Electrophoretic and viscometric properties of poly(dicarboxylic acids)

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The electrochemical and conformational properties of maleic acid—methyl vinyl ether copolymer, maleic acid—styrene copolymer and poly(itaconic acid) were investigated as functions of pH by means of electrophoresis and viscosity. The electrophoretic mobility and viscosity were measured in the pH range 3—10 by using different buffer solutions at 0.1 ionic strength. The curves of limiting mobility ($U_{c \to 0}$) and intrinsic viscosity ($[\eta]$) against pH and the relationship between $[\eta]$ and $U_{c \to 0}$ were obtained and compared with those of poly(monocarboxylic acid). The $U_{c \to 0}$ and $[\eta]$ curves were also compared with the potentiometric titration curve of each poly(dicarboxylic acid) obtained in 0.1N NaCl solution. These results are discussed in terms of the dissociation property of each poly(dicarboxylic acid).

INTRODUCTION

Polymeric acids, e.g. alternating copolymers of maleic acid with other vinyl monomers, are known as poly(dicarboxylic acids). The potentiometric titration behaviour of poly(dicarboxylic acids) has been studied by many authors investigating dissociation properties[1-9]. It is well known that titration curves of the poly(dicarboxylic acids) have a pronounced inflection around the half—neutralization point which is distinguishable from those of poly(monocarboxylic acids) such as poly(acrylic acid) (PAA), thus indicating that the carboxyl groups in the dicarboxylic polymer dissociate in two stages.

In previous studies, however, little attention has been paid to the influence of dissociation properties on the electrochemical and conformational changes of poly(dicarboxylate ion). It is of interest to investigate the electrochemical and conformational properties and compare them with potentiometric behaviour.

Electrophoresis is a useful method for obtaining information about the electrochemical properties of polyion. Conformational properties can be investigated by viscometry. Previously[10-14], we studied electrophoretic and viscometric behaviour of PAA[10,11,14], carboxymethyl cellulose[12,14] and potassium poly(vinyl alcohol) sulphate[13,14] as functions of pH and ionic strength. From the results obtained, changes in effective electrical charge and conformation were evaluated, and explained in terms of effects of dissociation or association of proton and counterion.

In the present study, electrophoretic and viscometric measurements were carried out for maleic acid—methyl vinyl ether (MA—MVE) copolymer, maleic acid—styrene (MA—St) copolymer, and poly(itaconic acid) (PIA), which are representative poly(dicarboxylic acids) and frequently used for studies of potentiometric titration behaviour. The dependence of electrophoretic mobility and viscosity on pH and the relationship between viscosity and mobility were investigated, and then compared with those of PAA already reported[10,11,14]. Results are discussed in terms of the dissocia-

tion properties of each poly(dicarboxylic acid) evaluated by potentiometric titration.

EXPERIMENTAL

Materials

MA—St copolymer was prepared by hydrolysis of maleic anhydride—styrene (MAn—St) copolymer. Maleic anhydride and styrene were purified by recrystallization from chloroform and by vacuum distillation, respectively. The copolymerization of a mixture of maleic anhydride (0.5 mol) and styrene (0.5 mol) was carried out in thiophene-free benzene (400 ml) with α,α'—azobisisobutyronitrile as initiator at 50°C for 4 h in a nitrogen atmosphere. The MAn—St copolymer was separated from the reaction mixture by filtration, washed with benzene, reprecipitated from acetone solution, and dried under reduced pressure. Fractionation was carried out by addition of benzene into acetone solution (2%) of the copolymer, and six fractions were obtained. The molecular weight (M_n) was estimated by viscometric measurement[15]. The MA—St copolymer used here was obtained from hydrolysis of the fourth fraction ($M_n = 3.22 \times 10^5$). Hydrolysis was carried out in 1N NaOH at 40°C for 2 h under nitrogen. The hydrolyzate was dialysed against distilled water for three days. The dialysed solution was passed through a column of Amberlite IR-120B. The copolymer was obtained by lyophilization, and dried at 40°C for two days under reduced pressure. The result of elemental analysis was H, 5.58% and C, 64.82%. The calculated values of $(C_{12}H_{12}O_4)_n$ are H, 5.49% and C, 65.45%. An i.r. spectrum (KBr disc) showed absorptions at 1720, 1600, 1490, and 1220 cm^{-1}.

PIA was prepared by the polymerization of itaconic acid (0.5 mol). Itaconic acid was purified by recrystallization from distilled water. Polymerization of itaconic acid was carried out in distilled water (350 ml) at 50°C for 30 h. with potassium peroxysulphate as initiator under nitrogen. The reaction mixture was poured slowly into acetone to preci-
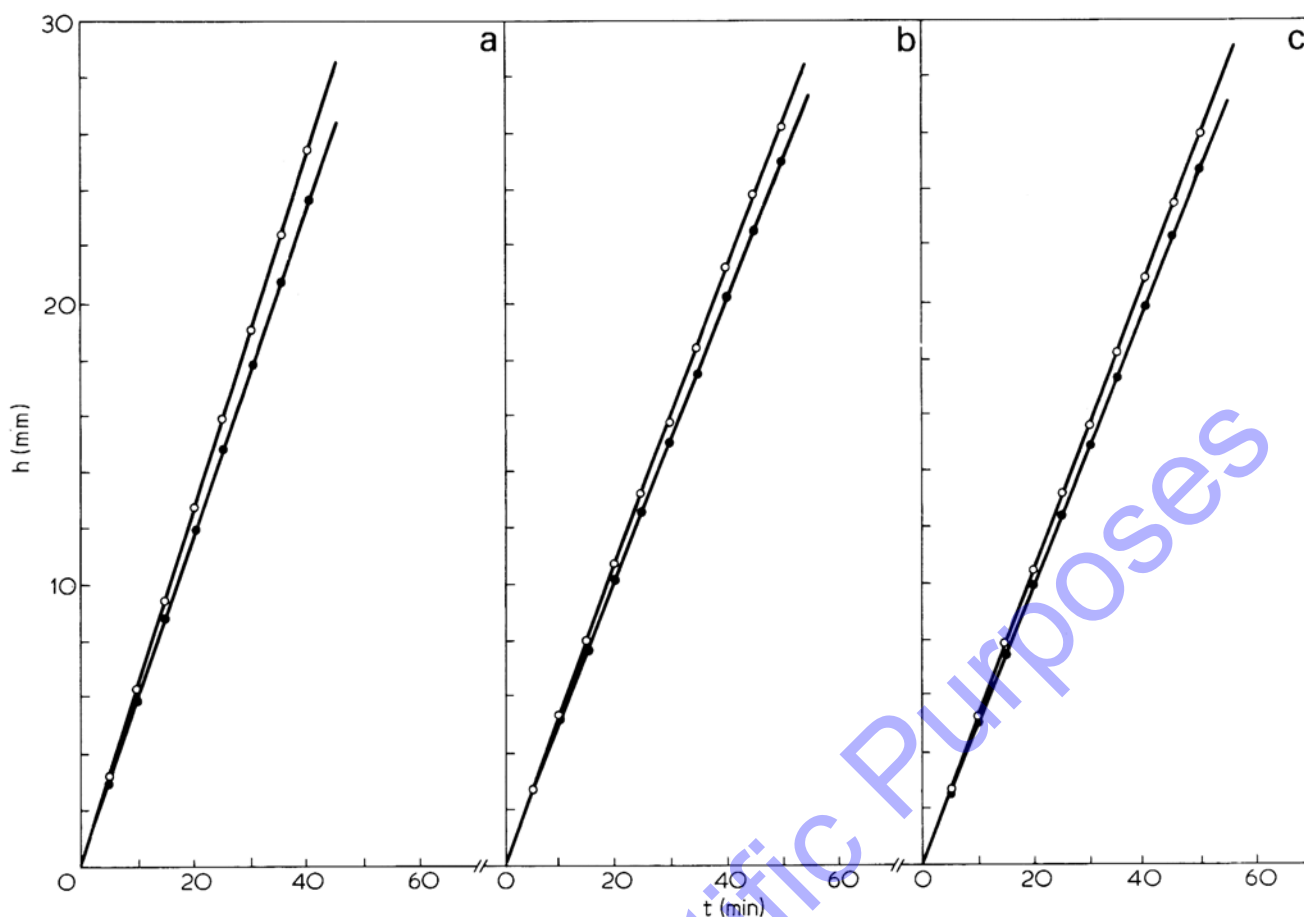
Figure 1 Determination of migrating velocities (h/t) for ascending ($\bigcirc$) and descending ($\bullet$) boundaries: a, MA–MVE copolymer at pH 7.01, specific conductance (κ) 6.080×10^{-3} ohm^{-1} cm^{-1}, polymer concentration (C) 0.1058 g dl^{-1}; b, MA–St copolymer at pH 6.98, $\kappa = 6.060 \times 10^{-3}$ ohm^{-1} cm^{-1}, C = 0.9992 g dl^{-1}; c, PIA at pH 6.98, $\kappa = 6.065 \times 10^{-3}$ ohm^{-1} cm^{-1}, C = 0.1153 g dl^{-1}

pitate polymer, which was separated by filtration, redissolved in water, and then dialysed against distilled water for five days. The dialysed solution was lyophilized and dried at 40°C for two days under reduced pressure. The result of elemental analysis was H, 4.62% and C, 45.91%. The calculated values of $(C_5H_6O_4)_n$ and H, 4.65% and C, 46.16%. An i.r. spectrum (KBr disc) showed absorptions at 1720 and 1230 cm^{-1}. The value of $[\eta]$ in 1 N NaCl at 25°C was 0.0786 dl g^{-1}.

The MA–MVE copolymer was prepared by hydrolysis of the copolymer of maleic anhydride–methyl vinyl ether manufactured by General Aniline & Film Co. The purification and preparation were described previously[16]. The result of elemental analysis was H, 5.83% and C, 47.19%. The calculated values of $(C_7H_{10}O_5)_n$ are H, 5.80% and C, 48.30%. An i.r. spectrum (KBr disc) showed absorptions at 1720, 1200 (broad), and 1100 cm^{-1}. The value of $[\eta]$ for sodium salt of MA–MVE copolymer in 1 N NaCl at 25°C was 1.56 dl g^{-1}.

Electrophoresis

The sample solution was prepared by using different buffer solutions at 0.1 ionic strength. Buffer solution systems are: CH$_3$COOH–CH$_3$COONa, pH 3–5; Na$_2$HPO$_4$–KH$_2$PO$_4$, pH 6–8; and NaHCO$_3$–Na$_2$CO$_3$, pH 9–10. Polymer (1.5 g) was dissolved in buffer solution (300 ml), and then dialysed against the same buffer solution in a cellophane tube until the Donnan equilibrium was reached. The polymer concentration of the dialysed solution was determined by evaporating to dryness. The sample solutions at different concentrations were prepared by diluting with the

buffer solution against which the sample solution was dialysed.

The electrophoretic velocity was measured at 25 ± 0.01°C using a Hitachi Tiselius Electrophoresis Apparatus (Model HTD-1). A micro-type cell with cross–sectional area of 0.1900 cm^2 was used. The migrating electric current was 3.2 mA. The Joule heat generated by this current was 4.45 × 10^{-2} W ml^{-1} s^{-1} at maximum. No effects of convection current and current leakage were observed during electrophoretic measurement. The migration distance (h) of the gravity centre of Schlieren pattern was measured on a photographic plate with a microcomparator. The migrating velocity (h/t) was determined by the slope of a straight line obtained by plotting h against time (t) (*Figure 1*).

Viscosity

The viscosity of the same sample solution used for the electrophoresis was measured at 25 ± 0.005°C by using an Ubbelohde viscometer having a follow time of 304.5 s for water at 25°C. Corrections for kinetic energy and rate of shear were found to be negligible. Relative viscosity (η_r) and specific viscosity (η_{sp}) were determined in the concentration (C) range of 0.04–0.24 g dl^{-1}. The plots of η_{sp}/C and $(\ln\eta_r)/C$ against C were given at least five points, and then extrapolated to $C \to 0$ by means of the least-squares method.

Potentiometric titration

The sample was dissolved in 100 ml of 0.1 N NaCl solution. The sample concentration (C_M) was 0.01 M, as expressed by the molarity of carboxyl groups attached to the
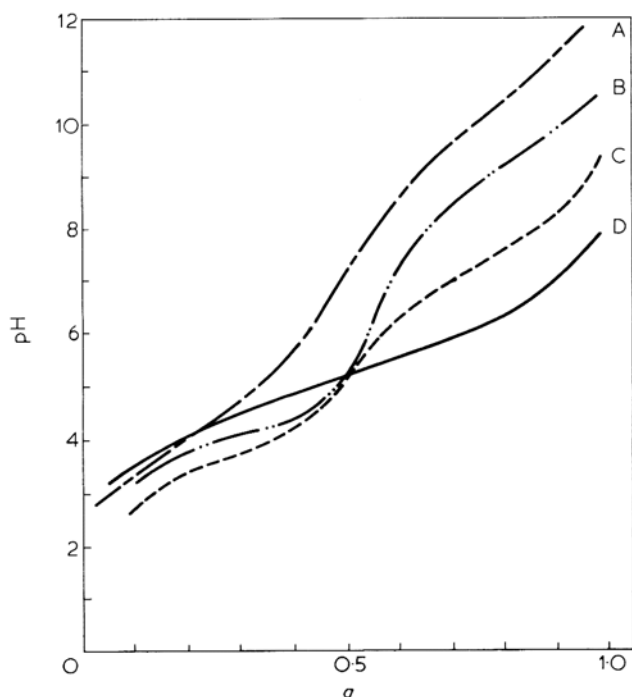
Figure 2 Potentiometric titration curves of PIA (A), MA—St co-polymer (B), MA—MVE copolymer (C), and PAA (D)[14]: curve D was obtained for the sample with $\bar{M}_n = 2.81 \times 10^5$ at $C_M = 0.05$ N in 0.1 N NaCl solution

polymer chain. The titration was carried out with 2 N NaOH at $25 \pm 0.1°C$ in a nitrogen atmosphere by using a Hirama Automatic Recording Titrator. To avoid the changes in concentration and ionic strength during the titration, high concentration titrant was added automatically to the sample solution from a microburet with a precision of 0.0005 ml. The neutralization points of two carboxyl groups in an MA—MVE residue were determined by means of first and second peaks of differential titration curve recorded together with the original titration curve. The titrant volume (V_f) at the first peak was in fair agreement with that (V_s) at the second peak. For the titrations of MA—St copolymer and PIA, however, no definite second peak was observed in the differential titration curve because the original titration curve did not inflect at the region where the second carboxyl group was completely neutralized. In these cases, the neutralization point of second carboxyl group was assigned to the double amount of V_f (i.e. $V_s = 2V_f$, since the results of elemental analysis showed that each poly(dicarboxylic acid) used here contains two carboxy groups in a monomeric residue.

RESULTS AND DISCUSSION

Potentiometric titration curve

The titration curve was expressed by the relation between pH and the degree of dissociation (α). The value of α was calculated by:

$$\alpha = \alpha_n + (C_{H^+} - C_{OH^-})/C_M \quad (1)$$

where α_n represents the degree of neutralization, and C_{H^+} and C_{OH^-} are the molarity of proton and hydroxyl ion. The titration curves of three poly(dicarboxylic acids) are shown in *Figure 2*, together with that[14] of PAA. The pattern of the curve for each poly(dicarboxylic acid) is in contrast

to that of PAA, and shows an inflection point around $\alpha = 0.5$. These indicate that each of the poly(dicarboxylic acids) investigated here has two species of the carboxyl groups of which the dissociation of protons occurs in two stages.

The dependence of apparent dissociation constant (pK_a) on α was also investigated to obtain information about the titrational behaviour of poly(dicarboxylic acids). The pK_a value was calculated by:

$$pK_a = pH + \log(1 - \alpha)/\alpha \quad (2)$$

The curves of pK_a *versus* α were shown in *Figure 3*. It is observed that the change in pK_a with α in the first dissociation stage ($\alpha < 0.5$) is smaller than that in the second dissociation stage ($\alpha > 0.5$). When poly(dicarboxylic acids) are neutralized, one of the two carboxyl groups in a monomeric residue dissociates relatively easily. However, if the neutralization is carried beyond 50%, protons have to be removed from the other carboxyl group which is situated very close to a carboxylate ion, and this is much more difficult. Thus, a remarkable inflection appears at $\alpha = 0.5$. It is also observed that the change of pK_a in the region of $\alpha < 0.5$ for MA—St copolymer is different from those for the other poly(dicarboxylic acids), and the value of pK_a is independent of α in the region of 0.25—0.35. Similar observation has been reported for poly(methacrylic acid)[17] and the copolymer of maleic acid—butyl vinyl ether[7]. These were explained by the conformational transition in the dissociation process. For the conformational transition of MA—St copolymer,
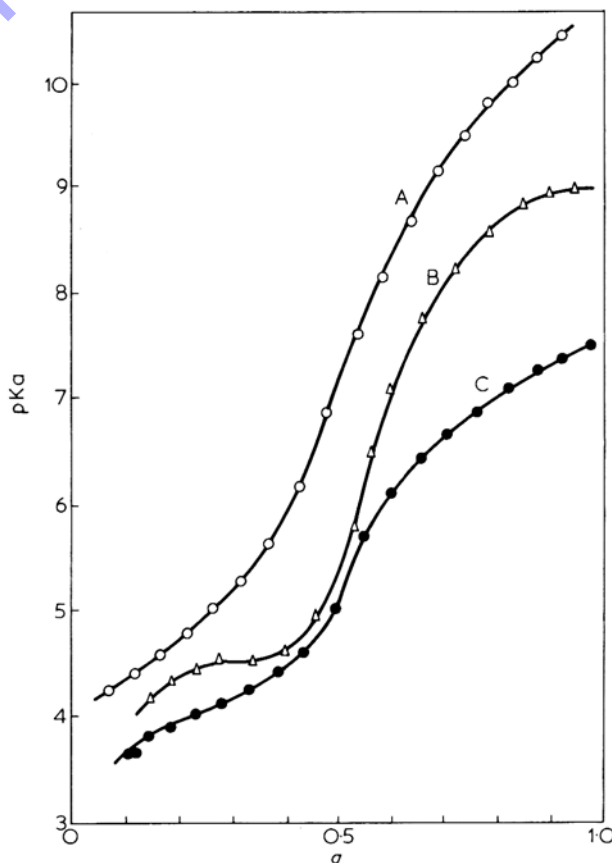

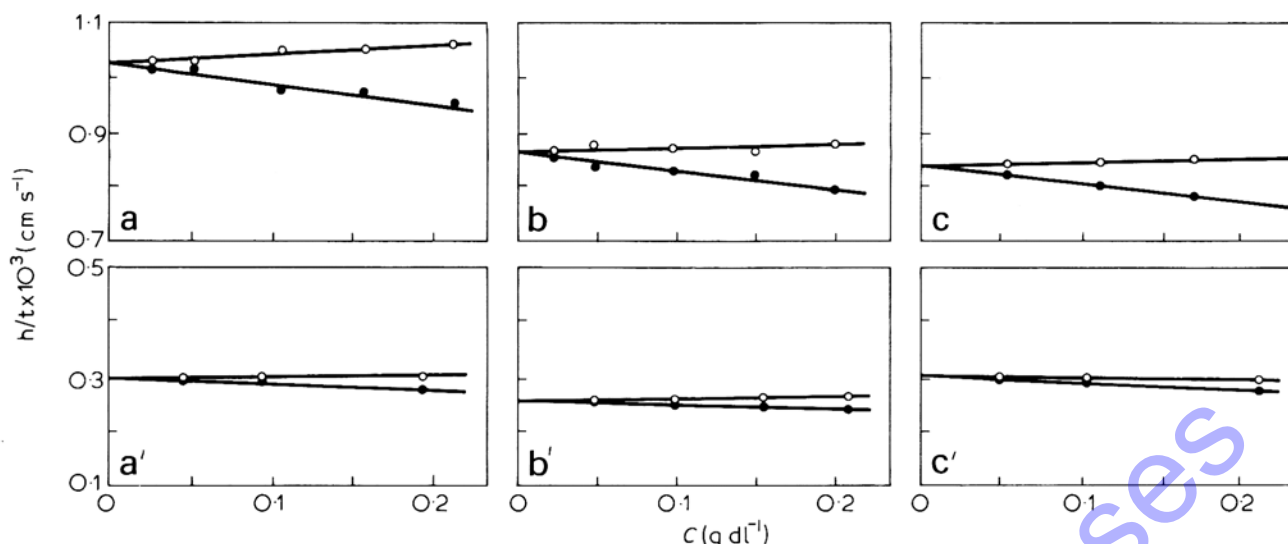*Figure 3* Curves of pK_a vs. α for PIA (A), MA—St copolymer (B), and MA—MVE copolymer (C)

Figure 4 Dependence of h/t of ascending (○) and descending (●) boundaries on C for MA—MVE copolymer (a, a'), MA—St copolymer (b, b'), and PIA (c, c'): a, b and c were obtained in the pH range 7.01—6.98 and $\kappa = 6.080 \times 10^{-3}$—$6.060 \times 10^{-3}$ ohm^{-1} cm^{-1}, and a', b', and c' were in the pH range 3.18—3.23 and $\kappa = 6.190 \times 10^{-3}$—$6.205 \times 10^{-3}$ ohm^{-1} cm^{-1}

the standard free energy change per monomole is 280—370 cal[8], as estimated from titrational data obtained in the range of ionic strength (NaCl) 0.27—0.009.

Dependence of electrophoretic mobility and viscosity on pH

The dependence of migrating velocity (h/t) on polymer concentration (C) was at first investigated to estimate precisely the electrophoretic mobility of poly(dicarboxylate ion) (*Figure 4*). It is found that the plots of h/t vs. C, obtained from ascending and descending boundaries, are expressed by straight line. Furthermore, the dependence of h/t on C is strengthened with increasing pH, and this tendency reaches a maximum at pH 7—8. The lack of symmetry between the Schlieren patterns of ascending and descending boundaries appears in the electrophoretic diagram, indicating that the pH gradient between polymer solution and solvent is produced in the electrophoretic cell during measurement, and this effect becomes progressively greater as the value of h/t increases. Thus, the h/t value obtained at a finite concentration was expected to implicate the effect of pH gradient. However, it is considered that the effect of pH gradient can be reduced infinitely if the value of h/t is extrapolated to $C \to 0$. The extrapolation was performed by the least-squares method. The value of limiting migration velocity $[(h/t)_{c \to 0}]$ obtained from the ascending boundary was in agreement with that from the descending boundary (*Figure 4*). The limiting mobility ($U_{c \to 0}$) is then calculated by:

$$U_{c \to 0} = (\kappa S/i)(h/t)_{c \to 0} \tag{3}$$

where S represents the cross-sectional area of the cell, κ is the specific conductance of solvent, and i is the migration electric current.

The plots of η_{sp}/C and $(\ln\eta_r)/C$ vs. C, obtained from the viscometric measurements, were expressed in all the cases by the equations of Huggins and Mead—Fouss:

$$\eta_{sp}/C = [\eta] + \kappa'[\eta]^2 C \tag{4}$$

$$(\ln\eta_r)/C = [\eta] - \beta[\eta]^2 C \tag{5}$$

where $[\eta]$ represents the intrinsic viscosity, κ' is Huggins's constant, and β is related to κ' by $\beta = 1/2 - \kappa'$. The difference between the values of $[\eta]$ estimated by equations (4) and (5) is smaller than 1%.

The curves of $U_{c \to 0}$ and $[\eta]$ vs. pH are shown in *Figure 5*, together with those[10,11,14] of PAA already reported. Both curves of each poly(dicarboxylic acid) are in contrast to those of PAA and have plateaux in specific pH regions. The potentiometric titration curves of each poly(dicarboxylic acid) indicate that two carboxyl groups in a monomeric residue dissociate in two stages. From the comparison of *Figure 5* with *Figure 2*, it is observed that the plateaux in the mobility and viscosity curves appear in the pH region around $\alpha = 0.5$ of the titration curve. Therefore, the changes of $U_{c \to 0}$ and $[\eta]$ in the pH region below and above the plateau can be assigned to the first and second dissociation stages of carboxyl groups in each poly(dicarboxylic acid), respectively.

To obtain accurate informations about the electrochemical properties of poly(dicarboxylic acids), the curve of $U_{c \to 0}$ vs. pH was investigated in detail. It is found that the increase in $U_{c \to 0}$ below the plateau is larger than that above the plateau. This finding indicates that each poly(dicarboxylate ion) carries a large portion of the effective charge in the first dissociation stage. In the second dissociation stage at the neutral region, there is little increase in the effective charge. However, the effective charge is reduced with increase in the basicity. As reasonable interpretation of the electrophoretic behaviour at the second dissociational stage, incomplete dissociation of proton and/or the binding effect of counterion could be considered. The differential titration curve of MA—MVE copolymer showed two peaks, and the titrant volume at the first peak agrees with one half of the titrant volume at the second peak. This indicates that the dissociation of protons from two carboxyl groups in a monomeric residue are stoichiometric. In the cases of MA—St copolymer and PIA, the second peak was not definite, and a slight amount of proton might be bound to the second carboxyl group. Even if this binding of proton is taken into account, however, the decrease in $U_{c \to 0}$ at the second dissociational stage is considerably larger. Thus, the electro-
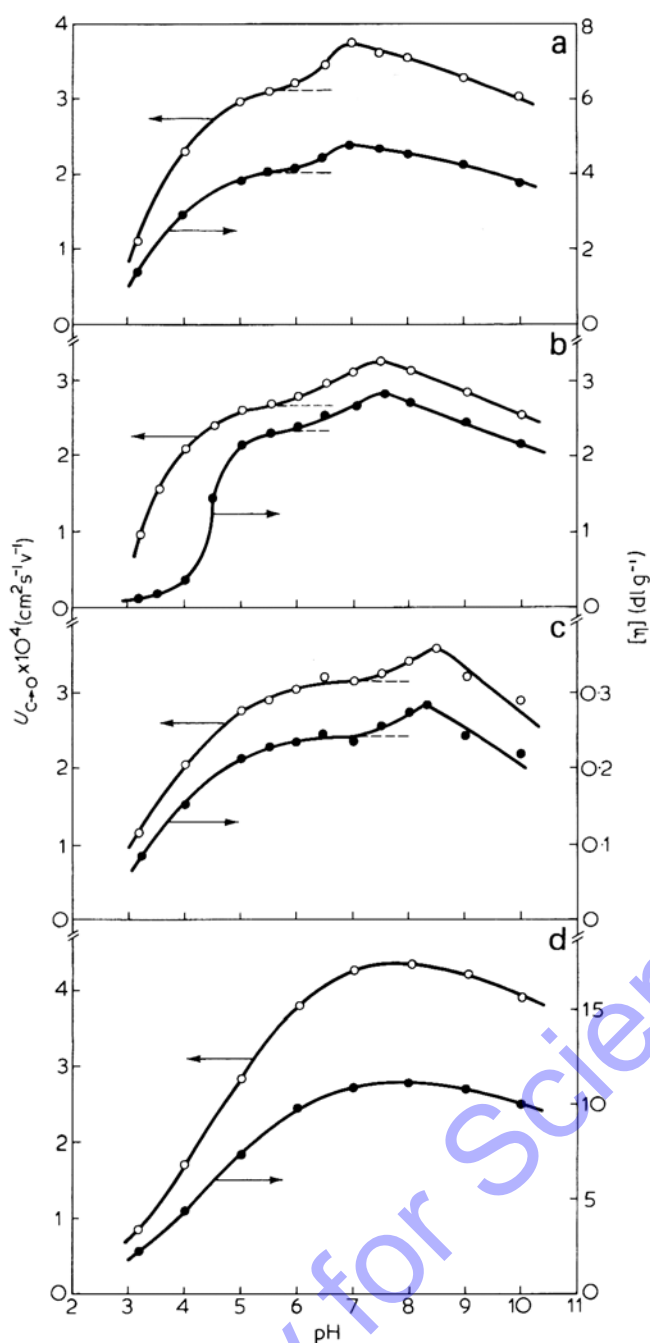
Figure 5 Curves of $U_{c \to 0}$ and $[\eta]$ vs. pH for MA–MVE copolymer (a), MA–St copolymer (b), PIA (c), and PAA (d)[10,11,14]: the results for PAA were obtained for the sodium salt of PAA with $\overline{M}_n$ = 3.67 x 10⁵ in the same manner as described here

phoretic property at the second dissociational stage seem to be influenced mainly by counterion binding. A similar result has been presented by the study on the degree of counterion binding (θ) for PIA ion[9]; the value of θ was 0.1 at $\alpha = 0.5$ and 0.3–0.7 at $\alpha = 1$, estimated by potentiometric titration in aqueous solution containing metal ions such as Li⁺, K⁺ and Na⁺. On the other hand, from the results shown in *Figures 2* and *5*, it is observed that the decrease in $U_{c \to 0}$ for each poly(dicarboxylic acid) commences at the region of pH 7–8.5 (i.e. $\alpha = 0.6$–0.7), while that for PAA is at pH 7.5 (i.e. $\alpha = 0.9$). These indicate that the type of counterion binding to poly(dicarboxylate ion) is different from that to poly(monocarboxylate ion). The binding of counterion to poly(dicarboxylate ion) could be understood by assuming

trapping of counterion between two carboxylate ions in a monomeric residue.

The conformational properties of poly(dicarboxylic acids) were evaluated by the curves of $[\eta]$ vs. pH. From the result shown in *Figure 5*, it is observed that the pattern of the viscosity curves for MA–MVE copolymer and PIA is similar to that of the mobility curves. In the case of MA–St copolymer, both the curves show a similar pattern in the region above pH 5. These indicate that the conformational change of poly(dicarboxylic acid) reflects the change in effective charge estimated by the mobility curve. However, the magnitude of the increase in $[\eta]$ for MA–St copolymer in the pH region below 5 is smaller than that in $U_{c \to 0}$. Ferry *et al.*[2] have been reported that the value of $[\eta]$ for MA–St copolymer in aqueous solution containing dioxane and HCl varies in a complicated manner with the contents of dioxane and HCl, whereas similar behaviour is not observed for the copolymer of maleic acid–ethyl vinyl ether. Other workers[5,8] also studied conformational properties of MA–St copolymer by potentiometric titration, viscosity, spectro-photometry and dilatometry and reported that the confor-mational transition occurs in the first dissociational stage. Thus, the results of viscosity for MA–St copolymer obtained here can be also explained by the conformational transition: a tightly coiled form of the copolymer chain in the region below pH 4 transforms to a loosely coiled one around pH 4.5, since the electrical repulsion force overcomes the hydrophobic force due to the interaction between phenyl groups in the copolymer. These are supported by the result of potentiometric titration (see *Figure 3*).

Relationship between viscosity and mobility

The change in effective electric charge can be evaluated by the curve of $U_{c \to 0}$ vs. pH. Furthermore, the $[\eta]$ vs. pH curve reflects the conformational change due to the effective charge. Thus, it can be expected that a relationship exists between $[\eta]$ and $U_{c \to 0}$. In previous studies on electro-phoresis and viscosity for different polymeric acids[10–14], the dependence of $[\eta]$ on $U_{c \to 0}$ was investigated to obtain the relationship between them. This was expressed by:

$$[\eta] = A U_{c \to 0} M^a \tag{6}$$

when ionic strength is greater than 0.1. M represents the molecular weight of the polymer. a and A are empirical constants; A is found to be independent of M and ionic strength. When equation (6) is combined with the Flory–Fox equation[19] for $[\eta]$, $U_{c \to 0}$ can be related to the expan-sion factor (α_η)[11,14]:

$$\alpha_\eta^3 = (A/K_0)(U_{c \to 0})M^c$$

$$K_0 = \Phi(\overline{\gamma}_0^{-2}/M)^{3/2} \tag{7}$$

$$c = a - 1/2$$

where Φ is a universal constant, and $\overline{\gamma}_0$ is the end-to-end dis-tance at the theta point.

The theoretical[20–22] and experimental[23–27] studies on electrophoresis of polyelectrolytes showed that the electro-phoretic mobility is independent of the coil dimenions as long as the ionic strength is higher relatively. These results indicate that the polyion coil behaves in electrophoresis as a free draining coil. Free draining behaviour can be confirmed also from the fact that the value of a in equation (6) is equal
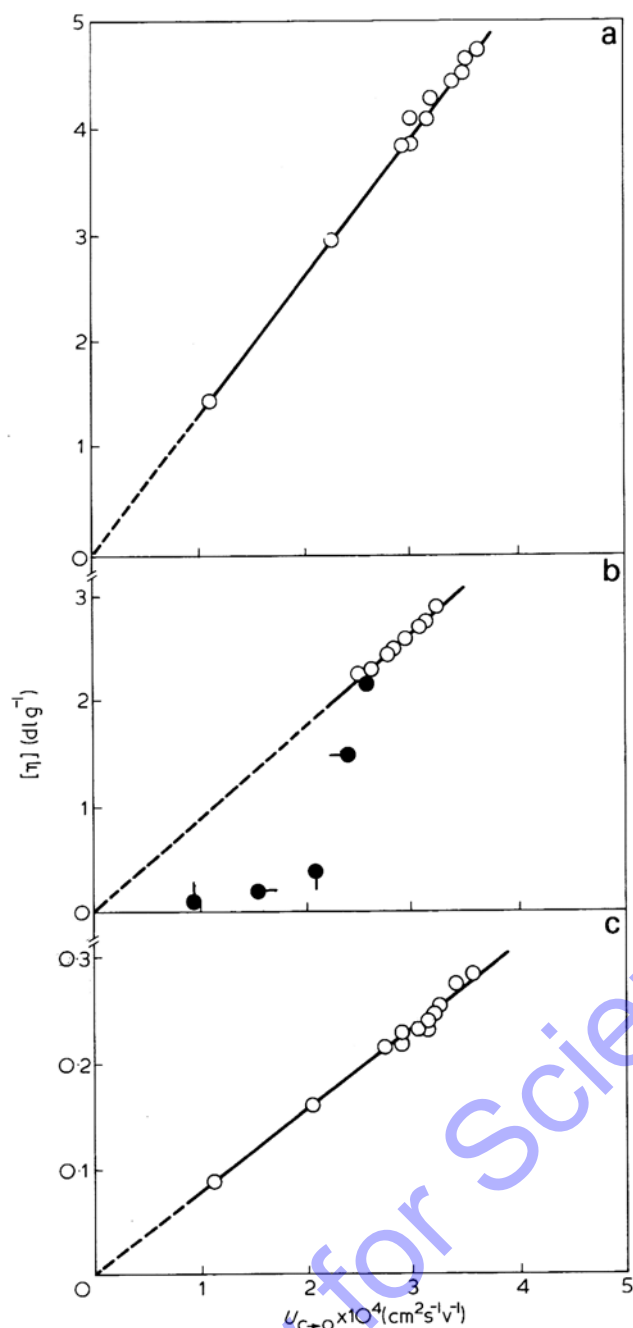
Figure 6 Relationship between [η] and $U_{c \to 0}$ for MA—MVE copolymer (a), MA—St copolymer (b), and PIA (c): plots of [η] vs. $U_{c \to 0}$ were obtained at different pH from the results shown in *Figure 5*. pH values are indicated in (b): ●, 3.21; ●, 3.49; ●, 4.01; ●, 4.50; ●, 5.02

to the value estimated by means of the slope of the logarithmic plots of [η] vs. M; in other words, $U_{c \to 0}$ is dependent on α_η^3 and not on M[11,14]. Thus, information about the electrophoretic behaviour of polyion coil can be obtained by investigation of the relationship between [η] and $U_{c \to 0}$.

In the present study, this relationship was investigated (*Figure 6*). It is found that the plots of [η] vs. $U_{c \to 0}$ for MA—MVE copolymer and PIA are expressed by straight lines passing through the origin. For MA—St copolymer, a similar relation was obtained in the pH region above 5. In the pH region below 5, however, the plots of [η] vs. $U_{c \to 0}$ for MA—St copolymer deviates from the straight line. For the polyelectrolytes used in previous studies on electrophoretic

behaviour[10–14,23–27], it was known that no specific change in the conformation is observed by other experimental methods such as viscosity and potentiometric titration. Moreover, similar observations for MA—MVE copolymer and PIA were obtained by the present investigation. In contrast to these polyelectrolytes, however, the MA—St copolymer forms a tighter coil in the pH region below 4, and this transforms to a looser coil at pH 4.5. Taking into account these results, the deviation of the plots of [η] vs $U_{c \to 0}$ for MA—St copolymer are explicable as follows: the viscometric behaviour of the tightly coiled form is different from that of the loosely coiled one, whereas the electrophoretic behaviour of the tightly coiled form is the same as that of the loosely coiled one since no difference between the mobility curves of MA—St copolymer and the other poly(dicarboxylic acids) was observed (*Figure 5*). The similarity of electrophoretic behaviour could be explained by the assumption that the tightly coiled form of MA—St copolymer behaves during electrophoresis as a free draining coil.

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