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CONCENTRATION DEPENDENCE OF EQUIVALENT CONDUCTIVITY OF POLYELECTROLYTE

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Equivalent conductivity of aqueous solutions of alternating copolymer of iso-butyl vinyl ether and maleic acid, [poly(iso BVE-co-MA)] was studied, especially its polymer-concentration dependence. Various species of counterions such as quaternary ammoniumions (NMe_4^+, NEt_4^+, NPr_4^+, NBu_4^+) and divalent ions (Ca^{2+}, Sr^{2+}, Ba^{2+}) were employed besides alkali metal ions. The applicability of Manning's conductivity theory was examined for the case of univalent counterions at various degrees of neutralization (β). A major discrepancy against the theory was observed at $\beta = 1.0$, while a comparatively good agreement was found at β around 0.5. This suggests that the rod-like polyion model, which is the basis of the theory, is applicable near $\beta = 0.5$, where polyions are most expanded. The low conductivities in the case of quaternary ammonium counterions suggested the ion-binding due to hydrophobic interaction with alkyl side chains. Molecular weight dependence was not appreciably observed near $\beta = 0.5$ similarly to usual polyelectrolytes, but it appeared slightly at $\beta = 1.0$.

1. Introduction

Recently, many experimental studies on electric conductivity of aqueous dilute polyelectrolyte solutions have been done to clarify the ion-binding characters of polyelectrolytes. The dependence of conductivity on polymer concentration, however, has not been theoretically well explained, since the theories of transport processes of polyions usually have assumed the infinite dilution of polyions. Some empirical formulae having been obtained suggest the essential properties of ion-binding of polyions.

For example the following empirical parameter ϕ, introduced by Eisenberg [1], has been found to be characteristic in polyelectrolyte solutions, being usually independent of the species of counterion pairs in many experiments;

$$\phi = (\Lambda_{MP} - \Lambda_{NP})/(\lambda^0_{M^+} - \lambda^0_{N^+}) \tag{1}$$

where Λ_{MP} and Λ_{NP} are the equivalent conductivities of polyion solutions having counterions M^+ and N^+, respectively, and $\lambda^0_{M^+}$ and $\lambda^0_{N^+}$ are the corresponding equivalent conductivities of the counterions at infinite dilution, respectively. Katchalsky showed that ϕ is related to osmotic coefficient and can be regarded as degree of ionic dissociation of polyelectrolytes [2].

If we assume as usual that the fraction f of the counterions is completely freely movable, and the remaining fraction $(1 - f)$ is bound to polyion and migrate with polyion without contributing to the total equivalent conductivity, the equivalent conductivity Λ of polyelectrolyte solutions can be expressed by

$$\Lambda = f(\lambda_p + \lambda_c^0), \tag{2}$$

where λ_p is the equivalent conductivity of polyion and λ_c^0 is the equivalent conductivity of counterion at infinite dilution.

According to Manning's polyelectrolyte theory the above fraction f of free counterions is given with the key parameter ξ by

$$f = 0.866|Z_c|^{-1}\xi^{-1}, \qquad (\xi > |Z_c|^{-1}) \tag{3}$$

where Z_c is the valence of the counterion,

$$\xi = e^2/\epsilon kTb,$$

e is protonic charge, ϵ the bulk dielectric constant, kT the Boltzmann factor and b the spacing between two charged groups along the axis of the polyion chain. Eq. (3) is established when $\xi > |Z_c|^{-1}$. When $\xi < |Z_c|^{-1}$, the interaction between a polyion and counterions are governed by the effect of simple

Debye-Hückel atmosphere [3].

The expression of Λ in eq. (2) neglects the interaction between free counterions and polyion charges in the polyion migration. Recently, Manning has derived an expression of Λ by extending his polyelectrolyte theory under the considerations of the relaxation and the electrophoretic effects which are essentially caused by the strong interaction between counterions and polyion charges in the electrophoresis process [4].

In this theory equivalent conductivity of polyion, λ_p, is written in the following form;

$$\lambda_p = \frac{279A|Z_c|^{-1}|\ln Ka|}{1 + 43.2A(|Z_c|\lambda_c^0)^{-1}|\ln Ka|}, \tag{4}$$

where

$$A = \frac{\epsilon kT}{3\pi\eta e}, \qquad K^2 = \frac{4\pi e^2}{\epsilon kT}\xi^{-1}n_e,$$

n_e is the stoichiometric equivalent polyion concentration (monovalent charged-groups per cm^3), a is the radius of the polyion-rod, and η is the kinetic viscosity of bulk solution.

In our study, the concentration dependence of λ_p was obtained for the cases of various species of counterions. From these data, we examined the applicability of Manning's theory to the solutions of alternating copolymer of maleic acid and iso-butyl vinyl ether, poly(iso BVE-co-MA). Since this copolymer has large hydrophobic alkyl side chains and has no equidistant spacing between the charged sites at β larger than 0.5, it is worth while to examine whether or not the above theory, based on the rod-like model, is applicable to our polyelectrolyte solutions with an uneven arrangement of side residues. The comparison of the experimental Λ-values with the predicted values by Manning's theory was made for polyelectrolyte salts in Li^+, Na^+ and K^+-forms etc.

In relation to the hydrophobic interaction between protein and quaternary ammoniumions recently recognized [5], our copolymer is thought to be also usable as a model polyelectrolyte. In our experiment, to confirm the interaction between hydrophobic alkyl side residues and quaternary ammoniumions and its influence on the over-all conformation of polyelectrolytes, the conductivity measurements were performed for polyelectrolytes having various counterions of quaternary ammoniumions, Me_4N^+, Et_4N^+, Pr_4N^+ and Bu_4N^+. These results were also compared with the theory.

Further, to examine the applicability of the theory to the dependence on polyion charge density, the conductivities Λ of polyelectrolyte salts having simple univalent counterions and quaternary ammonium counterions were measured at various degrees of neutralization in the region of $\xi > |Z_c|^{-1}$, where eq. (4) should be applicable to the calculation of λ_p.

On the other hand, this copolymer has a compact globular form at lower degrees of neutralization, but expands as β increases to the most expanded conformation at $\beta = 0.5$. It shrinks slightly with a further increase of β [6]. In our experiments, equivalent conductivities were measured at each stage of β and the applicability of the rod-like model was investigated especially at $\beta = 0.5$.

The influence of ion-specificity of divalent counterions on equivalent conductivity was also examined for the cases of Sr^{2+}, Ca^{2+} and Ba^{2+}. As anticipated, Λ values of polyelectrolyte salts with these divalent counterions were small. These results on the interaction between polyelectrolyte and divalent counterions were compared with other studies [7]. The equivalent conductivity of polyelectrolyte has been thought to be independent of molecular weight. Recently, many studies have shown that Λ of polyelectrolyte solutions is independent of degree of polymerization in the higher region ($D_p \geqslant 200$) [8,9]. On the other hand, Varoqui and Straus reported that Λ of polysoap increases with decreasing polymerization [10]. Our copolymer should undergo a conformational change when ionization progresses from the condition of compact polysoap-like conformation to that of expanded polyelectrolyte conformation. For the purpose of checking this point, the molecular weight dependences were measured at $\beta = 0.5$ and $\beta = 1.0$ in the molecular weight region from $\overline{M}_w = 49\,000$ to $\overline{M}_w = 609\,000$, and the applicability of the rod-like model was examined in these cases.

2. Experiments

2.1. Materials

Alternating copolymers consisting of iso-butyl-vinyl-ether and maleic anhydride poly(iso BVE-co-MA) were synthesized by a radical polymerization method and fractionated by a successive precipitation method as described elsewhere [6]. The fractionated copolymer was purified by dissolving it in tetrahydrofuran (THF) and precipitating in ethyl ether, prior to drying under vacuum at 40°C for 8 hrs. These procedures were repeated several times.

The molecular weight and the degree of polymerization were determined by viscometry in (THF) at 30°C.

The characteristics of each sample are listed in table 1.

The PAA samples used in this study were purchased from Scientific Polymer Products, Inc..

Each sample was dissolved completely in 1N NaOH under mild stirring for 2 hrs at 5°C and dialized against deionized distilled water for 4 days at 5°C to remove excess NaOH.

Acidic form of poly(iso-BVE-co-MA) was obtained from sodium salt by using the ion-exchange resin beds mixed with Dowex 50W-X8 cation exchange resin and Dowex 1-X8 anion exchange resin (mixing ratio, 5 : 1).

The final stock solutions of acidic form of poly(iso BVE-co-MA) were filtered through 4G-filter and stocked at 5°C. The other cationic forms were prepared by neutralization with the appropriate hydroxide solutions of Li, K, and Na etc. Each concentration of polyelectrolytes was determined by pH titration with saturated $Ba(OH)_2$ in 0.01 N $BaCl_2$ at 25°C.

In the case of PAA samples, the acidic form and the sodium salt were prepared by the same method.

Alkali solutions of Li(OH), Na(OH), $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ to obtain the corresponding polyelectrolyte salts through titration were prepared by diluting the supernatant of each saturated alkali solution to appropriate concentrations. The supernatant solutions were obtained by repeating several times the removal of supernatant with deionized water at every new equilibrium of the saturation. This procedure is to remove impure ions from alkali solids completely.

The solutions of $(CH_3)_4NOH$, $(C_2H_5)_4NOH$, $(C_3H_7)_4NOH$ and $(C_4H_9)_4NOH$ were prepared from corresponding quaternary ammonium bromides by the use of cation-exchange resin, and their concentrations were determined from corresponding quaternary hydrochloric acid solution. All the reagents used in our experiments are of special grades.

Table 1
Characteristics of poly(iso BVE-co-MA)

Fraction number	$[n]$ (100 ml . g^{-1}) in THF at 30°C	$\overline{M}_w \times 10^{-5}$
1	1.179	6.09
2	1.102	5.39
3	1.012	4.59
4	0.785	2.91
5	0.617	1.88
6	0.452	1.07
7	0.422	0.95
8	0.293	0.49

The molecular weights were calculated by the Mark-Houwink-Sakurada relation $[n] = 7.56 \times 10^{-4} \overline{M}_w^{0.552}$ (100 ml . g^{-1}) obtained by Endo et al. [11].

All the solutions were prepared with deionized water of specific conductivity ($K < 2.0 \times 10^{-7}$ ohm^{-1} cm^{-1} at 25°C), which was obtained with ion-exchanger after distillation and, refreshed at every measurement. The conductivity of the deionized water was checked before each measurement. Since even in the case of the lowest conductivity of the solutions, water did not contribute more than 2% of the total conductivity, the uncertainty in the measured polyelectrolyte conductivities must be negligible.

2.2. Measurement

The diagram of the conductance bridge and the detector are shown in fig. 1. The conductance bridge is constructed due to a symmetrical circuit by a variable resistance box (Yokogawa REV-601), imput transformers, an oscillator (Kikusui ORC-27A) and our own laboratory made L-C tuned amplifier. An oscilloscope (TRIO CO-1303) is used as a final null detector.

All measurements were performed at 25°C (±0.01°C) in an isothermal water bath, which was set in a steel shield box.

The cell constant of the used cell was 0.3892 cm^{-1}. This was determined with standard KCl solu- - tions [12] which was prepared by dissolving ultra pure KCl (Merch Analytical Grade) into ultra pure water immediately after drying in vacuum at 200°C

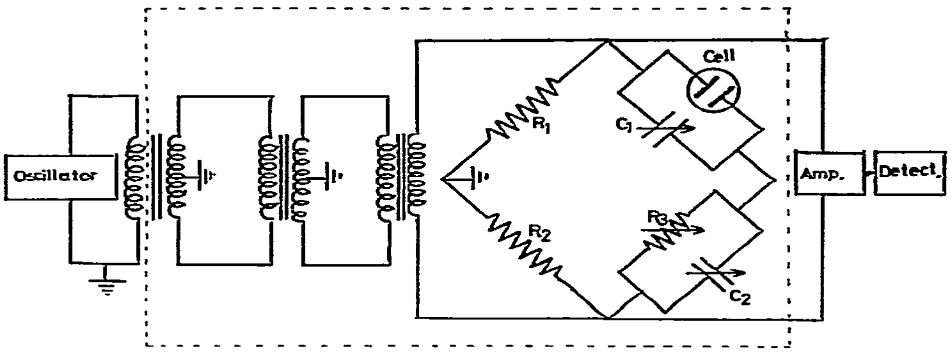

Fig. 1. Conductance bridge circuit.

for 10 hours. The electrodes were carefully black-platinized to avoid the effects of polarization, and immersed in deionized water when the cell was stocked.

The pH measurements were carried out at 25°C under N_2 gas by the use of a Hitachi-Horiba pH-meter.

The frequency dependence of the conductivities is shown in fig. 2, for the case of poly(iso BVE-co-MA) solutions neutralized with NaOH at $\beta = 1.0$. In the frequency range from 10 Hz to as high as 20 kHz, the change of Λ is very slight, the significant increment taking place only at more than 30 kHz.

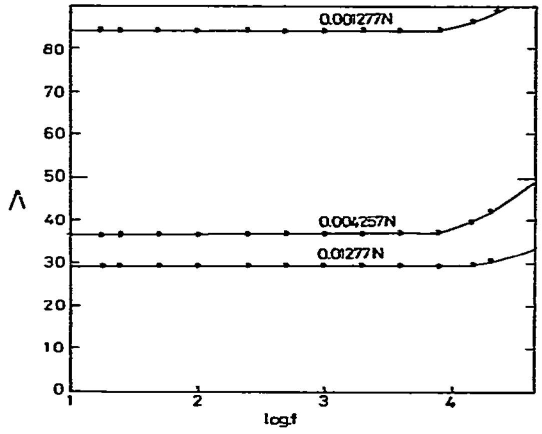

Fig. 2. Equivalent conductivities Λ ($\mathrm{ohm}^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1}$) of sodium salt of poly(iso BVE-co-MA) as a function of log f at 25°C.

The change of Λ against f decreased as polymer concentration increased. This fact agrees with the results of dielectric experiments which have shown that the range of the dispersion frequency generally moves to higher region when the concentration is increased.

The changes of Λ from 10 Hz to 10000 Hz did not exceed 0.5% through all our experiments. Under the consideration of this fact, all subsequent measurements were performed only at 8000 Hz. Since it is unlikely that low field relaxation mechanisms exist below 10 Hz, it is unquestionably correct to assume that the values of Λ at 8000 Hz can be regarded as DC conductivities.

3. Results and discussion

3.1. Results

The equivalent conductivities Λ of lithium, sodium, and potassium salts of poly(iso BVE-co-MA) with degree of polymerization ($D_p \approx 1000$) are shown in fig. 3.

In these plots, the contribution of conductivity due to free OH ions has been subtracted from the measured total conductivity whenever pH value of the solution exceeds 9.5. This contribution of OH ions was obtained from the calibration curves based on Harnd and Owen's tables [13]. The shapes of these curves are similar to the conductivities of other aqueous salt-free polyelectrolyte solutions in this concentration range.

For a given polyelectrolyte concentration, the ob-

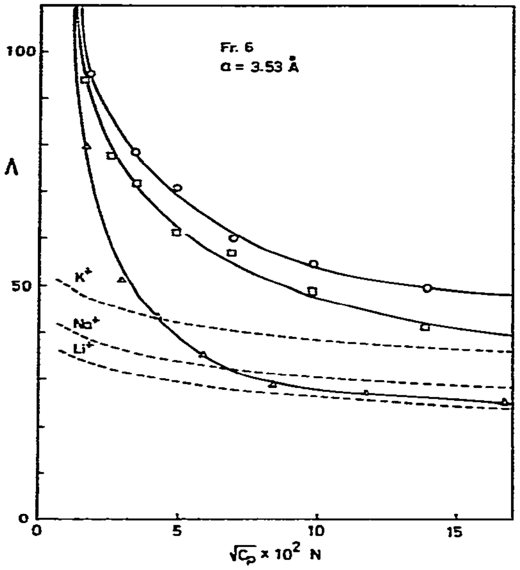

Fig. 3. Equivalent conductivities Λ (ohm^{-1} cm^{2} equiv^{-1}) of alkali metal salts of poly(iso BVE-co-MA) as a function of $C_p^{1/2}$ (equiv$^{1/2}$ l$^{-1/2}$) at 25°C. Counterions: △ = Li$^+$, □ = Na$^+$, ○ = K$^+$. The broken lines are predicted from Manning's theory.

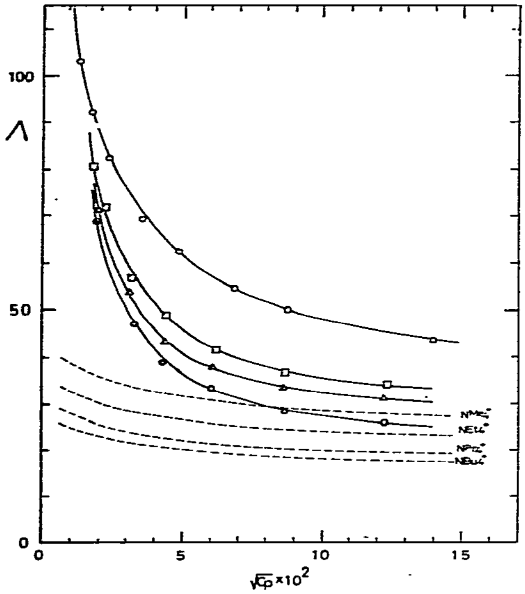

Fig. 4. Equivalent conductivities Λ (ohm^{-1} cm^{2} equiv^{-1}) of quaternary ammoniumion salts of poly(iso BVE-co-MA) as a function of $C_p^{1/2}$ (equiv$^{1/2}$ l$^{-1/2}$) at 25°C. Counterions: ○ = NMe_4^+, □ = NEt_4^+, △ = NPr_4^+, ● = NBu_4^+. The broken lines are predicted from Manning's theory.

served values of Λ are in the order of the values of equivalent conductivity of the cations at infinite dilution i.e. $Li^+ < Na^+ < K^+$.

A similar counterion dependence has been observed in salt-free aqueous solutions of many other polyelectrolytes such as PAA [14], PMA [1] and PSS [7,8,15] of simple univalent counterions. As seen in fig. 3, the conductivities of polyelectrolytes of these univalent counterions show the monotonous decrease when the polymer concentrations are increased in this concentration range. The distinct minimum found by Kwak et al. [7] in PSS salts of univalent counterions was not observed in our solutions.

The decrease of Λ in low concentration region is steeper than that predicted by eq. (2), when the values of λ_c^0 by Robinson and Stokes [12] are referred. This result also contradicts the conclusion obtained by Kwak et al. for PSS salts.

In the lower concentration region ($C_p < 0.0005$ N), the experimental ambiguity was unavoidable, so that the application of the theory was quite difficult. In the higher concentration region ($C_p > 0.002$ N) the absolute values of Λ are of the same order as those observed in other polyelectrolyte solutions.

The values of ϕ in eq. (1) were calculated by the use of the literature values of $\lambda_{M^+}^0$ (in cm^2 equiv^{-1} ohm^{-1}) which were 38.7 for Li^+, 50.1 for Na^+ and 73.5 for K^+ [12]. The ϕ-values ranged from 0.3 to 0.6, the constancy of ϕ was not always obtained because of the experimental difficulties in this concentration region.

In fig. 4, the conductivities Λ are plotted against $\sqrt{C_p}$ for the cases of large univalent counterions, i.e. Me_4N^+, Et_4N^+, Pr_4N^+ and Bu_4N^+ in the absence of added salt at 25°C. The behavior of these curves of $\Lambda - \sqrt{C_p}$ relation resembles those for the simple univalent counterions in fig. 3 although the absolute values of Λ are slightly smaller than those of the simple univalent counterion systems. This result is understandable in view of the fact that the equivalent conductivities of quaternary ammoniumions at infinite

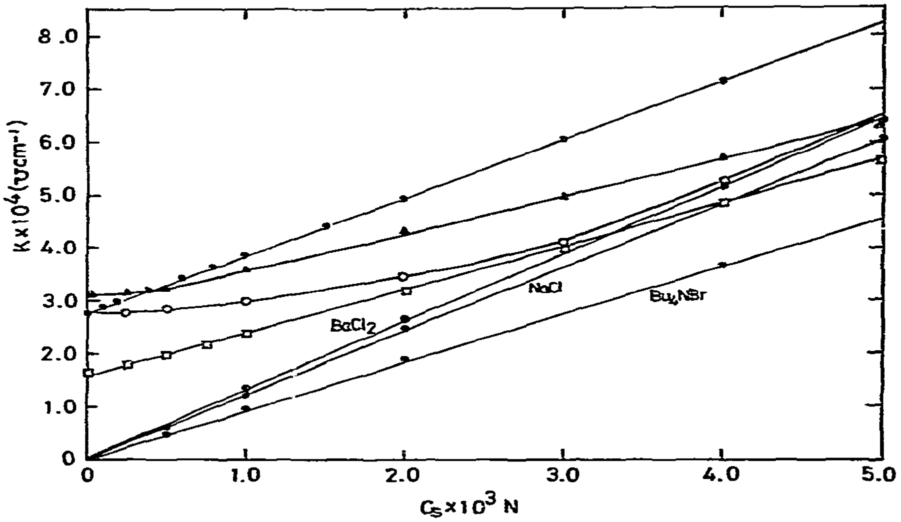

Fig. 5. Specific conductivities $K(\Omega\ \mathrm{cm}^{-1})$ of poly(iso BVE-co-MA) and PAA as a function of the added salt concentration at 25°C. The polyion concentrations are constant (0.0035 N). The polyion salt and the added salt; ● Na-poly(iso BVE-co-MA) in added NaCl, ○ Na-poly(iso BVE-co-MA) in added $BaCl_2$, ▲ Bu_4N^+-poly(iso BVE-co-MA) in added Bu_4NBr, □ Bu_4N^+-PAA in added Bu_4NBr.

dilution are much smaller than those of simple univalent cations. Also in the low concentration region, the decrease of Λ faster than that predicted by the theory is similar to the cases of simple univalent counterions.

In the higher concentration region the experimental values of Λ approach to those predicted by the theory. This tendency, however, does not always demonstrate the correctness of Manning's theory.

In fig. 5 the specific conductivity K ($\mho\,\mathrm{cm}^{-1}$) of the polyelectrolyte solutions are shown as a function of the added salt concentration. In the case of PAA, the curve of the specific conductivity of Bu_4N^+ salt of PAA is parallel to that of simple Bu_4NBr solution at any concentration of added salt, namely the additivity rule of the specific conductivity is perfectly established as observed in the case of sodium salt. This result implies that Bu_4N^+ ions are not specifically bound to polyions.

Also in the case of sodium salt of poly(iso BVE-co-MA) the additivity of the specific conductivity between the polyion and the added sodium chloride solution holds perfectly, however, the additivity is not established for the case of $BaCl_2$ added to sodium salt of this polymer.

The slope of the specific conductivity of the polyion solutions against salt concentration becomes nearly equal to that of simple $BaCl_2$ solution after the saturation of Ba^{2+} ion binding in the region where the concentration of the added $BaCl_2$ almost exceeds that of the polyion, e.g. 0.0035 N. This result indicates that the added Ba^{2+} ions are perfectly bound to polyions probably by a chelate formation and the dissociative groups are completely masked with Ba^{2+} ions.

Similar results to the case of Ba^{2+} ions were observed in the case of polyions neutralized with Bu_4NOH and added Bu_4NBr. These results suggest that Bu_4N^+ ions are bound to the polyions apparently by a chelate formation. However, under the consideration of the following results it is clearly shown that Bu_4N^+ ions are bound to the polyions due to the hydrophobic interaction. (a) The counterion condensation such as in the case of Na^+ ions does not clearly take place. (b) In the case of the polyion without hydrophobic side groups such as PAA the above

Table 2
Theoretical values of equivalent conductivities in several aqueous solutions at 25°C

C_p equiv. l^{-1}	$K \times 10^7$ $(cm)^{-1}$	K^+		Na^+		Li^+	
		λ_p ℧cm^2	Λ equiv^{-1}	λ_p ℧ cm^2	Λ equiv^{-1}	λ_p ℧ cm^2	Λ equiv^{-1}
0.05	0.3088	45.29	37.01	43.35	29.12	41.70	25.05
0.02	0.1953	53.72	39.64	51.03	31.51	48.76	27.25
0.01	0.1381	59.81	41.54	56.48	33.21	53.72	28.79
0.005	0.09765	65.72	43.38	61.73	34.85	58.44	30.26
0.002	0.06176	73.28	45.74	68.35	36.91	64.33	32.10
0.001	0.04367	78.81	47.46	73.14	38.40	68.56	33.42
0.0005	0.03088	84.21	49.14	77.76	39.84	62.61	34.68
0.0001	0.01381	96.16	52.87	87.84	42.98	81.32	37.39
0.00005	0.009765	101.09	54.40	91.94	44.26	84.82	38.48

λ_p; equivalent conductivity of the polyion calculated from eq. (4).
Λ; total conductivity of aqueous solutions.

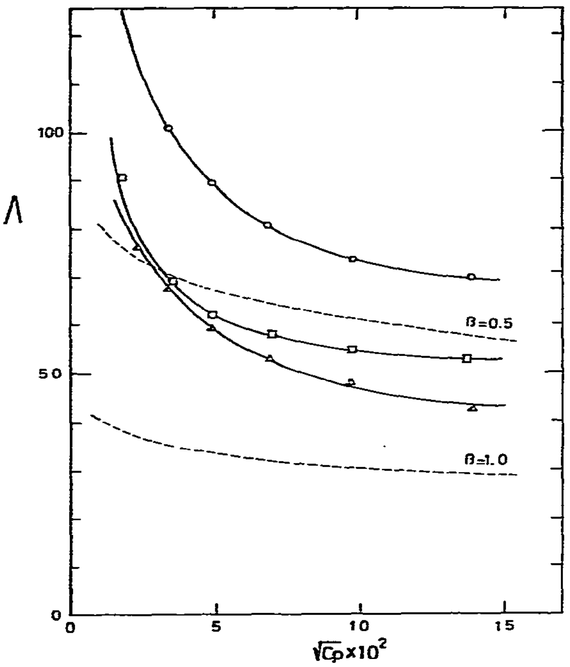

Fig. 6. Equivalent conductivities Λ (ohm^{-1} cm^2 equiv^{-1}) of sodium salts of poly(iso BVE-co-MA) as a function of $C_p^{1/2}$ (equiv$^{1/2}$ $l^{-1/2}$) at various degrees of neutralization at 25°C. Degrees of neutralization: ○ = 0.2, □ = 0.5, △ = 1.0.

results are not observed. (c) Bu_4N^+ ion does not form the chelate compound such as Ba^{2+} estimating from the molecular structure. (d) Both Bu_4N^+ ion and poly(iso BVE-co-MA) have hydrophobic groups; Bu_4N^+ has a tetrahedral structure with a central N atom and the polymer has a large alkyl side residue. The change of OH^- concentration in the process of salt addition was completely negligible in our salt concentration range.

The theoretical values of Λ used above were obtained from eq. (2) in which λ_p was calculated from eq. (4) and f from eq. (3) and λ_c^0 was quoted from Robinson and Stokes's table [12]. In this calculation of λ_p, the following numerical values were employed: 1.54 Å for C—C bond length, 1.27 Å for C—O bond length and 109° for bond angle of tetrahedral carbons.

As described before, this polyelectrolyte consists of alternating units of alkyl vinyl ether and maleic acid, and the charges on the chain are not arranged in equidistant spacing in the region of $\beta > 0.5$, so that we used the averaged charge distances b in eq. (3). Also, for simplicity we applied the theory based on the simple rod-like model by neglecting the existence of hydrophobic side residues. A little ambiguity due to the incomplete rod of polymer therefore arises, but a large deviation from the theory should not be likely. The radius of polyion rod was defined by the distance from the axis of polymer chain to a charge site which was calculated to be 3.53 Å from the molecular structure. For example, the theoretical values of

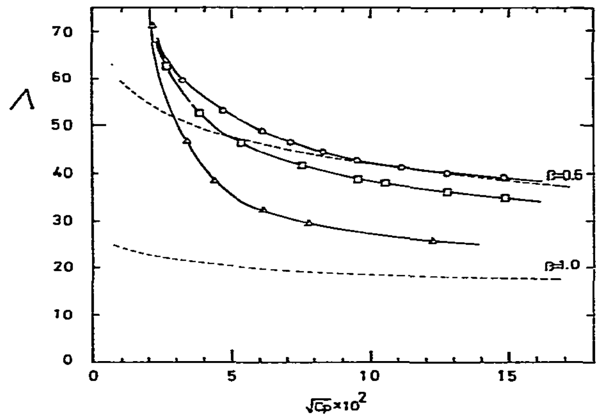

Fig. 7. Equivalent conductivities Λ (ohm^{-1} cm^2 equiv^{-1}) of poly(iso BVE-co-MA) partially neutralized with Bu_4NOH as a function of $C_p^{1/2}$ ($\text{equiv}^{1/2}$ $l^{-1/2}$) at 25°C. Degrees of neutralization: ○ = 0.4, □ = 0.6, △ = 1.0. The broken lines indicate the results predicted from Manning's theory in the cases of $\beta = 0.6$ and $\beta = 1.0$.

Λ of alkali ion salts of this copolymer are listed in table 2. These are obtained by the above described calculation. In the case of our polyelectrolyte, Manning's theory should be applicable only in the region of $\xi > 1$, corresponding to the region $\beta > 0.36$ at which the counterion condensation is thought to take place. The theoretical curves are shown by the broken lines in fig. 6. This figure shows the relation between Λ and $\sqrt{C_p}$ at various degrees of neutralization with NaOH, $\beta = 0.2$, $\beta = 0.5$ and $\beta = 1.0$. The conductivities shown in this figure are per stoichiometric monomolar ionized residue. In the higher concentration region, the values predicted by the theory were appreciably smaller than the experimental ones at $\beta = 1.0$. This fact shows that Manning's theory can neither explain the whole feature of the concentration dependence of equivalent conductivities nor give the absolute values of equivalent conductivity in the case of $\beta = 1.0$. According to Manning's theory, the specificity of counterions is expressed only by λ_c^0 in the denominater of eq. (4). In fact, the values of Λ are in the order of λ_c^0 in the whole concentration region as seen in figs. 3 and 4. The agreement with the theory is comparatively good at $\beta = 0.5$, and this result is reasonable in view of the fact that this polyelectrolyte takes the most expanded conformation at $\beta = 0.5$ as has been well known from other studies [6].

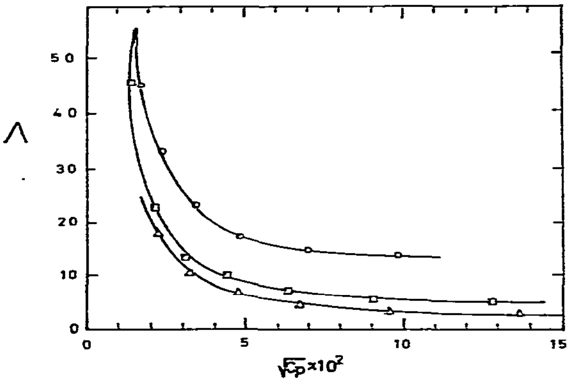

Fig. 8. Equivalent conductivities Λ (ohm^{-1} cm^2 $\text{equiv}^{-1/2}$) of alkali earth metal salts of poly(iso BVE-co-MA) as a function of $C_p^{1/2}$ ($\text{equiv}^{1/2}$ $l^{-1/2}$) at 25°C. Counterions: ○ = Sr^{2+}, □ = Ca^{2+}, △ = Ba^{2+}.

As shown in fig. 7, the values of Λ in the process of neutralization with Bu_4NOH, shift to values lower than the cases of the neutralization with NaOH. These results are expected from the small equivalent conductivity of Bu_4N^+ at infinite dilution as compared with other cations. This polyelectrolyte is known to take also the most expanded rod-like form in the vicinity of $\beta = 0.5$ even in the case of large monovalent counterions such as Bu_4N^+, and the rod-like model may be applied to the calculation if the equivalent conductivity λ_p. Clearly, at $\beta = 0.6$ in the concentration region between $C_p = 2 \times 10^{-2}$ N (monomole/l) and 2.5×10^{-3} N, the calculated values coincide with the corresponding experimental values, but in the region below 0.001 N, the experimental values much exceed the theoretical values. This may be partly due to the experimental ambiguities, however, the main steep decrease of Λ cannot be explained by Manning's theory in the lower concentration region. At $\beta = 1.0$, the experimental values surpass the calculated ones in the same manner as the case of sodium salt.

As seen in fig. 8, the conductivities of polyelectrolytes of divalent counterions show a similar concentration dependence of Λ in polyelectrolytes with univalent counterions. Because of the low conductivity of these divalent salts, the comparison of the concentration dependence with eq. (2) is difficult. In conformity with the general concept of counterion condensation

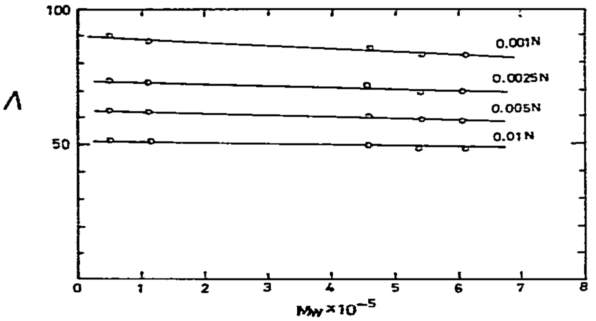

Fig. 9. Equivalent conductivities Λ (ohm^{-1} cm^2 equiv^{-1}) of sodium salts of poly(iso-BVE-co-MA) as a function of molecular weight $\overline{M}_w$ at 25°C. Polyion concentrations are 0.01 N, 0.005 N, 0.0025 N, and 0.001 from bottom to top.

[3,17], the equivalent conductivities of the polyelectrolytes of divalent counterions, especially Ca^{2+} and Ba^{2+}, were much smaller than Λs in the case of univalent counterions. The theory predicts that the order of conductivity is, $Sr(iso\ BVE\text{-}co\text{-}MA)_2 < Ca(iso\ BVE\text{-}co\text{-}MA)_2 < Ba(iso\ BVE\text{-}co\text{-}MA)_2$, but our experimental results show that this order is $Sr(iso\ BVE\text{-}co\text{-}MA)_2 > Ca(iso\ BVE\text{-}co\text{-}MA)_2 > Ba(iso\ BVE\text{-}co\text{-}MA)_2$.

Similar results have been found for PSS in the case of divalent counterions [7]. This tendency for divalent counterions has been also observed in the studies of osmometry and diffusion [17].

In fig. 9, the equivalent conductivities of the sodium salt at $\beta = 1.0$ are shown as a function of molecular weight. Clearly in higher concentration region, the variation of Λ when degree of polymerization is changed from a high value $D_p \approx 2800$ to a low value, $D_p \approx 200$ is less than 4%.

In the concentration region, lower than $C_p = 0.001$ N, however, the above variation of Λ increases more than 15%. It has been thought that the conductivities are independent of molecular weight in many usual polyelectrolyte solutions. For instance, for the case of PAA, Kern showed that Λ is constant in the region of degree of polymerization from 200 to 2000 [14]. Also for sodium polyphosphate, Schindwolf reported that Λ is strongly depend on the molecular weight when D_p is less than 100, but it is constant when D_p is more than 100 [18]. Similarly, Dolar et al. showed for NaPSS that Λ is constant in the region between $D_p = 1500$ and $D_p = 5400$, but when $D_p \leq 200$ it increases more than 10% [8].

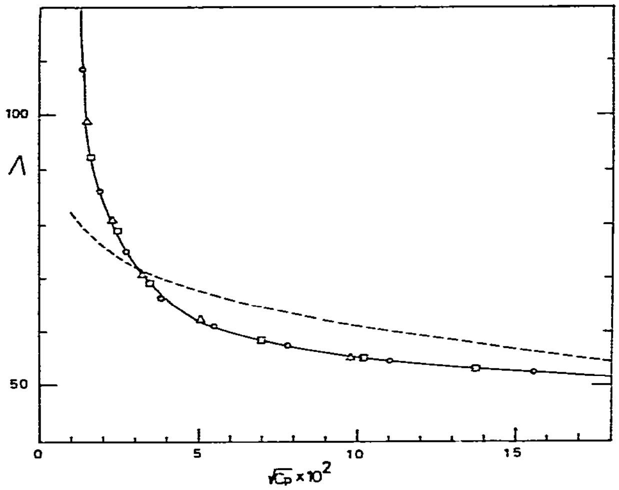

Fig. 10. Equivalent conductivities Λ (ohm^{-1} cm^2 equiv^{-1}) of sodium salt of partially neutralized poly(iso BVE-co-MA) as a function of $C_p^{1/2}$ (equiv$^{1/2}$ l$^{-1/2}$) of various molecular weights at 25°C. Molecular weight: □ = 0.49×10^5, ○ = 1.07×10^5, △ = 2.91×10^5.

Nagasawa et al. reported that the mobility $\overline{U}_p$ is perfectly independent of molecular weight in the region of degree of polymerization over 1300 [9]. Varoqui and Straus obtained the conductivities of univalent counterion solutions of the copolymer of alkyl vinyl ether and maleic acid with different lengthes of alkyl side chains [10]. They concluded that these copolymers take a polysoap-like conformation in the case of long alkyl side chains and behave as a usual polyelectrolyte in the case of short alkyl side chain. In the solutions of copolymer of methyl vinyl ether and maleic acid, Λ is independent of degree of polymerization in the same way as the other polyelectrolytes, and in the solutions of copolymer of decyl vinyl ether and maleic acid, which is well known as a typical polysoap, decreases with increasing D_p.

Since our copolymer, poly(iso BVE-co-MA), does not take a polysoap-like conformation in the region of $\beta \geq 0.5$, the obtained result that Λ is independent of the molecular weight coincides with the general results having been obtained. As shown in fig. 10, the equivalent conductivity of the polyelectrolytes at $\beta = 0.5$ is perfectly independent of degree of polymerization. This result also indicates that the polyelectrolyte takes a most expanded conformation near $\beta = 0.5$, suggesting again that the rod-like model is reasonable in this β range and thereby the experimental values of Λ coincide with the theoretical ones predicted by Manning's theory.

3.2. Discussion

3.2.1. Applicability of Manning's theory

The relation between equivalent conductivity and polymer concentration has been discussed by several theories. In simple polyelectrolyte solutions, a linear dependence of Λ on square root of solute concentration has been recognized experimentally.

Manning's theory is an approximative description having several delicate assumptions in question, that is, a polymer chain is assumed to be an infinitely long rod and the polyion charges are approximated to be uniformly distributed on the rod. The relations obtained from Manning's theory, however, have been useful and successful in understanding the characteristic properties of experimental results, for instance, counterion activity and osmotic coefficient etc, within a certain extent. In applying this theory to the conductivity experiments, the following questions always arise as the still undissolved problems. Can polyion mobility be described by surface potential ψ on the polyion rod?, that is, is Henry's cataphoresis theory acceptable for the present solutions? However Manning's theory has been the first attempt describing the polymer concentration dependence of equivalent conductivity Λ by the Debye screening parameter κ.

In the theory, the increase of λ_p is only 20% when the radius a of polyion-rod becomes even two times larger, and the increase of Λ is then less than 10% because of the multiplication of charge-density parameter ξ. The value of a we used was 3.54 Å. No large error is thought to occur in Λ by neglecting the size of the hydrophobic alkyl size chain.

In eq. (4), the specificity of counterions in λ_p is represented by λ_c^0. At a given polyelectrolyte concentration, eq. (4) is transformed into

$$1/\lambda_p = A + 0.155(1/\lambda_c^0),$$

where A is a constant. The parameter ϕ defined by eq. (1) is, therefore, given by

$$\phi = \frac{f\{\lambda_M^0 - \lambda_N^0 - 0.155(1/\lambda_M^0 - 1/\lambda_N^0)\}}{\lambda_M^0 - \lambda_N^0},$$

where the term $0.155(1/\lambda_M^0 - 1/\lambda_N^0)$ is so small that it may be neglected.

In using Manning's theory, the parameter ϕ was regarded as the ionization parameter f in good approximation. It should be emphasized that no numerical adjustment of a in the theory was made to fit the experimental data.

3.2.2. Molecular weight dependence

The conductivities of sodium salts of PAA and PSS which have an equidistant charge interval (both 2.49 Å) were independent of polyion concentrations when degrees of polymerization were more than 200 [8,9]. In the region, $D_p < 200$, Λ increases with decreasing D_p. A series of such polymers has a similar concentration dependence of Λ as will be shown in the next paper.

Our alternating copolymer without equidistant charge interval gave the same results as the above polymers.

These results coincide with above mentioned Nagasawa's conclusion that the polyion mobility U_p is independent of molecular weight. According to Nagasawa's theory [9], the more expanded the conformation of polyelectrolytes is, the more reasonably the rod-like polyelectrolyte model, in which the chains are surrounded by cylindrical ion atmosphere, should be applicable. As described elsewhere [6], it is turned out also from viscometric titration that this polymer has the most expanded conformation at $\beta = 0.5$ in the salt-free aqueous solutions. This is the reason why the theory based on the rod-like model was successfully available in the vicinity of $\beta = 0.5$.

As indicated in fig. 10, there is no molecular weight dependence of Λ at $\beta = 0.5$, and the coincidence of the experimental values with theoretical values are comparatively good.

Generally transport properties of complete rod-like polymers are thought to be independent of molecular weight, being different from equilibrium properties. Therefore, the molecular weight dependence found in fig. 9 at $\beta = 1.0$ is thought to be attributed to a slightly shrinked coiling conformation of polyions having a little molecular weight dependence.

3.2.3. Interaction with quaternary ammoniumions

A series of quaternary ammoniumions have been thought not to form the counterion condensation phase on the polyelectrolyte because of large size. If this is true, the polyion and the surrounding quaternary ammoniumions must migrate separatedly in the opposite directions, and consequently, the observed Λ must be a sum of λ_c^0 of quaternary ammonium ions and λ_p. (λ_p is about 20 as will be reported in the next paper [19].) The experimental result showed Λ appreciably smaller than this summation. (Refering to the literature, the λ_0^0-values of quaternary ammonium ions are, 44.92 for $(CH_3)_4N^+$, 32.66 for $(C_2H_5)_4N^+$, 23.42 for Pr_4N^+, and 19.40 for Bu_4N^+.) This result suggests that these quaternary ammonium ions are bound to polyelectrolytes. This binding is probably due to the hydrophobic interaction between quaternary ammoniumions and alkyl side chains. This may be concluded from the result shown in fig. 5.

The hydrophobic binding of quaternary ammoniumions to the macromolecules has been observed for example in protein solutions. Chan-Hwei-Chen et al. reported that Bu_4N^+ and Pr_4N^+ are significantly bound to protein in this order, and Me_4N^+ and Et_4N^+ are hardly bound to protein.

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References

[1] H. Eisenberg, J. Poly. Sci. 30 (1958) 47.
[2] A. Katchalsky, Z. Alexandcowicz and O. Kedem, in: Chemical physics of ionic solution, eds. B.E. Conway and R.G. Barradas (Wiley, New York, N.Y. 1966).
[3] G.S. Manning, J. Phys. Chem. 51 (1969) 924.
[4] G.S. Manning, J. Chem. Phys. 79 (1975) 262.
[5] CHan Hwei Chen and D.S. Berns, J. Phys. Chem. 81 (1977) 125.
[6] S. Miyamoto, to be submitted.
[7] J.C.T. Kwak and R.C. Hayes, J. Phys. Chem. 79 (1975) 265.
[8] D. Dolar, J. Span and S. Isakovic, Biophys. Chem. 1 (1974) 312.
[9] M. Nagasawa, I. Noda, T. Takahashi and N. Shimamoto, J. Phys. Chem. 76 (1972) 2286.
[10] R. Varoqui and U.P. Straus, J. Phys. Chem. 72 (1968) 2507.
[11] R. Endo, H. Imamura and M. Takeda, Rep. Prog. Polym. Phys. in Japan, XIV (1971) 43.
[12] R.A. Robinson and R.H. Stokes. Electrolyte solutions (Butterworths, London, 1970).
[13] H.S. Harned and B.B. Owen, Physical chemistry of electrolytes, 2nd ed. (Reinhold Publishing Corp., New York, 1950).
[14] W. Kern, Z. Phys. Chim. A 181 (1938) 249.
[15] J. Szymczak, P. Holyk and P. Ander, J. Phys. Chem. 79 (1975) 269.
[16] F. Oosawa, Polyelectrolytes (Marcel Dekker Inc., New York, N.Y., 1971).
[17] M. Reddy, J.A. Marinsky and A. Sarkar, J. Phys. Chem. 74 (1970) 3891.
[18] U. Schindewolf, Z. Physik. Chem. (Frankfurt) 1 (1954) 134.
[19] S. Miyamoto and N. Imai, to be submitted.