Excluded Volume of Alkali Poly(styrene sulfonates) in Solutions with Added Salt

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Summary

The intrinsic viscosities of sodium and potassium poly(styrene sulfonates) having different molecular weights were determined in sodium and potassium chloride solutions of various concentrations. The data were analyzed on the basis of the theory of Stockmayer and Fixman and the values of the mutal excluded volume of segments determined. The values obtained have been compared with those calculated using Ptitsyn's theory of excluded volume. To achieve semiquantitative agreement between theory and experiment, the effective and not the nominal charge of polyions has to be used in calculations. From the intrinsic viscosities the molecular expansion was also determined and the values obtained compared with those given by Fixman's theory of polyelectrolytes. Finally, the temperature coefficients of the intrinsic viscosities of some solutions having different ionic strength have also been ascertained.

INTRODUCTION

The problem of excluded volume of polyions in solutions of polyelectrolytes has for years attracted the attention of polymer

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scientists. Together with the problems of ion binding it belongs to those problems which have not been adequately solved. It is now well established that both excluded volume and ion binding are mainly due to electrostatic forces, the first to repulsive forces be-tween fixed charged groups and the second to the interaction of these groups with counterions (1). However, we still do not have a theory which would give satisfactory agreement with experiment on the basis of the same model.

This paper presents a viscometric study of the expansion and the excluded volume of polyions, respectively. The approach to the problem is based on the recent analysis of Kurata and Stockmayer (2) and the theory of Stockmayer and Fixman (3), respectively. Al-though definitive evaluation of these two as well as of the somewhat older theory of Flory (5) requires, according to Berry and Fox (4), data at high molecular weights and/or over a large temperature span, this is not so important in the present study. For considering the complexity of the problem of excluded volume and the present status of relevant theories we do not expect much more than a semi-quantitative agreement between theory and experiment. An inves-tigation along similar lines has already been reported by Taka-hashi and Nagasawa (6), but their treatment of experimental data on the basis of Ptitsyn's theory (7) is different from ours. Moreover, we have also applied the recent polyelectrolyte theory of Fixman (8), which is based on a fuzzy-sphere model, for the calculation of the molecular expansion.

The polyelectrolytes chosen for this investigation were sodium and potassium poly(styrene sulfonates), respectively. The intrinsic viscosities of their aqueous solutions at 20°C and various ionic strengths were determined and the data analyzed on the basis of the aforementioned theories. For some ionic strengths the intrinsic viscosities at 35, 50, and 70°C were also determined and their tem-perature coefficients ascertained.

EXPERIMENTAL

Materials

The fractionated samples of sodium poly(styrene sulfonate) (NaPSS) used in this investigation were kindly supplied by the Dow Chemical Co., Midland, Michigan. Aqueous solutions were

TABLE 1

Molecular Weights of Samples Used for Viscosity Measurements

Fraction	F_1	F_2	F_3	F_4
$M \times 10^{-4}$	1.6	8.1	24.9	33.0

purified by passage through columns containing anion and cation exchange resins in the hydroxide and hydrogen forms, respectively. From these pure solutions, NaPSS and potassium poly(styrene sulfonate) (KPSS) were obtained by passage through columns containing cation-exchange resin in the sodium and potassium forms, respectively. Molecular weights of the fractions of NaPSS were determined from the intrinsic viscosities at 20°C in 5.0×10^{-1} N NaCl solution using the equation

$$[\eta] = 6.7 \times 10^{-4} M_w^{0.62} \tag{1}$$

based on the M_w-viscosity chart of Vanderkooi (Dow Chemical Co.). The chart was obtained on the basis of light-scattering measurements. The values of the constants in the above equation are endowed with a certain degree of uncertitude, owing to difficulties encountered in the optical clarification of solutions. The same holds true for all other ionic strengths. Furthermore, the possible effects of heterogeneity of the fractions have also not been considered. Therefore we have deliberately avoided any discussion of the unperturbed dimensions of polyions. Molecular weights of the fractions are given in Table 1.

Viscosity Measurements

Viscosities were measured with two modified Ubbelohde viscometers having four bulbs with known volumes, which allows measurement of the shear dependence of solutions in a single run (9). The average shear gradients, $\bar{G}$, were calculated from Kroepelin's formula (10). For every concentration and temperature the relative viscosity was plotted for the four different shear gradients and the curve extrapolated to $G = 0$. These plots were linear in the range $G = 200$ to 1400 sec^{-1} covered by the measurements. The shear gradient corrections had to be considered mostly for solutions containing the two high-molecular-weight samples, F_3 and

F_4, at low ionic strength. The kinetic-energy correction factors were estimated from the efflux times of water at 15, 25, and 35°C and the relative viscosities were corrected for the kinetic energy whenever necessary. Temperatures were controlled to ±0.01°. Concentrations were appropriately corrected for the thermal expansion. The flow times were determined to 0.1 sec.

RESULTS

The experimental values of the intrinsic viscosities of NaPSS and KPSS in NaCl and KCl solutions having different ionic strength are presented in Table 2. In Figs. 1 and 2, the intrinsic viscosities are plotted vs. molecular weights in logarithmic scale. Linear depend-
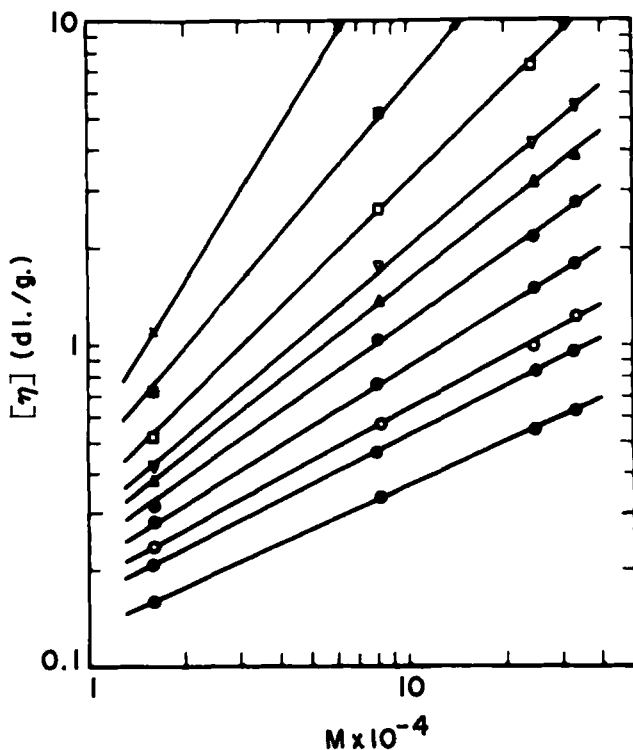

FIG. 1. Intrinsic viscosity vs. molecular weights of sodium poly(styrene sulfonate) in sodium chloride solutions at 20°C; ionic strength of NaCl, C_s: (●) 2.00; (◖) 1.31; (○) 1.00; (⊗) 5.01×10^{-1}; (◎) 2.00×10^{-1}; (△) 1.00×10^{-1}; (▽) 5.01×10^{-2}; (□) 1.00×10^{-2}; (⊠) 5.01×10^{-3}; (×) 0.
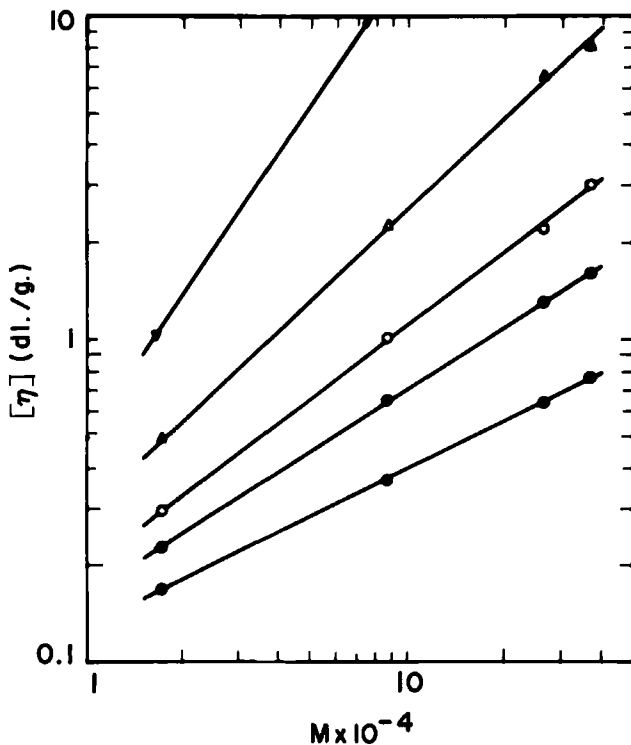
FIG. 2. Intrinsic viscosity vs. molecular weights of potassium poly(styrene sulfonate) in potassium chloride solutions at 20°C; ionic strength of KCl, C_s: (●) 1.18; (◑) 5.02 × 10⁻¹; (○) 1.00 × 10⁻¹; (△) 1.00 × 10⁻²; (▽) 0.

ence of log $[\eta]$ on log M is observed and, as expected, the slope of the lines increases with decreasing ionic strength. The values of K and ν calculated from Figs. 1 and 2 are given in Tables 2 and 3. The experimental results can now be treated in the following way. According to Stockmayer and Fixman (3) the intrinsic viscosities of flexible-chain polymers, provided draining effects are negligible, are given by the relation

$$[\eta] = KM^{1/2} + 0.51\Phi_0 BM \qquad (2)$$

where Φ_0 is the universal viscosity constant in theta solvents and B is the polymer-solvent interaction parameter, which is equal to

$$B = \beta/m_s^2 \qquad (3)$$

TABLE 2

Intrinsic Viscosities of Sodium and Potassium Poly(styrene sulfonate)
(NaPSS, KPSS) in Sodium and Potassium Chloride Solutions at 20°C

C_s, moles/liter	$[\eta]$, 100 ml/g			
	F_1	F_2	F_3	F_4
2.000	0.160	0.338	0.545	0.610
1.310	0.209	0.468	0.821	0.970
1.000	0.239	0.577	0.985	1.22
0.501	0.284	0.780	1.49	1.81
0.200	0.311	1.07	2.17	2.74
0.100	0.380	1.37	3.15	3.85
0.0501	0.422	1.75	4.18	5.47
0.0100	0.515	2.65	7.29	10.5
0.00501	0.715	5.15	19.4	23.4
0	1.10	14.8	88.3	134
KPSS in KCl				
1.180	0.165	0.367	0.652	0.771
0.502	0.230	0.661	1.28	1.60
0.200	0.295	1.01	2.20	2.97
0.010	0.489	2.31	6.45	7.21
0	1.05	12.4	53.1	91.9

TABLE 3

Dependence of K and ν in Mark-Houwink-Sakurada Equation
($[\eta] = KM^\nu$) on Ionic Strength at 20°C

NaPPS in NaCl			KPSS in KCl		
C_s, moles/liter	$K \times 10^4$	ν	C_s, moles/liter	$K \times 10^4$	ν
2.000	20.2	0.45			
1.310	15.4	0.50			
1.000	14.6	0.53	1.180	12.8	0.50
0.501	6.7	0.62	0.502	6.0	0.61
0.200	4.25	0.69			
0.100	2.10	0.77	0.100	2.41	0.75
0.501	1.24	0.84			
0.010	0.392	0.98	0.010	0.64	0.92
0.00501	0.114	1.15			
0	0.023	1.59	0	0.014	1.41

Here β is the mutual excluded volume of segment defined by

$$\beta = \int_0^\infty [1 - \exp\,(-V(r)/kT)]4\pi r^2\;dr \qquad (4)$$

where $V(r)$ is the potential of average force between two segments as a function of their distance r.

The value of B at single ionic strengths can be obtained from the slopes of plots of $[\eta]M^{1/2}$ vs. $M^{1/2}$. In Fig. 3 these plots for solutions of NaPSS are presented. They display the fact that B decreases with increasing ionic strength, which is in accord with the above-mentioned behavior of ν. The plots for large and moderate ionic strengths have a common ordinate intercept, whereas in 1.31 N and 2.00 N NaCl solutions it lies slightly lower. However, the plots for solutions of low ionic strength and water largely diverge, which means that in these solutions draining effects cannot be neglected.
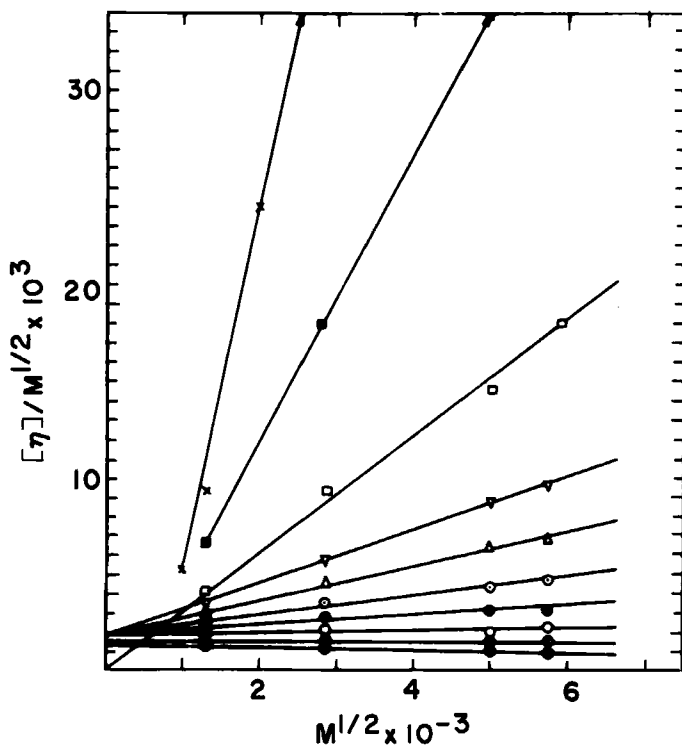

FIG. 3. Stockmayer-Fixman plots [Eq. (2)] for solutions of sodium poly(styrene sulfonate); ionic strengths are the same as in Fig. 1.

Moreover, it can be concluded that water and dilute salt solutions are good solvents for the polyelectrolyte.

The values of B should be proportional to the inverse square root of ionic strength, which in our case is set equal to the concentration of added salt (*11,12*) (C_s). In accordance with this, a straight line is obtained when B's are plotted vs. $1/C_s$ (Fig. 4). B may be assumed to be composed of two terms, B_0 and B_e, respectively. The first may be ascribed to nonelectrostatic and the second to electrostatic interactions. B_0 can be set equal to B at infinite ionic strength when all the charges on polyions are more or less completely screened off. Since water and aqueous salt solutions are very poor solvents for uncharged polymers in general, it is not surprising that the value of B_0 is negative. On the other hand, in the theta solvent B_0 equals B_e.
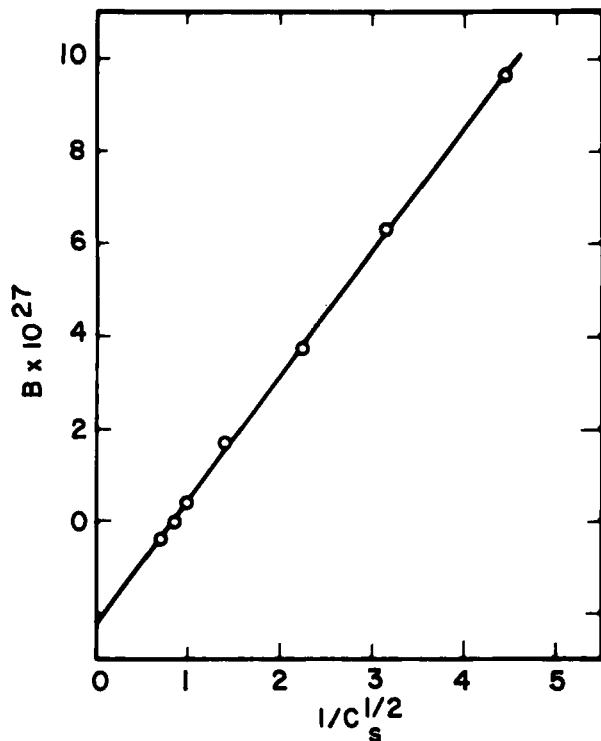

FIG. 4. B vs. inverse root of ionic strength $1/C_s^{1/2}$.

On the basis of this we can express B by the relation

$$B = B_0 + B_e = B_0 + A/C_s^{1/2} \tag{5}$$

where A is a constant.

Since theory and experiment in connection with B_0 have adequately been treated by others (13), we shall deal only with the experimental values of B_e, which can be compared with those given by Ptitsyn's theory (7). According to this theory B_e should be given by the relation

$$B_e = 10^3 i^2 / 2m^2 N_A C_s \tag{6}$$

where i is the ratio of the charged monomer units to their total number, m the molecular weight of a monomer unit, N_A Avogadro's number, and C_s the concentration of added salt of 1:1 type expressed in moles per liter. However, when treating the experimental data for the expansion of polyelectrolytes (7) it was necessary to introduce in Eq. (6) instead of i the effective charge parameter, i_{eff}, which is considerably lower than i and which accounts for ion binding. The same procedure can be followed in the present case. Since there is no theory giving i as a function of charge density and polyelectrolyte concentration, and considering further that to a first approximation the fraction of free ions, f, does not depend on ionic strength provided that the polyelectrolyte and the added salt contain a common ion, it is possible to replace i by f in Eq. (6). The values of f for solutions of NaPSS should be practically equal to those for solutions of the sodium polyacrylate; i.e., they should be close to 0.35, since they depend only slightly on the polyelectrolyte concentration (14). The values of B_e obtained on the basis of Eq. (6) are presented in Table 4 together with the observed values.

TABLE 4

Values of B_e Obtained from Stockmayer-Fixman Plots and Calculated from Eq. (6) $(B_0 = -0.22 \times 10^{-26})$

C_s, moles/liter	2.00	1.31	1.00	0.501	0.020	0.010	0.00501
$B_e \times 10^{26}$							
Obs.	0.20	0.22	0.26	0.29	0.59	0.85	1.19
Calcd.	0.14	0.18	0.24	0.48	1.21	2.42	4.84

Also, it is to be noted that Eq. (6) predicts a linear dependence on $1/C_s$ which is in contradiction with Eq. (5).

Comparison of the experimental results with the recent theory of Fixman (8) is also possible. His equation for the molecular expansion α^3 of polyelectrolyte in solution reads

$$\alpha^3 = 1 + C_n^{1/2} + D_0 q (2D\epsilon z_c b_0)^{-1}{}_n{}^{112} \cdot {}^{-1} \tag{7}$$

where C is a constant; n the number of segments of the length b_0 and charge q; ϵ the proton charge; D and D_0 the apparent and effective dielectric constants, respectively; z_c the charge number of counterions; and κ the Debye-Hückel parameter. The intrinsic viscosity is given by the relation

$$[\eta] = K M^{1/2} \alpha^3 \tag{8}$$

the difference between α^3 and $\alpha\eta^3$ being ignored.

It may be observed that Eq. (7) predicts a linear dependence of $[\eta]$ on $1/C_s^{1/2}$, as has indeed been found. Therefore, the plots of α^3,
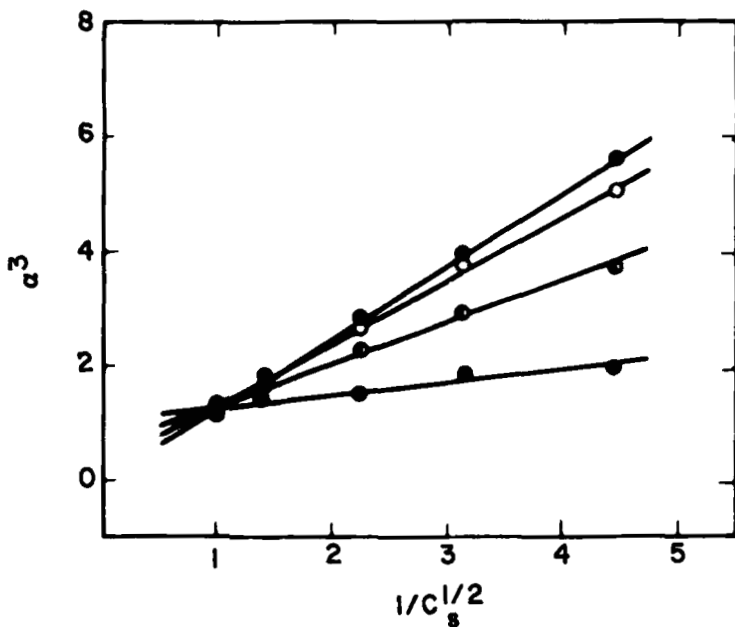

FIG. 5. Molecular expansion α^3 vs. inverse root of ionic strength $1/C_s^{1/2}$: (●) F_1; (◐) F_2; (○) F_3; (⊗) F_4.

TABLE 5

Values of $(D/D_0)b_0$ (in angstroms) for Sodium Poly(styrene sulfonate) in Sodium Chloride Solutions

Fraction	F_1	F_2	F_3	F_4
$(D/D_0)b_0$	58	44	53	51

computed from Eq. (8), vs. $1/C_s^{1/2}$ should be linear. In Fig. 5 these plots for all four fractions are given and their linearity is evident. The value of $(D/D_0)b_0$ calculated from the slopes by taking $q/\epsilon = 1$ and $n = M/206$ are seen to be around 50Å (cf. Table 5), which agrees satisfactorily with the values for sodium polyacrylate obtained by

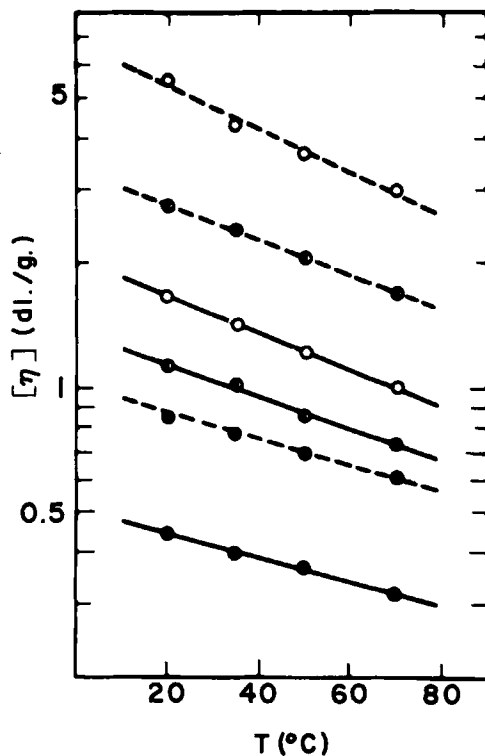**FIG. 6.** Intrinsic viscosity vs. temperature of sodium poly(styrene sulfonate) in sodium chloride solutions, ionic strengths of NaCl, C_s: (●) 5.01×10^{-1}; (◐) 2.00×10^{-1}; (○) 5.01×10^{-2}; F_2: ———, F_4: ----.

TABLE 6

Temperature Coefficients of Intrinsic Viscosities of Sodium
Poly(styrene sulfonate) in Sodium Chloride Solutions

C_s, moles/liter	5.01×10^{-1}		2.00×10^{-1}		5.01×10^{-2}	
Fraction	F_2	F_4	F_2	F_4	F_2	F_4
$-(d \ln [\eta]/dT) \times 10^2$, °C^{-1}	0.67	0.74	0.86	0.95	1.04	1.19

Fixman (8) on the basis of the experimental data of Takahashi and Nagasawa (6).

Finally, the results of the study of the temperature dependence of the intrinsic viscosities of solutions of NaPSS are presented in Fig. 6 and Table 6, respectively. In Fig. 6 intrinsic viscosities are plotted vs. temperature for the samples F_2 and F_4. The solvents used were $5.01 \times 10^{-2} N$, $2.0 \times 10^{-2} N$, and $15.01 \times 10^{-1} N$ NaCl. In Table 6 the values of temperature coefficients for the range 20 to 70°C are listed. They are seen to be large and negative and to depend on the solvent. Both these behaviors have been noted previously for cellulose derivatives (15,16).

DISCUSSION

Examination of Table 4 displays the fact that agreement between the observed and calculated values of B_e at lower ionic strengths is only semiquantitative, whereas for 1.0 N NaCl and higher ionic strengths the two values are quite close. Considering the relative simplicity of Ptitsyn's theory we can consider it a satisfactory approximation to the real situation. There is no need for dramatizing the fact that according to this theory B_e should be inversely proportional to C_s, for it may easily be shown that for high concentrations of C_s the linearity of the plot B_e vs. $1/C_s$ can be obtained, and considering further that f does slightly depend on C_s the observed agreement is not surprising. Since the shortcomings of Ptitsyn's theory, extensively discussed by Takahashi and Nagasawa (6), have in our treatment been to a large extent removed by considering the effective charge on polyions, we would like to concentrate our discussion more on the appropriateness of Eq. (2) for polyelectrolyte solutions. As has been mentioned above, it should be strictly applicable only when draining effects are negligible. It is more or less

certain that these effects disappear at higher ionic strengths. However, when the concentration of added salt is becoming less and less, draining effects must manifest themselves, for the dimension of polyions increase quite considerably and in addition their stiffness is larger. In accordance with this the Stockmayer-Fixman plot for 1.00×10^{-2} N and lower concentrations of NaCl does not pass through the common ordinate intercept, and, moreover, it can be concluded (cf. Fig. 3) that the divergence is greater the lower the ionic strength. Therefore, it has no use to analyze the data for these solutions. Furthermore, we can assume that at intermediate ionic strengths draining effects are also present, although to a lesser extent. So we can attribute the relatively poor agreement between theory and experiment in these cases partially to the inappropriateness of a completely nondraining model. That draining effects under similar conditions have to be considered has recently been proved by Kamide and Moore (17) for solutions of cellulose derivatives. Fixman's theory (8) also does not provide better agreement with experiment. It predicts the experimentally observed dependence of $[\eta]$ on C_s, but the values of $(D/D_0)b_0$ are too large. Following the suggestion of the author we can replace q in Eq. (7) with qf corresponding to the introduction of the effective charge in Ptitsyn's expression, Eq. (16), which would result in values of $(D/D_0)b_0$ around 16 Å. However, for exactly the same purpose D_0 has been introduced in the theory. Therefore D/D_0 should be equal to 1 and b_0 would be far too large.

All that has been said for solutions of NaPSS can be assumed to hold also for solutions of KPSS as well as other alkali poly(styrene sulfonates), although experimental results should reflect the influence of ionic size, whereas in both theories there is no such parameter.

The large negative temperature coefficients of intrinsic viscosity for solutions of NaPSS with added salt (cf. Table 6) can partially be interpreted in the same way as in the case of cellulose derivatives (15,16). They may be attributed to increasing chain flexibility toward higher temperatures. Besides, decreased ionic hydration at higher temperatures also has to be considered (12,18). Finally, and this is especially important for polyelectrolyte solutions, the decrease of the dielectric constant of water with temperature which in turn increases the degree of ion binding, also has to be taken into account. Now, all these factors cause a decrease of polyion

dimensions, which explains the observed dependence of the intrinsic viscosity on temperature. To determine the extent of the contribution of single factors additional studies are necessary.

Acknowledgments

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Zusammenfassung

Die grundmolare Viskosität von Natrium- und Kaliumpoly(styrolsulfonaten) verschiedenen Molekulargewichts in Natrium- und Kaliumchloridlösung wurde bei verschiedenen Konzentrationen bestimmt. Die erhaltenen Daten wurden auf der Basis der Stockmayer-Fixman Theorie analysiert und die Werte des sich gegenseitig ausschliessenden Volumens der Segmente bestimmt. Die so erhaltenen Werte wurden mit den nach der Ptitsyn Theorie berechneten verglichen. Um halbquantitative Uberein-

stimmung zwischen Theorie und Experiment zu erreichen, wurden die effektiven und nicht die nominellen Ladungen der Polyionen für die Berechnungen benutzt. Aus der grundmolaren Viskosität wurde auch die molekulare Ausdehnung bestimmt und mit nach Fixman's Theorie der Polyelektrolyten erhaltenen Werten verglichen. Schliesslich wurden noch die Temperaturkoeffizienten der grundmolaren Viskositäten einiger Lösungen von verschiedener Ionenstärke bestimmt.

Résumé

On a determiné les viscosités intrinsèques des poly(styrène sulfonates) de sodium et de potassium, possedant des masses moléculaires différentes, en solution dans le chlorure de sodium et chlorure de potassium à des concentrations variées. On a analysé les données en se basant sur la théorie de Stockmayer et Fixman et on a determiné les valeurs du volume exlu des segments. On a comparé les résultats avec les valeurs calculées à l'aide de la théorie de Ptitsyn sur le volume exclu. Dans le but d'obtenir un accord sémiquantitatif entre la théorie et l'expérience on a utilisé dans les calculs la charge éffective, pas la charge nominale des polyions. On a aussi determiné l'expansion moléculaire à parti des viscosités intrinsèques et les valeurs obtenues comparées avec celles données par la théorie de Fixman sur les polyélectrolytes. Finallement, on a verifié les coëfficients de température des viscosités intrinsèques de quelques solutions possédant une force ionique différente.