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ESTIMATION OF BOUND QUATERNARY AMMONIUMION TO A ROD-LIKE POLYION WITH A LARGE ALKYL RESIDUE

S. MIYAMOTO and N. IMAI
Department of Physics, Faculty of Science, Nagoya University,
Nagoya 464, Japan

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The amount of quaternary ammonium ion (Bu_4N^+), which is believed not to be bound to general carboxylpolyelectrolytes, bound to poly(iso BVE-co-MA) was estimated by conductivity measurements. In the region of the density of polyion charge in which the polyions are thought to take a free draining conformation, it has been confirmed that the activity coefficient of Bu_4N^+ ions is less than 0.5 in the presence of a small amount of Bu_4NCl, showing that the force between the counterions and the polyion is probably due to the hydrophobic interaction. Moreover, from the electrophoretic mobility U_p of the polyion observed from the data of conductivity, it has been ascertained that U_p of this polyion is two times larger than PAA, and the behavior of the quantity e/ξ_p with changing degree of ionization corresponds to that of the viscosity.

1. Introduction

The interaction between a linear polyion and its counterions has been investigated by many experimental works in irreversible transport processes. Wall and his coworkers [1] have shown on the basis of their experiments on transport number and conductivity in the polyelectrolyte solutions that in salt-free solutions the polyion transfers together with a considerable fraction of the counterions dissociated from polyions. On the other hand, Gregor et al. [2] reported on the basis of the equivalent conductivity that various quaternary ammoniumions, such as Bu_4N^+ or Pr_4N^+ ions migrate independently of the polyion in the opposite direction to the polyion transference. In theoretical studies Hermans and Fujita [3,4], and Overbeek and Stigter [5] have derived the expressions of the polyion mobility, U_p in concentrated salt solutions. These theories gave the results that the apparent hydrodynamic interaction between polymer segments vanished in the limit of high ionic strength, that is, the polyion behaved with regard to transfer like a free draining sphere as if the charge effect of polyion had disappeared. It has been shown by one of the authors of this paper that the distortion effect of the applied electric field in the vicinity of polyions due to the counterions, which is neglected by Hermans and Fujita, is essentially important [6]. Recently Manning [7] constructed the theory of the equivalent conductivity of the polyion on the basis of a rod-like model of the polyion under the considerations of both the relaxation and the electrophoretic effects. The appreciable contradiction between the theory and experiments, however, have been observed in the case of low polyion concentration.

It is pointed out by Nagasawa [8] that in the derivation of polyion mobility, it is important to take into consideration the interaction between the ionic atmosphere and the polyion, the skeletons of which are surrounded by the cylindrical ionic atmosphere.

In this work, the attention is mainly paid to the interaction between polyion and counterions and this problem is experimentally investigated by conductmetric titration, activity measurement and viscometric titration. The polymer sample we used here is p(iso BVE-co-MA), which has both the dissociative groups and the hydrophobic residues and is supposed to take a rod-like conformation under the appropriate experimental conditions. One of our aims is to recognize the importance of the hydrophobic interaction

Table 1
Characteristic properties of p(iso BVE-co-MA) used in this study

$\bar{M}_w \times 10^{-5}$ (Na form)	$\bar{M}_v \times 10^{-5}$ in MEK	$\bar{M}_v \times 10^{-5}$ in aceton	$[\eta]$ $\beta = 1.0$ in 1N NaCl	$\bar{M}_w \times 10^{-5}$ in aqueous solution $\beta = 1.0$ in 1N NaCl (H form)
3.7	1.75	2.14	1.25 ($g\,d\ell^{-1}$)	2.73

between this polyion and quaternary ammonium counterions having bulky hydrophobic residues. This study will offer some suggestions on the studies of aggregation phenomena of protein molecules having hydrophobic parts.

Through our studies, firstly it is demonstrated that the binding of quaternary ammonium ions to the polyion is appreciably strong, in contrast to the non-binding of quaternary ammoniumions to PAA as concluded by Gregor et al. Secondly, it is suggested that in the limit of low ionic strength this polyion should take the most expanded conformation in the region of high degree of neutralization, so that we must apply a rod-like model in the theoretical approach.

2. Experiments

2.1. Materials

2.1.1. Copolymer and reagent

Alternating 1:1 copolymer of maleic anhydride with isobutyl vinyl ether p(iso BVE-co-MA) was synthesized as had been described elsewhere [9]. In the fractionation of copolymer, acetone and normal hexan were used as a solvent and a precipitant, respectively. Some characteristic properties of the copolymer used are listed in table 1. The reagents used in this study were special grade ones. Tetra-butyl ammonium hydroxide (Tokyo Kasei Kogyo Co. Ltd.) was used after removing the impure anions and cations with exchange resin beds. It was important to use Bu_4NOH immediately after elution, for avoiding the contaminations of the impure ions.

2.1.2. Preparation of aqueous polymer solution

1 gr of poly(iso BVE-co-MA) was dissolved perfectly in 100 ml of 1 N aqueous NaOH solution at 5°C under mild stirring for 3 h for the complete hydrolysis of carboxyl groups of maleic anhydride.

After dissolving the polymers perfectly, the excess sodium hydroxide was removed by dialysis against deionized water at 5°C for 3 days.

The polymer solutions were then completely deionized by passing through the column packed with the ion-exchange resin bed, Dowex-50 cation exchange resin and Dowex-1 anion exchange resin (mixing ratio 5:1), filtrated through 3-G glass filter and stocked at 5°C.

All aqueous solvents used were distilled and deionized till each electric resistance exceeded 500 kΩ/cm.

Sodium hydroxide and Barium hydroxide solutions were obtained by dilution of each saturated solution (almost CO_2-free), and their concentrations were determined by the titration with a standard hydrochloric acid solution prior to each measurement.

2.2. Measurements

2.2.1. Viscosity measurements

In all viscosity measurements a couple of Cannon-Ubelode type viscometers were used.

The viscometer having flow time 312 ± 0.1 s in water at 25.00° ± 0.01°C with capillary diameter 0.40 ± 0.01 mm was used, and the other one having a shorter flow time 115.4 ± 0.1 mm was used for the aqueous solutions.

The kinetic energy correction could be neglected within the accuracy of the present experiments. The drainage error was assumed to be negligible and the correction against shear-rate effects was also ignored for the dilute concentration range in our viscosity measurements as described elsewhere [9].

2.2.2. pH measurements

In the pH measurements, Yokogawa pH meter

(Tokyo) with the Hitachi-Horiba glass electrodes was used.

The determination of polymer concentrations was made by the titration.

The titrant (Barium hydroxide solution) was added under nitrogen gas from a 0.5 ml micro-buret (METROHM. Co. Ltd. type; E. 475) through a polyethylene capillary into the titration vessel containing 20 ml of the polymer solution in the presence of 0.2 N $BaCl_2$ solution.

The temperature was controlled within 25°C ± 0.01°C for all of the pH measurements.

2.2.3. Conductivity measurements

In the measurements of the conductivity the improved Kohlrausch bridge was used, whose method and bridge were described in the previous paper [10].

In the concentration range in our present experiments, the capacitance of the supplementary variable condensor to correct the electrode polarization was inappreciable.

Referring to the results of our preliminary experiments and the results by Eisenberg et al. [11], we chose a constant frequency of 8 kHz, because of the non-frequency dependence on conductivities around this frequency range.

The cell was set in the isothermal water bath of 25.0° ± 0.01°C during each measurement.

2.2.4. Measurement of activity

The measurements of sodium ion activity, were carried out at constant C_p with changing degree of neutralization with a sodium-ion sensitive electrode (Toko Kagaku CE 1100) and Hitachi Horiba ion meter at 25° ± 0.01°C. The attainment of the equilibrium was ascertained by the recorder connected with the ion meter. This recorder reading was an important technic for reliability.

3. Results and discussion

3.1. Results

The expression of the specific conductivity for polyelectrolyte solutions can be derived under the considerations of both the relaxation and the electrophoretic effects in the following way.

At first, the specific conductivity $K_p(\Omega^{-1}\ \mathrm{cm}^{-1})$ of single polyion is given by

$$K_p = N e n^* u_p, \tag{1}$$

where N is the number of polyion in 1 cm^3, n^* the apparent charge of polyion, e the protonic charge, and u_p is the electrophoretic (electrical) mobility of polyion defined by

$$u_p = n^* e/\xi_p, \tag{2}$$

with the friction coefficient of a polyion, ξ_p. Now, let us assume that C_b equivalents per liter of simple counterion are bound to the polyion due to not only covalent formation but also atmospheric counterion-binding. Then, the following relation should be established.

$$10^3 N n^*/N_0 = \beta C_p - C_b, \tag{3a}$$

$$10^3 N n/N_0 = C_p, \tag{3b}$$

where C_p is the concentration (equivalents of monomeric unit per liter) of polyion having number, n, of ionizable carboxyl groups per molecule, β is the degree of neutralization, and N_0 is Avogadro's number.

Substitution of eq. (3a) and (3b) into eq. (2) leads the following expression;

$$u_p = \frac{ne}{\xi_p}\frac{\beta C_p - C_b}{C_p} = \frac{ze}{\xi_{se}}\frac{\beta C_p - C_b}{C_p}, \tag{4}$$

where ξ_{se} is the apparent frictional coefficient of polyion segment, and z is the number of monomers in a segment. Eq. (4) is valid generally for free-drained polymers and our present polymer may be thought to obey this relation in the absence of salt because of the expansion [8].

Substituting eq. (4) into eq. (1), we have the expression of conductivity;

$$K_p = 10^{-3} N_0 e \frac{ze}{\xi_{se}} \frac{(\beta C_p - C_b)^2}{C_p}. \tag{5}$$

On the other hand, u_p is related to the equivalent conductivity of polyion, Λ_p, as follows

$$\Lambda_p = 10^{-3} N_0 e u_p = 10^{-3} F u_p.$$

Here, we introduce the equivalent conductivity of the segment, Λ_{se}, defined by

$$\Lambda_{se} = 10^{-3}\, Fe/\xi_{se}. \tag{6}$$

The specific conductivity, K, of polyelectrolyte solutions with added salt concentration C_s may be expressed by λ_{se} ($= 10^{-3}\, \Lambda_{se}$) and the limiting equivalent conductivities of positive and negative low molecular ions from added salt, λ_+° ($= 10^{-3}\, \Lambda_+^\circ$) and λ_-° ($= 10^{-3}\, \Lambda_-^\circ$), and that of original counterions λ_c° ($= 10^{-3}\, \Lambda_c^\circ$) as follows,

$$K = z(\beta C_p - C_b)^2/C_p\, \lambda_{se} + (\beta C_p - C_{bg})\lambda_c^\circ + \gamma_+(C_s - C_{bs})\lambda_+^\circ + \gamma_- C_s \lambda_-^\circ + a_H \lambda_H^\circ + a_{OH}\lambda_{OH}^\circ, \tag{7}$$

where C_{bg} is the concentration of the bound counterions of the species in the absence of salt, C_{bs} is the increment of the bound counterions from added salt, γ_+ and γ_- are the activity coefficients of positive and negative low molecular ions from added salt not bound to polyions, and λ_H° ($= 10^{-3}\, \Lambda_H^\circ$) and λ_{OH}° ($= 10^{-3}\, \Lambda_{OH}^\circ$) are limiting equivalent conductivities of H^+ ion and OH^- ion whose activities are a_H and a_{OH}, respectively. The concentration of total bound low molecular ions, C_b, is given by

$$C_b = C_{bg} + C_{bs}. \tag{8}$$

Now, if the counterion activity of polyion solution at the degree of neutralization β is denoted by a_c, the following relation may be established,

$$a_c = \gamma_c(\beta C_p + C_s) = \gamma_p C_p + \gamma_+ C_s, \tag{9}$$

where γ_c denotes the activity coefficient of counterions, and γ_p expresses the degree of effective polyion charge. In the case of counterions which are bound to polyion by only electrostatic interaction, γ_p has been known to be a constant against C_s according to the additivity rule.

When HCl is added to a salt-free polyelectrolyte solution, the initially bound counterions are replaced by the H^+ ions, and all added H^+ ions are completely bound to the polyion before pH is acidic. Eq. (7) is applicable to this case if the added HCl is regarded as a simple added salt. (The added HCl concentration is C_s.) If we put $C_{bs} = m(C_s)\, C_s$, this parameter $m(C_s)$ becomes nearly unity for added H^+ ions. The concentration C_{bg} of the bound counterion (Na^+) decreases with the addition of HCl as expressed by the following relation

$$C_{bg} = (1 - \gamma_p)\beta C_p - m(C_s)\, C_s = (1 - \gamma_{Na})\beta C_p \tag{9'}$$

where γ_{Na} is γ_c for Na^+ in eq. (9). Substitution of eq. (9′) and eq. (8) into eq. (7) gives the following relation

$$K = z(\gamma_{Na}\beta C_p - C_{bs})^2 C_p^{-1}\lambda_{se} + \gamma_{Na}\beta C_p\lambda_c^\circ + \gamma_+(C_s - C_{bs})\lambda_+^\circ + \gamma_- C_s\lambda_-^\circ + a_{H^+}\lambda_H^\circ + a_{OH^-}\lambda_{OH}^\circ. \tag{10}$$

Particularly in the case of HCl addition, since $C_{bs} = C_s$ ($m = 1$), this equation is transformed into,

$$K = z(\gamma_{Na}\beta C_p - C_s)^2 C_p^{-1}\lambda_{se} + \gamma_{Na}\beta C_p\lambda_c^\circ + \gamma_- C_s\lambda_-^\circ + a_{H^+}\lambda_H^\circ + a_{OH^-}\lambda_{OH}^\circ. \tag{10'}$$

The method of this HCl-addition is convenient to obtain λ_{se}, that is λ_p, in eq. (6), for carboxyl poly electrolytes. In fig. 1, the specific conductivities of the partially neutralized p(iso BVE-co-MA) solutions are plotted against added HCl concentration for various β's. In this figure the specific conductivity of simple HCl solution is also indicated. In the HCl concentration region over βC_p each line of the specific conductivities is parallel to that of simple HCl.

The specific conductivity K and pH are listed in table 2 as a function of added HCl concentration.

The equivalent conductivities of the polyion at various degrees of neutralization were obtained from eq. (10′) on the basis of the limiting equivalent conductivities of sodium ion (50.10), chloride ion (76.35), hydrogen ion (349.81) and hydroxide ion (199.18) cited from Robinson and Stokes's tables [12].

In the region of pH < 4.5, the correction of the free H^+ ion contribution was inevitable.

The activity coefficient and the exchange parameter were directly obtained from the activity measurements of Na^+ ions by the use of a sodium sensitive electrode under the assumption of the constant activity coefficient of polyion in the C_p range from 0.003 N to 0.01 N. In fig. 2 the activity coefficient γ_{Na} is plotted against various degrees of neutralization with NaOH, and fig. 3 shows γ_{Na} as a function of the degree of neutralization in the process of HCl addition starting from the different initial degrees of neutralization.

In calculation of Λ_{se}, the observed values of K, pH and γ_{Na} listed in the tables 2 and 3 were used, and the

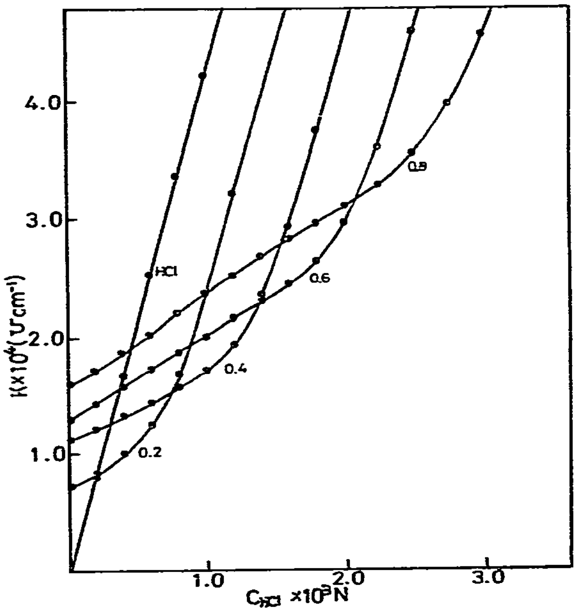

Fig. 1. Specific conductivity of p(iso-BVE-co-MA) neutralized with NaOH at various degree of neutralization are shown as a function of the concentration of added HCl. Degree of neutralization: $\beta = 0.2$, $\beta = 0.4$, $\beta = 0.6$, $\beta = 0.8$ from bottom to top. Polyion concentration $C_p = 0.0035$ N.

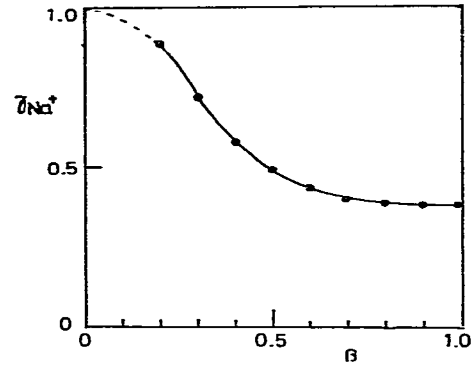

Fig. 2. Activity coefficient of Na^+ ion γ_{Na^+} versus degree of neutralization with NaOH in the salt-free condition. Concentration of the polyion $C_p = 0.0035$ N.

assumption that $\gamma_- \approx 1$, which should be established in low concentration Cl^- ion activities as our case, was employed.

In table 3, are indicated the equivalent conductivity Λ_s of the polymer segment, the polyion equivalent conductivity Λ_p, the effective charge fraction of polyion γ^*, and the activity coefficient of counterions γ_{Na}.

The specific conductivities of poly(iso BVE-co-MA)

Table 2
Specific conductivity and pH dependence on HCl concentrations of constant polymer concentration ($C_p = 0.0035$ N) at various degree of neutralization with NaOH

		$\beta = 0.2$		$\beta = 0.4$		$\beta = 0.6$		$\beta = 0.8$	
C_{HCl}	$K_{HCl} \times 10^4$	pH	$K \times 10^4$	pH	$K \times 10^4$	pH	$K \times 10^4$	pH	$K \times 10^4$
0	0	5.11	0.677	5.82	1.110	7.42	1.266	9.32	1.585
0.0002	0.837	4.74	0.803	5.48	1.205	6.68	1.433	9.21	1.715
0.0004	1.678	4.45	1.007	5.08	1.329	6.22	1.501	8.75	1.829
0.0006	2.525	3.99	1.244	4.91	1.430	5.86	1.721	7.42	2.047
0.0008	3.372	3.59	1.910	4.77	1.568	5.53	1.860	6.96	2.201
0.0010	4.226			4.59	1.714	5.26	1.997	6.38	2.364
0.0012				4.24	1.938	5.04	2.152	5.86	2.480
0.0014				3.85	2.351	4.89	2.302	5.63	2.650
0.0016				3.58	2.932	4.73	2.441	5.35	2.826
0.0018						4.41	2.635	5.11	2.957
0.0020						4.21	2.960	4.92	3.107
0.00225						3.61	3.617	4.78	3.283
0.0025						3.35	4.600	4.49	3.556
0.00275								3.99	3.972
0.0030								3.79	4.567

K (Ω^{-1} cm^{-1})

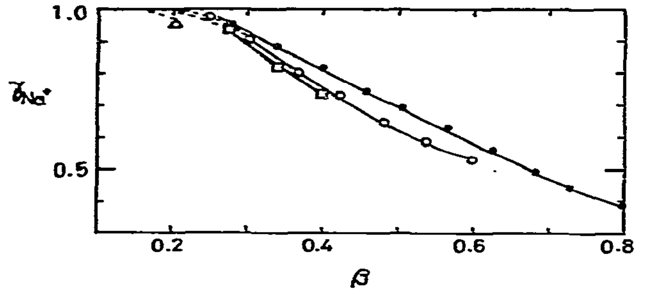

Fig. 3. Activity coefficient of Na^+ ion versus degree of neutralization in the presence of added HCl at $C_p = 0.0035$ N. The initial degree of neutralization with NaOH: ● $\beta = 0.8$, ○ $\beta = 0.6$, □ $\beta = 0.4$, △ $\beta = 0.2$.

in the case of NaCl addition at various degrees of neutralizations are shown in fig. 4. As seen in this figure the rate of the increase of specific conductivities against the added salt-concentration C_s is the same as in the case of simple NaCl solution, indicating the constant value of γ_p against C_s. This means the perfect establishment of the additivity rule in the conductivity. The same results have been observed for other simple counterions, such as Li^+ ion and K^+ ion [13].

Table 3
Equivalent conductivity and activity coefficient

	β^*	γ_{Na^+}	Λ_p^*	γ^*	Λ_p
$\beta = 0.8$	0.8	0.385	302	0.308	93.0
	0.743	0.441	298	0.295	87.9
	0.686	0.498	288	0.284	81.8
	0.629	0.568	282	0.283	79.8
	0.571	0.640	246	0.283	69.6
	0.514	0.695	244	0.270	65.9
	0.457	0.740	242	0.254	64.5
	0.400	0.816	190	0.253	48.1
$\beta = 0.6$	0.6	0.530	200	0.318	63.6
	0.543	0.592	198	0.298	59.0
	0.486	0.650	192	0.275	52.8
	0.429	0.740	186	0.273	50.8
	0.371	0.800	179	0.252	44.9
$\beta = 0.4$	0.4	0.746	186	0.300	55.8
	0.343	0.820	181	0.273	49.4
	0.286	0.955	129	0.270	34.8
$\beta = 0.2$	0.2	0.880	226	0.196	44.3

γ_{Na^+} : activity coefficient of sodium ion.
γ^* effective activity coefficient of the polyion $(\gamma_{Na^+}\beta C_p - C_{bs})/C_p$.
Λ_p^* : $z\Lambda_s$ (Ω^{-1} cm^2 equiv^{-1}).
Λ_p : equivalent conductivity of monomeric unit (Ω^{-1} cm^2 equiv^{-1}).
β^* : $(\beta C_p - C_{HCl})/C_p$.

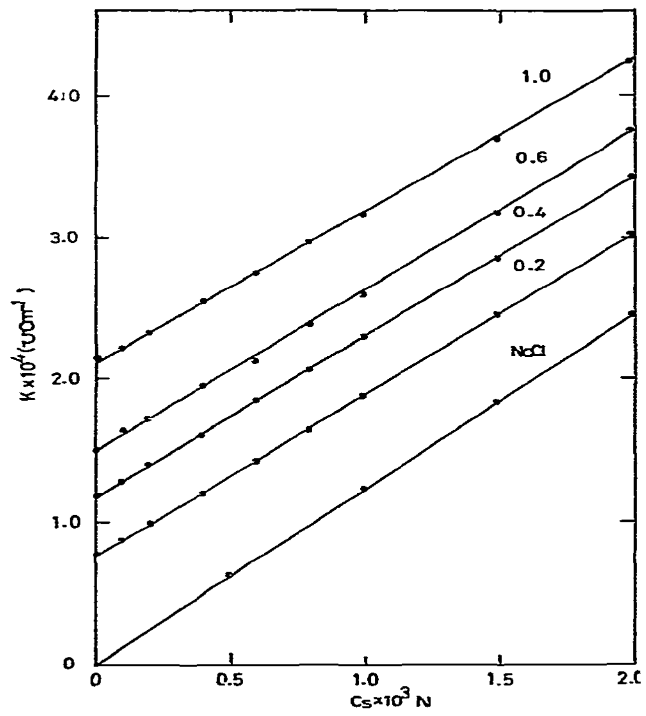

Fig. 4. Specific conductivity of the solution versus added NaC concentration at various degree of neutralization: ● $\beta = 0.2$, $\beta = 0.4$, $\beta = 0.6$, $\beta = 1.0$ from bottom to top at $C_p = 0.0035$. The straight line drawn through origin shows the specific conductivity of NaCl.

As shown in fig. 5, however, the specific conductivities of p(iso BVE-co-MA) at partial degrees of neutralization with Bu_4N^+OH deviate far from the dotted line representing the conductivity in the case of perfect additivity rule, drawing a downward concave curv This means that the effective polyion charge is decreased by added Bu_4NCl. The values of γ_p in this case, calculated from the specific conductivities on the basis of Λ_p in table 3 obtained in the process of simple NaOH neutralization, are listed in table 4. In this calculation, we have assumed that the equivalent conductivities, Λ_p, of the polyion neutralized with Bu_4N^+OH

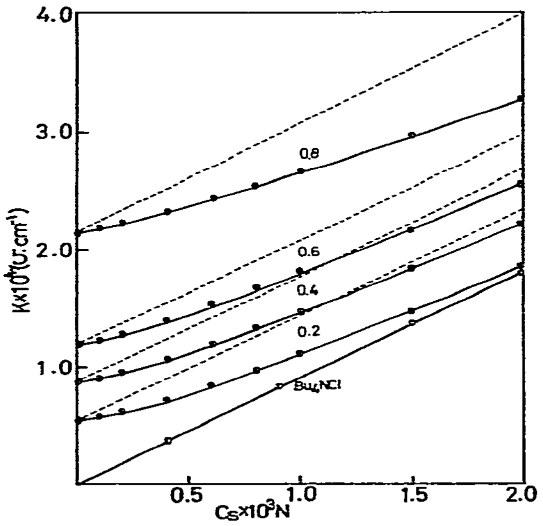

Fig. 5. Specific conductivity of the polyelectrolyte solution neutralized with Bu_4NOH versus added Bu_4NCl concentration at various degree of neutralization: ● $\beta = 0.2$, $\beta = 0.4$, $\beta = 0.6$, $\beta = 0.8$ from bottom to top at $C_p = 0.00345$, ○ = Bu_4NCl alone.

are the same as that of the case of Na^+ counterion at each corresponding degree of neutralization.

Obviously table 4 and fig. 5 both demonstrate that Bu_4N^+ ions are bound specifically to the polyion. This specific binding of Bu_4N^+ ions is undoubtedly due to the hydrophobic interaction between Bu_4N^+ ions and alkyl residues of the polyion chain. The feature of fraction of the effective charge, represented by γ_p, in the case of Bu_4N polyion solutions is plotted against the ratio of the added Bu_4NCl concentration C_s to βC_p, denoted by X in fig. 6. This ion-binding has been also examined by H^+ titration [18].

Table 4
Degree of effective polyion charge in the presence of Bu_4N^+ ion

$\beta = 0.8$		$\beta = 0.6$		$\beta = 0.4$		$\beta = 0.2$	
X	γ_p	X	γ_p	X	γ_p	X	γ_p
0	0.678	0	0.675	0	0.873	0	1.0
0.073	0.635	0.097	0.625	0.145	0.765	0.290	0.986
0.145	0.615	0.193	0.584	0.290	0.696	0.580	0.795
0.217	0.591	0.290	0.566	0.435	0.652	0.870	0.668
0.290	0.569	0.386	0.544	0.580	0.602	1.159	0.568
0.362	0.548	0.483	0.520	0.725	0.564	1.449	0.493
0.435	0.527	0.580	0.496	0.870	0.520	1.739	0.382
0.507	0.507	0.676	0.478	1.014	0.496	2.029	0.307
0.580	0.478	0.773	0.460	1.159	0.465	2.319	0.227
0.652	0.470	0.870	0.448	1.307	0.448	2.609	0.189
0.725	0.453	0.966	0.433	1.449	0.427	2.899	0.154

X: $C_s/\beta C_p$; γ_p: degree of effective charge of the polyion

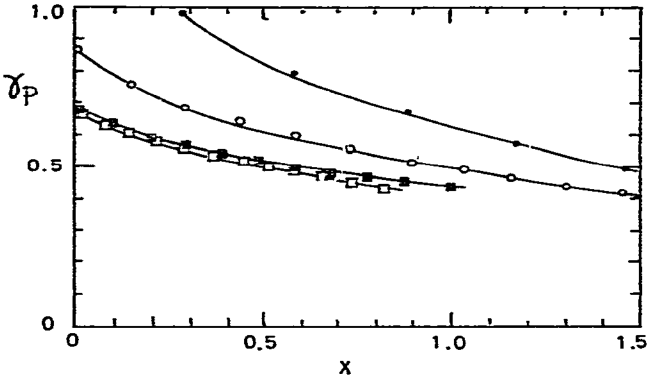

Fig. 6. Degree of effective polyion charge, neutralized with Bu_4NOH versus X at various degree of neutralization: □ $\beta = 0.8$, ■ $\beta = 0.6$, ○ $\beta = 0.4$, ● $\beta = 0.2$ from bottom to top. X is the ratio of added Bu_4NCl concentration to βC_p.

3.2. Discussion

Generally the term "counterion binding" may cover the following types of interaction between counterion and polyion: (1) the formation of undissociated or complex molecules such as undissociated carboxylic acid or the interaction between carboxylate ion and Ba^{++}, Ca^{++}, and Cu^{++}: (2) the trap of counterions inside the polyion domain: and (3) the ion-pair formation between counterions and fixed charges due to the electrostatic force, including the cylindrical ionic atmosphere strongly attracted around the polyion skeleton. The counterion condensation may also be included in the last category.

The interaction between counterions and polyion in the case of Bu_4N^+ counterions observed in our experiments cannot be explained by the second type of ion-binding. It has already been pointed out that in the first type of counterion binding, the additivity of the specific conducitivity is not established, while the third type satisfies the additivity rule almost perfectly. The behavior of conductivity in the third type has the same feature as activity or osmotic pressure, that is to say, the degree of ion-binding calculated from conductivity gives almost the same value as that from the activity measurement or osmotic pressure measurement.

The present experimental data, however, show that no additivity of specific conductivities of the polyion and the added salt holds, although this does not always mean the first type counterion-binding. Since in the case of quaternary ammonium ions, the covalent formation can never take place, it may be concluded that the present counterion binding is the association counterions with the hydrophobic alkyiside residues from the following reasons; (1) The activity coefficient of the polyion decreases with increase of the concentration of added tetra-n-butyl ammonium chloride. If this case were of the third type of counterion binding (including the counterion condensation), the activity coefficient γ_p should have been a constant independently of the added salt concentration: (2) Tetra-n-butyl ammonium ion cannot form the ion-complex with carboxylate residue as Cu^{++} ion, which is known to form the metal chelate with carboxylates, showing a similar behaviors of conductivity to the case of Bu_4N^+: and (3) A tetra-n-butyl ammonium ion has a tetra-hedral structure with four big alkyl side residues around a central nitrogen atom, so that the electrostatic force between the fixed charges on the polyion and quaternary ammonium ions is much weakened.

Gregor et al. [2] concluded that in PAA or PMA solutions, tetra-n-propyl ammonium ions or tetra-n-butyl ammonium ions were not bound to the polyion and under the applied electrical field polyions and quaternary ammonium ions migrated independently in the opposite direction. In the case of PAA or PMA having no large hydrophobic residues, no such hydrophobic interaction between polyion and quaternary ammonium ions can take place.

Ikegami also reported that in the process of neutralization of PAA with tetra-n-butyl ammonium hydroxide, Bu_4N^+ ion operates as a breaker of a special water structure [14].

This result is explained as due to the effect that Bu_4N^+ ions cannot reach the region of special water structure around the rodlike polyion because of its bulky hydrophobic residues. On the other hand, Chang-Hwei Chen and Berns showed on the basis of microcalorimetry measurements that the aggregation of phycocyanin is inhibited by the strong interaction between the hydrophobic area of the protein and the bulky hydrophobic groups of Bu_4NBr, that is, Bu_4NBr may operate as a strong solvent structure maker [15].

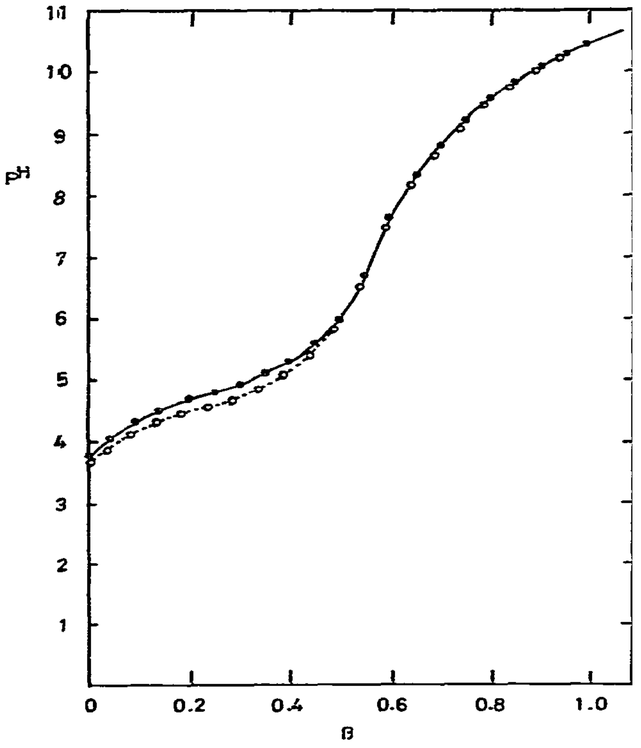

Fig. 7. Titration curve of pH versus β: —•— forward with NaO titration, ---o--- backward titration with HCl at C_p = 0.0035 N in the salt-free solution at 25°C.

In the previous section, we calculated the polyion equivalent conductivity Λ_p, by using the method of HCl-addition to various initial degrees of neutralization. As shown in fig. 7 the pH titration curve of forward titration with NaOH coincided with the curve of backward titration with HCl in the region over $\beta = 0.5$. Even in the region of low degrees of neutralization the pH-difference between the forward and the backward titrations was less than 0.2 pH unit. This result suggests that the conformational change of the polyion is a perfectly reversible phenomenon, and therefore it seems reasonable to use the method of HCl addition in obtaining the equivalent conductivity Λ_p of the polyion in the salt-free system.

As shown in fig. 8 the behaviour of the specific vis-

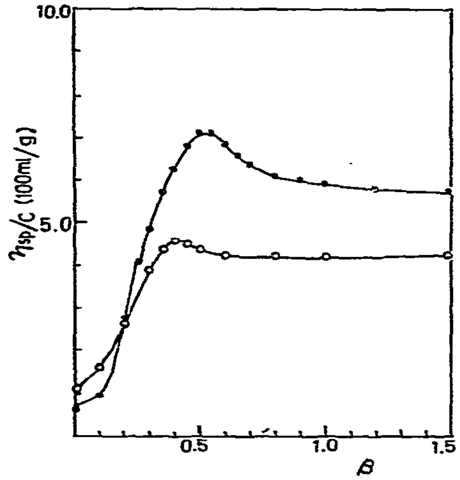

Fig. 8. η_{sp}/c versus degree of neutralization with NaOH, in 0.02 N NaCl solution at 25.00 ± 0.02°C: ● p(iso BVE-co-MA) (C_p = 0.00345), ○ p(EVE-co-MA) (C_p = 0.00326 N).

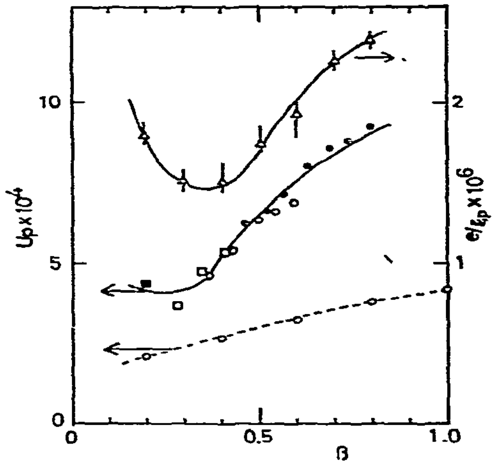

Fig. 9. Electrophoretic mobility U_p(cm^2/s V) of the polyion versus degree of neutralization. Initial degree of neutralization; ● β = 0.8, ○ β = 0.6, □ β = 0.4, ■ β = 0.2. And △ = e/ξ_p (cm^2/s V) versus β. Dotted line is the electrophoretic mobility of PAA referred from Nagasawa et al.'s data [17].

Table 5
Electrophoretic mobility of the polyion

	β*	$u_p^* \times 10^4$	$u_p \times 10^4$
β = 0.8	0.8	31.3	9.54
	0.743	30.8	9.09
	0.686	29.8	8.27
	0.629	29.2	8.26
	0.571	25.5	7.22
	0.514	25.3	6.83
	0.457	25.1	6.38
	0.400	19.7	4.98
β = 0.6	0.6	20.7	6.58
	0.543	20.5	6.11
	0.486	19.9	5.47
	0.429	19.3	5.26
	0.371	18.5	4.65
β = 0.4	0.4	19.3	5.78
	0.343	18.8	5.12
	0.286	13.4	3.61
β = 0.2	0.2	23.4	4.59

u_p^*: electrophoretic mobility of the segment (cm^2/s V) (= Λ_p^*/F);
u_p: usual electrophoretic mobility of the polyion (cm^2/s V) (= Λ_p/F);
F : Faraday constant (= 96500).

cosity of p(iso BVE-co-MA) at low ionic strength is characteristic in contrast to the cases of other usual polyelectrolytes such as PAA and PMA, that is, the value of η_{np}/c is extremely low in the vicinity of β = 0.2 having a maximum at β = 0.5. Also, in the case of p(St-co-MA) an abnormal maximum has been observed at β = 0.5 [16]. This means that in the region of low degrees of neutralization this polyelectrolyte takes an extremely compact globular conformation, which extends on increase of degree of neutralization till the most expanded conformation at β = 0.5.

As shown in tables 3 and 5, and in fig. 9 the values of the equivalent conductivity Λ_p and the electrophoretic mobility U_p are two times larger than those of PAA [17]. There are two possibilities to explain these effects; the first is the effect that one monomeric unit is thought to be divalent because of the structure of monomeric unit $-CH_2-CH(OC_4H_9)-CH(COOH)-CH(COOH)-$, while the friction coefficient behaves like PAA, and the second is the effect that a segment in a polymer chain is composed of more than two monomeric units ($z \geqslant 2$) and the friction coefficient of the segment varies with the charge density. In the case of this polyelectrolyte, the above two effects must be taken into consideration. In fig. 9 the behaviour of Λ_p and U_p against the degree of neutralization are indicated, and a considerable difference from the viscosity behaviour is observed. That is to say, the electrophoretic mobility, takes a rather larger value in the ionization region in which the viscosity has also larger values. This result implies that the traditional electrophoretic mobility U_p is not always consistent with the polyion transport phenomenon exactly, while the behaviour of the quantity e/ξ_p, corresponding to the electrophoretic mobility of whole polyion, coincides with that of the viscosity.

These results show that the friction coefficient of whole polyion (or the segment of the polymer chain) varies with the degree of ionization. It may be necessary to take into consideration the distortion of electric field in the vicinity of the polyion, which is appreciably dependent on polyion charge [6].

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