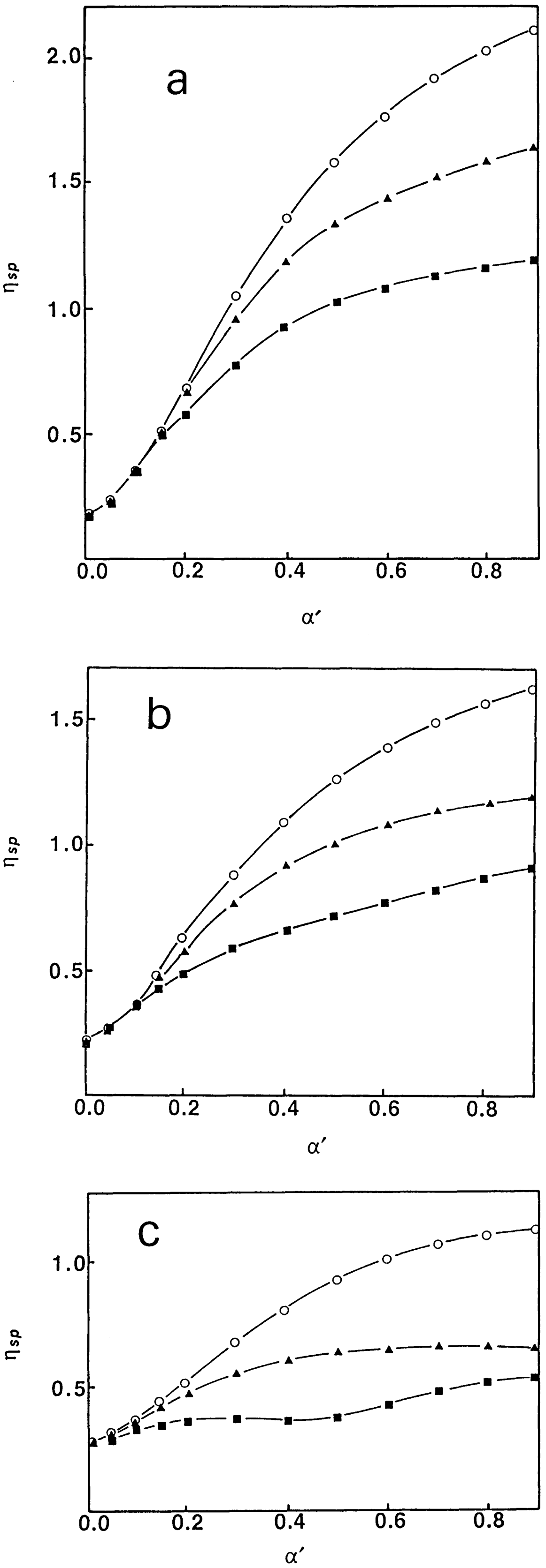

Fig. 7. Specific viscosities of PAA solutions in the presence of either Mg ion(▲) or Mn ion(■) and in the absence of both ions(○) at different dioxane contents: (a), 0%; (b), 10%; (c), 20%. [PAA]=1.00×10⁻² M, [Mg]=1.00×10⁻³ M, [Mn]=1.00×10⁻³ M, I=0.1 M (KCl).

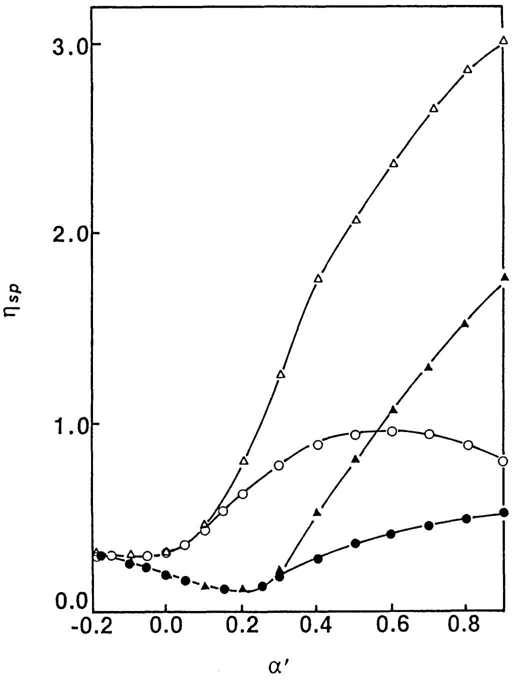

Fig. 8. Specific viscosities of PAA solutions in the presence of Pb ion(●,▲) and in the absence of Pb ion(○,△) in 20% dioxane mixed solvent at different added salts: (○,●), $NaClO_4$; (△,▲), Et_4NClO_4. [PAA]=1.01×10⁻² M, [Pb]=1.01×10⁻³ M.

were dissociated, so that the complexes are considered to be chelated with two adjacent carboxylate groups.

The viscosity of PAA solutions containing 20% dioxane in the presence and absence of Pb(II) ion are shown in Fig 8. The viscosity of the solutions containing Pb(II) ions decreased with increase in α' until α' of 0.2 and increased with α' above this. This minimum at α' of 0.2 corresponds to the maximum in the formation curve as is shown in Fig. 6. The viscosity at α' of 0.2 was lower than that at α' of 0, suggesting that the constriction of polymer coil accompanied by chelate complex formation overcame the expansion of that by repulsive force between carboxylate groups in this region. Since $\bar{n}$ of the complex was nearly two even at α of 0.2, the complex at α of 0.2 is presumably chelated with two remote carboxylate groups on a polymer chain which are situated in relatively near distance of random coil state. The viscosity of Pb(II)–PAA solution above α' of 0.2 is lower than that of Pb(II) free PAA solution; the viscosity at α' of 0.9 was 50—60% of that of free Pb(II) solution. This value was comparable to those of Mn–PAA solutions, therefore, at high α', the local structure of the polymer chain surrounding the Pb complex is assumed to be similar to that of Mn complex. Thus, the Pb complex is also chelated with two adjacent carboxylate groups at high α'.

Finally, turn back to discuss the anomalous behavior of $\bar{n}$ as is shown in Fig. 6.

In the case of Pb–PAA system, the decrease in $\bar{n}$ depended on the kinds of added salts in the α range from 0.3 to 0.6 as is shown in Fig. 6. That is, $\bar{n}$ value decreased in the order of $Li^+ < Na^+ < Et_4N^+$. Among monovalent ions, the viscosity reducing effect on PAA solution increases in the order of $Et_4N^+ < K^+ < Na^+ < Li^+$ as the reciprocal of the ionic radius. The increase of the viscosity in the presence of Et_4N^+ ion was larger than that in the presence of Na^+ ion as is shown in Fig. 8, indicating that the polymer chain more remarkably expanded with α' in the presence of the former ion than in the latter ion.

It is concluded that Pb-dicarboxylate complex formed at low α' is the intramolecular complex chelated with two remote carboxylate groups on a polymer chain owing to the contraction of polymer coil. As α increases, the complex is gradually broken by the expansion of polymer coil and is transformed into the another form of the complex which consists of two adjacent carboxylate groups.

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