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technique is expected to be closer to 100 Å. The latter result is in agreement with SIMS analysis of polystyrene–poly(methyl methacrylate) diblock copolymers by Coulon et al.[20]

Summary and Outlook

The interdiffusion coefficient for a 111K DPS/93K HPS bilayer specimen healed at 125 °C was found to be 5.6 × 10^{-16} cm^2/s, in close agreement with FRES results. SIMS combines excellent depth resolution, Δz = 138 Å, with high sensitivity to hydrogen and deuterium. SIMS also has the advantage of direct depth profile measurement.

Measurement of diffusion at short times will require deconvolution of the measured profiles as well as a method for enhancing adhesion between the sample layers. Future work will include investigation of molecular weight effects on polymer diffusion. Correlated motion effects for high molecular weights will also be examined in future experiments and compared with results obtained with neutron specular reflectance techniques.[21]

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Registry No. PS, 9003-53-6.

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Raman Spectroscopic Study of the Ionization of Polyelectrolytes. 1. Poly(styrenesulfonic acid) and Poly(ethylenesulfonic acid)

Naoki Tanaka, Hiromi Kitano, and Norio Ise*

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.
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ABSTRACT: The dissociation behavior of polyelectrolytes such as poly(styrenesulfonic acid) and poly(ethylenesulfonic acid) was examined in aqueous solutions by using laser Raman spectroscopy. These polymeric acids are not completely dissociated: the macroions had a smaller degree of dissociation than the corresponding low molecular weight compounds. The degree of dissociation decreases with increasing concentration of macroions.

Since Kern observed the marked nonideality of polyelectrolyte solutions in terms of the osmotic pressure and single-ion activity coefficients of counterions,[1,2] the association phenomena of couterions with macroions have been one of the central topics for experimentalists and theoreticians working on polyelectrolyte solutions. Unfortunately, however, the exact nature of the interaction between counterions and macroions is still not fully understood. Even some of the conclusions concerning the degree of dissociation of the ionizable groups have varied; for example, Lapanje and Rice[3] stated that poly(styrenesulfonate) is fully dissociated on the basis of the agreement between the Raman spectra of the polymer and its low molecular weight homologue (ethylbenzenesulfonic acid). However, the dissociation of another homologue, *p*-toluenesulfonic acid, was found to be incomplete by Dinius and Choppin[4] using NMR spectroscopy and by Bonner and Torres[5] using Raman spectroscopy. The Raman effect is the reflection of a change in the finite electron density at the bond; in general, purely ionic or ion dipole bonding does not give rise to a Raman band characteristic of the bond.[6] Therefore Raman spectroscopy can be used to measure the state of "true" dissociation in a polyelectrolyte solution. In the present paper, we were interested in studying the reason for the discrepancy mentioned above and also in studying the state of dissociation of poly(styrenesulfonic acid) by using this technique. The state of dissociation of polyacrylate has been previously studied by this method.[7]

Experimental Section

Materials. Sodium poly(styrenesulfonate)s (NaPSS, $\bar{M}_w$ 4000, 16 000, 65 000, and 100 000; $\bar{M}_w/\bar{M}_n$ 1.04–1.06) and sodium poly-

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* To whom correspondence should be addressed.

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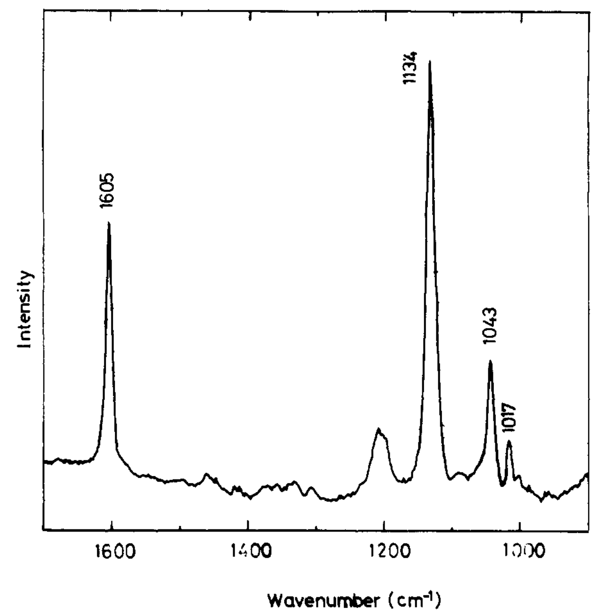

Figure 1. Raman spectrum of poly(styrenesulfonic acid) ($\bar{M}_w$ 3600) at 25 °C; [polymer] = 0.156 equiv L^{-1}.

(ethylenesulfonate)s (NaPES, $\bar{M}_w$ 2000) were obtained from Pressure Chemicals, Pittsburgh, PA, and Polyscience, Warrington, PA, respectively. Poly(styrenesulfonate)s were purified by repeated ultrafiltration using an Amicon apparatus (Model 202, membrane; Diaflo YM 5, exclusion limit 2000) and finally converted to the protonated form by passing through an ion-exchange resin column (IR-120B, 2 × 30 cm). In the case of poly(ethylenesulfonate)s, its solution was washed with active charcoal powder before passage through the ion-exchange column. *p*-Toluenesulfonic acid (HTS), methanesulfonic acid (HMS), and *p*-toluenesulfonamide were purchased from Nacalai Tesque, Kyoto, and dodecylbenzenesulfonic acid was supplied by Tokyo Kasei Co, Tokyo. Dimethyl sulfoxide and acetonitrile were guaranteed reagents for spectroscopy from Merck. A Milli-Q grade water was used for preparation of sample solutions.

Spectroscopic Measurements. The Raman spectra of polymer solutions were examined by using an NR-1100 Raman spectrophotometer (Japan Spectroscopic Co., Tokyo). An argon ion laser (GLG 3200, NEC, Tokyo) was used as a light source (power 300 mW). The wavelength was 514.5 nm for dodecylbenzenesulfonic acid and 488 nm for other compounds. Sample solutions were put into a small glass tube (i.d. 0.28 mm; length 12 mm), and the tube was set in a small thermostated chamber of the spectrophotometer, which was controlled at 25 ± 0.5 °C by using a Peltier device (Model RT-IC, Japan Spectroscopic Co.).

Conductometric Measurements. To estimate the concentration of polymer solutions, conductometric titration was carried out using a Wayne-Kerr autobalance precision bridge (B-311).

Results and Discussion

***p*-Toluenesulfonic Acid and Poly(styrenesulfonic acid).** Figure 1 shows the Raman spectrum of poly(styrenesulfonic acid) ($\bar{M}_w$ 3600). The spectra of poly(styrenesulfonic acid)s of higher molecular weight were quite similar to this spectrum. A monomeric analogue (*p*-toluenesulfonic acid) showed a very similar spectrum, though there was a slight shift in the wavelength of the highest peak. Precisely speaking, the shape of the peak at 1206 cm^{-1} of *p*-toluenesulfonic acid was different from that of HPSS, and a new peak appeared at 1387 cm^{-1}, but these differences were not essential for the present purpose.

The peaks at 1017, 1043, and 1134 cm^{-1} in the figure correspond to a sulfonic acid residue.[8,9] A peak at 1605 cm^{-1} was due to the C–C stretching vibration of benzene ring,[10] and we adopted the intensity of this peak as a reference to evaluate the degree of dissociation.

Lapanje and Rice[3] and Bonner and Torres[5] assigned the peak at 1125 cm^{-1} to the characteristic peak of sulfonate ion. Lapanje and Rice compared the peaks of HPSS and ethylbenzenesulfonate ion and concluded that HPSS dissociated completely,[3] because the relative intensities of the peak at 1125 cm^{-1} of the two compounds were the same. The underlying assumption was the complete dissociation of ethylbenzenesulfonate. Bonner and Torres claimed that, from the ratio of the peaks at 1125 and 2925 cm^{-1}, *p*-toluenesulfonic acid is not completely dissociated.

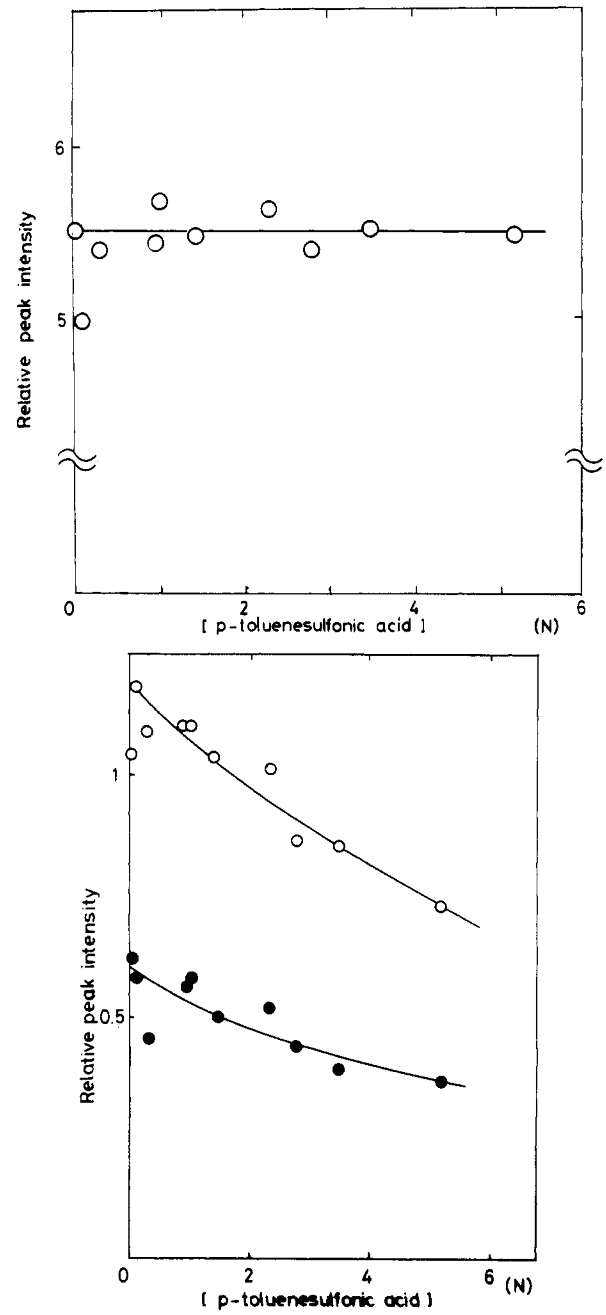

Figure 2. Concentration dependences of relative peak intensities of *p*-toluenesulfonic acid at 25 °C: (top) ○, I_{1134}/I_{1605}; (bottom) ○, I_{1043}/I_{1605}, ●, I_{1017}/I_{1605}.

We reexamined the concentration dependence of the peak intensity at 1017, 1043, and 1134 cm^{-1} (corresponding to the 1125 cm^{-1} peak in the previous studies), normalized to the peak intensity at 1605 cm^{-1}. Figure 2 shows that the peak intensity at 1134 cm^{-1} did *not* display a concentration dependence, but the peaks at 1017 and 1043 cm^{-1} were clearly concentration dependent.

The Raman spectrum of *p*-toluenesulfonamide showed a peak at 1166 cm^{-1} in DMSO–H_2O. *p*-Dodecylbenzenesulfonic acid (anhydrous pure compound, not dissociated) had a peak at 1154 cm^{-1} (Figure 3), which means that the

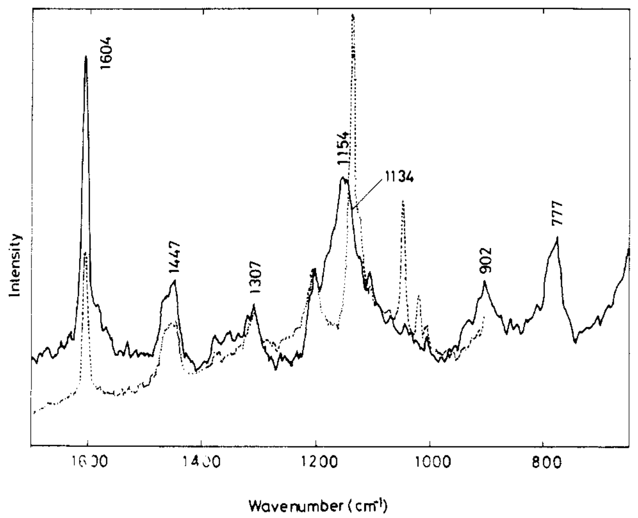

Figure 3. Raman spectrum of *p*-dodecylbenzenesulfonic acid at 25 °C: —, pure compound; ---, aqueous solution.

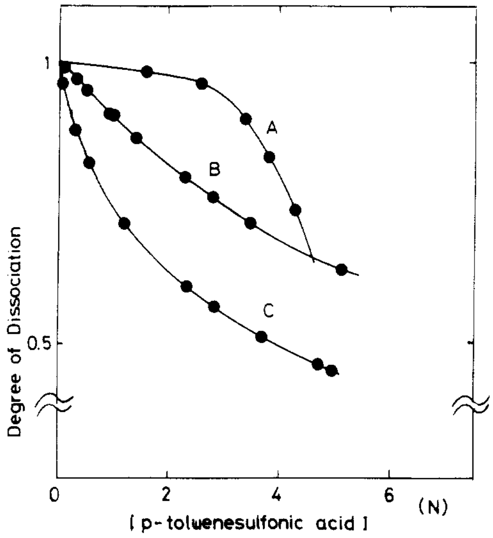

Figure 4. Effect of concentration of *p*-toluenesulfonic acid on the degree of dissociation: A, by Bonner et al. (Raman); B, this work (Raman); C, by Dinius et al. (NMR).

intensity of the peak around 1134 cm^{-1} would not correctly reflect the ionic dissociation of the sulfonate group, because these compounds are not dissociated.

From the intensity at 1043 cm^{-1}, the degree of ionization, α, was calculated. The proportionality between the peak intensity, I, and the concentration of the species observed, C, is expressed by

$$C = JI \quad (J^{-1}\text{: molar intensity}) \qquad (1)$$

The relative peak intensity of the peak at 1043 cm^{-1} (I_{1043}) to that at 1605 cm^{-1} (I_{1605}) is given by

$$\frac{I_{1043}}{I_{1605}} = \frac{C_{SO_3^-}J_{1605}}{C_{stoich}J_{1043}} = J'\alpha \qquad (2)$$

where $C_{SO_3^-}$ and C_{stoich} are the concentration of sulfonic acid residue and unit concentration, respectively.

Since $\alpha \rightarrow 1$ as $C_{stoich} \rightarrow 0$, a plot of $J'\alpha$ against C_{stoich} should approach J' at $C_{stoich} = 0$. α of HTS aqueous solution at several concentrations was calculated from this J' value.

Figure 4 shows the concentration dependence of the degree of dissociation (α) of *p*-toluenesulfonic acid obtained in this work together with those of other workers. Our finding is in rough agreement with that of Dinius and Choppin evaluated by using NMR methods.[4] They measured the degree of dissociation of *p*-toluenesulfonic acid by using

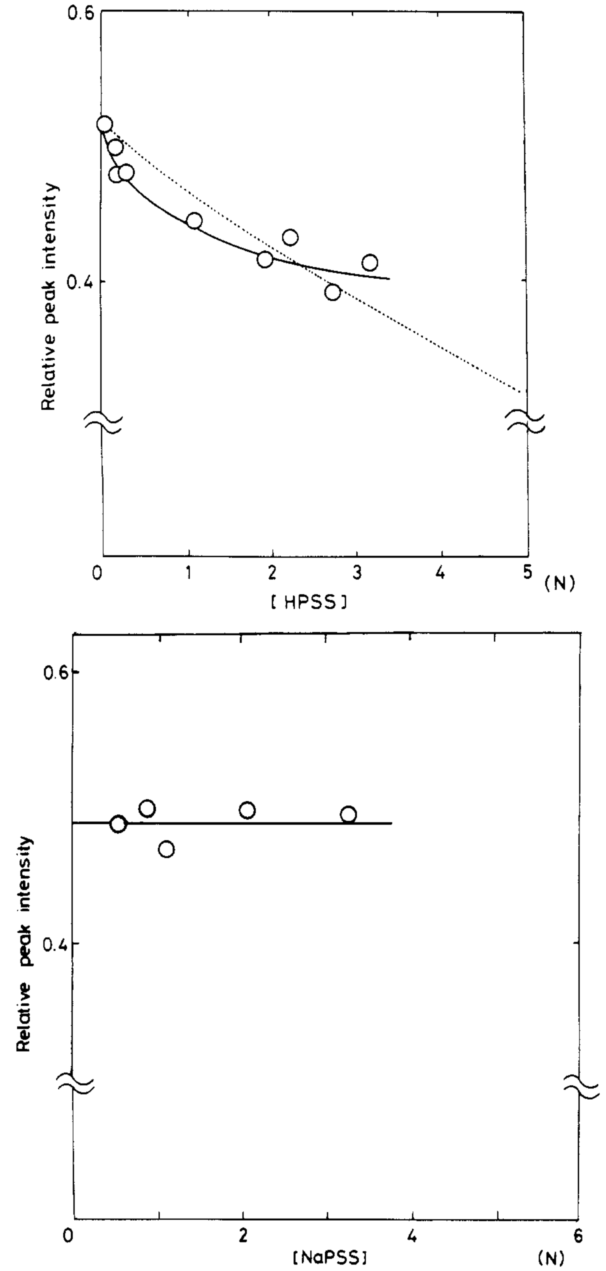

Figure 5. Concentration dependence of the relative intensity of observed I_{1043}/I_{1605} at 25 °C: (top) -○-, HPSS ($\bar{M}_w$ 3600), ---, *p*-toluenesulfonic acid; (bottom) NaPSS ($\bar{M}_w$ 4000).

$$S/P = \alpha S_1 + (1 - \alpha)S_2 \qquad (3)$$

where S, P, S_1, and S_2 are total chemical shift, mole fraction, shift of the hydronium ion, and shift of the undissociated acid, respectively. S_1 was the value extrapolated to $P = 0$ in the $S/P - P$ plots, and S_2 was estimated by assuming that the chemical shift of *p*-toluenesulfonic acid in CHCl$_3$ or heptane was equal to S_2. Considering that anhydrous *p*-toluenesulfonic acid is not very soluble in these solvents, their sample (*p*-toluenesulfonic acid dissolved in these solvents) must have been highly hydrated and partly dissociated. If so, the true value of the degree of dissociation would be larger than that reported by Dinius and Choppin: the agreement with our results would then be more satisfactory. This agreement appears to suggest that the peak intensities at 1017 and 1043 cm^{-1} (not at 1134 or 1125 cm^{-1}) should be used to estimate the degree of dissociation.

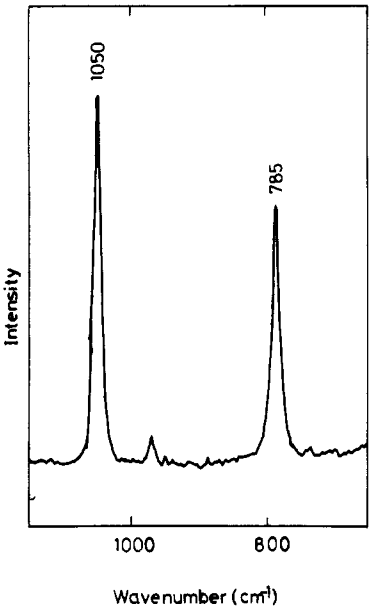

Figure 6. Raman spectrum of methanesulfonic acid at 25 °C; [methanesulfonic acid] = 0.865 equiv L^{-1}.

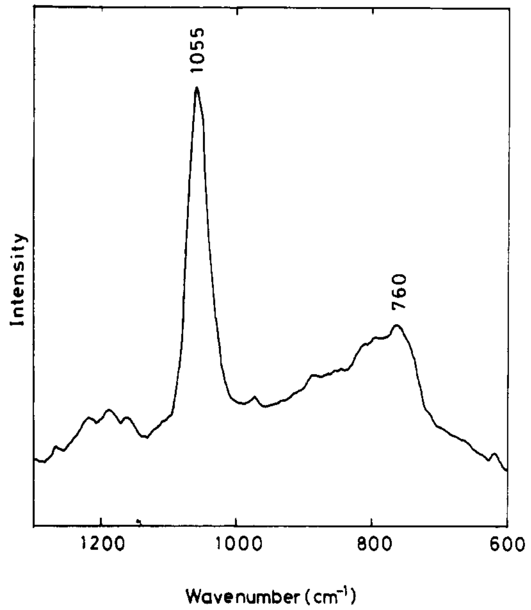

Figure 7. Raman spectrum of poly(ethylenesulfonic acid) (HPES) at 25 °C; [HPES] = 0.50 equiv L^{-1}.

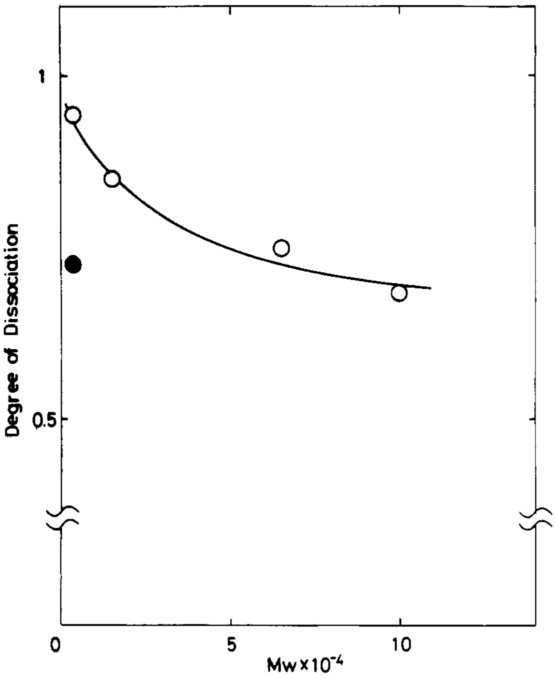

Figure 8. Effects of molecular weight and solution medium on the relative peak intensity of HPSS at 25 °C: ○, in H_2O; ●, in 33 v/v % CH_3CN-H_2O.

Similar measurements were carried out on HPSS (Figure 5, top; $\bar{M}_w$ 3600) and NaPSS (Figure 5, bottom; $\bar{M}_w$ 4000). We could not observe concentration dependence in the peak intensity for NaPSS at 1043 cm^{-1}, whereas dependences in the peak intensity for HPSS are very obvious. This means that the relative intensity at 1043 cm^{-1} reflects the dissociation of sulfonate groups and, in addition, the high concentration of the polymer did not simply quench the peak intensity of the solution.

Methanesulfonic Acid and Poly(ethylenesulfonic acid). Next we examined the concentration dependence of the peak intensity for methanesulfonic acid (HMS) and poly(ethylenesulfonic acid) (HPES). Figure 6 shows the Raman spectrum of methanesulfonic acid. The peaks at 1050 and 785 cm^{-1} corresponded to the symmetric stretching vibration of $-SO_3^-$ and to the C–S stretching vibration, respectively. The relative intensity of the former peak to that of the latter one was estimated. The concentration dependence for HMS was consistent with that found by Covington et al.[11] As for HPES, we used the peak of C–H stretching vibration (2946 cm^{-1}) as a reference peak, because the peak intensity of HPES at 785 cm^{-1} was quite indefinite (Figure 7).

Effects of Molecular Weight and Solvent. Figure 8 shows the degree of dissociation α of HPSS of various molecular weights (0.25 equiv L^{-1}); α was calculated in the same manner as for HTS. In the figure the degree of dissociation of HPSS ($\bar{M}_w$ 3600) in 33 v/v % acetonitrile–water is also shown. It is clear that the increase in molecular weight of HPSS and the decrease in dielectric constant of the medium reduce the degree of dissociation of HPSS.

In a previous work using transference measurements, the degree of counterion dissociation of HPSS was found to be 0.38–0.58 in the concentration region from 0.148 to 0.0049 equiv L^{-1}.[12] The present results obtained at much higher concentrations were 0.75–0.95 from Figure 8. The large value from the Raman method is reasonable since the counterions that are in a very closed proximity to the ionizable groups are recognized as "associated" by the transference measurements and as "dissociated" by the Raman method.

On the basis of recent viscosity measurements the macroions are believed to assume a rather coiled-up conformation in aqueous solution[13] at the concentration range used in the Raman spectroscopy. Then, the *intra*molecular interaction would be substantial with increasing molecular weight, although the distance between adjacent charged groups is fixed. Under such a circumstance, the dissociation must take place under higher electrostatic potentials for higher molecular weight samples. This accounts for the observed reduction of the degree of dissociation.

Comparison of Dissociation Behavior of Sulfonate Derivatives. Figure 9 shows the concentration dependences of the degree of dissociation of methanesulfonic acid and poly(ethylenesulfonic acid). For comparison, the corresponding data for *p*-toluenesulfonic acid and poly(styrenesulfonic acid) are shown as dotted curves. It is clear that at high concentration the polyelectrolytes show less dissociation than the low molecular weight compounds. This is inconsistent with the previous results reported by

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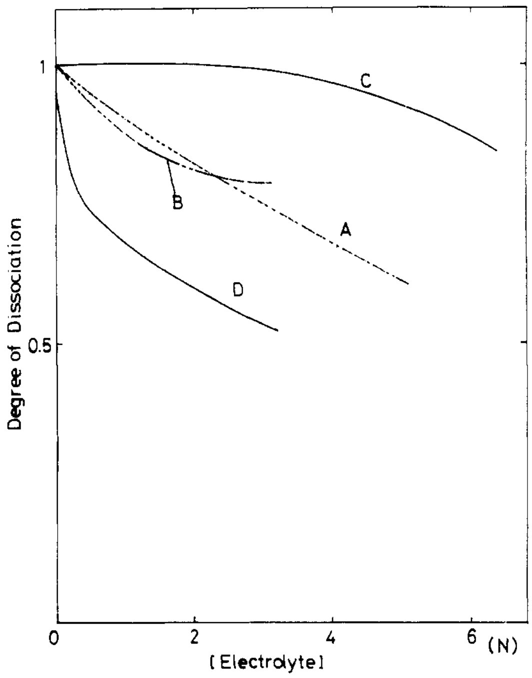

Figure 9. Effect of concentration on the dissociation of sulfonate groups of methanesulfonic acid and poly(ethylenesulfonic acid) at 25 °C: A, *p*-toluenesulfonic acid (dotted curve); B, poly(styrenesulfonic acid) (dotted curve); C, methanesulfonic acid; D, poly(ethylenesulfonic acid).

Lapanje et al.[3] and by Kotin et al.[14] The lower degree of dissociation of HPES compared to HPSS may be due to the phenyl side chains in the latter, which would make the main chains of poly(styrenesulfonate) ions less flexible.

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Registry No. HPSS, 50851-57-5; HPES, 26101-52-0.

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Complex Formation in Polymer-Ion Solutions. 2. Polyelectrolyte Effects

E. Pezron,*,† L. Leibler,* and F. Lafuma

Laboratoire de Physico-Chimie Macromoléculaire,‡ *E.S.P.C.I. 10, rue Vauquelin, 75231 Paris Cedex 05, France.* *Received July 28, 1988*

ABSTRACT: We have studied the effect of electrostatic interactions on ion complexation in polymer solutions. Using a simple self-consistent argument, we show that the complexation constants strongly depend on the ionic strength of the solution and in particular on the complexing ion concentration. We have performed a ^{11}B NMR experimental study of complexation in three different poly(hydroxy compound)-borax systems over a wide range of borax concentration. As theoretically expected, a sharp decrease of complexation constants with increasing borax concentration is observed. This electrostatic effect, specific to macromolecular systems, is absent in corresponding low molecular weight model systems.

I. Introduction

Considerable effort has been devoted to the study of ion complexation by polymer chains over the past 4 decades. Electrostatic repulsion between charged complexes on macromolecular chains plays a major role in various phenomena such as phase separation,[1-2] the swelling of gels,[3] and the rheological properties of semidilute[4] or dilute solutions[5,6] of polymer-ion systems. Electrostatic interactions strongly affect the formation of polymer-ion complexes in many different systems such as polyelectrolyte-metallic ion[7-9] or neutral polymer-anion solutions.[1] The importance of this polyelectrolyte effect in polymer-ion complexation is generally evaluated on the basis of a comparison with the classical complexation picture for small model molecules. In the preceding paper of this series,[9] it has been shown that this classical mass action law scheme is inadequate for dilute polymer solutions when intrachain complexes are formed. The aim of this paper is to present a theoretical analysis of the importance of the polyelectrolyte effect on complex formation in a simple neutral polymer-ion system and to test the predictions for polyelectrolyte effects in poly(hydroxy compound)-borate solutions.

In many situations complexation chemical equilibria between polymers and ions in aqueous solutions may be reduced to the two following successive reactions:

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† Present address: Institute for Surface Chemistry, Box 5607, S.11486, Stockholm, Sweden.
‡ Université Pierre et Marie Curie, CNRS U.A. 278.