Diffusion Coefficients for Amorphous Polymer and Water Systems

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Recent studies of absorption and desorption of low-molecular-weight substances in amorphous polymers olids have demonstrated a sharp distinction between organic solvents and water. In systems of amorphous polymer + organic vapor the processes are of the Fickian type[1-4], usually with a diffusion coefficient which depends appreciably on penetrant concentration, when the systems are well above the glass transition temperatures, T_g, of respective polymers. At temperatures below T_g they exhibit various non-Fickian features[5-8]. No definite information has as yet been obtained about the behavior at temperatures slightly above T_g[9]. On the other hand, the processes of water are Fickian both above and below T_g, if in the latter region the system is not greatly removed from T_g[10]. In addition, the diffusion coefficients for amorphous polymer +water systems are practically independent of water concentration at any given temperature in the region mentioned above[10-13]. It is also reported that while the apparent activation energies, ΔH_d, for diffusion of organic solvents in amorphous polymers increase as the temperature is lowered toward T_g[3,4], the ΔH_d for aqueous systems are constant in the corresponding temperature region[10-12]. Furthermore, there are some experimental data[13] which show that plots of $\log D$ vs. $1/T$ for a water system

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are represented by two straight lines intersecting at T_g, where D is the mutual diffusion coefficient of the system and T is the absolute temperature. This implies that the ΔH_d of such a system changes discontinuously to another constant value when the temperature is lowered through T_g. These features suggest that the molecular mechanism responsible for the diffusion of water in amorphous polymers must be different from that for the diffusion of organic solvents in the same polymers. No adequate explanation has yet been presented concerning this problem.

In a recent publication⁴⁾ we have shown that the dependence on temperature and also on concentration of diffusion coefficients for systems of amorphous polymer + organic solvent above T_g can be interpreted quite satisfactorily in terms of a simple theory based on the free volume model of polymer network. One will find it natural that in view of this previous success we were interested in examining the extent to which our free volume theory can account for data of diffusion coefficients for polymer + water systems. One of the purposes of the study reported in this paper is to obtain experimental data pertinent to this problem. The other purpose is concerned with the re-examination of the previously reported variation of D for polymer + water systems with temperature. This arose from a close inspection of existing data and also from the prediction that if the free volume of the polymer network is the controlling factor for the diffusion of water, the linear relation between $\log D$ and $1/T$ should be only approximate.

Experimental

Materials.—Two amorphous polymers, polyvinyl acetate (PVAc) and polymethyl acrylate (PMA), were chosen for the present study. These were purified, unfractionated materials obtained from the Institute for Chemical Research, University of Kyoto. The number-average molecular weight of the PVAc, determined osmotically in a mixture of methanol (80) and ethanol (20) at 17°C, was 8.3×10^4. According to Naito¹⁴⁾, this is a thata solvent for PVAc. In fact, our osmotic measurements gave a second virial coefficient which was zero within the accuracy of the experiment. The films for sorption experiments were prepared in the same manner as described previously¹⁵⁾. Their thicknesses were varied from 1.0×10^{-2} to 4.1×10^{-2} cm., depending upon the rate of absorption or desorption in respective cases.

The PMA used was identical to that used for obtaining the data reported in reference (4) and had a number-average molecular weight of 3.1×10^5 (determined osmotically in acetone at 25°C). Films of this polymer prepared for sorption measurements were 1.1×10^{-2} to 4.9×10^{-2} cm. thick.

Apparatus and Procedure. — Our sorption apparatus has been described previously¹⁵⁾. Integral absorption from and integral desorption to zero pressure were measured for several external pressures of water vapor at a number of temperatures in the range 10 to 60°C for PMA and in the range 5 to 60°C for PVAc. In each experiment the temperature of the system was controlled to within ±0.1°C. According to the literature¹⁶⁾, the glass transition temperatures, T_g, of dry PMA and PVAc are about 3°C and about 28°C, respectively. Thus the present study for PVAc covered the temperature range both above and below T_g, and that for PMA treated the range above T_g only. Pressures of water vapor in the sorption tube were measured to ±1 mm. on a dioctyl phthalate manometer. This corresponded to an accuracy of ±0.07 mmHg. At every temperature studied, especially at temperatures below T_g, it was essential to use well-annealed specimens in order to obtain reproducible results.

For PVAc we performed steady-state permeation measurements at three temperatures, 10, 30 and 40°C, by using the cup method.

Results and Discussion

Diffusion Coefficients.—It was found that for both PVAc and PMA the equilibrium water concentrations, Q_∞ (grams of water sorbed per gram of dry polymer), at given relative humidities are independent of the temperature, over the ranges studied, within the accuracy of the present measurements. Those isotherm data are not shown here.

All the absorption and desorption data obtained were plotted in the form of Q_t/Q_∞ against $(t)^{1/2}$, where Q_t denotes the amount (in grams) of water absorbed or desorbed per gram of dry polymer for a time t from the start of a particular run. For all the external pressure and temperature measured, these plots had shapes expected from the normal Fickian diffusion mechanism. Furthermore, in each case, the absorption curve and the corresponding desorption curve coincided with each other over the entire range of time-scale of the experiment. According to theory¹⁷⁾, these features indicate that the mutual diffusion coefficient, D, of such a system should be independent of the penetrant concentration and may be evaluated from the initial slope, I, of the coincident absorption-desorption plot by means of the equation:

$$D=\pi I^2X^2/16 \tag{1}$$

where X is the thickness of the sample film.

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15) H. Fujita and A. Kishimoto, *J. Polymer Sci.*, **28**, 547 (1958).

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Fig. 1 illustrates how well a pair of absorption and desorption curves coincided with each other. The solid line in the figure represents the curve which has been calculated from the Fick diffusion equation by using for D the value determined by Eq. 1. A similar agreement between observed and calculated values was found for almost all the experimental data obtained. In Fig. 2 the values of D calculated by Eq. 1 from the data for the PVAc system are semi-logarithmically plotted against the equilibrium water concentration Q_∞. It is seen that the D values for each temperature are independent of Q_∞, and hence of the penetrant concentration, within errors of experiment. In the figure the filled circles give results from the steady-state permeation measurements. There are good agreements between the D values from the two different types of measurement at all temperatures where comparison can be made. It is of interest to note that this agreement was obtained even at 10°C, a tempetature about 20°C below T_g of PVAc. The indication from these results is that the diffusion of water into PVAc is controlled by the purely Fickian mechanism not only above T_g but also below T_g, provided that in the latter region the temperature is not too low from T_g. In this connection it is of significance to recall that the sorption processes of organic vapors in amorphous polymers generally exhibit marked deviations from the behavior expected from the normal Fickian mechanism when the systems are studied at temperatures below T_g of respective polymers.

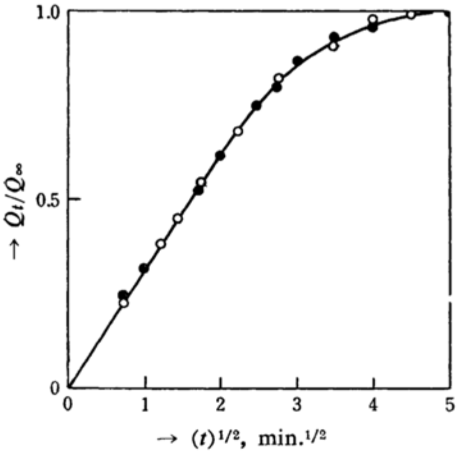

Fig. 1. Absorption and desorption curves for water in PMA. Water vapor pressure =17.2 mmHg; thickness of film=1.83×10^{-2} cm; temperature=30°C; concentration of water at sorption equilibrium= 0.99×10^{-2} g./g. Open circles, absorption; filled circles, desorption; solid line, theoretical.

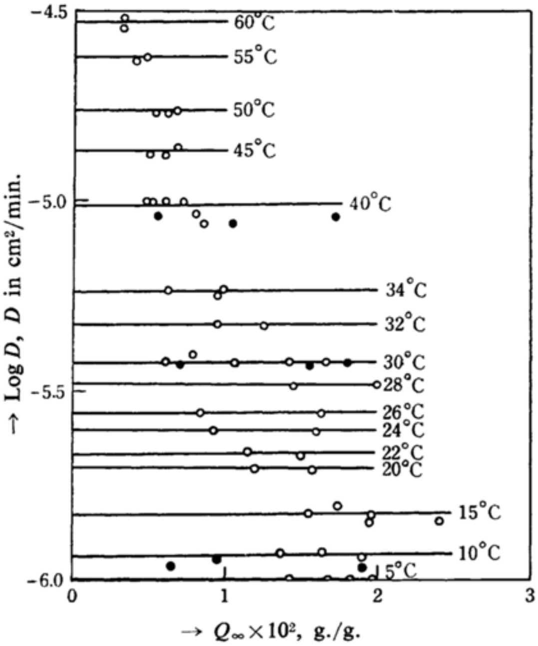

Fig. 2. Mutual diffusion coefficient vs. concentration relations on the system PVAc+water.
○ sorption studies;
● steady-state permeation studies.

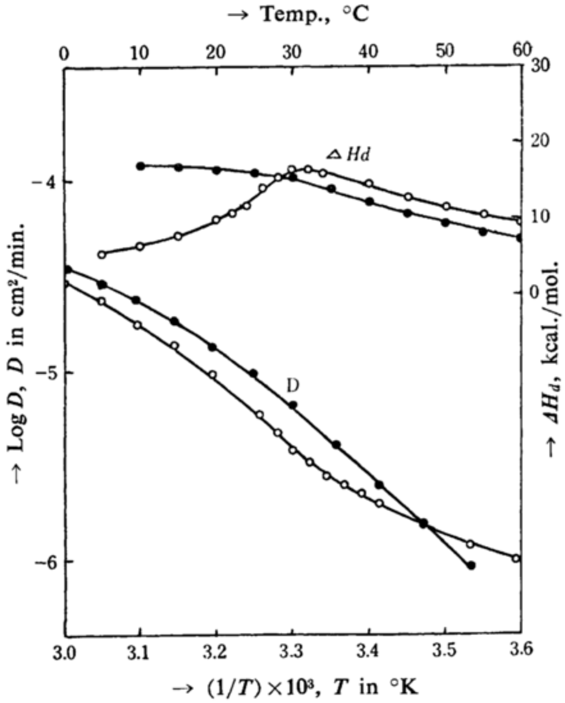

Fig. 3. Mutual diffusion coefficient vs. reciprocal absolute temperature (lower part); Apparent activation energies for diffusion, ΔH_d, vs. temperature (upper part).
○ PVAc; ● PMA.

The data for the PMA system were exactly similar to those for the PVAc system described above, although the behavior below T_g could not be studied on this polymer in the present work.

In Fig. 3 the values of D for the two systems are semi-logarithmically plotted against the reciprocal of absolute temperature T. First it will be seen that the plots for the two systems are not linear but curved. Of special interest is the inflection point which appeared on the plot for PVAc at a temperature near T_g of the polymer. Values of ΔH_d, the activation energy for diffusion of water in a polymer, were calculated from the smooth $\log D$ vs. $1/T$ curves drawn in Fig. 3, and are plotted against T in the upper part of the same figure. One finds that for both systems ΔH_d increases as the temperature is lowered toward T_g of respective polymers, and for PVAc it reaches a maximum at a temperature near T_g and then decreases gradually with further decrease in temperature. This appearance of a maximum ΔH_d is the reflection of the fact that the corresponding $\log D$ vs. $1/T$ plot has an inflection point. We wish to emphasize that this is the first experimental demonstration of a ΔH_d vs. T curve which goes through a maximum at a temperature in the vicinity of which the system undergoes glass transition. It should also be mentioned that our data for PVAc do not conform to the previous finding[13] for the system polymethyl methacrylate + water where the plots for $\log D$ vs. $1/T$ were represented by two straight lines intersecting at a temperature near T_g.

By employing the steady-state permeation method Meares[18,19] measured diffusion coefficients of several gases in PVAc and found that the slope of the plots for $\log D$ vs. $1/T$ showed distinct discontinuities at two temperatures, about 10°C apart from one another, in the region encompassing T_g of the polymer. Then he suggested that the glass transition of PVAc must take place over a range of temperature, rather than at a particular temperature. Although our PVAc data do not show any break in the temperature region studied, it appears that the occurrence of a broad maximum in ΔH_d has some correlation with Meares' suggestion on the "glass transition region". Recently, there are similar arguments from measurements of viscoelastic properties of dry polymers[20].

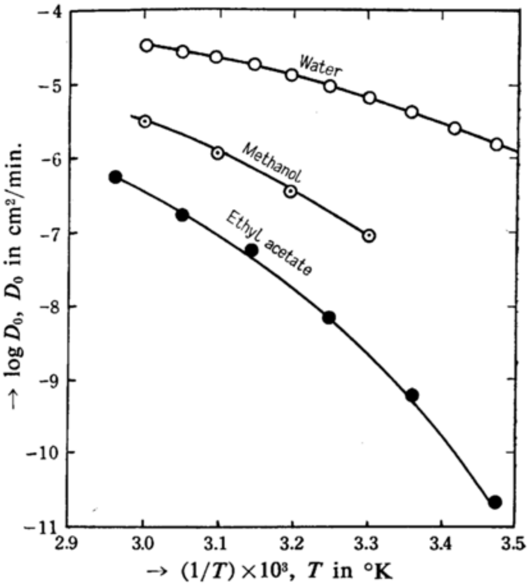

Fig. 4. Mutual diffusion coefficients at the limit of zero penetrant concentration as a function of reciprocal absolute temperature.

Comparison with Amorphous Polymer + Organic Solvent Systems.—Fig. 4 compares the temperature dependence of D_0 (the value of D at the limit of zero penetrant concentration) for systems PMA + ethyl acetate, PMA + methanol, and PMA + water. The data for the first two systems were taken from our previous publication[4]. The graph shows that with increasing molecular size as well as chemical affinity to PMA of the penetrant the values of $\log D_0$ at fixed temperatures decrease and their temperature dependence becomes more pronounced. This latter fact implies that more activation energy for diffusion into PMA is required at any given temperature (above T_g) for organic solvents than for water.

As noted in the introduction to this article, we have recently shown that the dependence on temperature and also on penetrant concentration of diffusions coefficients for amorphous polymer + organic solvent systems (above T_g of respective polymers) can be accounted for satisfactorily by a simple free volume theory[4]. According to this theory, the thermodynamic diffusion coefficient, $\mathfrak{D}_T$, of a penetrant in an amorphous polymer at a temperature T is represented by the equation:

$$\ln\ (\mathfrak{D}_T/\mathfrak{D}_0) = B_d\beta'(T)/[f(T,0)^2 + \beta'(T)f(T,0)v_1] \qquad (2)$$

Here $\mathfrak{D}_0$ is the value of $\mathfrak{D}_T$ at the limit of zero penetrant concentration, $f(T,0)$ is the average fractional free volume in the dry polymer at temperature T, v_1 is the volume fraction of the penetrant in the mixture, B_d is

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a constant characteristic of the system, and $\beta'(T)$ is a parameter representing the plasticizing effect of the penetrant. The value of $\mathfrak{D}_T$ can be calculated from D when the corrections for the volume expansion of the polymer by the addition of penetrant and for the thermodynamic non-ideality of the mixture are applied. The former correction can be made under the assumption that no volume change on mixing occurs and the latter correction may be derived from the analysis of the isotherm curve of the system.

We examined the applicability of Eq. 2 to the present data, by assigning to $\beta'(T)$ the values which we had previously deduced from measurements of stress-relaxation on these systems(15). It was found that in order that Eq. 2 may fit the concentration dependence data obtained, the values of B_d have to be chosen as almost equal to zero for both PVAc and PMA systems. On the other hand, as shown previously(4), the constant B_d may also be determined from the ratio of ΔH_d to ΔH_v, where ΔH_v is the apparent activation energy for the steady-flow viscosity of the pure polymer. Comparison of the ΔH_d data given in Fig. 3 with the ΔH_v values calculated from the equation of Williams, Landel and Ferry(16) yielded $B_d=0.16$ for PVAc and 0.25 for PMA. These B_d values are inconsistent with those derived above from the analysis of concentration dependence data, indicating that Eq. 2 is no longer applicable to the polymer+water systems investigated here. This result leads us to the conjecture that the amount of free volume must not be a major controlling factor for the diffusion of small molecules, such as water, through amorphous polymers. Previously we have inferred(4) that for penetrants very small in size and less soluble in the given polymer only a very local cooperation of the solid-like vibrations of two or three monomer units on the polymer chain would be sufficient to give a cross-section for the penetrant molecules to pass. This cooperative motion is so local that the probability of its occurrence, and hence the rate of diffusion of the penetrant molecule in the mixture, may be, in a first approximation, independent of how large the free volume in the mixture is. This will explain why the D values for the polymer+water systems studied did not exhibit measurable variation with water content. If the above is the case, then we would have to ascribe the observed temperature dependence of D for these systems to a temperature variation of solid-like vibration of monomer units, rather than to the temperature dependence of the free volume which is thought to be associated with larger-scale cooperative motions of several polymer segments.

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