Diffusion Coefficient Measurements by Solvent Absorption in Concentrated Polymer Solution

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Synopsis

Diffusion coefficient measurements for solvents in concentrated polymer solutions require consideration of both concentration dependence of the diffusion coefficient and surface resistance to mass transport. Solutions to the diffusion equation have been generated where these effects are explored. A method to account for both concentration dependence and surface (absorption) resistance in the experimental determination of diffusion coefficients is given and demonstrated with an example where a multiplying factor of over 300 is required to adjust the apparent diffusion coefficient to the value sought.

INTRODUCTION

Diffusion in concentrated polymer solutions is of considerable practical interest to coatings, for instance, since film formation by solvent evaporation requires transport of the solvent within the film to the air/film surface from which evaporation then takes place. Early work in the coatings industry lead to a mathematical description of the film formation process by solvent evaporation.[1-3] In all its simplicity the description involved collecting diffusion coefficient data over the entire concentration range of interest (all concentrations) and then solving the diffusion equation by a finite difference technique for the given solvent diffusion coefficient/concentration at various (small) time intervals at each point in the film. It was found that the solvent diffusion coefficient was quite important for the phenomena known as solvent retention, where bulk solvent concentrations are below about 0.2 volume fraction and the surface concentration is essentially zero. It was also found that surface evaporation phenomena became increasingly significant at increasing bulk concentrations above this, since the surface concentration was not zero and was higher for higher bulk concentrations. Surface resistance, including solvent latent heat (heat transfer), solvent vapor pressure, and the solvent/air diffusion coefficient all become important. In practice these are combined into a factor called the relative evaporation rate, which is widely used in the trade and has some theoretical justification,[4] to estimate solvent evaporation phenomena, i.e., film drying rates.

The question which then arises is that if surface effects are important at bulk concentrations greater than about 0.2 volume fraction in desorption, are they not also important in the same concentration range for absorption? The answer is decidedly affirmative as will be shown below (and can be seen in Fig. 1).
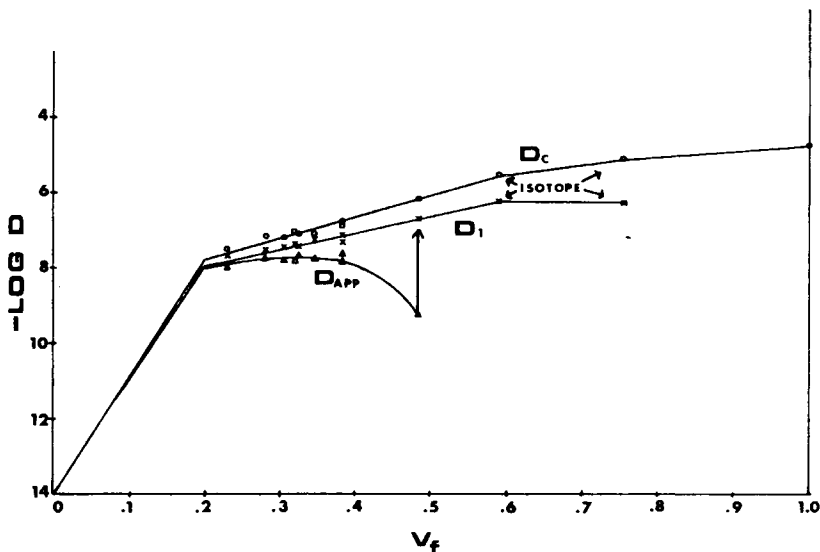
Fig. 1. Diffusion coefficient data for the system chlorobenzene–poly(vinyl acetate) at 23°C.

ABSORPTION WITH A SURFACE RESISTANCE AND CONCENTRATION DEPENDENT DIFFUSION COEFFICIENT

In order to test the significance of surface resistance for absorption, the same mathematical treatment previously applied to desorption[1,2] was applied to absorption. This basically involved adding a minus sign to direct the mass (and heat) transfer in the opposite direction than for desorption. Diffusion coefficient data for the system chlorobenzene/poly(vinyl acetate) are used here to test the calculations. These data are shown in Figure 1. D_{app} is found from the dry film thickness L and the half-time of the absorption experiment $t_{1/2}$ using the customary equation[5]

$$T_{1/2} = \frac{D_{app}t_{1/2}}{L^2} = 0.049 \tag{1}$$

D_c, the diffusion coefficient based on total film thickness is related to D_1, the diffusion coefficient based on the dry film thickness by

$$D_1 = D_c (1 - v)^2 \tag{2}$$

where v is the volume fraction of solvent present. The concentration dependence is exponential both above and below a value which for this system is 0.2 volume fraction.

D_1 is found by correcting D_{app} for both concentration dependence and surface resistance as shown below. The correction for concentration dependence alone is equivalent to the "integral" method of treating such data.[5,6] The surface resistance correction is based on the data summarized for absorption in Figure 2.

Here V is the concentration dependence (in decades) involved in the experiment, and B is the relative value of diffusional resistance, R_d, to surface resistance, R_s:

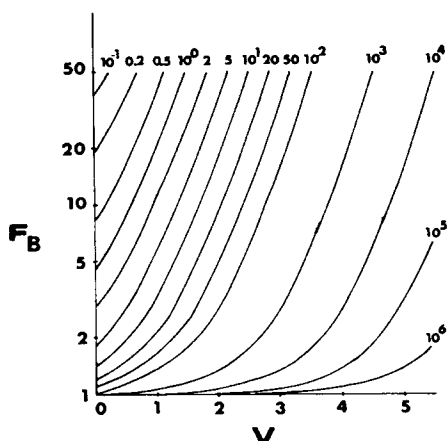$$^{10}\log V = \frac{D_1 \text{ (at final } C_0)}{D_1 \text{ (at initial } C_0)} \tag{3}$$

Fig. 2. Correction factors, F_B, for surface resistance for diffusion coefficient measurements by the absorption technique where the diffusion coefficient depends exponentially on concentration. Various curves are for B values as defined in the text.

$$B = \frac{R_d}{R_s} = \frac{L/D_1}{1/h} = \frac{hL}{D_1} \quad \text{(dimensionless)} \quad (4)$$

Here the flux F is given by

$$F = D_1 \frac{dc}{dx} = h(\Delta C) \quad (5)$$

and D_1 is the diffusion coefficient (cm²/s), C is the solvent concentration (g/cm³), x is distance into the film (cm), h is the surface mass transfer coefficient (s/cm) ΔC is the concentration difference, surface concentration at equilibrium with the prevailing vapor pressure (C_∞) less the prevailing surface concentration (g/cm³), L is the dry film thickness (cm). D_1 is found from

$$D_1 = D_{app} \, (F_M)(F_B) \quad (6)$$

where F_M is a multiplying factor to account for concentration dependence and F_B is a multiplying factor to account for surface resistance.

These factors essentially replace the constant 0.049 in Eq. (1) by one representing the conditions of the experiment. F_M has been reported previously for absorption and desorption.[6] F_M is based on the ratio of the calculated (dimensionless) half-time with the specified concentration dependence to 0.049, the dimensionless half-time for absorption or desorption for a constant diffusion coefficient.[6]

F_B has been calculated in a similar manner using the ratio of the half-time calculated for absorption with a significant surface resistance to that where surface resistance had no significant affect, i.e., sufficiently high B. F_B data are given in Figure 2 for absorption. Both these absorption data and corresponding desorption data are reported elsewhere.[7] In effect this is a simplified curve fitting procedure based on half-times. The diffusion equation has been solved many times to generate the data in Figure 2. For a constant diffusion coefficient:

$$F_B = \frac{3.7}{B} + 1 \quad (7)$$

The additional data in Figure 1 are for independent diffusion coefficient measurements. Radioactive chlorobenzene was used in the experimental technique of contacting two liquid columns with each other reported by Walker[8] at the intermediate concentrations, and the self-diffusion coefficient for chlorobenzene was found in the literature.[9] All curves in the figure are smooth, and no deviations require special explanation other than that presented here.

Example

A quartz spring experiment for the absorption of chlorobenzene into polyvinyl acetate applied to both sides of a 5-μm-thick aluminium foil yielded the following data:

L $\quad$ = 7.35 μm
v_0 $\quad$ = 0.433 volume fraction (initial)
v_∞ $\quad$ = 0.482 volume fraction (final)
$t_{1/2}$ $\quad$ = 167 s
D_{app} = 6.34 × 10^{-10} cm^2/s
V $\quad$ = 0.2 decades (from Fig. 1)
F_M $\quad$ = 1.2 (Ref. 6)
h $\quad$ = 3.4 × 10^{-6} cm/s (from F/Δ C at t ≈ 0)
B $\quad$ = 0.0208 [eq. (4)] with D_1 = 1.2 × 10^{-7} from Figure 1 at $v = v_0$
F_B $\quad$ = 254 (extrapolated in Fig. 2)
$D_{1(C)}$ = 1.9 × 10^{-7} cm^2/s (eq. 6) at $v = v_\infty$

This data point falls exactly on the D_1 curve. The total correction to D_{app} required in this case is a multiplier greater than 300.

DISCUSSION

Surface effects must be considered in solvent absorption or desorption experiments where solvent concentrations are greater than about 0.2 volume fraction (reference to present system). This concentration may be lower for other systems. The important factor is the ratio of diffusional to surface resistance, which should be checked for each experiment in question. We have found surface resistance to be significant for the absorption of water into poly(vinyl acetate) and other polymers where only a few percent of water absorb,[7] for interpreting time-lag experimentals,[10] and for correcting permeation cup experiments for evaporation resistance within the cup.[11] This cup resistance has been shown significant for proper interpretation of permeation cup data to determine the transport properties of paper and wood, for example.[12]

The diffusion equation solved with realistic boundary conditions, as described above, predicts Case II type behavior[13] (where weight increases linearly with time) as normal absorption with concentration dependence and no significant surface resistance. Super Case II type behavior[14] (where weight increases more rapidly than with linear time) occurs when resistance at the surface becomes a significant factor.

A critical review of literature data reveals an exceptionally large number of reports which presumably would have been interpreted otherwise had surface resistance been included in the interpretation of the data. Such a review would be beyond the scope of the present article and is, in fact, practically impossible,

because the necessary data are not specifically reported in the articles in question.

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