Diffusion of a Polyelectrolyte in Aqueous Solution in the Absence of Added Salt

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The diffusion of poly(styrenesulfonic acid) and its sodium salt in pure aqueous solutions was studied with the Rayleigh and schlieren optical systems. It was shown that the pattern has a discontinuous diffusion front though most of the schlieren pattern has the normal distribution curve. It was concluded that the abnormal diffusion patterns arise from the characteristic concentration dependence of the diffusion coefficients of the polyelectrolytes. The moving distance of the diffusion front was found to be proportional to the square root of time and to be in fair agreement with the distance calculated from Fick's equation by taking into account the abnormal concentration dependence of the diffusion coefficient.

Introduction

It has been pointed out by several authors[2,3] that an interesting feature is observed in the diffusion patterns of linear polyelectrolytes (such as poly(acrylic acid) and nucleic acid), when there is no added simple electrolyte in the solution. It is found that the schlieren pattern of the diffusion boundary does not have the normal distribution curve, but, rather, a discontinuous front, as shown in Fig. 1 and 2. Because of the appearance of the diffusion front, the diffusion of a soluble polyelectrolyte into water, if the concentration of polymer is high, sometimes looks like the swelling of a gel which has an insoluble network structure. In the papers thus far published,[4-6] the discontinuous diffusion front described has been little studied. Perhaps the lack of attention is to be expected since the optical abnormality is observed only at the diffusion front and, in most parts of the diffusion boundary, the schlieren pattern approximately follows the normal distribution function. If instead of a schlieren optical system, a Rayleigh or Lamm optical system is used for the observations, the existence of the discontinuous diffusion front may easily be overlooked.

No satisfactory explanation has been presented for the appearance of the discontinuous diffusion front; it has been speculated that polyelectrolyte molecules may have a network structure in aqueous solutions.[3] The purpose of the present paper is to show that the discontinuous diffusion front is caused by a characteristic concentration dependence of the diffusion coefficient of polyelectrolytes in solution (see Fig. 7). Although it is certainly important to determine the diffusion coefficient and therefrom the molecular characteristics of the polyelectrolyte, this will not be considered herein. In this paper attention is focused on the concentration dependence of the diffusion coefficient. As a characterization of polyelectrolyte solutions, this concentration dependence may be as important as that of activity coefficient, osmotic coefficient, etc.

As is well known, the unidimensional diffusion of a substance with a concentration-dependent diffusion coefficient, $D(C)$, is governed by Fick's equation

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(2) M. Nagasawa, T. Matsubara, H. Fujita, and I. Kagawa, *Kogyo Kagaku Zasshi*, **61**, 1611 (1958).
(3) K. Iso, *ibid.*, **84**, 100, 199 (1963).
(4) Y. Nishijima and H. Inagaki, *Nippon Kagaku Zasshi*, **73**, 191 (1952).
(5) (a) O. Kedem and A. Katchalsky, *J. Polymer Sci.*, **15**, 321 (1955); (b) G. J. Howard and D. Jordan, *ibid.*, **12**, 209 (1954).
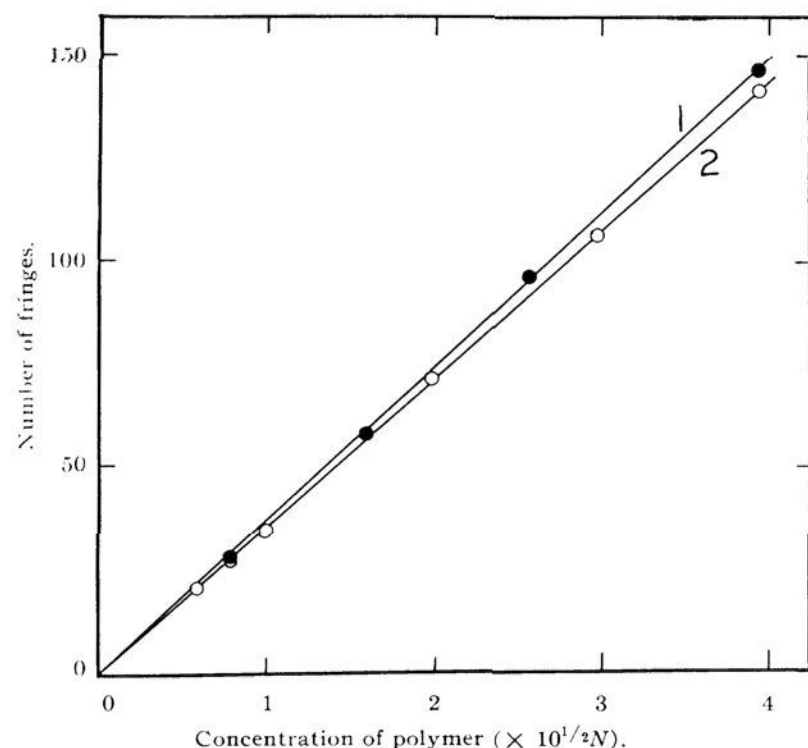(6) G. Sitaramaiah and D. A. I. Goring, *ibid.*, **58**, 1107 (1962).

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right) \qquad (1)$$

If $D(C)$ is independent of concentration C and the initial conditions are

$$C(x,0) = C_0 \qquad -\infty < x < 0$$

$$C(x,0) = 0 \qquad \infty > x > 0 \qquad (2)$$

Then eq. 1 can readily be solved. The following is obtained

$$C(x,t) = \frac{C_0}{2}\left[1 - \Phi\left(\frac{x}{2\sqrt{D_0 t}}\right)\right] \qquad (3)$$

and

$$\frac{dC}{dx} = \frac{C_0}{2}\frac{1}{\sqrt{\pi D_0 t}}\exp\left(-x^2/4D_0 t\right) \qquad (4)$$

where

$$\Phi(Z) = \frac{2}{\sqrt{\pi}}\int_0^Z \exp\left(-Z^2\right)dZ \qquad (5)$$

If $D(C)$ depends on concentration, in general no analytical solution can be obtained. In such cases, eq. 1 is conveniently recast in a different form[7]

$$-2\eta\,\frac{dC}{d\eta} = \frac{d}{d\eta}\left[D(C)\,\frac{dC}{d\eta}\right] \qquad (6)$$

using the Boltzmann transformation

$$\eta = x/2\sqrt{t} \qquad (7)$$

The diffusion coefficient, $D(C)$, is obtained from integration of eq. 6

$$D(C) = \frac{-2\int_0^C \eta\,dC}{(dC/d\eta)C} \qquad (8)$$

where the condition

$$\left[D(C)\,\frac{dC}{d\eta}\right]_{C=0} = 0$$

has been used. The integral in eq. 8 can be calculated graphically from the experimental Rayleigh patterns. This method of calculating $D(C)$ is often referred to as the Boltzmann–Matano procedure.

(7) J. Crank, "The Mathematics of Diffusion," Oxford University Press, Oxford, England, 1956.

Fig. 1.—Linear relationship between polymer analytical concentration and fringe numbers: (1) Na-PSSA, (2) H-PSSA.

Experimental

(1) Samples.—Since the concentration of polymer at the diffusion front is very low, for the studies considered herein it is necessary to use a polymer sample which does not hydrolyze. For this reason, poly(styrenesulfonic acid) (H-PSSA) and its sodium salt (Na-PSSA) were used in all our experiments. The sample was a gift from The Dow Chemical Co., and its degree of polymerization was of the order of 1 million according to Dr. Vanderkooi ([η] in 0.5 M NaCl at 25° = 1.45).[8] No fractionation was effected because the aim of this work was not to study the magnitude of the diffusion coefficient, but rather to clarify the origin of the abnormal diffusion patterns. The molecular weight dependence of the diffusion coefficients of polyelectrolytes in solution has not yet been studied fully, but it is likely that the dependence is not too appreciable because of the large mobility of the counterions.

(2) Optical Systems.—As stated in the Introduction, a schlieren optical system is suitable for examining a diffusion front which has a discontinuity, while a Rayleigh optical system is most convenient for calculating the diffusion coefficient as a function of concentration (using the Boltzmann–Matano graphical method described above). In the present experiments, both the schlieren and Rayleigh optical systems of a Beckman Spinco Model H diffusion apparatus were used.

(3) Experimental Procedures.—Crude poly(sodium styrenesulfonate) provided by The Dow Chemical Co.[8] was dissolved in NaOH solutions of about 1 M and precipitated with ethanol three or four times. The sodium salt thus purified was converted to the acid form by passing through Amberlite 120. The sample solution when in the acid form was kept in a refrigerator. Poly-(sodium styrenesulfonate) was made by neutralizing the acid sample with NaOH. The concentration of the stock solution was determined by titration with a Fisher standard 0.100 N HCl solution. Dilution of the sample solution was carried out volumetrically at room temperature. To eliminate errors due to dilution, in this paper the concentrations are expressed in terms of the numbers of Rayleigh fringes. One fringe corresponds to the following concentration of the acid and the salt, respectively.

1 fringe of H-PSSA   = 0.0002797 N of sulfonic acid group

               = 0.005148 g./100 ml. of polymer

1 fringe of Na-PSSA = 0.0002703 N of sulfonate group

               = 0.005570 g./100 ml. of polymer

These are the average values obtained from the linear relationships between analytical concentrations and the numbers of fringes (Fig. 1).

We used a standard 11-ml. cell supplied with the Spinco Model H diffusion apparatus. The temperature was maintained at 25.0 ± 0.01°. Boundary sharpening was carried out by sucking up the solution with a capillary as suggested in the instruction

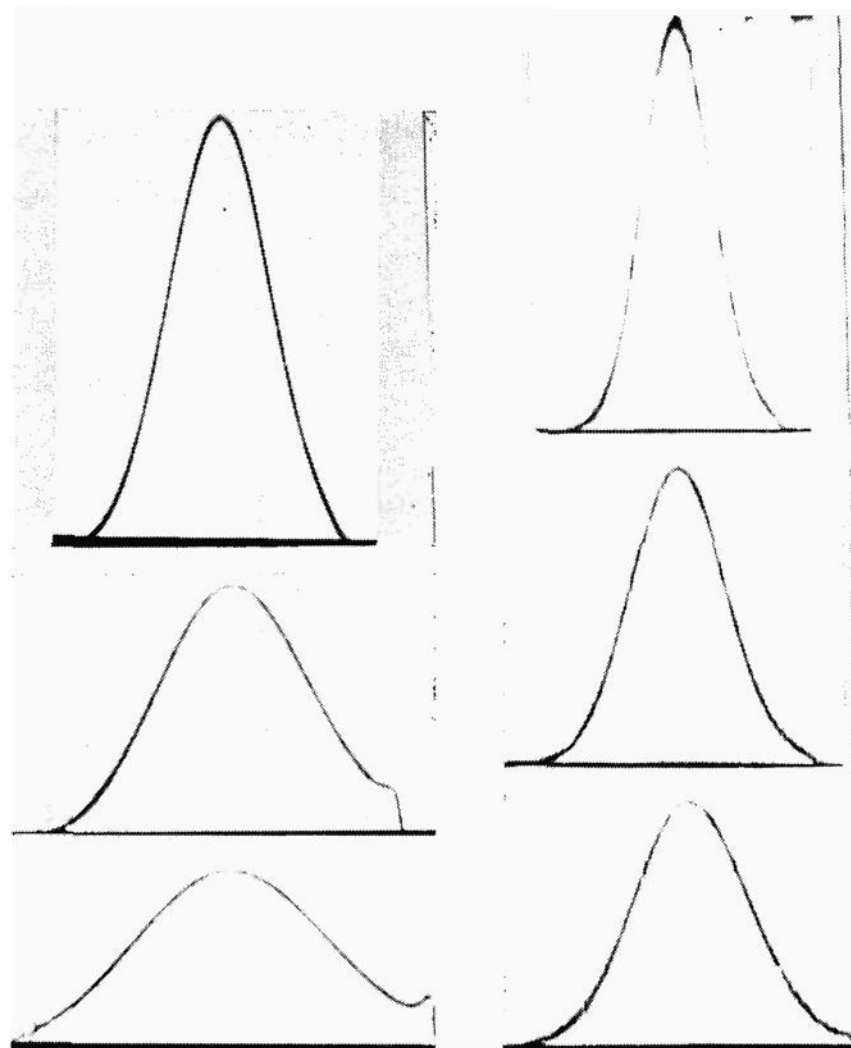(8) L. Kotin and M. Nagasawa, *J. Am. Chem. Soc.*, **83**, 1026 (1961).

Fig. 2.—Creation of the diffusion front in the schlieren patterns: (a) Na-PSSA concentration 0.0793 N (289 fringes), t = 5400, 21,600, 43,200 sec. from the top; (b) H-PSSA, concentration 0.793 N, t = 39600, 7560, 11160 sec. from the top.

manual for the instrument. As at least several hours was necessary for completion of one experiment, the zero time correction was negligible. The diffusion experiment was carried out in a closed cell, but the measurements were stopped long before the diffusion front reached the ends of the cell so that the end effect may be assumed to be negligible. In general, the experimental procedures were the same as those described in a previous paper.[9]

Results and Discussion

On the Characteristic Features of the Diffusion of a Polyelectrolyte.—The diffusion front characteristic of a polyelectrolyte in solution does not disappear so long as diffusion proceeds. Moreover, even if the diffusion boundary is disturbed with a fringe so that the schlieren pattern does not show a discontinuity, a discontinuous diffusion front is gradually set up as the time goes on. Figure 2 illustrate this process. The diffusion front is set up more quickly in Na-PSSA solutions than in H-PSSA solutions. In Fig. 3, the diffusion fronts are enlarged to show that they can be clearly defined as the point where $C = 0$ and $dC/dx = 0$ and also that the maximum ($dC/dx = \infty$) is located a little behind the front. In experiments other than those displayed in Fig. 1 and 2, only Rayleigh photographs were taken, but the diffusion front ($C = 0$, $dC/dx = 0$) was clearly observed even in very diffuse patterns.

The position X of the diffusion front as a function of time t, measured from the Rayleigh patterns, is shown in Fig. 4. It is observed that X is strictly proportional to the square root of t. This same behavior has been observed in many gel–solvent systems.[7,10] Thus, we have

$$X = kt^{1/2} \qquad (9)$$

(9) G. Thomson, S. A. Rice, and M. Nagasawa, *ibid.*, **85**, 2537 (1963)

(10) J. J. Hermans, *J. Colloid Sci.*, **2**, 387 (1947).
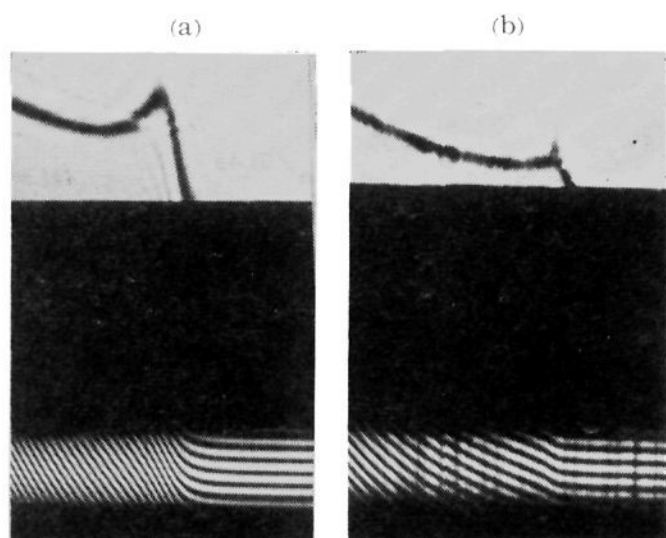
(a)   (b)

Fig. 3.—Diffusion fronts of Na-PSSA ($t = 81,000$ sec.) and H-PSSA ($t = 40,192$ sec.); concentrations are the same as those in Fig. 2.

Calculation of the Average Diffusion Coefficients from the Rayleigh Patterns.

The average diffusion coefficient can be calculated from the spreading of the Rayleigh patterns with time using Longsworth's method.[11] The results of the calculations are shown in Fig. 5. One or two fringes on both extreme sides of the diffusion patterns were discarded because of the difficulty in determining the exact positions of the fringes. The probable error in the average diffusion coefficients obtained is about ±1%. Since eq. 2 and 3 are used for the calculation, the value obtained is an average over the concentration region $0 \sim C$ of the polymer, and, hence, it is not possible to determine the concentration dependence of the diffusion coefficient by this method. In particular, the anomalies in the very dilute solution region cannot be revealed by this method.

Diffusion Coefficient as a Function of Concentration.

The details of the concentration dependence of the diffusion coefficient can be manifested by applying the Boltzmann–Matano method described above. The position of a fringe in the Rayleigh pattern, x, is plotted against the square root of the time, $t^{1/2}$, first to test the linear relationship (see Fig. 6). With the established linear relationship, we now plot the concentration (i.e., fringe number) against η ($\eta = x/2t^{1/2}$). Graphical integration of the reduced pattern so obtained gives values of $\int_0^C \eta \mathrm{d}C$, so that the diffusion coefficient can be calculated as a function of concentration (using eq. 8). The diffusion coefficients thus obtained are shown in Fig. 7. The results depend slightly on the initial concentration C_0. The reason for the disagreement is not clear at present, but the ambiguity involved is not serious and does not influence our conclusion. As seen in Fig. 7, the diffusion coefficients of H-PSSA and Na-PSSA display very unusual concentration dependences: that of H-PSSA has an almost constant value at concentrations higher than a concentration, C_x, but rapidly decreases as the concentration becomes lower than C_x, while that of Na-PSSA smoothly decreases with decrease of concentration over the whole range of concentration examined.

It is clear then that the characteristic behavior of polyelectrolytes in diffusion arises from the abnormal concentration dependence of the diffusion coefficient, as shown in Fig. 7. For example, in the solution of

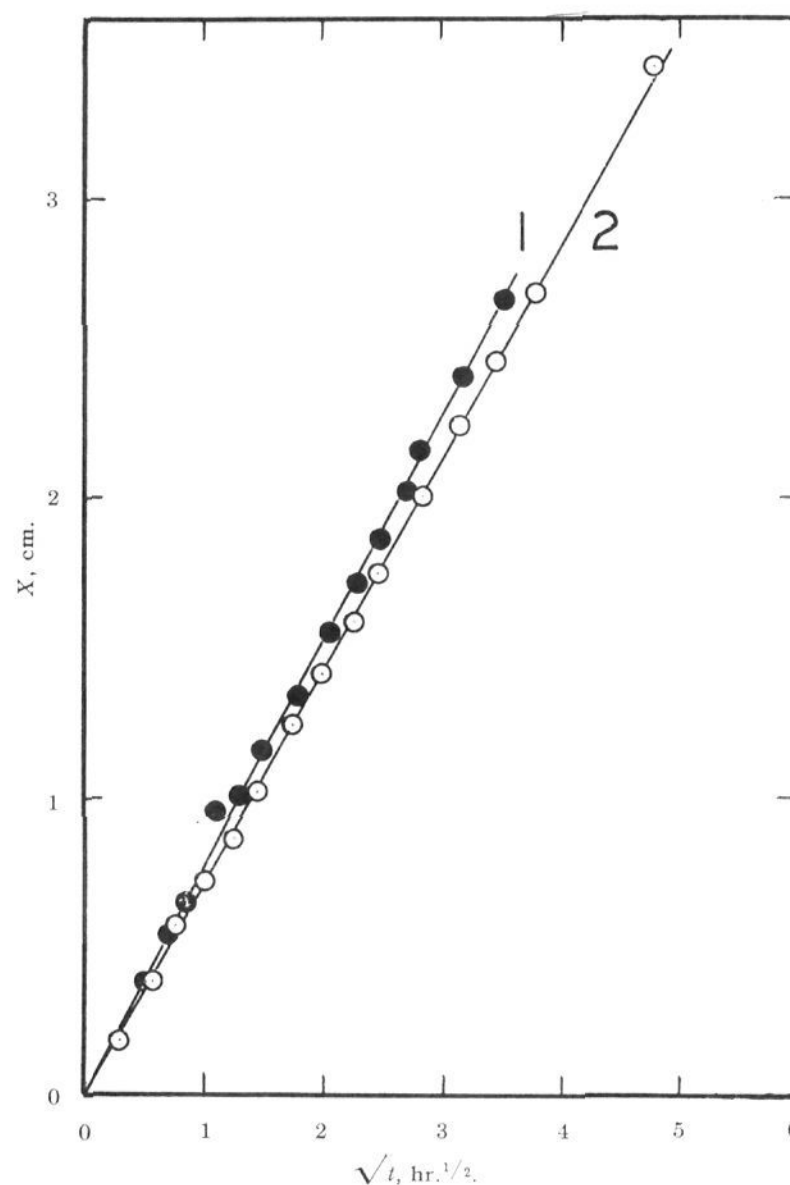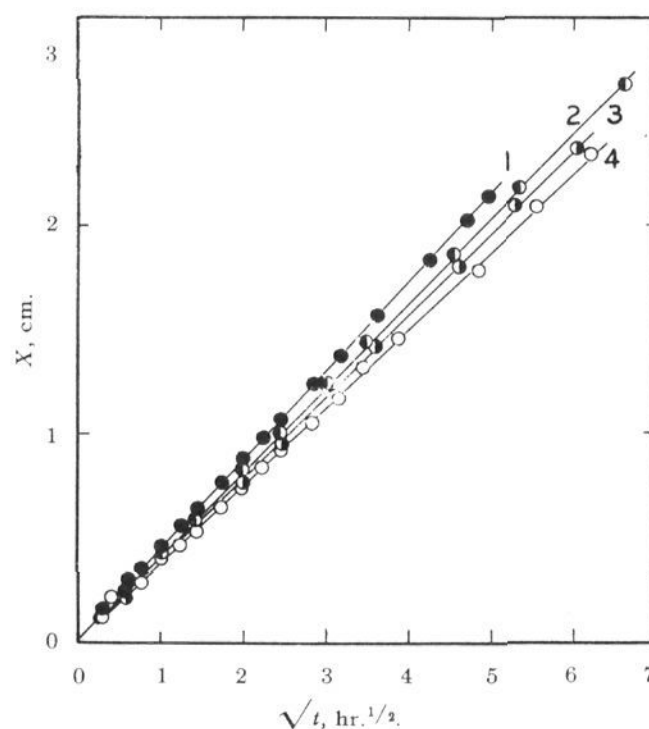(11) L. G. Longsworth, *J. Am. Chem. Soc.*, **74**, 4155 (1952).

Fig. 4.—Moving velocity of the diffusion front: (a) Na-PSSA, concentration (1) 141.4, (2) 96.62, (3) 58.6, (4) 28.7 fringes; (b) H-PSSA, concentration (1) 107.4, (2) 141.3 fringes.

H-PSSA, the polymer molecules hardly diffuses toward the less concentrated region if the concentration becomes lower than C_x. Hence, a discontinuous point must appear in the diffusion pattern. Except near the diffusion front, the diffusion pattern shows no anomaly as the diffusion coefficient is almost constant at concentrations higher than C_x. The schlieren pattern can be calculated from the following equation which is a transformation of eq. 6

$$\left(\frac{\mathrm{d}C}{\mathrm{d}\eta}\right)_C = -\frac{2\int_0^C \eta \mathrm{d}C}{D(C)} \qquad (6')$$
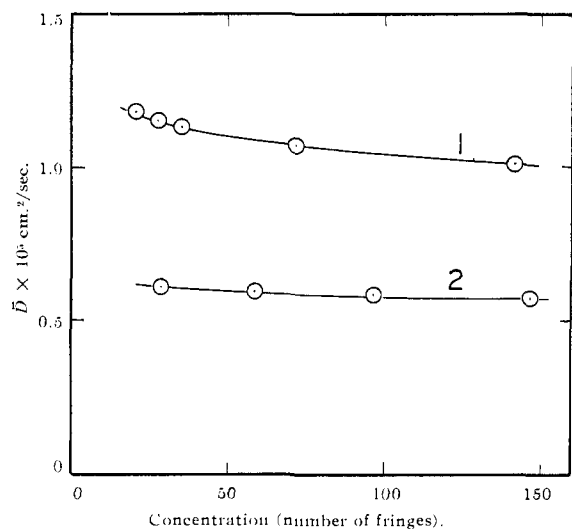
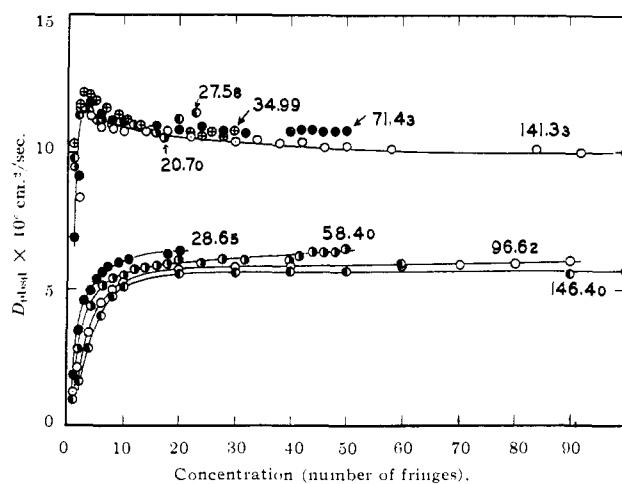Fig. 5.—Average diffusion coefficients calculated from the Rayleigh patterns: (1) H-PSSA, (2) Na-PSSA.

Fig. 7.—Concentration dependence of the diffusion coefficients of Na-PSSA (upper) and H-PSSA (lower): Numbers show concentrations (fringe numbers).
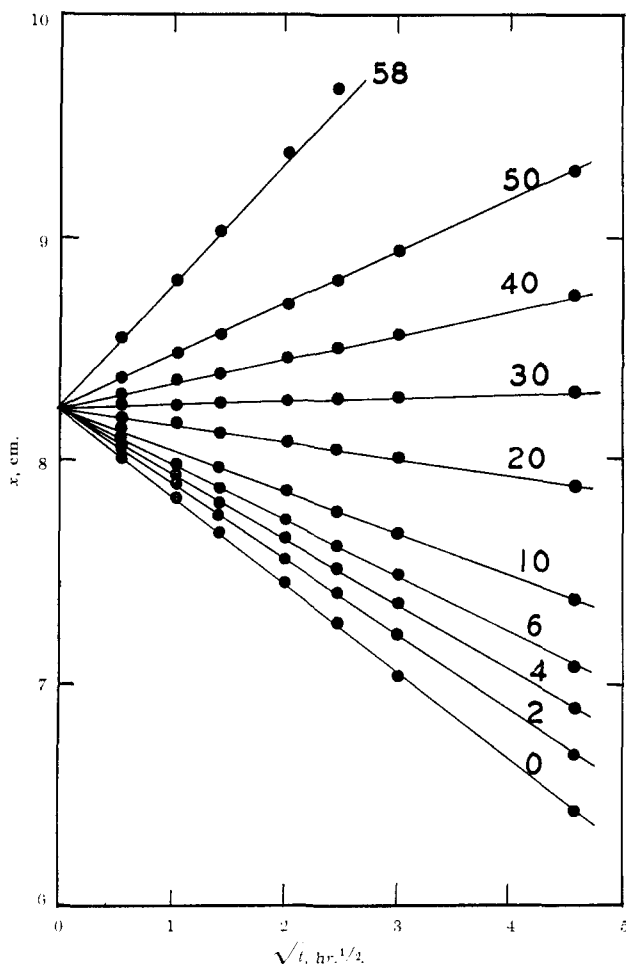

Fig. 6.—Linear relationship between x and $\sqrt{t}$ at various concentrations: sample, Na-PSSA, concentration, 58.60 fringes.
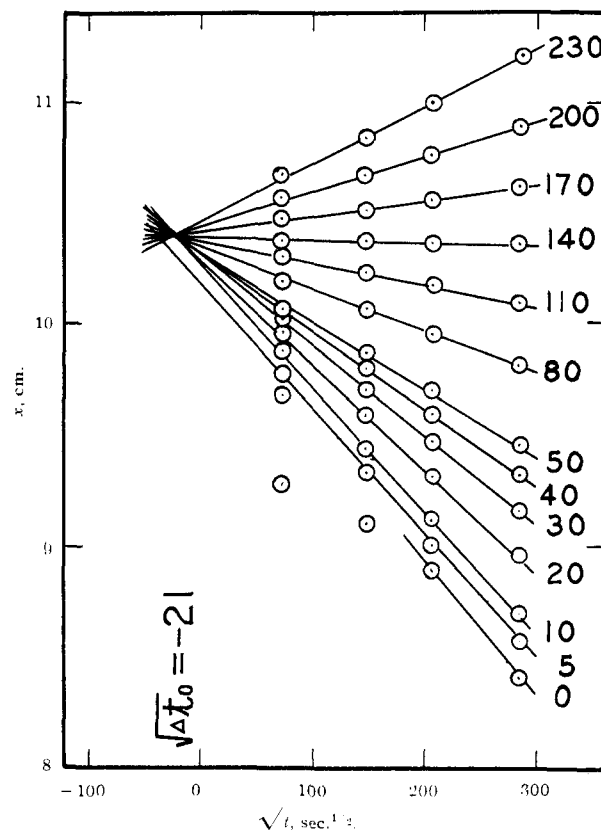

Fig. 8.—Boltzmann-Matano's plot for the experiment of Na-PSSA in Fig. 2: concentration = 0.0793 N (289 fringes).

Since the denominator decreases faster than the numerator with a decrease of the concentration, $(dC/d\eta)_C$, that is, $(dC/dx)_C$ can have a maximum at some concentration. To confirm this deduction, we have calculated $(dC/dx)_C$ for Na-PSSA (see Fig. 2) using the data displayed in Fig. 7, and compared the calculation with experiment. To make this comparison, the zero time correction for the experiment shown in Fig. 2 must be determined, as the boundary was disturbed

intentionally at $t = 0$. In Fig. 8, are plotted x vs. $t^{1/2}$ at various concentrations. From the figure, it is clear that the square root of the zero time correction is -21 sec.$^{1/2}$. The values of $(dC/dx)_C$ calculated from eq. 6' using this zero time correction and the concentration dependence of $D(C)$ in Fig. 7 are shown by a dotted line in Fig. 9. The agreement between the calculated pattern and the experimental one is not perfect, but it is good enough to confirm the conclusion that the appearance of the discontinuous diffusion front is due to the abnormal concentration dependence of the diffusion coefficient.

Calculation of the Velocity of the Moving Front of H-PSSA.—The diffusion coefficient of H-PSSA, as shown in Fig. 7, may be approximated by

$$D = D_0 \quad \text{for } C_x < C < \infty$$

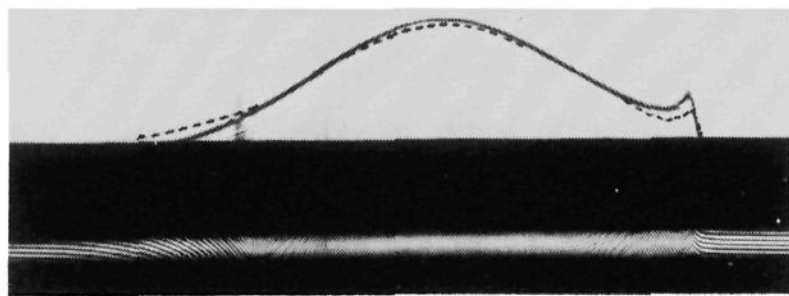$$D = 0 \quad \text{for } C < C_x$$

Fig. 9.—Comparison between the observed schlieren pattern and the expected one of Na-PSSA. The experiment is the same shown in Fig. 2 ($t = 81,000$ sec.).

The solution of eq. 1 with such a diffusion coefficient can be obtained as follows.[12] Equation 1 is now transformed to

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial^2 C}{\partial x^2} \quad (-\infty < x < X) \qquad (10)$$

As a particular solution of this equation we may take

$$C(x,t) = A + B\Phi(x/2\sqrt{D_0 t}) \qquad (11)$$

The auxiliary conditions pertinent to the problem are

$$C(x,0) = C_0 \quad (t = 0, -\infty < x < 0)$$
$$C(X,t) = C_x \quad (x = X) \qquad (12)$$

Substitution of these conditions into eq. 11 leads to

$$A - B = C_0$$
$$A + B\Phi(X/2D_0 t) = C_x \qquad (13)$$

As eq. 13 must be valid for all t, it follows that

$$X/2\sqrt{D_0 t} = \beta = \text{constant} \qquad (14)$$

which accords with the experimentally obtained relation 9. Inserting A and B from eq. 13 into eq. 11 and differentiating with respect of t, we have

$$\frac{dC(x,t)}{dt} = \frac{C_0 - C_x}{1 + \Phi(\beta)} \frac{1}{\sqrt{\pi D_0 t}} e^{-\frac{x^2}{4D_0 t}} \quad (-\infty < x < X) \qquad (15)$$

Since $C_0 \gg C_x$, it is seen that the diffusion pattern is almost a normal distribution curve except for the existence of the discontinuous diffusion front at $x = X$. From the comparison between eq. 9 and 14, we have

$$k = 2\sqrt{D_0}\beta \qquad (16)$$

If the diffusion front moves dX in a time dt, the amount of the polymer which diffuses into the region between X and $X + dX$ must be equal to the total decrease of the polymer over the range $-\infty < x < X$ in the same time interval. Thus

$$\int_{-\infty}^{X} \frac{\partial C}{\partial t} S dx dt = S dX C_x \qquad (17)$$

where S is the cross-sectional area of the diffusion cell. The substitution of eq. 10 into eq. 17 gives

$$\frac{dX}{dt} = \frac{1}{C_x} D_0 \left(\frac{dC}{dx}\right)_{x=X} \qquad (18)$$
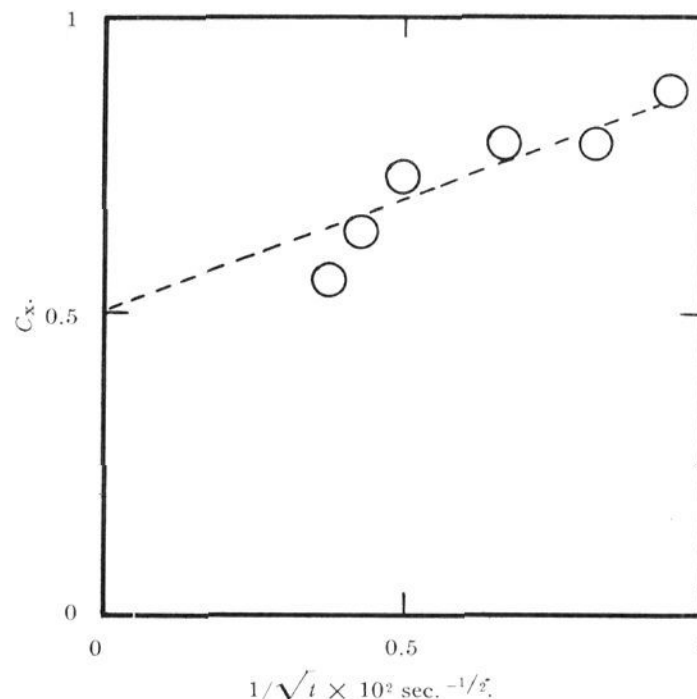
(12) See ref. 7, p. 106.

Fig. 10.—Variation of C_x with time obtained from the comparison between schlieren and Rayleigh patterns.

Inserting the value of eq. 15 at $x = X$ into eq. 18 and comparing the result with eq. 14, we have

$$\pi \cdot \beta \cdot \{1 + \Phi(\beta)\} e^{\beta^2} = (C_0/C_x) - 1 \qquad (19)$$

If we know C_0 and C_x, β can be calculated from eq. 19 and then the value of k can be calculated from eq. 16. This is to be compared with the experimental value of k.

Figure 7 seems to show that C_x is roughly between the first and second fringes, but it is not proper to determine C_x from the figure since the diffusion coefficient in Fig. 7 was calculated only for every fringe. It is more desirable to determine C_x from direct comparison between the maximum point in the schlieren pattern and the Rayleigh pattern (see Fig. 3). Moreover, as the value of C_x obtained from the comparison depends on the diffusion time, we must extrapolate the values obtained to $t = \infty$ to obtain a reliable value of C_x. A plot of the apparent C_x against $1/t$, shown in Fig. 10, gives about 0.5 fringe for C_x in the solution for which $C_0 = 0.0793$ N. Although there is a possibility that even the extrapolated value may depend on the initial concentration used, $C_x = 0.5$ fringe seems to be reliable as judged from examination of the Rayleigh patterns taken for different initial concentrations. The ambiguity in C_x has only a small influence on the calculated velocity of the moving boundary for $C_0 \gg C_x$.

Assuming $C_x = 0.5$ fringe, β can be calculated from eq. 19 and then k can be calculated from eq. 16. The calculated values, k_{calcd}, are listed together with the observed values, k_{obsd} in Table I. Although it is observed that k_{calcd} shows a small systematic change with C_0, while k_{obsd} does not, the agreement between the calculated and experimental values must be considered satisfactory in view of the crudeness of our assumption concerning the concentration dependence of the diffusion coefficient.

Discussion on the Concentration Dependence of the Diffusion Coefficient.—The diffusion coefficient D measured in this work is the mutual diffusion coefficient and can be related to the diffusion coefficient of the polymer component, D_p, relative to the solvent-

TABLE I

MOVING VELOCITY OF THE DIFFUSION FRONT OF H-PSSA

Concentration		k_{obsd},	k_{calcd},
Fringe no.	Moles/l.	cm./sec.$^{1/2}$	cm./sec.$^{1/2}$
20.7$_0$	0.695 × 10^{-2}	11.6$_3$	9.5$_4$
27.5$_8$	.792	12.4$_0$	10.0$_4$
34.9$_9$	.991	12.1$_6$	10.4$_7$
71.4$_3$	1.98	11.8$_1$	11.6$_1$
107.3$_7$	3.00	12.1$_5$	12.6$_6$
141.3$_3$	3.96	12.0$_3$	12.2$_3$

fixed frame of reference by the equation[13,14]

$$D = D_p(1 - \bar{v}_p C_p) \quad (20)$$

where $\bar{v}_p$ is the partial molar volume of the polymer and C_p is the polymer concentration expressed in moles/ml. In very dilute solutions such as in the present experiments eq. 20 may be replaced by the relation

$$D \doteq D_p \quad (21)$$

The diffusion coefficient D_p of an electrolyte may be written in the form[15,16]

$$D_p = (D_p{}^0 + \Delta D) \frac{d \ln a_p}{d \ln C_p}$$

$$= (D_p{}^0 + \Delta D) \left(1 + \frac{d \ln \gamma_p}{d \ln C_p}\right) \quad (22)$$

where a_p is the mean activity and γ_p is the mean activity coefficient of an electrolyte. ΔD is a term arising from the electrophoretic interaction between the ions and the solvent. The mean activity of an electrolyte of 1-Z type, a_p, is formally defined as[17]

$$(Z + 1) \ln a_p = \ln a_{p^{-z}} + Z \ln a_{c^+} \quad (23)$$

where $a_{p^{-z}}$ and a_{c^-} are the ionic activities of the Z-valent anion and the univalent cation, respectively. The charge of the polyion, Z, is so large that we may assume

$$\ln a_p \doteq \ln a_{c^+} \quad (24)$$

Therefore, eq. 22 may be put in the form

$$D_p = (D_p{}^0 + \Delta D) \frac{d \ln a_{c^+}}{d \ln C_p} \quad (25)$$

or

$$D_p = (D_p{}^0 + \Delta D) \left(1 + \frac{d \ln \gamma_{c^-}}{d \ln C_p}\right) \quad (26)$$

Here, γ_{c^+} is the activity coefficient of the counterion; it can be determined experimentally if we assume that $\gamma_{K^+} = \gamma_{Cl^-}$ in KCl solutions. (This assumption is not serious since only the differential term $d \ln \gamma_{c^+}/d \ln C_p$ is included in eq. 26.)

Moreover, the activity of the solute can, in general, be transformed into the osmotic coefficient, g, by using the Gibbs–Duhem relationship. That is, if we express the molar concentration of solvent by C_0 and the

(13) R. P. Wendt and L. J. Gosting, J. Phys. Chem., **63**, 1287 (1959).

(14) H. Fujita, Kagaku Kogaku, **25**, 74 (1961).

(15) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955.

(16) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publishing Corp., New York, N. Y., 1950.

(17) S. A. Rice and M. Nagasawa, "Polyelectrolyte Solutions," Academic Press, Inc., New York, N. Y., 1961.

activity by a_0, we know that

$$-C_{p^{-z}} d \ln a_{p^{-z}} + C_{c^+} d \ln C_{c^+} +$$

$$C_0 d \ln a_0 = 0 \quad (27)$$

As $C_{p^{-z}} = C_p$ and $C_{c^-} = Z C_p$, we have

$$(Z + 1)C_p d \ln a_p = -C_0 x d \ln a_0 \quad (28)$$

which gives

$$(Z + 1)C_p \frac{d \ln a_p}{dC_p} = -C_0 \frac{d \ln a_0}{dC_p} \quad (29)$$

Since

$$\ln a_0 = -g \frac{(Z + 1)M_0}{1000} C_p$$

$$C_0 \doteq \frac{1000}{M_0}$$

where M_0 is the molecular weight of water, eq. 29 becomes

$$\frac{d \ln a_p}{d \ln C_p} \doteq \left(g + C_p \frac{dg}{dC_p}\right)$$

Substituting this relationship into eq. 22, we finally obtain

$$D_p = (D_p{}^0 + \Delta D) \left(g + C_p \frac{dg}{dC_p}\right) \quad (30)$$

Thus, there are three factors which can influence the diffusion coefficient D_p of a polyelectrolyte: (1) changes of $D_p{}^0$, which may be caused by changes in molecular configuration with dilution; (2) ΔD which arises from the electrophoretic interaction between the ions and solvent; (3) the term $d \ln \gamma_{c^+}/d \ln C_p$ or $(g + C_p dg/dC_p)$.

Kedem and Katchalsky[5a] explained the diffusion behavior of polyelectrolytes using only the concentration dependence of g and the assumption that $C_p dg/dC_p$ is negligible compared with g. However, this assumption seems incorrect: experimental studies of g for poly(styrenesulfonic acid) solutions by Takahashi and Kagawa[18] show that g and $C_p dg/dC_p$ are comparable, and both of the other factors should be taken into account.

The experimental data of Takahashi and Kagawa[18] do not permit accurate estimation of $(g + C_p dg/dC_p)$ at the concentration of interest: other data on the osmotic coefficients of polyelectrolytes in aqueous solutions do not seem available. At present, then, eq. 30 is not suitable for determining the effect of the activity coefficient or of the osmotic coefficient on D_p. Moreover, as detailed in the Appendix, there remains an important unsolved problem in the conversion of the activity coefficient of a solute to the osmotic coefficient of the solution for the case of linear polyelectrolyte solutions. Therefore, we prefer to use eq. 26 rather than eq. 30 to discuss the effects of the activity coefficient.

The activity coefficient of the hydrogen ion in poly(styrenesulfonic acid) solution was measured by Mock and Marshall[19] using a glass electrode. From

(18) A. Takahashi and I. Kagawa, Nippon Kagaku Zasshi, **83**, 9 (1962).

(19) R. A. Mock and C. A. Marshall, J. Polymer Sci., **13**, 263 (1955).

their data, it is clear that the activity coefficient of the hydrogen ion does not change much with changing concentration of the polymer. Therefore for H-PSSA

$$1 + d \ln \gamma_{H^-}/d \ln C_p = 1$$

except for very dilute solutions. No reliable data are available for the sodium ion activity coefficients of poly(sodium styrenesulfonate). The cryoscopic data of Mock[20] cannot be used here. If it is assumed that the concentration dependence of the activity coefficient of Na^+ in poly(sodium vinyl alcohol sulfate) solution is similar to that in poly(sodium styrenesulfonate) solutions, we may use measurements of the Na^+ activity coefficient in poly(sodium vinyl alcohol sulfate) (shown in Fig. 7 of ref. 21). It is then possible to estimate the values of $(1 + d \ln \gamma_{Na'}/d \ln C_p)$ (see Table II). From the table it is clear that the characteristic concentration dependence of the diffusion coefficient, D_p, is not due to the activity coefficient term. Even taking into account the difference between two polymers, the calculated values are unlikely to change with concentration so much as to change this conclusion.

TABLE II

CONTRIBUTION OF THE ACTIVITY COEFFICIENT TERM TO DIFFUSION COEFFICIENT

Concn. of polymer, moles/1.	$1 + \dfrac{d \ln \gamma_{Na^+}}{d \ln C_p}$	Concn. of polymer, moles/1.	$1 + \dfrac{d \ln \gamma_{Na^+}}{d \ln C_p}$
0.1×10^{-2}	1.15	1.0	1.17
.2	1.16	2.0	1.15
.4	1.17	4.0	1.17
.8	1.17		

We conclude that the characteristic concentration dependence of the diffusion coefficient arises mainly from the changes in $D_p{}^0$ due to configurational changes of the polymer on diffusion, and from the electrophoretic interaction between the polyion, counterions, and solvent (ΔD). Though the electrophoretic effects in linear polyelectrolyte solutions without added salt have not yet been fully clarified, this conclusion seems to be supported by the fact that if the mobilities of the polyion and the counterion in solution are $l_{p^{-z}}$ and l_{c^-}, respectively, D_p is approximately given by[15,16]

$$D_p = \frac{RT}{F^2} \frac{Z+1}{Z} \frac{l_{p^{-z}}l_{c^+}}{l_{p^{-z}} + l_{c^-}} \left(1 + \frac{d \ln \gamma_{c^-}}{d \ln C_p}\right) \quad (31)$$

From the comparison between eq. 31 and 26, we know that

$$\frac{l_{p^{-z}} \, l_{c^+}}{l_{p^{-z}} + l_{c^-}} \propto (D_p{}^0 + \Delta D)$$

It is true that the mobilities determined by ordinary methods are influenced not only by the electrophoretic effect but also by the relaxation effect of the ionic atmosphere around the ions, while in diffusion they are influenced only by the electrophoretic effect, but, for the present qualitative discussion, it is acceptable to assume that the mobilities determined by ordinary methods may safely be used in eq. 31. The values of $(l_{p^{-z}}l_{c^-})/(l_{p^{-z}} + l_{c^+})$ for poly(sodium vinyl alcohol sulfate), calculated from data reported pre-

(20) R. A. Mock, *J. Polymer Sci.*, **44**, 271 (1960).
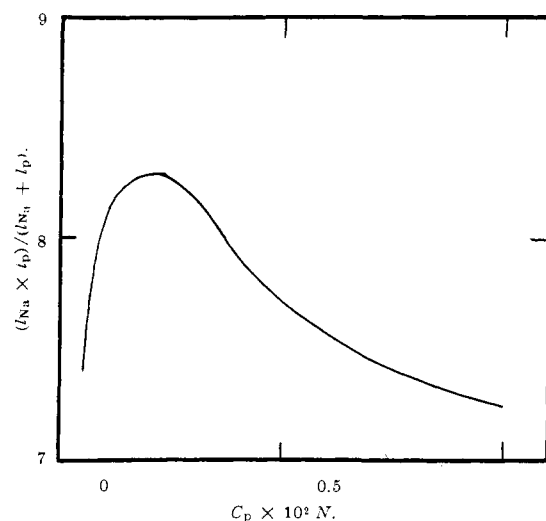(21) M. Nagasawa and I. Kagawa, *ibid.*, **25**, 61 (1957); **31**, 256 (1958).

Fig. 11.—Concentration dependence of $(l_{p^{-z}}l_{c^-})/(l_{p^{-z}} + l_{c^+})$ of poly(vinyl alcohol sulfate).

viously,[22,23] are shown in Fig. 11. Of course, we cannot expect quantitative agreement between the concentration dependence of D_p shown in Fig. 7 and that of $(l_{p^{-z}}l_{c^+})/(l_{p^{-z}} + l_{c^+})$ in Fig. 11, but, at the least, it may be concluded that the observed decrease of D_p with dilution is due to the decrease of $(l_{p^{-z}}l_{c^+})/(l_{p^{-z}} + l_{c^+})$, that is of $(D_p{}^0 + \Delta D)$.

Finally, it is to be pointed out that characteristic concentration dependences such as seen in Fig. 7 are observed not only in diffusion but also in the thermodynamic properties of linear polyelectrolytes in pure aqueous solutions. The activity coefficient of the counterion and the osmotic coefficient of linear polyelectrolyte solutions are much smaller than unity and, moreover, they show a characteristic concentration dependence very similar to that of D_p. The hydrogen ion activity coefficient[19] and the osmotic coefficient[18] in poly(styrenesulfonic acid) solutions has a constant value over the whole concentration range. (The low concentration where D_p begins to drop, C_x, cannot be reached in activity coefficient and osmotic coefficient experiments.) On the other hand, the sodium ion activity coefficient and the osmotic coefficient in sodium polyelectrolyte solutions decrease smoothly with dilution just as observed for D_p.[24] Since D_p, as well as the activity coefficient and osmotic coefficient, are governed by the interionic interaction, it is not unexpected that there exist qualitative similarities between these properties.

The value of $D_p{}^0$, which is directly related to the molecular configuration of the polymer, cannot be obtained under the present circumstances if there is no added salt.

(22) M. Nagasawa, S. Ozawa, and K. Kimura, *Kogyo Kagaku Zasshi*, **59**, 1201 (1956); M. Nagasawa, S. Ozawa, K. Kimura, and I. Kagawa, *Mem. Fac. Eng. Nagoya Univ.*, **8**, 50 (1956).
(23) M. Nagasawa, A. Soda, and I. Kagawa, *J. Polymer Sci.*, **31**, 539 (1958), Fig. 1.
(24) See ref. 17, p. 398.

Appendix

In general, if a practical osmotic coefficient, ϕ, is measured, it can be converted to the activity coefficient of the solute, $\gamma_{\pm}$, by using the Gibbs–Duhem relationship. That is

$$d \{m(1 - \phi)\} + m \, d \ln \gamma_{\pm} = 0 \quad (32)^{23}$$

where m is the molal concentration of the solute. Integration of eq. 32 with the assumption of eq. 24 gives

$$\ln \frac{(\gamma_{c^+})_{m_1}}{(\gamma_{c^+})_{m_2}} = (\phi_{m_1} - \phi_{m_2}) - 2 \int_{m_1}^{m_2} \left(\frac{1 - \phi}{m^{1/2}} \right) dm^{1/2} \quad (33)^{24}$$

If we apply this relationship to polyelectrolyte solutions

and insert the experimental values of ϕ into eq. 33 to calculate γ_{c^-}, the calculated values are not only in numerical disagreement with values determined by other direct methods but also show a concentration dependence quite different from the expermental one. Although the contribution of the polyion to the chemical potential of the polyelectrolyte component is assumed to be negligible compared with the contribution of the counterion, and, also, the calculation of γ_{c^+} involves the assumptiont hat $\gamma_{K^-} = \gamma_{Cl^-}$ in KCl solutions, it is inconceivable that these assumptions cause this contradiction, so far as our discussion is limited to a ratio of the activity coefficients at two different concentrations, $(\gamma_{c^+})_{m_1}/(\gamma_{c^+})_{m_2}$. At present, we have no idea of the origin of this contradiction.

Exchange of Parts between Molecules at Equilibrium. V. Alkyl-Terminated Chain Polysulfides and Polyselenides

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The proton nuclear magnetic resonance chemical shift of appropriate alkyl end groups for polysulfides (i.e., sulfanes) or polyselenides (i.e., selenanes) varies with the length of the sulfur or selenium chain, reaching in any particular solution or mixture a constant value for the very long chains. Thus the smaller molecules containing from a single sulfur or selenium atom up to six or ten such atoms may be quantitatively measured in mixtures. This technique has been employed to study the equilibria between variously sized chains in the reorganizing systems obtained by mixing various proportions of elemental sulfur with either dimethyl or di-t-butyl disulfide. In addition to a study of the kinetics of this equilibration process, the method was also applied to the investigation of the course of condensation polymerization between dialkyl and dichloro sulfides or selenides to form the alkyl chloride plus the respective sulfide or selenide chains. A study was also made of the reaction between dimethyl sulfide and elemental sulfur—a reaction which gives complicated mixtures consisting of the dialkyl polysulfides as well as methyl-terminated methylene sulfide chain molecules.

Primarily due to the work of Feher and colleagues,[2] a great deal is known about various molecules based on chains of sulfur atoms terminated by a variety of monofunctional substituents. However, the unique capability inherent in nuclear magnetic resonance (n.m.r.) for simultaneously identifying and carrying out a quantitative assay of individual species in complicated mixtures of molecules[3] has not previously been applied to this chemistry to which the technique is so well suited. N.m.r. is a particularly useful tool in the study of polysulfides (also called α,ω-disubstituted sulfanes) and polyselenides (also called α,ω-disubstituted selenanes) because these systems are sufficiently labile so that quantitative conclusions based on classical separations methods for molecules automatically become suspect.

Another reason for carrying out this study was to extend the broad investigation of equilibrium chemistry now underway in this laboratory[3] to the molecules having –S–S– chains in their backbone. Since the achievement of disproportionation equilibrium between two symmetric alkyl disulfides to give the corresponding mixed one has been demonstrated,[4] equilibration between a range of different sizes of alkyl polysulfides is to be expected.

Experimental

Reagents.—Sulfur dichloride obtained from Matheson Coleman and Bell was taken from fresh bottles which had not been opened until being placed in a drybox. Dimethyl sulfide and t-butyl disulfide were procured from Columbia Chemical Co., of Columbia, S. C. Dimethyl disulfide and dibenzyl disulfide came from Eastman Kodak Co. and the Waterlee Chemical Co. of Lugoff, S. C., respectively. The 2,2'-dithiobisbenzothiazole was a recrystallized sample from the Monsanto Chemical Co., and the elemental sulfur was a precipitated U.S.P. grade bearing the Baker and Adamson reagent chemical label.

Dimethyl diselenide (i.e., methyl selenide) and dichloro diselenide (i.e. selenium monochloride) were purchased from Metallomer Laboratories, Maynard, Mass., and Peninsular Chemical Research, Gainsville, Fla., respectively. Dimethyl selenide was prepared by modification of a published procedure,[5] a modification in which the stated proportion of reagents was mixed with cooling and the reaction mixture was then stirred at room temperature for 1 week. The n.m.r. analysis for hydrogen-containing substituents as well as standard wet-chemical procedures for sulfur and selenium showed that the compounds prepared by us and those purchased on special order from the custom manufacturers were free from gross amounts of impurities.

Reactions.—Equilibration studies of mixtures of dimethyl or di-t-butyl sulfide with elemental sulfur were carried out in 5-mm.

(1) Postdoctoral Fellow from the University of Glasgow, Sept., 1962–1963.

(2) F. Fehér, Special Publication, No. 12, The Chemical Society, London, 1958, p. 305 [Chemical Society Conference, "Recent Work on the Inorganic Chemistry of Sulfur," Bristol, England]. Also see M. Schmidt, "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press, Inc., New York, N. Y., pp. 98–158.

(3) See papers I, II, and IV in this series; i.e., K. Moedritzer and J. R. Van Wazer, J. Am. Chem. Soc., **86**, 802, 807, 814 (1964).

(4) L. Haraldson, C. J. Olander, S. Sunner, and E. Varde, Acta Chem. Scand., **14**, 1509 (1960). For other similar exchange reactions, see C. A. M. Mauritzen and P. Stewart, Nature, **197**, 48 (1963), and K. W. Bowers, Dissertation Abstr., **23**, 1512 (1962). A related mechanism study is given by A. J. Parker and N. Kharasch, J. Am. Chem. Soc., **82**, 3071 (1960), and related thermodynamic data by W. D. Good, J. L. Lancina, and J. P. McCullough, J. Phys. Chem., **65**, 860 (1961).

(5) M. L. Bird and F. Challenger, J. Chem. Soc., 572 (1942).