# Diffusion Studies with Poly(vinyl alcohol) in Aqueous Solution

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ABSTRACT: The diffusion behavior of two widely different samples of poly(vinyl alcohol) in aqueous solution was studied by the frit method. The experimental data were summarized in semilog plots that attained linearity after an induction effect had subsided. A convenient procedure was devised to test for quasi-ideal behavior during the induction period, and only solute of high molecular weight exhibited strongly nonideal characteristics. However, even this nonideality was removed under changed experimental conditions. The determined diffusion coefficients showed a predicted dependence on solute molecular weight but remained unaffected by changes in the initial concentration within the frit. In diffusion experiments with dissolved blends of the two polymers, no evidence was found to indicate preferential depletion of the low molecular weight component during experimental observation. The determined diffusion coefficients were found to depend linearly on the blend composition, and it appears that the method served to characterize the diffusion behavior of these solute mixtures as a whole.

Diffusion studies with polymer samples in solution yield rather direct information about the effective mobility of the individual polymer coils in averaged conformations that remain undistorted by shear or extraneous forces. Because of these properties, the diffusion coefficients of polymers describe the effective molecular volume, which is primarily a function of the molecular weight, the degree of branching, and the extension of the polymer coil due to specific solute–solvent interactions.

While several highly precise experimental methods are available for measuring polymer diffusion coefficients in solution,[1,2] a convenient gravimetric procedure is afforded by the "frit method,"[3,4] which was used in this investigation. According to this method, determinations of buoyant weight are carried out with a thin porous frit that is submersed in a thermostated bath of solvent. If the porous frit had previously been filled with a solution, then the time dependence of the weight changes would reflect on the diffusion characteristics of the solute. The method has been found suitable for evaluating quantitatively the diffusion characteristics of small dissolved molecules as well as polymeric solutes.[5] Even the behavior of mixed polymeric solutes in experiments of this kind has been investigated to a limited extent.[6] In the present investigation, detailed studies of polymer diffusion have been performed over considerable ranges of solute concentration, and further information has been obtained to define the effect of sample polydispersity on the experimental results.

## Discussion of the Experimental Method

The experimental procedure outlined above serves to determine the apparent weight $w$ of the polymer solution contained within the submerged frit at various times. The quantity $w$ is given as the difference of the frit weights at time $t$ and the weight at infinite time. Since the contained volume of liquid within the frit remains constant, the experimental observations reflect on the time dependence of the average solution density $d$. The latter quantity is assumed to be given in terms of the solute concentration $C$, the solvent density $d_0$, and an empirical constant $k$ according to simple relations of the type

$$d = d_0 + kC \qquad (1)$$

Depending on the nature of the solute–solvent system, $k$ may be positive or negative, and $w$ attains positive or negative values accordingly. Many solution systems, involving polymeric and nonpolymeric solutes, have been found to conform well to the requirements of eq 1 over considerable ranges of concentration. But the empirical constant $k$, being a measure of the partial specific volume for the solute, may depend to a detectable extent on the molecular weight of a polymeric solute.

Under the boundary conditions that are suggested by the experimental procedure, the time dependence of the average concentration $\bar{C}$ (within the frit) is obtainable from the Fickian diffusion law as

$$\bar{C} = (8C_0/\pi^2)\sum_{n=1}^{\infty}(2n-1)^{-2}\exp[-(2n-1)^2D\alpha t] \qquad (2)$$

where $C_0$ is the initially uniform concentration within the frit; $D$ is the diffusion coefficient that is assumed to be independent of any local concentration encountered inside the frit; and $\alpha$ is an apparatus constant whose theoretical magnitude is $(\pi/L)^2$, where $L$ denotes the effective frit thickness. Since $L$ gives the average length of the tortuous channels (available to the solution) across the frit, this distance may well exceed the linear thickness of the frit. These tortuous channels through the porous frit material must succeed in preventing any motion other than Brownian movement within the frit in order for eq 2 to apply. Such immobilization of the solution must be in effect despite the existence of density gradients within the frit and despite the agitation that is needed to keep the frit surfaces precisely at the negligible bath concentration. Although stringent requirements are imposed on the experimental conditions, many sensitive solution sys-

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(1) E. L. Cussler and E. N. Lightfoot, *J. Phys. Chem.*, **69**, 1135 (1965).

(2) V. N. Tsvetkov and S. I. Klenin, *J. Polym. Sci.*, **30**, 187 (1958).

(3) G. Schulze, *Z. Phys. Chem.*, **89**, 168 (1914).

(4) F. T. Wall, P. F. Grieger, and C. W. Childers, *J. Amer. Chem. Soc.*, **74**, 3562 (1952).

(5) F. T. Wall and C. W. Childers, *ibid.*, **75**, 3550 (1953).

(6) G. B. Taylor and F. T. Wall, *ibid.*, **75**, 6340 (1953).

tems, involving low molecular weight solutes, have been found to conform quantitatively to the anticipated ideal diffusion behavior.[4,7]

In actual experimental investigations of this nature, it is advantageous to enter the experimental data into semilog plots of $w$ *vs.* $t$. This procedure is suggested by the properties of eq 2, since the summation becomes dominated by its first term after a limited induction time. Thereafter, the diffusion process can be described adequately by the derivable relation

$$\log w = -(0.4343)D\alpha t + \log [(8/\pi^2)w_0] \quad (3)$$

Here $w_0$ is the value of $w$ at the precise instant when the solution-filled frit becomes immersed into solvent. Direct observations of $w_0$ are not possible experimentally, and, if $w_0$ is to be determined, one must resort to an extrapolation of the experimental data to zero time, along a nonlinear portion of the semilog plot described above. For nonpolymeric solutes, the curved region of these plots have been found to be in good agreement with results computed according to eq 2. However, in diffusion experiments with polymeric solutes the initial change in apparent weight has been found to be usually more rapid[5,6] than can be accounted for theoretically. In either case the described plotting procedure eventually yields straight lines, from whose slopes the product $D\alpha$ can be evaluated.

## Experimental Section

Our apparatus was quite similar to the one described elsewhere.[4] Instead of using a "chainomatic" balance, an automatic single-pan balance was used to follow the immersed frit weight. In all diffusion experiments the temperature of the solvent bath was maintained at 34.0 ± 0.1°. Two frits of porous porcelain were used; they were hand-ground from 10 × 10 cm porcelain plates (purchased from Will Scientific, Inc.) to attain thicknesses of about 1.1 and 1.6 mm. The samples of poly(vinyl alcohol) used in this investigation were unfractionated samples of "Elvanol" 50-42 and 51-05 supplied by Du Pont. The polymer samples had widely different molecular weights, as reflected by their respective intrinsic viscosity values of 0.85 and 0.334 in aqueous solution at 30°. A correlation of intrinsic viscosity with polymer molecular weight can be established using literature results.[8] However, this procedure can provide only a rough estimate of molecular weight, since the published correlation[8] ($[\eta] = 0.0425M_v^{0.64}$) is based upon experience with polymer samples that were almost completely hydrolyzed, while our samples were actually copolymers, in which 12% of the polymer units were retained as unhydrolyzed vinyl acetate groups.

Prior to each diffusion experiment, the porous frits were soaked in unagitated solutions at room temperature for a minimum of 20 hr. Calibration experiments were performed with sucrose solutions in order to determine $\alpha$ for the frits under investigation, using a solute with a known diffusion coefficient. Although a 0.25 *M* sucrose solution was employed, we applied in calculations the diffusion coefficient at infinite dilution ($6.4 \times 10^{-6}$ cm²/sec at 34°). This approach is justified since detailed computer calculations[9] have corroborated the plausible conclusion that the frit method actually measures the rate of departure of solute from the frit surface, where the concentration is only infinitesimally different from the bath concentration. The diffusion coefficient cited above was obtained by a short extrapolation to the desired temperature along the virtually linear trend in the literature data.[10] In order to provide a comparison to the diffusion behavior of polymers (discussed below), the results of the calibration experiments are presented in Figure 1.

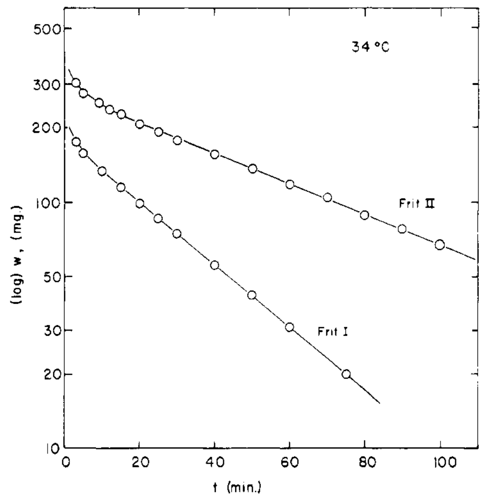

Figure 1. Frit calibration experiments, using 0.25 *M* sucrose solution.

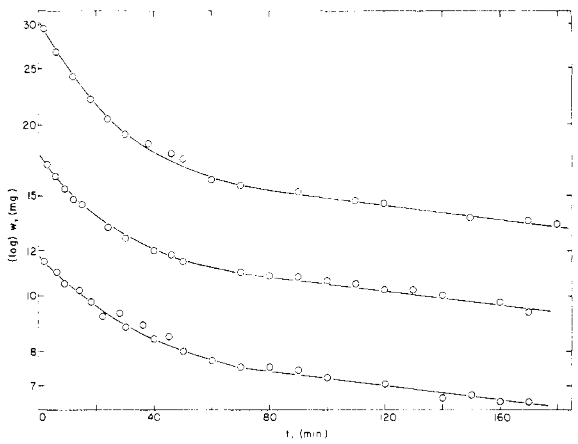

Figure 2. Diffusion experiments with high molecular weight polymer, using frit II.

## Diffusion Behavior of Individual Polymer Samples

The results of diffusion experiments with polymeric solutes are summarized in Figures 2 and 3. Over various ranges of solute concentration the slope of our diffusion plots remained essentially constant, independent of the initial concentration within the frit. No significant trends have been detected to indicate less ideal behavior. Even if it were established that the diffusion coefficient is dependent on concentration within the frit, then this experimental finding would lend support to the view, cited above, that the diffusion coefficient at the concentration of the frit surface is

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(7) D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw Hill Book Co., Inc., New York, N. Y., 1962, p 154.

(8) M. Matsumoto and Y. Oyanagi, *Kobunishi Kagaku*, **17**, 191 (1960).

(9) F. T. Wall and R. C. Wendt, *J. Phys. Chem.*, **62**, 1581 (1958).

(10) International Critical Tables, Vol. V, E. W. Washburn Ed., McGraw Hill Book Co., Inc., New York, N. Y., 1929, p 71.

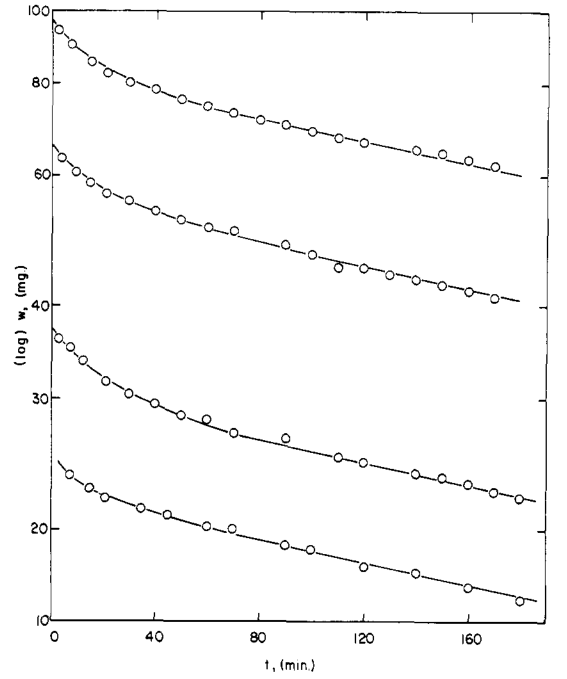

Figure 3. Diffusion experiments with low molecular weight polymer, using frit I.

measured by the experimental method. In agreement with theoretical considerations,[11] the diffusion coefficients of our polymer samples decreased with increasing molecular weight, and the numerical values of $D$ were calculated to be $2.4 \times 10^{-7}$ and $8.3 \times 10^{-7}$ cm$^2$/sec for samples 50-42 and 51-05, respectively.

The most conspicuous difference in the diffusion behavior of polymeric and nonpolymeric solutes is the severity of the induction effect, *i.e.*, the size of the curved portions in the diffusion plots. It appears that this nonlinear section is oversize with respect to the decrease along the logarithmic coordinate and with respect to the duration of the induction period. However, it had been shown previously,[4] using eq 2, that the deviation from linearity is attenuated to a contribution of about 1% only when the effective diffusion variable ($Dt/L^2$) has progressed to a value of about 0.030. As a consequence of this condition, it follows that the induction period may appear to be long if the diffusion coefficient is correspondingly small.

Concerning the extent of the induction effect along the vertical direction of the diffusion plots, a convenient test for quasi-ideal behavior can be devised. According to this test, the linear trend in the diffusion plots is extrapolated to zero time, and then the distance along the logarithmic axis is determined to the extrapolation of the experimental points at zero time. As can be seen from eq 3, ideal behavior would demand that this distance is represented by the logarithm of $(8/\pi^2)$. Ordinarily, polymer samples cause the induction effect to be more severe (as shown in Figure 2) than can be accounted for theoretically. However, it appears that the data of Figure 3 have been obtained with a polymer of sufficiently low molecular weight, so that nearly ideal behavior is conformed to, according to the criteria considered here.

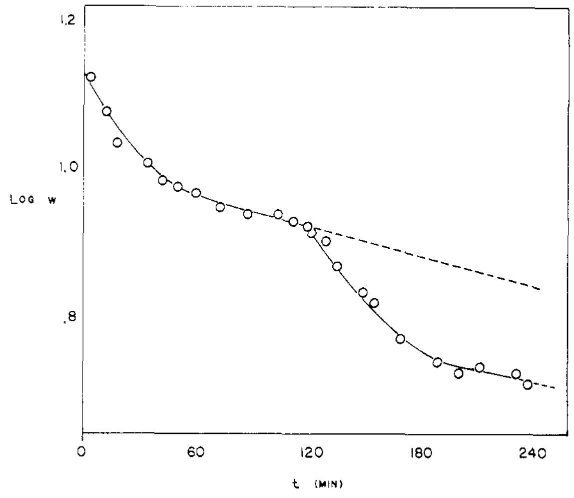

Figure 4. An "interrupted" diffusion experiment with high molecular weight polymer, using frit I.

In an attempt to gain some insight into the physical cause of an anomalous induction effect, a critical experiment, described in Figure 4, was carried out. A regular diffusion experiment was interrupted after a 2-hr duration. Thereafter the concentration profile was given an opportunity to distribute itself uniformly across the frit while the latter was stored apart from solvent for about 28 hr. The frit was stored in a water-saturated atmosphere, and the macroscopic loss of solution from the frit remained negligible. Subsequent experimental procedures subjected the contents of the frit to a resumed diffusion experiment, which is described in the second leg of the plot in Figure 4. If the second induction effect had shown up to be significantly less severe than the first, then we might have concluded that preferential effusion of low molecular weight fractions had taken place during the first 2-hr period. As seen in the diagram, the two induction effects appeared with essentially equal magnitude, but our study of solute fractionation effects remained unresolved, since the previously encountered, anomalous, induction effect adjusted itself to become nearly ideal when the high molecular weight polymer was studied in our thinner frit. The latter observation provides an important clue that nonideal induction effects may be remedied by a suitable choice of experimental conditions. In a subsequent publication[12] these indications have been pursued further.

## Diffusion Studies with Mixed Polymeric Solutes

In order to investigate the joint diffusion of solute species with different molecular weights, a number of polymer blends in solution were studied according to the frit method. Although some systems of this nature had been investigated previously,[6] important new conclusions can be derived from our data, summarized in Figure 5. Using the same polymers that have been described previously in this investigation, it is seen that a gradual decrease in the effective diffusion coefficient takes place as the polymer blends become more con-

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[11] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 629.

[12] M. J. Eitel, submitted for publication.

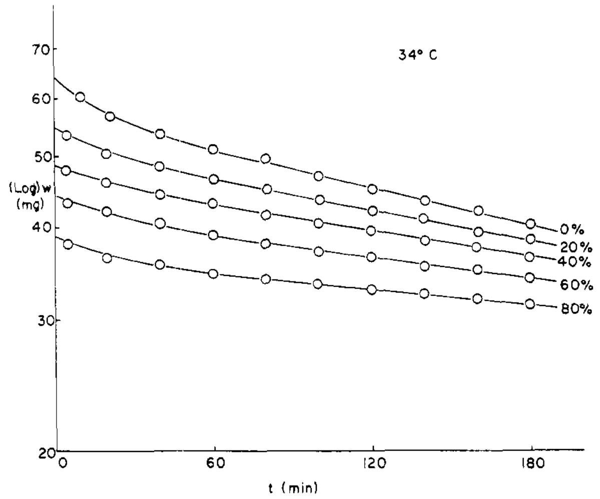

Figure 5. Diffusion experiments with dissolved polymer blends, prepared with the indicated content of the high molecular weight component; experimentation with frit I.

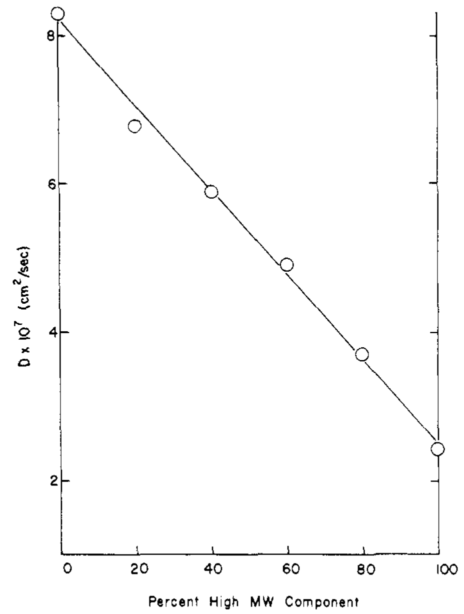

Figure 6. The effect of the composition of dissolved polymer blends on the effective diffusion coefficient.

centrated with respect to the high molecular weight constituent. It should be mentioned that the differences in the extrapolation values of $w_0$ must not be misunderstood to reflect on differences in density alone. Although the solutions of polymers with different molecular weight are capable of showing different densities, these effects are expected to be quite small.

The individual diffusion plots of polymer blends are expected to be curved and concave upward if the low molecular weight constituents were depleted within the frit significantly faster than high molecular weight fractions. As shown in Figure 5, this behavior has not been encountered at the frit thickness employed and under the particular conditions of the experiments. Because of the absence of fractionation effects, it appears that our experiments provide a measure of an average diffusion coefficient that applies to each polymer blend as a whole. As shown in Figure 6, the determined diffusion coefficients are described well by a linear function of the weight composition for the prepared blends

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# Multicomponent Polymerization. I. Integration of the Rate Equations

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ABSTRACT: The equation describing instantaneous copolymer composition in free-radical vinyl copolymerization has been known and verified for many years. Although this equation has been integrated to give composition as a function of conversion, no analytical expression has been presented which gives conversion as a simple function of time. In this paper a derivation and experimental verification of such an equation is presented. Applications of this equation to problems in copolymerization kinetics are also considered. Extension of the equation to systems of more than two monomers is postulated.

In order to describe completely the course of a copolymerization it is necessary to know both monomer feed and polymer composition as functions of conversion and time.

Copolymer and monomer feed composition are related by the well-known copolymer composition equation

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \qquad (1)$$

where the mole fractions of monomer $i$ in the feed and instantaneous copolymer are $f_i$ and $F_i$, respectively. The variation of composition $f_i$, with conversion, $m$, is governed, in turn, by a simple material balance. This relationship, known widely as the Skeist equation, has been successfully integrated by Meyer and Lowry[1] to give

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(1) V. Meyer and G. Lowry, *J. Polym. Sci., Part A*, 3, 2843 (1965).