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The Interaction of Polymer Ions with Counterions. II. Polymethacrylates

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The equivalent conductivities and the electrophoretic mobilities of sodium, tetramethyl-, tetraethyl-, and tetrabutyl- ammonium salts of polymethacrylic acid (PMA) in 0.05 M solutions of the simple salts of the corresponding cations are measured at 25°C, and the results obtained are interpreted in terms of the counterion binding. The calculated values of the apparent degree of ionization for sodium, tetramethyl-, and tetraethylammonium salts of PMA are found to be larger than those of the corresponding salts of polyacrylic acid (PAA), indicating that the methyl groups in PMA generally hinder the binding of counterions with polyions. With tetrabutylammonium salt of PMA, the apparent degree of ionization is nearly equal to that of the tetrabutylammonium salt of PAA. This fact suggests hydrophobic interaction between the methyl groups in PMA and tetrabutylammonium ions.

The role of the nonpolar side chains of polyelectrolytes in the water phase is of great interest in connection with hydrophobic interaction in grobular proteins. Polymethacrylic acid contains extra methyl groups in the main chain compared with polyacrylic acid. In the previous paper,[1] the conductivities and electrophoretic mobilities of polystyrenesulfonates, polyethylenesulfonates, and polyacrylates, measured in 0.05M solutions of the simple salt of the corresponding cations at 25°C, were discussed on the basis of the apparent degree of ionization of the polyelectrolytes. The object of the present paper is to compare the additional data on polymethacrylate with those of polyacrylates.

Experimental

Polymethacrylic acid (PMA) was prepared by the polymerization of methacrylic acid in water, in the presence of hydrogen peroxide as an initiator, according to the method described by Leyte and Mandel.[2] A commercial sample of methacrylic acid was distilled under reduced pressure before polymerization. The polymer was dissolved in methanol and fractionally precipitated by the gradual addition of ether to give different molecular weights. The fraction used in this experiment had a molecular weight of 1.11×10^6, determined from the viscosity measurement of the polymer solution in methanol using the equation proposed by Wiederhorn and Brown.[3] Sodium, tetramethylammonium (Me_4N), tetraethylammonium (Et_4N), and tetrabutylammonium (Bu_4N) salts of PMA were prepared by the neutralization of PMA with the corresponding hydroxides. The sodium hydroxide solution was preapred by diluting its saturated aqueous solution. Tetraalkylammonium hydroxides were prepared by the reaction of the respective bromide salts in aqueous solutions with silver oxide. The tetraalkylammonium bromides were purchased from the Tokyo Kasei Kogyo Co. and were recrystallized from suitable solvents: an ethanol-water mixture for Me_4NBr_4, ethanol for Et_4NBr, and ethyl acetate for Bu_4NBr. Sodium chloride was a reagent-grade sample. Water was obtained by redistillation from an alkaline permanganate solution.

The detailed procedure for measuring the equivalent conductivities and electrophoretic mobilities of polyelectrolytes in 0.05M solutions of the simple salts of the corresponding cations at 25°C was described in the previous paper.[1] As simple salts, sodium chloride was used for Na-PMA and tetraalkylammonium bromides were used for respective tetraalkylammonium salts of PMA.

The electrical conductivities were measured with a Yokogawa BVZ-13A auto-frequency bridge, using a frequency of 1000 Hz. The electrophoretic mobilities were measured with a Hitachi HTB-2 Tiselius electrophoresis apparatus, varying the electric currents from 1 to 2 mA. A polyelectrolyte solution was dialysed in a cellophane tube against a large volume of a 0.05M solution of a simple salt for 2 days. From the boundaries recorded on a photographic plate at a different time, the electrophoretic mobility was then calculated.

Results

The equivalent conductivity of polyelectrolyte in a simple salt solution, Λ_p, may be expressed;[4]

$$\Lambda_p = 10^3(K_{ps}-K_s)/N_p$$

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[1] K. Tamaki, M. Ozaki, M. Ogiwara and I. Takemura, *Nippon Kagaku Zasshi*, **88**, 711 (1967).

[2] J. C. Leyte and M. Mandel, *J. Polymer Sci.*, *A*, **2**, 1879 (1964).

[3] N. M. Wiederhorn and A. R. Brown, *J. Polymer Sci.*, **8**, 651 (1952).

[4] U. P. Strauss and S. Bluestone, *J. Amer. Chem. Soc.*, **81**, 5295 (1959).

where K_{ps} and K_s are the specific conductivities of the salt solution with and without an added polyelectrolyte, and N_p is the polyelectrolyte concentration, expressed in terms of equiv./*l*. Although K_s in a salt solution containing polyelectrolyte is not generally equal to that of the same concentration of a simple salt solution without an added polyelectrolyte, in this study K_s may be considered to be equal to the value of a 0.05M solution of a simple salt; this means that the 0.05M solution of a simple salt is taken to be serving as the solvent. The values of Λ_p calculated in this manner are given as a function of the polyelectrolyte concentration in Fig. 1. Λ_p shows no noticeable trend with the variation in the polyelectrolyte concentration.[4,5] Therefore, the values of Λ_p, taken as the intrinsic equivalent conductivities, are listed in Table 1, in which the values of polyacrylates under the same conditions are also included.

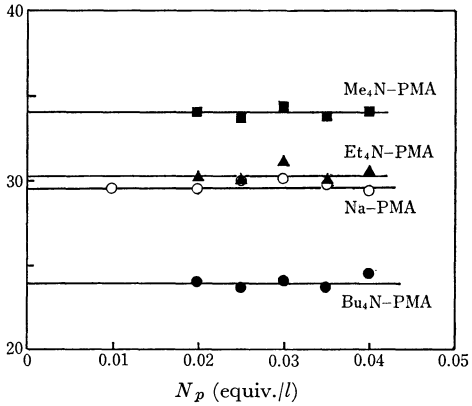

Fig. 1. Equivalent conductance in 0.05M simple salt solution as a function of the polymer concentration.

The observed electrophoretic mobility varied generally with the polyelectrolyte concentration, and it was found that the descending boudary became diffuse with the time. Thus, the mobilities of the ascending boudary as a function of the polyelectrolyte concentration are shown in Fig. 2. By extrapolation to an infinite dilution, the intrinsic mobilities of polyelectrolytes in 0.05M solutions of simple salts are obtained. The values are listed in Table 1.

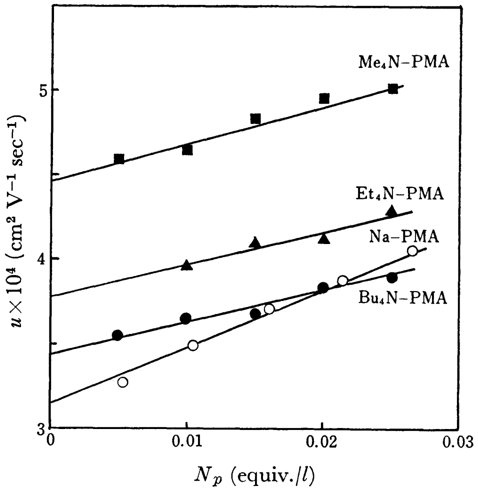

Fig. 2. Electrophoretic mobility in 0.05M simple salt solution as a function of the polymer concentration.

Discussion

As may be seen in Table 1, the electrical transport properties of the salts of PMA vary with the kinds of their counterions, indicating the difference in the strength of the interaction of this polymer with counterions. As an quantitative analysis of the data is not possible at present, the counterion-binding theory[6] is adopted as in the previous work.[1] This theory implies that part of the counterions, associated with the region of the polyion, does not contribute to the conductivity, whereas the other part of counterions remains free and behaves as in a corresponding solution of simple salt. The equivalent conductivity of polyelectrolyte can thus be written:[4]

$$\Lambda_p = i\,(\boldsymbol{F}u + l_c)$$

where i is the apparent degree of ionization, $\boldsymbol{F}$ is the faraday, and l_c is the equivalent ionic conduc-

TABLE 1

Counterion	PMA				PAA		
	$u \times 10^4$ (cm^2·V^{-1}·sec^{-1})	l_c (ohm^{-1}·cm^2)	Λ_p (ohm^{-1}·cm^2)	i	$u \times 10^4$ (cm^2·V^{-1}·sec^{-1})	Λ_p (ohm^{-1}·cm^2)	i
Na$^+$	3.15	43.1	29.4	0.40	3.27	24.4	0.33
Me$_4$N$^+$	4.45	38.2	33.9	0.42	4.84	27.3	0.32
Et$_4$N$^+$	3.77	27.3	30.2	0.47	3.89	24.4	0.38
Bu$_4$N$^+$	3.44	15.5	23.8	0.49	2.57	19.5	0.48

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[5] R. Varoqui and U. P. Strauss, *J. Phys. Chem.*, **72**, 2507 (1968).

[6] S. A. Rice and M. Nagasawa, "Polyelectrolyte Solutions," Academic Press, London and New York (1961), p. 427.

tivity of the counterion in the solution of a simple salt. In this case, l_c can be taken as the value of the ionic conductivity of counterions in a 0.05M concentration of a simple 1-1 electrolyte.[1)] Therefore, we can regard the apparent degree of ionization, i, or the apparent degree of binding, $1-i$, as a means of interpreting the strength of the interaction of the polyion with the counterion. The calculated values of i for polymethacylates are listed in Table 1; the values of polyacrylates are also shown in the table for purpose of comparison. With sodium salts, the values of i are larger in PMA than in PAA; that is, the methyl groups in PMA tend to hinder the binding of counterions with polyions. This is consistent with the finding of Crescenzi *et al.*[7)] and Strauss and Leung.[8)] With tetramethyl- and tetraethylammonium salts, the values of i are also about 1.2—1.3 times larger in PMA than in PAA; in fact, the binding of counterions with polycarboxylic acids is mainly determined by the size of the counterions.[1,9,10)]

The value of i for Bu_4N-PMA does not increase so much as that of Et_4N-PMA, being rather equal to that of Bu_4N-PAA. From the size effect of the counterions, the values of i for Bu_4N-PMA should be much larger; however, in this case the methyl groups in PMA may play an additional part in the interaction with counterions, although the effect of the methyl groups is not so remarkable as to reverse the sequence of Et_4N and Bu_4N ions in the apparent degree of binding.

Many investigators[2,11,12)] have reported the pH-induced transition of the molecular configuration of PMA in relation to the intramolecular hydrophobic or van der Waals interactions due to the methyl groups at low degrees of neutralization. However, as for the interaction of methyl groups in PMA with counterions at the full degree of neutralization, as in this study, it may be concluded that the hydrophobic effect is apparent with a strongly hydrophobic ion such as Bu_4N ion.

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