

diffusing molecule encountered a local viscous resistance, which varied as the melt viscosity of the polymer-solvent mixture, we obtained the relation:

$$\log D = A - B(\omega_2)^{1/2} \quad (1)$$

where D is the diffusion constant at a given concentration, ω_2 is the weight fraction of polymer, and A and B are constants. Figure 1 shows the application of this equation to the calculated data of Crank and Park. The fit of the points is not as good as would be desired, but on the whole describes the behavior fairly well. A plot of $\log D$ versus weight fraction of polymer is somewhat poorer. As Crank and Park show in the accompanying letter, $\log D$ is linear in the volume fraction of plasticizer, and this is mathematically equivalent to equation (1) at low concentrations of plasticizer.³ The fact that equation (1) has now been shown to apply to two sets of data suggests that it merits further attention for describing the functional dependence between diffusion and concentration. Moreover, this equation emphasizes how strongly the diffusion constant does increase with solvent concentration, and, hence, the necessity of allowing for this variation in treating experimental data.

References

1. J. Crank and G. S. Park, *Trans. Faraday Soc.*, **45**, 240 (1949).
2. R. F. Boyer, *J. Applied Phys.*, **20**, No. 6, 540 (1949).
3. R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **2**, 157 (1949).

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We are indebted to R. F. Boyer for allowing us to see his letter on "Concentration Dependence of Diffusion of Chloroform in Polystyrene" prior to publication and we take this opportunity to mention the results of some further work carried out by one of us (G. S. P.).

Using the same experimental technique but graphically better methods of analysis, diffusion coefficient-concentration curves have been obtained for methylene chloride, chloroform, carbon tetrachloride, methylene bromide, bromoform, and methyl iodide in polystyrene. These results have all been shown to fit the expression:

$$\log D = \alpha + \beta\nu_1$$

where α and β are parameters, D is the diffusion coefficient and ν_1 is the volume fraction of the diffusing molecule. This expression and the expression:

$$\log D = A + B\omega_2^{1/2}$$

given by Boyer can be shown with a fair degree of approximation to be mathematically equivalent forms over the range of concentrations considered. This means in effect that the general behavior of all our diffusion coefficients so far obtained is consistent with the prediction based on the Flory expression for melt viscosity, though as yet the agreement has not been examined quantitatively.

A full account of this work will be published elsewhere.

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Viscosities of Very Dilute Polymer Solutions

In determinations of intrinsic viscosities, extrapolations are often made from a concentration range in which hydrodynamic interaction is pronounced since the average intermolecular distances are comparable with the molecular dimensions. In connection with the theory of the concentration dependence,¹ there is interest in the behavior at extreme dilution. A concave downward trend in the plot of η_{sp}/c vs. c at low concentration has been reported.^{2,2} This suggests careful examination of the viscosity of solutions at concentrations well below the limit of 0.1% ordinarily used for polymers of molecular weight 10^5 to 10^6 .

With this in view, we report a few results obtained with toluene solutions of a polystyrene fraction with molecular weight $\bar{M}_n = 500,000$ in the concentration range from 0.017 g./dl. upward. (The molecular weight was determined osmotically by G. A. Hanks.)

The viscometers used were of the Ubbelohde suspended level type, modified by expanding the reservoir to permit successive dilutions in the viscometer.⁴ The two viscometers used for the lowest concentration (J_1 and J_2 , see Fig. 1) were fitted with a filtering and dispensing unit,⁵ eliminating artifacts which might otherwise arise from occlusion of the capillary by foreign particles. Because of the long flow times for toluene in viscometers J_1 and J_2 (467.8 and 369.8 sec., respectively), kinetic energy corrections were unnecessary. The other viscometers were calibrated and kinetic energy corrections applied. The maximum velocity gradients in the J_1 and J_2 viscometers were less than 1800 sec.^{-1} ; in the R , S , and G , less than 1250 sec.^{-1} ; and in the U_2 , less than 435 sec.^{-1} .

The results of the viscosity measurements are shown in Figure 1 as a plot of η_{sp}/c vs. c . It might be of interest that the curve can be adequately represented up to $c = 3$ by a Baker type of equation:

$$\eta_r = \left(1 + \frac{[\eta]c}{2.9}\right)^{2.9}$$