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Counterion Effect on the Titration Behavior of Poly(itaconic acid)

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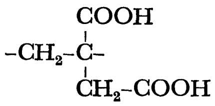
The effect of counterions on the titration behavior of poly(itaconic acid) (PIA) was studied by titrating PIA in aqueous solutions containing alkali metal salts and a tetramethylammonium salt at 25 °C. The acidity of the primary carboxylic groups of PIA increases in the order $(CH_3)_4N^+ < Li^+ < Na^+ < K^+$, whereas that of the secondary carboxylic groups increases with the decrease in the crystallographical radii of the counterions, in the order $(CH_3)_4N^+ < K^+ < Na^+ < Li^+$, in agreement with the results for ordinary polycarboxylic acids. The order $K^+ > Na^+ > Li^+$ on the binding strength to the primary carboxylate groups in the first dissociation step is interpreted in terms of the radii of the hydrated cations; it can be ascribed to the stable ring structure of the monoanion of the itaconic acid residue, resulting from the hydrogen bonding between two adjacent carboxylate groups. In apparent complete dissociation, about 80, 60, and 40% of the itaconate residues bind to Li^+, Na^+, and K^+ ions, respectively, when it is assumed that no $(CH_3)_4N^+$ ions are bound to the carboxylate groups.

The specific effect of counterions on the titration behavior of weak polyelectrolytes is of interest in connection with the selective accumulation of specific ions in biological systems. This can be ascribed to the counterion binding by the polyion with an enormously high electrostatic potential. For polycarboxylic acids, the counterion effect has been studied extensively.[1-7] Gregor and Frederick,[1] and Kagawa and Gregor[2] demonstrated that the acidity of ordinary polycarboxylic acids, *e.g.*, poly(acrylic acid) and poly(methacrylic acid), decreases with the increase in the counterion size; that is, the alkali metal ions are bound to the polyanions in the affinity order $Li^+ > Na^+ > K^+$. Similar phenomena have been observed with viscosity,[3] conductivity,[3,4] counterion activity,[5] counterion mobility,[6] and dilatometry[7] in alkali metal polycarboxylate systems.

Recently, some investigators[7,8] have dealt with the specific binding of the alkali metal ions with the anions of maleic acid copolymers. The counterion binding for polydicarboxylic acids, however, has not yet been clarified. From a study of the effect of the counterions on the titration behavior of poly(maleic acid), it was found that the binding strength of the alkali metal ions to the primary carboxylate groups decreases in the order $K^+ > Na^+ > Li^+$, whereas that to the secondary ones $Li^+ > Na^+ > K^+$.[9] The latter finding agrees with those for ordinary polycarboxylic acids. On the other hand, the affinity order in the first dissociation step is interpreted in terms of the radii of the hydrated cations; it can be attributed to the hydrogen-bonded ring structure of the monoanion of the maleic acid residue.[9]

The present study is concerned with poly(itaconic acid) (PIA):



$$-CH_2-\overset{\displaystyle COOH}{\underset{\displaystyle CH_2-COOH}{C}}-$$

The number of carbon atoms between two adjacent carboxylic groups in the itaconic acid residue is equal to that in the maleic acid group. The author has synthesized PIA and carried out potentiometric titrations in aqueous solutions containing salts. The effect of Li^+, Na^+, K^+, and tetramethylammonium ions $(CH_3)_4N^+$, on the titration behavior of PIA, in particular the binding of the alkali metal ions to the primary and secondary carboxylate groups of PIA, is reported herewith.

Experimental

Materials. The PIA sample was prepared by the procedures of Marvel and Shepherd,[10] and Sakurada *et al.*[11] as follows. Itaconic acid was recrystallized in water[12] twice before use. The itaconic acid was polymerized in a 0.5 mol/l HCl solution containing 20 wt% monomer and 0.1 wt% potassium peroxysulfate at 50 °C for 140 hr under a nitrogen atmosphere. The reaction mixture was then added slowly dropwise to acetone to precipitate the polymer. The PIA was separated by filtration, redissolved in water, reprecipitated in acetone, and dried *in vacuo* at 35 °C. white powdery product was obtained in a 20% yield. Found: C, 45.08; H, 4.86%. Calcd for $(C_5H_6O_4)_n$: C, 46.16; H, 4.65%. The polymer seems to be slightly hydrated.[10] Figure 1 shows the dependence of the reduced viscosity of aqueous PIA solutions on polymer concentration. The molecular weight of the present PIA sample may be estimated to be about 10^5, by comparison with the viscosity data of

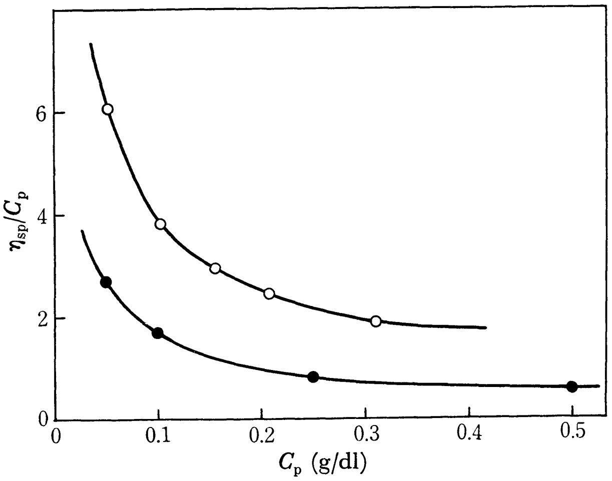


Fig. 1. The dependence of the reduced viscosity (η_{sp}/C_p) of aqueous PIA solutions on polymer concentration (C_p) at 25.0 °C. ○: present PIA and ●: PIA by Marvel and Shepherd.[10]

the PIA sample obtained by Marvel and Shepherd[10] who estimated it to be about 5×10^4. A concentrated aqueous PIA solution (*ca.* 1 wt%) was stored in a polyethylene container at 5 °C.

Carbonate-free titrants, NaOH and LiOH solutions, were prepared. The neutral salts added, $LiNO_3$, $NaNO_3$, KNO_3, and tetramethylammonium chloride, $(CH_3)_4NCl$, were thoroughly dried at 110 °C or *in vacuo* prior to weighing. All the chemicals used were of a guaranteed reagent grade. All the aqueous solutions were prepared by the use of deionized water.

Potentiometric Titrations. The pH values were measured with a Yokogawa KPH-51A pH meter equipped with Toadenpa HG-4005 glass and HC-205 calomel electrodes separated by a saturated KCl-agar salt bridge. The titrations were carried out in a special titration vessel maintained at 25.0±0.05 °C under a nitrogen atmosphere. It was found that the acid-base equilibrium was not immediately attained in the region around the half-neutralization point of PIA. The tendency was more pronounced in the case of the PIA solution without added salts. Similar phenomena have been observed in the cases of poly(maleic acid)[9] and other polyacids.[13,14] In this region, the solutions were stirred for 15 min—1 hr after each addition of a certain amount of the base until the pH readings became constant. The repeated titration curves were reproducible to within ±0.01 pH unit.

Results and Discussion

pH Titration Curves. The pH titration curves of PIA with NaOH in 0.1 mol/l solutions of four kinds of 1-1 salts are shown in Fig. 2, where α' is the degree of the neutralization of the carboxylic groups of PIA (originally proportional to the gram equivalent numbers of the added base). Each titration curve has an inflection point at the same degree of neutralization ($\alpha'=1.0$), which corresponds to the equivalence point of the primary carboxylic groups of PIA. The end point of the secondary ones ($\alpha'=2.0$) lies in a high pH region. Thus, no definite inflection points are observed, though a somewhat obscure inflection point is noticed in the PIA–$LiNO_3$ system (Figs. 2 and 3). It has been found that the carboxylic groups of PIA dissociate in two distinct steps,[11,15] whereas the titration curve of monomeric itaconic acid has an inflection point only at $\alpha'=2.0$.

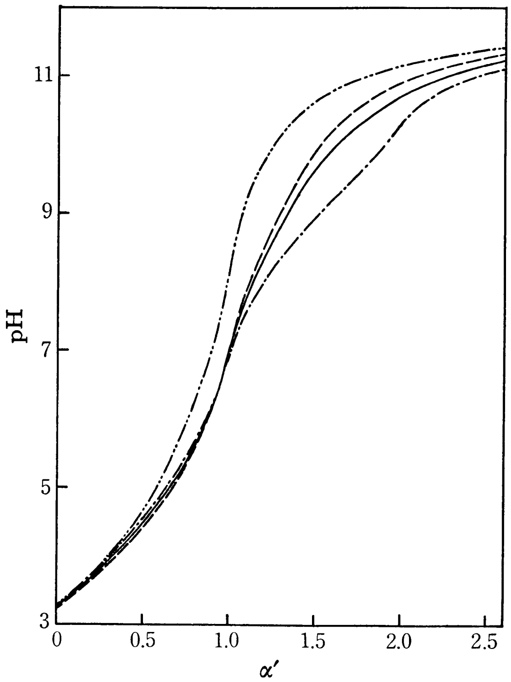


Fig. 2. The pH titration curves of 3.79×10^{-3} monomol/l PIA with NaOH in 0.1 mol/l $LiNO_3$ (-·-·-·), $NaNO_3$ (——), KNO_3 (------), and $(CH_3)_4NCl$ (-·-·-).

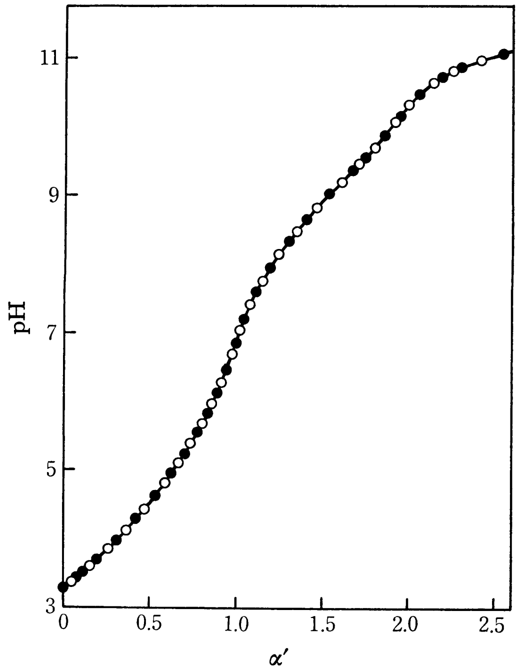


Fig. 3. The pH titration curves of 3.79×10^{-3} monomol/l PIA in 0.1 mol/l $LiNO_3$ with LiOH (○) and with NaOH (●).

The precise concentration of PIA, expressed in monomol/l (one monomole contains one itaconic acid residue), was determined from the gram equivalent numbers of the base added up to the first inflection point, already designated in $\alpha'=1.0$. This concentration was in fair agreement with that predicted from gravimetry of the aqueous stock solution of PIA. It has been confirmed that the PIA obtained by radical polymerization in an aqueous HCl solution has a linear chain structure consisting of repeated itaconic acid units.[10,11,16,17] Thus, in the later analysis of the dissociation behavior of PIA, it could be assumed that the amount of the secondary carboxylic groups is equal to that of the primary ones in the present PIA sample.

The added salt concentration (0.1 mol/l) is much higher than that of polyacid (*ca.* 10^{-3} monomol/l) (Fig. 2). Thus, the dissociation behavior of PIA must be substantially influenced by the cations of added salts, in spite of the use of NaOH as a titrant. For the sake of confirmation, the PIA solution in 0.1 mol/l $LiNO_3$ was titrated with LiOH as well. The titration curves with NaOH and with LiOH in 0.1 mol/l $LiNO_3$ are both in excellent agreement, as shown in Fig. 3. Such a titration procedure with NaOH in solutions containing different added salts is useful for examination of the counterion effect, since preparing different bases so that they are carbonate-free and at approximately the same concentration is troublesome.

The effect of the four cations in the first dissociation step of PIA seems to differ from that in the second one (Fig. 2). In the second step ($\alpha' \geq 1.0$), the pH values at a given α' decrease obviously in the order $(CH_3)_4N^+ > K^+ > Na^+ > Li^+$, in agreement with the cases of ordinary polycarboxylic acids.[1,2] On the other hand, in the first step a peculiar effect of the alkali metal ions is observed; the pH values decrease in the order $(CH_3)_4N^+ > Li^+ > Na^+ > K^+$. The present findings are entirely analogous to those in the first and second dissociation steps of poly(maleic acid).[9]

Apparent Dissociation Constants. In order to characterize the counterion effect on the titration behavior of PIA, the apparent acid-dissociation constants (K_1 and K_2) of the primary and secondary carboxylic groups were calculated from the curves in Fig. 2, by the following equations:

$$pK_1 = \text{pH} + \log \frac{1-\alpha_1}{\alpha_1} \tag{1}$$

$$pK_2 = \text{pH} + \log \frac{1-\alpha_2}{\alpha_2} \tag{2}$$

where α_1 and α_2 are the degrees of dissociation of the primary and secondary carboxylic groups, respectively. The α_1 and α_2 values were determined on the basis of the electroneutrality and conservation conditions in acidic and alkaline solutions, respectively;

$$\alpha_1 = \frac{[\text{NaOH}]+[\text{H}^+]}{[\text{A}_t]} = \alpha' + \frac{[\text{H}^+]}{[\text{A}_t]} \tag{3}$$

$$\alpha_2 = \frac{[\text{NaOH}]-[\text{A}_t]-[\text{OH}^-]}{[\text{A}_t]} = \alpha' - 1 - \frac{[\text{OH}^-]}{[\text{A}_t]} \tag{4}$$

where [NaOH] is the molarity of the added titrant diluted in test solutions, and $[\text{A}_t]$ the total concentration of the itaconic acid residues, expressed in monomol/l; $[\text{H}^+]$ and $[\text{OH}^-]$ are values calculated from the measured pH values and the ionization constant of water,[18] with corrections for the activity coefficients ($y_{\text{H}^+}=0.83$ and $y_{\text{OH}^-}=0.76$ at the ionic strength of 0.1[19]). It is well-known that the apparent dissociation constants for weak polyacids continuously decrease with the increase in the degree of dissociation, that is, the increase in the charge on a polymer chain.[20]

Figures 4 and 5 show the pK_1 *vs.* α_1 and pK_2 *vs.* α_2 curves, respectively. The plots were omitted in the regions of $\alpha_1 \geq 0.9$ and $\alpha_2 \leq 0.1$ around the half-neutralization point of PIA, where Eqs. (1) and (2) hardly hold. The pK_1 values at a given α_1 are seen to decrease in the order $(CH_3)_4N^+ > Li^+ > Na^+ > K^+$, and the pK_1 curves in the presence of the alkali metal ions deviate to a greater extent from each other in the region of $0.3 \leq \alpha_1 \leq 0.6$ (Fig. 4). On the other hand, the pK_2 values at a given α_2 decrease in the order $(CH_3)_4N^+ > K^+ > Na^+ > Li^+$, the differences in the pK_2 values with the counterions being much greater than in the pK_1 values, and the effect of the alkali cations increasing with the increase in α_2 (Fig. 5).

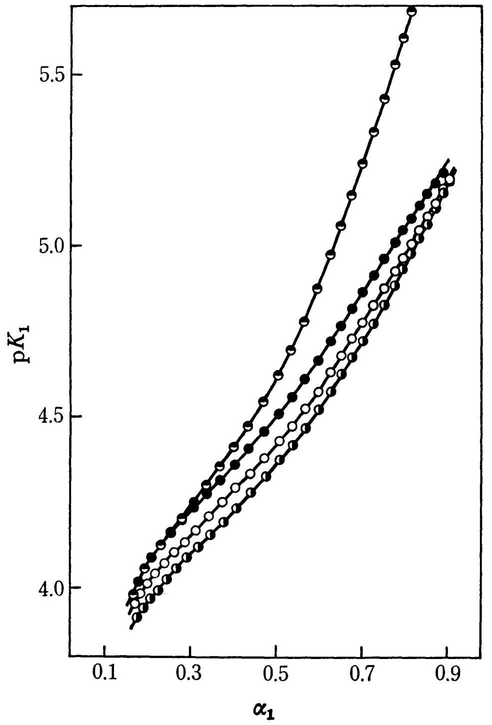


Fig. 4. The dependence of pK_1 on α_1, calculated from the curves in Fig. 2. ●: $LiNO_3$, ○: $NaNO_3$, ◑: KNO_3, and ◓: $(CH_3)_4NCl$.

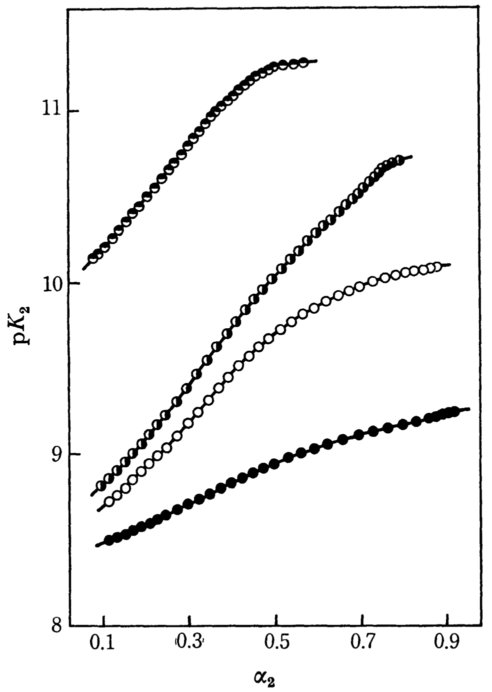


Fig. 5. The dependence of pK_2 on α_2, calculated from the curves in Fig. 2. ●: $LiNO_3$, ○: $NaNO_3$, ◑: KNO_3, and ◓: $(CH_3)_4NCl$.

Table 1 gives the average dissociation constants ($pK_{1,\text{av}}$ and $pK_{2,\text{av}}$) with the dffierent counterions; the pK_1 values at $\alpha_1=0.5$ and pK_2 values at $\alpha_2=0.5$, respectively, were determined in Figs. 4 and 5. The differences in $pK_{1,\text{av}}$ with the counterions (0.06—0.12) are sufficiently larger than the estimated accuracy of pK (0.02), and hence the order of the decrease in the $pK_{1,\text{av}}$ is regarded as significant. On the other hand,

TABLE 1. AVERAGE DISSOCIATION CONSTANTS OF THE PRIMARY AND SECONDARY CARBOXYLIC GROUPS OF PIA[a] IN 0.1 mol/l ADDED SALTS

Counterion	$pK_{1,av}$	$pK_{2,av}$
Li^+	4.50	8.95
Na^+	4.42	9.70
K^+	4.36	10.04
$(CH_3)_4N^+$	4.62	11.26

a) 3.79×10^{-3} monomol/l

such marked differences in $pK_{2,av}$ with the counterions (*e.g.*, 1.22 between K^+ and $(CH_3)_4N^+$ ions) are not known for other polycarboxylic acids. For example, the difference in pK_{av} between K^+ and $(CH_3)_4N^+$ ions for poly(acrylic acid) is 0.33 under the same conditions as the ionic strength of 0.1.[1] As for monomeric itaconic acid, the two dissociation constants have been reported to be $pK_{a,1}=3.68$ and $pK_{a,2}=5.14$ at the ionic strength of 0.1 ($NaClO_4$) at 25.0 °C.[21] Because of the increasing difficulty in the removal of protons from polyions with an enormously high electrostatic potential, the pK_{av} values of polyacids are higher than the pK_a values of the corresponding monomeric acids. Even if the effect is taken into account, the $pK_{2,av}$ values are considerably higher than the $pK_{a,2}$ of itaconic acid. Consequently, it is presumed that the protons of the secondary carboxylic groups of PIA tend to be bound to the adjacent primary carboxylate groups in each itaconic acid residue. Similar findings have been presented for poly(maleic acid).[9]

In order to support this presumption, the dependence of the titration behavior of PIA on the ionic strength in aqueous solutions was examined. Figure 6 shows the pK_1 *vs.* α_1 curves of PIA in water and in the presence of $NaNO_3$ (0.01 and 0.1 mol/l), derived from the corresponding pH titration curves according to Eqs. (1) and (3). In the cases of ordinary weak polyacids which are free from a conformational transition with the dissociation, the dependence of the apparent dissociation constant (pK) on the degree of dissociation can be represented by a second-degree polynomial.[22] The dependence in the first dissociation step, however, appears to be represented by an at least third-degree polynomial (Fig. 6). Similar findings have been presented for the primary carboxylic groups of poly(maleic acid)[23] and for poly(acrylic acid) of a relatively high molecular weight (*ca.* 10^6) without added salts.[22,24] This can be attributed to the intramolecular hydrogen bonding by the ionizable groups, in particular between the adjacent carboxylic groups.[23,24] In the absence of added salts, the portion of the pK_1 *vs.* α_1 curve in the lower α_1 region is more convex upward; hence, the structure resulting from the cooperative hydrogen bonding between two adjacent carboxylate groups in each itaconic acid residue seems to be more stable.

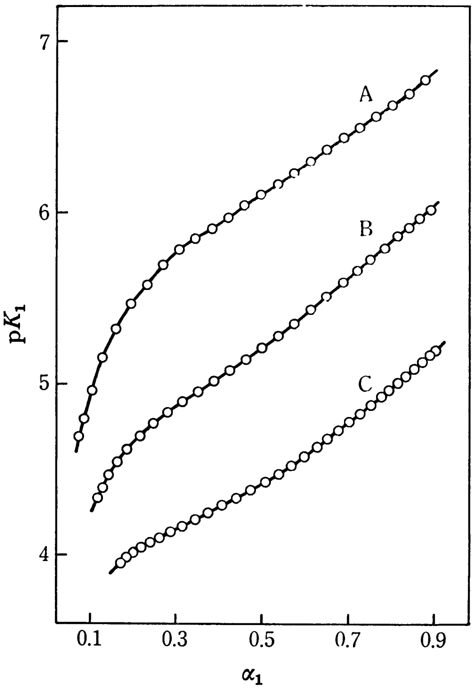
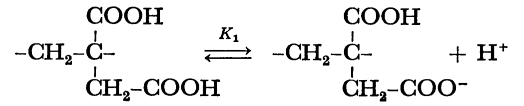


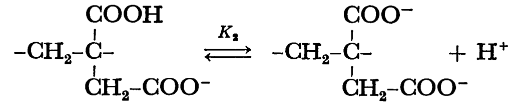
Fig. 6. The pK_1 *vs.* α_1 curves of 3.79×10^{-3} monomol/l PIA in water (curve A) and in the presence of $NaNO_3$ at 0.01 mol/l (B) and 0.1 mol/l (C).

Binding of Alkali Metal Ions. We see from Figs. 4 and 5 that the acidity of the primary carboxylic groups of PIA increases in the order $(CH_3)_4N^+ < Li^+ < Na^+ < K^+$, and that of the secondary ones $(CH_3)_4N^+ < K^+ < Na^+ < Li^+$. In such a case, the increment in acidity gives a measure of the interaction between carboxylic groups and counterions. Thus, the alkali metal ions are bound to the carboxylate groups of PIA in a certain way.

The carboxylic groups of PIA dissociate in the following two steps:



$$\begin{array}{c}\mathrm{COOH}\\ \mathrm{-CH_2\text{-}\overset{|}{\underset{|}{C}}\text{-}}\\ \mathrm{CH_2\text{-}COOH}\end{array} \underset{}{\overset{K_1}{\rightleftharpoons}} \begin{array}{c}\mathrm{COOH}\\ \mathrm{-CH_2\text{-}\overset{|}{\underset{|}{C}}\text{-}}\\ \mathrm{CH_2\text{-}COO^-}\end{array} + H^+ \quad (5)$$



$$\begin{array}{c}\mathrm{COOH}\\ \mathrm{-CH_2\text{-}\overset{|}{\underset{|}{C}}\text{-}}\\ \mathrm{CH_2\text{-}COO^-}\end{array} \underset{}{\overset{K_2}{\rightleftharpoons}} \begin{array}{c}\mathrm{COO^-}\\ \mathrm{-CH_2\text{-}\overset{|}{\underset{|}{C}}\text{-}}\\ \mathrm{CH_2\text{-}COO^-}\end{array} + H^+ \quad (6)$$

These equilibria are represented by the following simplified expressions:

$$H_2A \rightleftharpoons HA^- + H^+ \quad (7)$$

$$HA^- \rightleftharpoons A^{2-} + H^+ \quad (8)$$

On the assumption that no $(CH_3)_4N^+$ ions are bound to the carboxylate groups in the PIA–$(CH_3)_4NCl$ system, the degree of binding (θ) of the alkali metal ions (M^+) with the monoanion (HA^-) and dianion (A^{2-}) of the itaconic acid residue was calculated from the titration curves. The θ value is defined as the average number of the alkali metal ions bound to each itaconic acid residue. In the first dissociation step, MHA must be the only species of the primary carboxylate groups binding to M^+ ions. Therefore, θ can be calculated by the use of the scheme described previously.[9] In the second step, however, the scheme cannot be applied because of the presence of various species (*e.g.*, MHA, MA^-, and M_2A) as a mixture.

Thus, θ throughout the first and second steps is expressed by the equation:

$$\theta = \frac{[ML]}{[A_t]} = \frac{[L_t]-[HL]-[L^-]}{[A_t]} \quad (9)$$

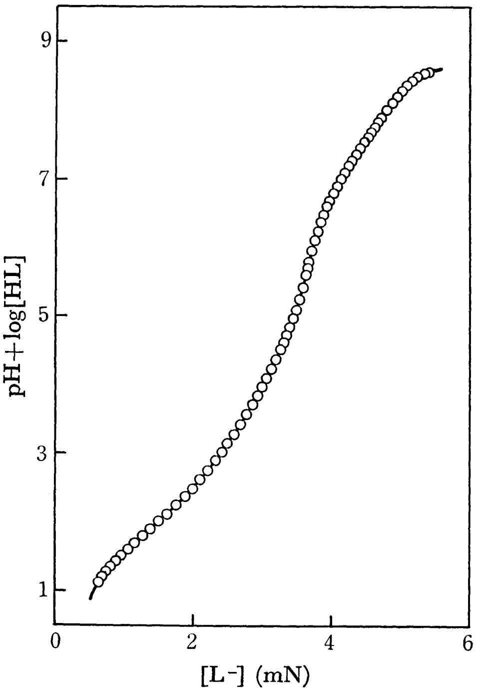


Fig. 7. The reference plot of 3.79×10^{-3} monomol/l PIA in 0.1 mol/l $(CH_3)_4NCl$, for calculation of θ.

where $[L_t]$ is the total concentration of the carboxylic groups without differentiation between the primary and secondary carboxylic groups (*i.e.*, $[L_t]=2[A_t]$), and [ML] is that of the primary and/or secondary carboxylate groups combined with M^+ ions. The [HL] related to undissociated carboxylic groups is found to be:

$$[HL] = [L_t] - [NaOH] - [H^+] + [OH^-] \qquad (10)$$

from the conservation and electroneutrality conditions. The $[L^-]$ value related to free carboxylate groups in the 0.1 mol/l MNO_3 solutions is calculated by the use of a reference plot for the 0.1 mol/l $(CH_3)_4NCl$ solution of PIA (Fig. 7).[9] After the determination of (pH+log[HL]) values for the 0.1 mol/l MNO_3 solutions of PIA, the appropriate $[L^-]$ values in the MNO_3 solutions can be found in the reference curve for the $(CH_3)_4$NCl solution. Such a scheme with the reference plot has been devised by Mandel and Leyte.[25]

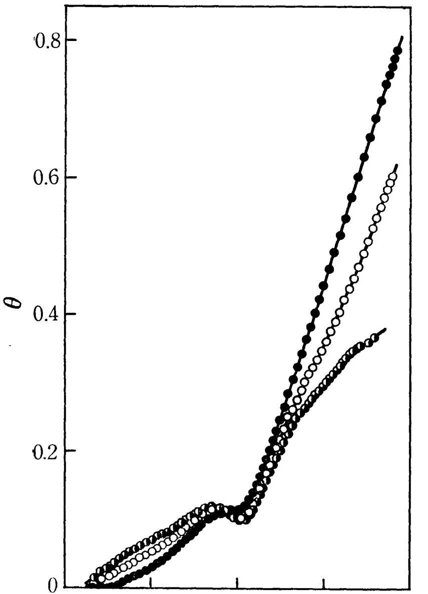


Fig. 8. The dependence of θ on α, calculated from the curves in Fig. 2. ●: Li^+, ○: Na^+, and ◑: K^+.

Figure 8 shows the dependence of θ on α, where α is the total apparent degree of dissociation of the itaconic acid groups; $\alpha=\alpha_1$ or $=1+\alpha_2$, and hence $\alpha=2$ at the apparent complete dissociation. According to the assumption on the calculation of θ, we have $\theta=0$ for $(CH_3)_4N^+$ ions over the whole α range. In the first dissociation step ($\alpha\leq1.0$), the θ values at a given α decrease in the order $K^+>Na^+>Li^+$, whereas in the second step the order of the binding strength is completely reversed. With the increase in α, the θ values in the first step gradually increase and then become practically constant (0.11—0.12) in the region near $\alpha=0.9$. The θ values in the region beyond $\alpha=1.0$ increase steeply with α, linearly for Li^+ ions. Those around $\alpha=1.0$ for Na^+ and K^+ ions appear to decrease slightly with α. However, this is not definite because of the increase in the errors inherent in the scheme with the reference plot near the half-neutralization point.

We see from Fig. 8 that when α approaches 2, about 80, 60, and 40% of the itaconic acid residues bind to Li^+, Na^+, and K^+ ions, respectively. For polyacrylate and copolymers of maleate, the binding fractions with the alkali metal ions have been evaluated from such various measurements as of counterion mobility,[6,26,27] counterion activity,[28] conductivity,[4] viscosity,[29] and apparent molal volumes[8] in the polyelectrolyte systems. The present values for polyitaconate seem to be comparable in magnitude to those for the above polycarboxylates. However, such marked differences in the θ values with the alkali cations for polyitaconate have not been found for ordinary polycarboxylates.[4,8]

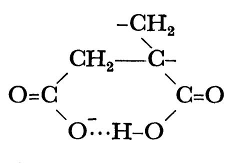
The order $Li^+>Na^+>K^+$ on binding strength in the second dissociation step of PIA agrees with the results for polymonocarboxylates[1,4] and for the second step of maleic acid polymers.[7,9] These results can be explained in terms of the crystallographical ionic radii of alkali metals;[2] the smallest Li^+ ion is bound to the largest extent. This contact binding between the alkali metal ions and the carboxylate groups in these polyelectrolyte systems resembles the so-called contact ion-pairs for weak electrolytes.

It is noteworthy that, in the first dissociation step, the binding strength of the alkali metal ions to the primary carboxylate groups is in the order $K^+>Na^+>Li^+$. This can be explained in terms of the radii of the hydrated alkali cations, which increase in the order $K^+<Na^+<Li^+$. The so-called solvent-separated ion-pairs between the hydrated cations and the carboxylate groups are predominant in the first step. The same affinity sequence of the alkali metal ions has been found for polysulfonates.[4,30] For polycarboxylates, however, it has been reported only in the case of the

primary carboxylate groups of poly(maleic acid).[9]

Interpretation on Specific Counterion Binding. A common structural feature to PIA and poly(maleic acid) is that the local density of ionizable groups along the polymer chain is much higher than that for polymonocarboxylic acids; hence, the interaction between neighboring groups must be considerable. Since the binding behavior of the counterions for PIA is quite analogous to that for poly(maleic acid),[9] a similar interpretation on the specific counterion binding in the first dissociation step is given as follows.

The monoanion of the itaconic acid residue is considered to have the structure:



involving cooperative hydrogen bonding by two adjacent carboxylate groups; hence, a single electronic charge is distributed by resonance over a wide range. Tate, who examined the titration behavior of PIA, has proposed the same structure.[15] The stability of the seven-membered ring is comparable to that of six-membered ones because of the very small volume of the hydrogen-bonded proton. Similar hydrogen-bonded seven-membered rings have been confirmed for the monoanion of maleic acid copolymers[7,31] and for the hydrogen maleate anion.[32,33] Although no sufficient evidence has been presented, it is expected that the formation of the structure leads to a rather compact conformation of the PIA chain.

Such a stable ring structure resulting from the hydrogen bonding should be effective at least in the first dissociation step. Thus, the primary carboxylate groups, which would bind to the alkali metal ions by nature, are more tightly bound to the protons of the secondary carboxylic groups. The present findings that hydrated alkali cations are more loosely bound to the primary carboxylate groups can be ascribed to such a chelation of a proton with two adjacent carboxylate groups. The intramolecular hydrogen bonding is gradually broken up with the increase in α. This results in a conformational change from a compact form to an extended form of the PIA chain. In the absence of added salts, the compact form resulting from the hydrogen-bonded structure is more stable; the pK_1 values in the lower α_1 region are fairly high (Fig. 6).

In the second dissociation step, the contact binding between the alkali metal ions and the carboxylate groups, which is much stronger than the solvent-separated binding with the hydrated cations, is predominant. Even if part of the monoanions assume the hydrogen-bonded structure, the effect should be negligible in comparison with that of the contact binding by the dianions or the carboxylate groups free from the hydrogen-bonded protons. Incidentally, the Li^+ ion is considerably smaller than the Na^+ and K^+ ions. In the high pH region, therefore, it is presumed that the Li^+ ions are more favorably located than the others in the place of the hydrogen-bonded protons. Such a chelation of a Li^+ ion with two adjacent carboxylate groups results in the higher θ values at high α. A similar structure has been proposed for the poly(maleic acid)-LiCl system in connection with the precipitation from the concentrated solution at higher α.[34]

In conclusion, we can safely say that the counterion binding for PIA is affected throughout by the interaction between the vicinal carboxylic groups.

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References

1) H. P. Gregor and M. Frederick, *J. Polym. Sci.*, **23**, 451 (1957).
2) I. Kagawa and H. P. Gregor, *ibid.*, **23**, 477 (1957).
3) H. P. Gregor, D. H. Gold, and M. Frederick, *ibid.*, **23**, 467 (1957).
4) K. Tamaki, M. Ozaki, M. Ogiwara, and I. Takemura, *Nippon Kagaku Zasshi*, **88**, 711 (1967).
5) I. Kagawa and K. Katsuura, *J. Polym. Sci.*, **17**, 365 (1955).
6) G. V. Ferry and S. J. Gill, *J. Phys. Chem.*, **66**, 999 (1962).
7) A. J. Begala and U. P. Strauss, *ibid.*, **76**, 254 (1972).
8) C. Tondre and R. Zana, *ibid.*, **76**, 3451 (1972).
9) N. Muto, T. Komatsu, and T. Nakagawa, This Bulletin, **46**, 2711 (1973).
10) C. S. Marvel and T. H. Shepherd, *J. Org. Chem.*, **24**, 599 (1959).
11) I. Sakurada, Y. Sakaguchi, S. Hōrin, and H. Ueda, *Kobunshi Kagaku*, **27**, 74 (1970).
12) R. G. Fordyce and G. E. Ham, *J. Amer. Chem. Soc.*, **69**, 695 (1947).
13) H. P. Gregor, L. B. Luttinger, and E. M. Loebl, *J. Phys. Chem.*, **59**, 34 (1955).
14) N. Muto, T. Komatsu, and T. Nakagawa, *Nippon Kagaku Zasshi*, **92**, 43 (1971).
15) B. E. Tate, *Adv. Polym. Sci.*, **5**, 214 (1967).
16) S. Nagai and K. Yoshida, *Kobunshi Kagaku*, **17**, 748 (1960).
17) S. Nagai and F. Fujiwara, *Polym. Lett.*, **7**, 177 (1969).
18) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York (1958), p. 638.
19) J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).
20) J. Th. G. Overbeek, *Bull. Soc. Chim. Belges*, **57**, 252 (1948).
21) M. Yasuda, K. Yamasaki, and H. Ohtaki, This Bulletin, **33**, 1067 (1960).
22) M. Mandel, *Europ. Polym. J.*, **6**, 807 (1970).
23) N. Muto, T. Komatsu, and T. Nakagawa, *Repts. Progr. Polym. Phys. Japan*, **15**, 75 (1972).
24) A. R. Mathieson and J. V. McLaren, *J. Polym. Sci., Ser. A*, **3**, 2555 (1965).
25) M. Mandel and J. C. Leyte, *ibid., Ser. A*, **2**, 2883 (1964).
26) J. R. Huizenga, P. F. Grieger, and F. T. Wall, *J. Amer. Chem. Soc.*, **72**, 2636, 4228 (1950).
27) M. Nagasawa and S. A. Rice, *ibid.*, **82**, 5070 (1960).
28) J. W. Lyons and L. Kotin, *ibid.*, **87**, 1670 (1965).
29) H. Terayama and F. T. Wall, *J. Polym. Sci.*, **16**, 357 (1955).

30) H. Eisenberg and R. Mohan, *J. Phys. Chem.*, **63**, 671 (1959).

31) B. J. Felber and N. Purdie, *ibid.*, **75**, 1136 (1971).

32) S. Nagakura, *J. Chim. Phys.*, **61**, 217 (1964).

33) J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Amer. Chem. Soc.*, **89**, 213 (1967).

34) J. L. Lang, W. A. Pavelich, and H. D. Clarey, *J. Polym. Sci., Ser. A*, **1**, 1123 (1963).