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DIELECTRIC DISPERSION OF ALTERNATING COPOLYMERS OF MALEIC ACID

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Dielectric dispersions of three kinds of copolymers of maleic acid, poly(maleic acid-co-methyl vinyl ether) (PMAMVE), poly(maleic acid-co-ethyl vinyl ether) (PMAEVE) and poly(maleic acid-co-styrene) (PMAST), were measured by use of a pseudorandom noise dielectric spectrometer. A large dielectric increment was observed in the low frequency region (10–20 Hz), and was explained in terms of our theory of ion fluctuation. When these copolymers were neutralized with mixtures of NaOH and $Ca(OH)_2$ by changing their ratio, enhancement of the static dielectric increment was observed in the intermediate ratios of both ion species. This phenomenon was analyzed by modifying our theory of ion fluctuation to the case of alternating copolymers. Quantitative agreement with experimental results was obtained by using values of parameters representing binding energies and mutual repulsion, which are chosen to fit the calculated degree of ion binding to the experimental data on activities of Na^+ and Ca^{2+} ions. At large fractions of divalent ions, the increment, relaxation time and specific viscosity were found to decrease sharply due to chelation by divalent ions.

1. Introduction

Polyelectrolyte solutions exhibit high dielectric constant resulting from high polarizability of polyions. Such high polarizability is provided by the motion of loosely bound ions along the polymer chain [1–7]. Various experimental findings indicate that the dielectric increment is enhanced by loosely bound ions but reduced by strongly bound ions. For example, solutions of strong polyacids such as poly(styrene sulfonic acid, PSS) show high dielectric increment both in the neutralized and unneutralized states, whereas those of weak polyacids such as poly(acrylic acid, PAA) show high dielectric increment only when neutralized with strong bases.

Other possible factors responsible for the polarizability of polyions are considered to be of minor importance. Orientation of permanent dipole seems unlikely, because in most cases, a polyelectrolyte molecule has no net permanent dipole along its main chain from a structural point of view, or the permanent dipole is easily canceled by ionic charge if it exists. Contribution of electrophoretic motion of the polyion to the dielectric increment is negligible, because it provides an opposite dispersion, i.e. dielectric constant increases with increasing frequency [8]. The opposite dispersion has never been observed in polyelectrolyte solutions. Interfacial polarization such as the Maxwell–Wagner effect also provides a small contribution [9]. In addition, the dispersion frequency predicted by this mechanism is usually too high.

Theoretically, the enhancement of the dielectric increment by loosely bound ions is explained by the enhancement of charge fluctuation of bound ions. According to the fluctuation-dissipation theorem [5,10], the charge fluctuation is related to the mean square of dipole moment of the polyion. Our previous theoretical works [1–4] demonstrated that the charge fluctuation of a linear lattice molecule calculated in terms of the Ising model was in agreement with the experimental results.

Besides these facts, it is known that divalent counterions enhance the static dielectric increment ($\Delta\epsilon_0$) of the polyelectrolyte solutions. This phenomenon, found in various kinds of polyelectrolytes, is due to a specific effect of divalent ions, because divalent ions are bound more strongly to the polyion than monovalent alkali metal ions. The enhancement of $\Delta\epsilon_0$ is also understood on the basis of the charge fluctuation by using a lattice model [1,11]. Here the lattice model represents the properties that a divalent ion as well as a monovalent ion is capable of occupying a single lattice point and is mobile along the polymer chain if the next lattice point is vacant. The calculation reveals that the bound divalent ions provide larger charge fluctuation at the lattice point, by assuming reasonable values of the binding energy which are consistent with the results of activity measurements of single ions. The theory also predicts the disappearance of the enhancement in the solutions containing very tightly bound ions, as the cases of the transition metals. It should be noted that the effect of the divalent ions is observed in $\Delta\epsilon_0$ or in the low frequency dispersion region (below 10^4 Hz) for fairly wide polymer concentration range (C_p = 0.1 mN to 5 mN), whereas not observed in the high frequency dispersion region (above 10^4 Hz). This fact means that the linear lattice model is applicable only to the low frequency dielectric properties.

Dielectric study of the copolymers of maleic acid has been made for a few kinds of the copolymers [4,12,13]. These copolymers exhibit several unique characteristics, as compared with the homopolymers of monoprotic acids [14–18]. They are due to the high local charge density resulting from two carboxyl groups in close proximity as well as to the hydrophobic interaction among nonpolar chains incorporated into the copolymers as constituents.

Concerning the effect of divalent ions on the dielectric increment, the enhancement of $\Delta\epsilon_0$ has been observed only in the limited cases, which was ascribed to the strong affinity of the divalent ion to a single pair of the carboxyl groups. Our previous experiments, however, were limited to 200 Hz as the lowest frequency, so that they were still insufficient to determine accurate values of $\Delta\epsilon_0$.

The present method [19–22], by use of a pseudo-random noise dielectric spectrometer, is quite effective in determining the values of $\Delta\epsilon_0$ as well as the low frequency dispersion profiles, because the frequency domain is extended to 10 or 20 Hz, and the electrode polarization effect is removed by use of a 4-terminal electrode cell. The increment is found to be enhanced by mutual presence of calcium and sodium ions in solutions of poly(maleic acid-co-methyl vinyl ether) (PMAMVE), poly(maleic acid-co-ethyl vinyl ether) (PMAEVE) and poly(maleic acid-co-styrene) (PMAST), as compared with the respective solutions neutralized with sodium hydroxide.

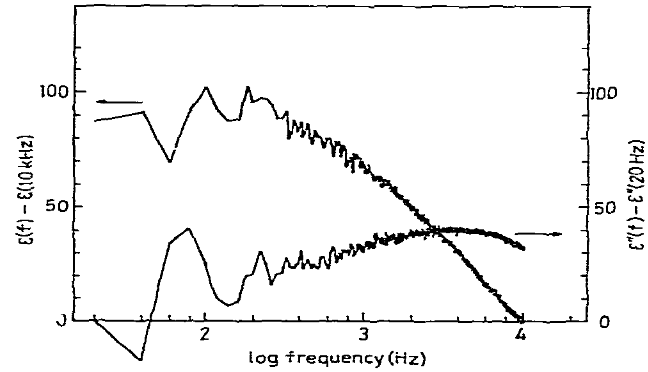

Fig. 1. An example of the recording of the dielectric increment and dielectric loss increment of PMAEVE. The ordinate is either the difference in dielectric constant $\epsilon(f) - \epsilon(10\ \mathrm{kHz})$, or the difference in the dielectric loss $\epsilon''(f) - \epsilon''(20\ \mathrm{Hz})$. Polymer concentration C_p = 1 mN, degree of neutralization $\alpha = 0.5$, and the counterion ratio of Na^+ to Ca^{2+} = 8:2.

2. Materials and methods

PMAMVE was a generous gift of Professor M. Nagasawa, Nagoya University. PMAEVE and PMAST were synthesized by copolymerization of maleic anhydride with ethyl vinyl ether or styrene. Synthesis and purification of these copolymers and preparation of the salt-free solutions have been described in the previous works [2,18].

Measurements of dielectric constant in the low frequency region (below 10 kHz) were carried out with a pseudo-random noise dielectric spectrometer. Details of the apparatus and measuring techniques have already been described [19–22]. In most cases, measuremenst were made at 20.8 ± 0.05°C, over frequency region from 10 kHz to 10 or 20 Hz, by using about 30 ml of freshly prepared solution at concentration 1 mN. For high frequency region, dielectric measurements were made with an Ando TR-1B bridge. Experimental details have also been described [23].

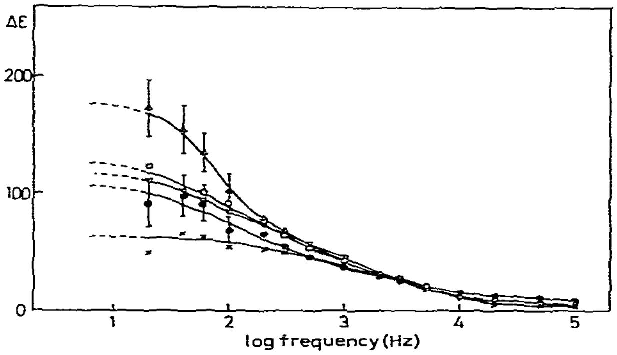

Fig. 2. Dielectric dispersion of PMAEVE neutralized with mixtures of NaOH and $Ca(OH)_2$. Experimental conditions are: $C_p = 1$ mN, $\alpha = 1$, and counterion ratio (Na^+:Ca^{2+}) = 10:0 (●), 8:2 (○), 6:4 (△), 4:6 (▽), 2:8 (×). Vertical bars express the magnitude of the precision.

3. Results

Fig. 1 shows a typical example of the recording of the dielectric increment ($\Delta\epsilon$) and dielectric loss increment ($\Delta\epsilon''$) of PMAEVE partially neutralized with mixtures of NaOH and $Ca(OH)_2$. The ordinate expresses either the difference in dielectric constant at any frequency and that at 10 kHz, or the difference in dielectric loss at any frequency and that at 20 Hz. Experimental errors of both quantities increase as frequency decreases. Although the apparatus records $\Delta\epsilon$, $\Delta\epsilon''$ and the Cole-Cole plot in each measurement, the latter two quantities are usually not adopted in this paper because of the large error of $\Delta\epsilon''$ in the low frequency region and of the lack of the value at the reference frequency, $\Delta\epsilon''$ (20 Hz).

Fig. 2 shows the dispersion curves of PMAEVE neutralized with mixtures of NaOH and $Ca(OH)_2$. In the low frequency region, the dielectric increment is not always saturated to a certain value but still has a tendency to increase. So the values of $\Delta\epsilon_0$ are mostly estimated by extrapolation of the dispersion curves. It seems appropriate to use the values of $\Delta\epsilon_0$ thus obtained for examination of the effect of divalent ions, although these values may contain fairly large amounts of errors, as indicated by vertical bars in the figure. Evidently, previous observation above 200 Hz is found to be insufficient to determine $\Delta\epsilon_0$.

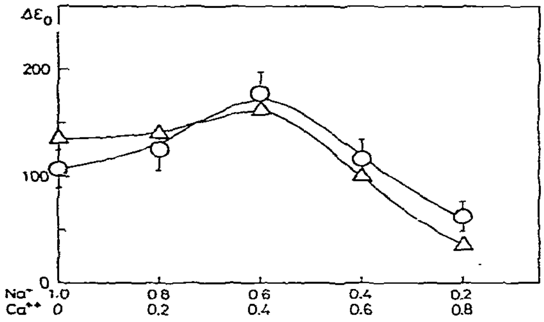

Fig. 3. Dependence of the static dielectric increment $\Delta\epsilon_0$ of (PMAEVE (○) and PMAMVE (△) on the counterion ratio of Na^+ to Ca^{2+}. $C_p = 1$ mN, $\alpha = 1$.

There is another dispersion in the high frequency region (above 100 kHz). The increment of this dispersion is, however, much smaller than $\Delta\epsilon_0$, so that the study is focused to the low frequency dispersion process.

Dependence of the dielectric increment on the counterion ratio was examined at concentration 1 mN, and at degree of neutralization 1, so that the total counterion concentration, $C_{Na} + C_{Ca}$ was 1 mN. Values of $\Delta\epsilon_0$ of PMAEVE and PMAMVE, and those of PMAST are plotted as a function of the counterion ratio in figs. 3 and 4, respectively. In the case of

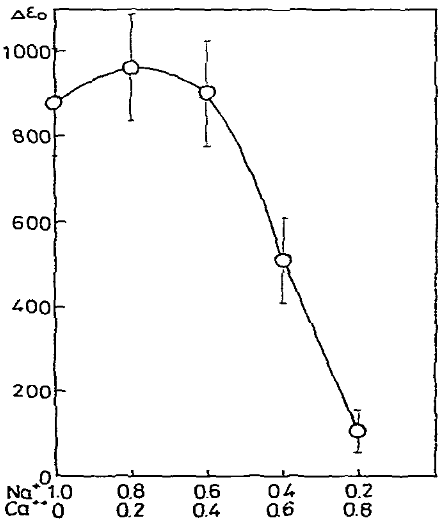

Fig. 4. Dependence of $\Delta\epsilon_0$ of PMAST (○) on the counterion ratio of Na^+ to Ca^{2+}. $C_p = 1$ mN, $\alpha = 1$.

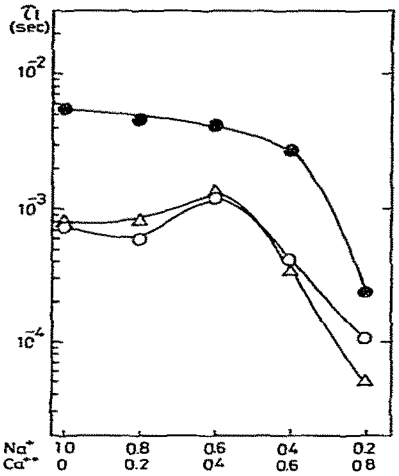

Fig. 5. Dependence of the mean relaxation time of the low frequency dispersion τ_ℓ of PMAEVE (○), PMAMVE (△) and PMAST (●) on the counterion ratio of Na^+ to Ca^{2+}. C_p = 1 mN, α = 1.

PMAEVE, $\Delta\epsilon_0$ increases as the fraction of Ca^{2+} increases, reaches a maximum at about 40% replacement, and then decreases sharply. Similar tendency is observed for PMAMVE. In the case of PMAST, much larger increment is observed, and calcium ion seems less effective to enhance $\Delta\epsilon_0$, as compared with other two cases. These differences are ascribed primarily to the difference in the molecular weight (M_w = 1.8 × 10^5 for PMAEVE and ca. 5 × 10^5 for PMAST), as discussed later.

The mean relaxation time of the low frequency dispersion, τ_ℓ, is plotted in fig. 5 as a function of the counterion ratio for the three kinds of copolymers. Much larger values of τ_ℓ for PMAST are also due to the large molecular weight of the sample. In each case, τ_ℓ decreases sharply for large fraction of Ca^{2+}, suggesting the shrinkage of the polyion. Dependence of specific viscosity, η_{sp}, on the counterion ratio indicates the same tendency as shown in fig. 6. The viscosity decreases slightly as the fraction of Ca^{2+} increases, and then decreases sharply. Values of η_{sp} for PMAST are larger than those for PMAEVE, corresponding to the larger molecular weight of PMAST. Relative decrease in η_{sp} due to the replacement by Ca^{2+} is more drastic for PMAST than for PMAEVE. This is also ascribed to the difference in the molecular weight, as discussed later.

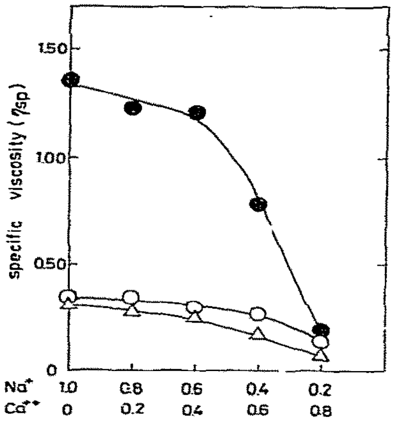

Fig. 6. Dependence of the specific viscosity η_{sp} of PMAEVE (○), PMAMVE (△) and PMAST (●) on the counterion ratio of Na^+ to Ca^{2+}. C_p = 1 mN, α = 1.

On the other hand, conductance at 667 Hz decreases almost linearly with the counterion ratio, as shown in fig. 7. The conductance at this frequency is considered to be almost the same as dc conductance. Decrease in the conductance with the fraction of Ca^{2+} is mainly due to decrease in the amounts of free ions in solution.

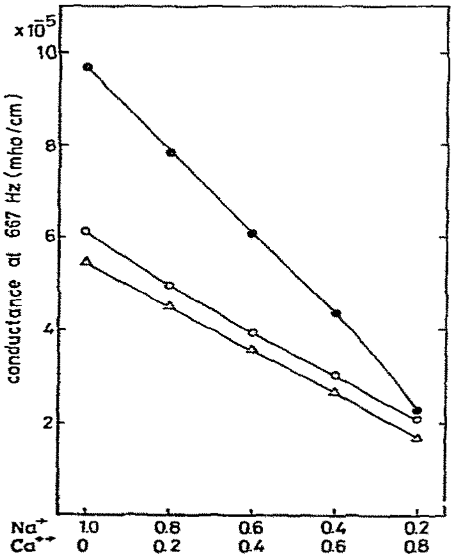

Fig. 7. Dependence of the specific conductance at 667 Hz of PMAEVE (○), PMAMVE (△) and PMAST (●) on the counterion ratio of Na^+ to Ca^{2+}. C_p = 1 mN, α = 1.

Nature of ion binding or conformation of the polyion seems not so effective in the dc conductance.

4. Discussion

As mentioned before, the dielectric increment of polyelectrolytes is understood on the basis of the fluctuation of bound ions on the polyion which is described by a linear lattice model. Theoretically, the increment as well as the relaxation time is proportional to the square of the length or the mean radius of gyration of the polyion, and this relation has been found for several cases [1–7,11–13,23,24].

The effect due to the coexistence of divalent ions is also explained by the lattice model. We have derived an expression for the dielectric increment of rodlike polyions in solution [1]

$$\Delta\epsilon_0 = \frac{\pi N e^2 \beta n l^2}{9 k_B T} f(m)\,, \tag{1}$$

where N is the number of polyions per unit volume, β, the internal field correction factor, n, the number of charged sites on a single polyion, and l, the length of a single polyion. In the above equation, $f(m)$ is a function of the mean degree of binding, m, and consists of terms for the charge fluctuation due to the bound ion at a single site and the correlation of charges due to mutual repulsion between counterions bound to different sites. The latter term provides a negative contribution to the increment. If the system contains only monovalent ions and the neighbor interactions between ions are negligible, $f(m)$ is simply given by

$$f(m) = m(1-m)\,. \tag{2}$$

When mono- and divalent ions coexist, $f(m)$ is not a simple form as eq. (2), depending on the mutual interaction energies between counterions. If the mutual interaction is negligible, then $f(m)$ increases gradually as the monovalent ions are replaced by the divalent ions. The mutual interaction stabilizes the charge fluctuation, so that $f(m)$ increases slowly with the ratio of the divalent ions and has a maximum at an intermediate ratio of the two ion species, and then decreases.

In the case of the copolymers of maleic acid, two carboxyl groups in the maleic acid unit are in close proximity, which leads to a strong affinity to counterions. The bound ions are assumed to be more or less localized in the vicinity of a pair of dicarboxyl groups. This situation is taken into account in calculating the fluctuation of bound ions by use of a lattice model.

A simplified model is presented for the calculation of ion binding and fluctuation of bound ions. A polymer molecule is represented by a linear lattice composed of n pairs of ionized dicarboxylate groups, since the experiments were made at degree of neutralization $\alpha = 1$. Each pair is regarded as an independent unit of ion binding. Consequently, mutual interaction between bound ions to different pairs is neglected. To obtain a partition function of the system, the following five possibilities of ion binding are considered for a single pair: 1) no counterion is bound, 2) a monovalent ion is bound to either of the sites, 3) two monovalent ions are bound to the sites, 4) a divalent ion is bound to either of the sites, and 5) a monovalent ion and a divalent ion are bound to the sites. Other possibilities are neglected, because they are either equivalent to one of the above mentioned five states or practically improbable. Interaction energies between the site and the bound mono- and divalent ions are assumed to be, $-eV_1$ and $-2eV_2$, respectively. Mutual repulsion is considered for case 5), that is, a monovalent ion and a divalent ion are bound to a single pair with interaction energy W_{12}.

The partition function of the system Z is simply given by

$$\begin{aligned} Z &= x^n \\ &= (1 + u\lambda_1 + u^2\lambda_1^2 + v\lambda_2 + uvw\lambda_1\lambda_2)^n\,, \end{aligned} \tag{3}$$

where λ_1 and λ_2 are activities of mono- and divalent ions, respectively, and u, v and w are defined as,

$$\begin{aligned} &u = \exp(eV_1/k_B T)\,, \qquad v = \exp(2eV_2/k_B T)\,, \\ &w = \exp(-W_{12}/k_B T)\,. \end{aligned} \tag{4}$$

According to the standard method of the statistical mechanics, the mean degree of ion binding m and the fluctuation $f(m)$ are derived from eq. (3) as,

$$m = \frac{1}{2}\left[\frac{1}{x_k}\frac{\partial x_k}{\partial k}\right]_{k=1}\,, \tag{5}$$

$$f(m) = \frac{1}{2}\frac{\partial}{\partial k}\left[\frac{k}{x_k}\frac{\partial x_k}{\partial k}\right]_{k=1}\,, \tag{6}$$

where parameter k is introduced to replace λ_1 and λ_2

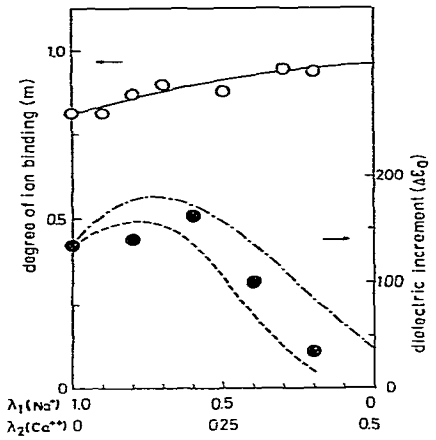

Fig. 8. Upper part: Comparison of the calculated degree of ion binding m as a function of the counterion ratio (——) with the experimental data on activities of Na$^+$ and Ca^{2+} ions in the solutions of PMAMVE (○). Parameters used in the calculation are: $u = 3.0$, $v = 60.0$ and $w = 0.02$. Lower part: Comparison of the calculated fluctuation $f(m)$ by using the above mentioned parameters (· — · —) and the experimental data on $\Delta\epsilon_0$ of PMAMVE (●). (- - -), Corrected values of $f(m)$ by multiplying the ratio of specific viscosity η_{sp}/η_{sp}^{I}, where η_{sp}^{I} is the specific viscosity of the sodium salt (10 : 0). Details are written in the text.

by $\lambda_1 k$ and $\lambda_2 k^2$, respectively, and x_k is defined as

$$x_k = 1 + u\lambda_1 k + (u^2\lambda_1^2 + v\lambda_2)k^2 + uvw\lambda_1\lambda_2 k^3 . \qquad (7)$$

Explicit expressions of eqs. (5) and (6) are given by,

$$m = (1/2x)(y + 2z + 2y^2 + 3wyz) , \qquad (8)$$

$$f(m) = (1/2x^2)\,[4z + (1 + z + 9wz + wz^2)y + 4(1 + wz)y^2 + (1 + wz)y^3] , \qquad (9)$$

where $y = u\lambda_1$, $z = v\lambda_2$, and x, defined in eq. (3), is equal to $[x_k]_{k=1}$. The static dielectric increment $\Delta\epsilon_0$ is expressed as eq. (1) by replacing n by $2n$, because the number of the sites are twice.

When the ratio of divalent ions to monovalent ions is changed, the sum of the values $\lambda_1 + 2\lambda_2$ can be assumed to be constant. Hence the calculation is carried out under the condition

$$\lambda_1 + 2\lambda_2 = 1 ,$$

by changing the values of u, v and w. As shown in the upper part of fig. 8, values of the parameters, $u = 3.0$, $v = 60.0$ and $w = 0.02$, are chosen to fit the calculated curve of the degree of binding to the experimental data obtained by the measurements of activities of Na$^+$ and Ca^{2+} ions. By using these values, the fluctuation $f(m)$ is calculated as a function of the counterion ratio, and compared with the experimental values of $\Delta\epsilon_0$. The results are shown in the lower part of fig. 8.

The fluctuation $f(m)$ explains the over-all profile of the enhancement of $\Delta\epsilon_0$ by the coexistence of both ion species, although quantitative agreement with experimental values is incomplete. With increasing the ratio of divalent ions, $f(m)$ increases and has a maximum at intermediate values of λ_1 and λ_2, and then decreases, while the total degree of ion binding m increases monotonically. Value of $f(m)$ at $\lambda_1 = 1$ is higher than that at $\lambda_1 = 0$ ($\lambda_2 = 0.5$), corresponding to higher affinity of the divalent ion to the polyion. Enhancement of the fluctuation in the intermediate values of λ_1 and λ_2 is related to the possibility of simultaneous binding of both ion species to a single pair, noted as case 5). In the curve fitting procedure, parameter w (= 0.02) is chosen rather arbitrarily to represent low probability of case 5). This is a reasonable assumption, because the local net charge is reversed in this case. However, prohibition of this case, $w = 0$, is inconsistent with the basic assumption of the lattice model, that is, a divalent ion as well as a monovalent ion is capable of occupying a single site.

At large fractions of divalent ions, contraction of the polyion is expected due to chelation by divalent ions between distant parts of the chain. The dielectric increment is greatly reduced by this effect. In fig. 8, the effect of the contraction is corrected by multiplying η_{sp}/η_{sp}^{I} with $\Delta\epsilon_0$, where η_{sp}^{I} is the specific viscosity of the sodium salt, taken as a reference state [1]. The reduction of the apparent length is considered to be dependent on the total length of the polyion. Therefore, the reduction of $\Delta\epsilon_0$ or η_{sp} due to the chelation is more drastic for PMAST than for PMAEVE or PMAMVE.

In the present model, the fluctuation of bound ions at a single pair is assumed to be independent of that at the neighboring pairs. This assumption seems too simple to describe the fluctuation of bound ions in the actual polymer systems, since in the copolymers of maleic acid, the distance between two adjacent sites belonging to the next pair each other is at most three times larger than that between two sites forming a pair. However, the distance between carboxylate groups of the copolymers in solution is an averaged quantity which seems to have a wide distribution depending on the condition of the solution as well as on the nature of the nonpolar side groups incorporated into the copolymers. So the interaction between ions bound to the neighboring pairs as well as the long range interaction is omitted in the theory because of the difficulty in formulation. Present study shows how a simplified model can explain the enhancement of $\Delta\epsilon_0$ due to the coexistence of mono- and divalent ions in relation to the ion binding.

The enhancement of $\Delta\epsilon_0$ by divalent ions seems to be dependent on the concentration of the polyion [25]. In dilute solutions, however, several artifacts such as contamination of CO_2 are anticipated to be amplified. In addition, our previous study on poly (acrylic acid) revealed that the enhancement was observed for fairly wide concentration range (0.1 mN to 5 mN). At present, it seems reasonable to consider that the effect of divalent ions can be explained on the basis of the lattice model as a phenomenon of a single macromolecule.

In many cases, the dielectric increment still has a tendency to increase at the lowest frequency observed. The frequency domain should be extended to lower region for the measurements on these copolymers. Other techniques may also be useful for the dielectric study of polyelectrolytes [26].

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