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Regions of Fickian Diffusion in Polymer–Solvent Systems

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ABSTRACT: Oscillatory and step-change sorption experiments are used to help locate regions of Fickian diffusion for amorphous polymer–solvent systems. Sorption experiments are characterized by using a dimensionless group, the diffusion Deborah number, and sorption data are reported for water and methanol diffusion in poly(vinyl acetate). It is found that there are at least two Fickian regions for polymer–solvent diffusion which can be observed by varying the time scale of the experiment at fixed temperature, concentration, and polymer molecular weight. A low-frequency region is a viscous Fickian diffusion region, and a high-frequency region is a rubberlike elastic Fickian diffusion region.

It is well-known that diffusion processes in polymer–solvent systems often do not follow the laws of the classical theory of molecular diffusion.[1,2] There is thus not only considerable interest in understanding the anomalous effects observed in mass-transfer processes for polymer–penetrant systems but also interest in anticipating conditions for which it is possible to utilize the classical or Fickian theory in analyzing the diffusion process. In general, Fickian diffusion can be observed for polymer–solvent systems at sufficiently high temperatures and solvent concentrations since the polymer–solvent system behaves like a purely viscous fluid mixture under such conditions. In addition, it is commonly accepted[3-7] that diffusion at low penetrant concentrations below the polymer glass transition temperature can be analyzed by using the classical theory since the system appears to have the properties of an elastic solid. At intermediate temperatures and concentrations, a polymer–solvent mixture can exhibit anomalous or non-Fickian diffusion phenomena which are caused by viscoelastic effects in the polymer–penetrant system. As a penetrant diffuses through a polymeric material, the polymer chains must take on new conformations consistent with the new penetrant concentration. If this polymer chain rearrangement occurs on a time scale comparable to that of the diffusion process, behavior which is not consistent with classical diffusion theory will result. It is thus possible to observe widely different diffusional behavior in polymer–solvent systems by performing experiments that traverse large enough ranges of temperature, concentration, and polymer molecular weight.

Another way of investigating the diverse behavior exhibited in diffusion processes for polymer–solvent systems is to conduct a series of experiments by varying the characteristic time of an experiment at fixed temperature, concentration, and polymer molecular weight. This can be done for step-change sorption experiments by changing the thickness of the sample[8] and for oscillatory sorption experiments by varying the oscillation frequency.[9] Similarly, different characteristic experimental times can be obtained in quasi-elastic light-scattering experiments by varying the momentum-transfer range.[10,11] The principal objective of this study is to use oscillatory diffusion experiments, carried out at different oscillation frequencies and at fixed temperature, average concentration, and polymer molecular weight, to help locate regions of Fickian diffusion for amorphous polymer–solvent systems. The utilization of a dimensionless group, the diffusion Deborah number, in the characterization of sorption experiments is discussed in the second section of the paper, and a description of oscillatory and step-change sorption experiments is presented in the third section of the paper. Data for the water–poly(vinyl acetate) (PVAc) and methanol–PVAc systems are presented and discussed in the fourth section of the paper.

Diffusion Deborah Number

The presence of Fickian diffusion in polymer–solvent systems can be anticipated by comparing the rate of diffusion to the rate of rearrangement of polymer molecules. In the absence of externally induced flow in a concentration field, all deformations are the direct result of concentration gradients. In such cases, the nature of the diffusional transport in a polymer–solvent system can conveniently be ascertained by defining a diffusion Deborah number $(\mathrm{DEB})_{\mathrm{D}}$ as the ratio of a characteristic time λ_m of the fluid to the characteristic time θ_{D} of the diffusion process:[12-14]

$$(\mathrm{DEB})_{\mathrm{D}} = \lambda_m/\theta_{\mathrm{D}} \tag{1}$$

This dimensionless group will provide a useful characterization of a diffusion process if single values of θ_{D} and λ_m suffice to give an adequate representation of a particular mass-transfer operation. This point will be discussed further below.

For very small values of the diffusion Deborah number, molecular relaxation is much faster than the diffusive transport, and the diffusion process involves what is es-

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sentially a purely viscous binary mixture since conformational changes in polymer structure appear to take place instantaneously. A diffusion process at small values of $(\mathrm{DEB})_\mathrm{D}$ is simply diffusion in the classical sense, and it can be denoted as a viscous diffusion process. For very large values of the diffusion Deborah number, there is a negligible time variation of the polymer structure during the diffusion process so that a diffusing penetrant molecule is moving in a material that effectively has the properties of an elastic solid. This type of diffusional transport can be denoted as elastic diffusion. Finally, when the diffusion Deborah number is of the order of unity, rearrangement of polymer chains and the movement of solvent molecules take place simultaneously since the molecular relaxation and diffusive transport processes occur in comparable time scales. It seems appropriate to denote this type of diffusional transport as viscoelastic diffusion. Since the diffusion Deborah number is a convenient and useful way of characterizing a diffusion process, there is ample incentive for computing representative values of $(\mathrm{DEB})_\mathrm{D}$ by careful evaluation of the quantities λ_m and θ_D.

The characteristic time θ_D of a diffusion process must in general be defined differently for each mass-transfer operation. In many instances, it is an oversimplification to utilize a single value of the characteristic time to describe a mass-transfer process since different particles in the system of interest can have different characteristic times. In such cases, the utilization of a single characteristic diffusion time gives an overall indication of the type of diffusion process that is occurring since this characteristic time describes the time scale of the diffusion process only in some average way. For example, in a step-change sorption experiment involving the diffusion of a penetrant into a polymer film of initial thickness L, the usual definition of an average characteristic time for this unsteady one-dimensional mass-transfer process is[12-14]

$$\theta_\mathrm{D} = L^2/D^* \quad (2)$$

where D^* is a diffusion coefficient that is an appropriate measure of the diffusional transport in the system. Clearly, in this case, the utilization of a single value of θ_D is not completely satisfactory since a particle near the surface of the film undergoes a history different from that of a particle located a significant distance from the surface, and the diffusion behavior of the two particles should be described by different characteristic diffusion times. An additional difficulty in this case is the need to introduce an appropriate definition for the diffusion coefficient D^*. On the other hand, for an oscillatory sorption experiment for which the solvent pressure in the gas phase above the polymer film varies periodically, θ_D can be defined as[9]

$$\theta_\mathrm{D} = 1/\omega \quad (3)$$

where ω is the oscillation frequency in cycles/s. In this experiment, a single value of the characteristic diffusion time is applicable at every point in the diffusion field since the cycle time of the oscillation is the same for every particle in the system. Material particles at different distances from the vapor–polymer interface do however experience different phases of the cycle with different concentration amplitudes. Thus, it is clear that an oscillatory sorption experiment provides a more meaningful method of investigating nonclassical diffusion behavior than does a step-change sorption experiment.

There are two difficulties in choosing an appropriate value of λ_m for the calculation of $(\mathrm{DEB})_\mathrm{D}$. First, since λ_m can be a strong function of temperature and concentration for a given polymer–solvent system, it will be possible to define a single value of the Deborah number for an entire diffusion process only if the spatial and time variations of these variables are negligible. For an isothermal, step-change sorption experiment, this can be accomplished if the difference in final and initial equilibrium concentrations is sufficiently small. Similarly, for an oscillatory experiment, a single value of the Deborah number could provide an adequate representation of the diffusion process at a given temperature if the concentration amplitude of the experiment is suitably small. It will be supposed here that a Deborah number calculated for a particular diffusion process is computed by using material properties which are representative of the temperature, polymer molecular weight, average pressure, and average concentration of the system. Hence, for an oscillatory diffusion experiment, a single value of the Deborah number can be computed by using the equation

$$(\mathrm{DEB})_\mathrm{D} = \lambda_\mathrm{m}\omega \quad (4)$$

if a single definition of the characteristic time λ_m is adequate for the representation of the pertinent relaxation mechanisms in the polymer–solvent system.

A second difficulty is that there are of course many possible definitions for λ_m. It seems reasonable to define λ_m as a mean relaxation time for the polymer–solvent system at the conditions of interest[12-14]

$$\lambda_\mathrm{m} \doteq \int_0^\infty tG(t)\,\mathrm{d}t \Big/ \int_0^\infty G(t)\,\mathrm{d}t \quad (5)$$

where $G(t)$ is the shear relaxation modulus which appears in the theory of linear viscoelasticity. Utilization of $G(t)$ data provides a convenient way of characterizing the response of the polymer–solvent system to deformations. It is important to remember, however, that this definition for λ_m represents an average over the various relaxation mechanisms that the polymer–solvent system undergoes. Hence, although eq 5 may be an adequate definition for step-change sorption experiments since θ_D is also an average value, this definition is not satisfactory for an oscillatory experiment since a precise definition for θ_D is available for this case. Consequently, it seems appropriate to modify the definition of the diffusion Deborah number as given by eq 1 or 4 to more carefully portray the various relaxation mechanisms that characterize a typical polymer–solvent system.

A convenient way to focus on the relaxation behavior for polymer–solvent systems that may be pertinent to oscillatory diffusion experiments is to examine the frequency dependence of the shear storage modulus $G'(\omega)$ and the shear loss modulus $G''(\omega)$. Although these quantities give information on relaxation mechanisms in systems deformed by surface tractions, comparable molecular responses should be evident in systems where deformations are caused by concentration gradients. An example of the frequency dependence of G' and G'' is presented in Figure 1 for a narrow molecular weight distribution sample of pure PVAc at 60 °C. This diagram is based on data collected by Plazek[15] for a polymer sample with a weight-average molecular weight of 6.5×10^5. For high frequencies, $\omega > \omega_\mathrm{E}$, there is very little frequency dependence of G' over many decades of logarithmic frequency since negligible backbone configurational changes occur and the system behaves like an elastic solid. This frequency range represents the elastic diffusion region where it is supposed that the diffusion process is Fickian with a mutual diffusion coefficient D, which we shall denote as D_E. For very low frequencies, $\omega < \omega_\mathrm{V}$, the polymeric liquid behaves like a Newtonian liquid and G'' is directly proportional to ω.[16] In this region, the material behaves like a viscous liquid since all relaxation mechanisms are complete in a small

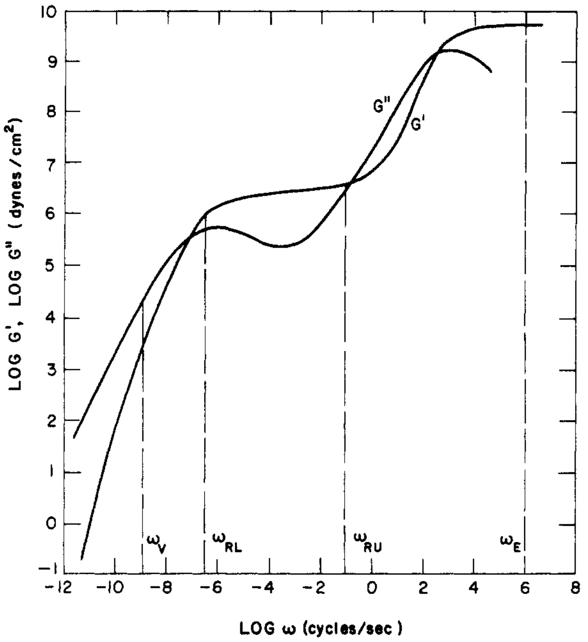

Figure 1. Frequency dependence of G' and G'' at 60 °C for PVAc sample studied by Plazek.[15] The frequencies ω_E, ω_{RU}, ω_{RL}, and ω_V are explained in the text.

fraction of the oscillation cycle. This is obviously the viscous diffusion region, which can be described by the classical Fickian theory with a mutual diffusion coefficient denoted as D_V. Finally, for an intermediate range of frequencies, $\omega_{RL} < \omega < \omega_{RU}$, $G'(\omega)$ changes slowly and the behavior of the polymeric system approximates that of an elastic material. Indeed, the presence of a plateau region where G' changes only slightly confers rubberlike elastic properties on the material over an intermediate-frequency range since the slow and fast relaxation processes have been effectively separated by the persistence of entanglements in the material. Although $G'(\omega)$ appears to be relatively flat on log–log plots (especially for high molecular weight samples with narrow molecular weight distributions), it should be remembered that the plateau region is not entirely devoid of relaxation processes. It certainly is possible, however, that these relaxations will prove to be inconsequential for diffusional transport and that the approach to rubberlike elastic behavior will lead to a third region for Fickian diffusion characterized by a mutual diffusion coefficient D_R.

If a diffusion Deborah number is now defined as

$$(\mathrm{DEB})_D = \omega/\omega_E \qquad (6)$$

then there will be elastic diffusion with $D = D_E$ for

$$(\mathrm{DEB})_D > 1 \qquad (7)$$

rubberlike elastic diffusion with $D = D_R$ for

$$\omega_{RL}/\omega_E < (\mathrm{DEB})_D < \omega_{RU}/\omega_E \qquad (8)$$

and viscous diffusion with $D = D_V$ for

$$(\mathrm{DEB})_D < \omega_V/\omega_E \qquad (9)$$

For all other values of $(\mathrm{DEB})_D$, nonclassical or viscoelastic diffusion processes would be expected, and these must be described by a theory that is presumably considerably more complex than the classical Fickian theory of diffusion. Since conformations in the polymer–solvent system can be quite different in the elastic, rubberlike, and viscous regions, there is no reason to expect that D_E, D_R, and D_V will be equal to each other at a given concentration and temperature. Finally, it is important to note that the above discussion is based on Figure 1, which represents the dynamic behavior of a narrow molecular weight distribution polymer sample of relatively high molecular weight in the absence of solvent. For a broad molecular weight distribution sample with a lower molecular weight, the plateau region is shorter and less flat. Also, the addition of solvent will modify the G' and G'' vs. ω curves; an important change will of course be the shift of these curves to higher frequencies with increasing solvent concentration.

The above discussion has been concerned with classification of the diffusion process inside the polymer film. In a sorption experiment, consideration must also be given to the possibility that the surface concentration of the film does not instantaneously achieve the equilibrium value consistent with the solvent pressure in the gas phase.[17] Consequently, it is possible that although the diffusion process in the bulk phase may be Fickian, the total mass-transport process does not exhibit classical behavior because of surface nonequilibrium effects.[13] Hence, a combination of an appropriate value of the diffusion Deborah number and of the attainment of instantaneous equilibrium at the phase boundary are needed to ensure that a mass-transfer process will exhibit classical behavior.

In this study, we shall conduct oscillatory experiments over a frequency range that will make it possible to measure D_V and D_R if both Fickian regions exist. The frequencies needed to measure D_E are, however, much higher than are possible when the present diffusion apparatus is used.

Experimental Section

Step-change sorption (both absorption and desorption) and oscillatory sorption experiments were carried out for the water–PVAc system at 90 °C and for the methanol–PVAc system at 60 °C. A step change in the surface concentration was effected by introducing a sudden increase or decrease in the solvent pressure in the gas phase above a polymer sample. For sufficiently small concentration amplitudes in an oscillatory experiment, the pressure–concentration relationship is approximately linear, so that a sinusoidal variation in the solvent pressure in the gas phase should produce a penetrant surface concentration for the polymer sample which is a sinusoidal function of time. These experiments were carried out by using a sorption balance controlled by a computer so that any desired pressure–time forcing function could be produced in the gas phase.

The experimental apparatus utilized in this study is similar to one described in an earlier investigation[9] with two important modifications. In the previous study, the sorption experiment was carried out by using a Cahn electrobalance. Since this unit has temperature and solvent restrictions, it was replaced in this investigation by a quartz spring sorption balance. The cylindrical sorption column was 1.2 m in length with an inside diameter of 10 cm, and it was surrounded by a jacket that was used to circulate heat-transfer fluid for control of the temperature of the experiment. Quartz springs and quartz buckets for the column were provided by Worden Quartz Products, Inc., and a cathetometer was used to measure spring extension. A second modification of the original apparatus was the introduction of a computer-controlled cooling system for the solvent boiler.

Samples of polymer were prepared directly in quartz buckets with a diameter of 1.7 cm by using a solvent-casting technique. The PVAc used in this study was a commercial sample with a weight-average molecular weight of 2.3×10^5. Additional details on the experimental apparatus and procedure are given elsewhere.[9,18] One important aspect of sorption measurements with quartz spring systems is the correction for buoyancy effects. The buoyancy effect can be accounted for in a straightforward manner for step-change experiments since the density of the gas phase is constant after the initial jump in pressure. For oscillatory experiments the buoyancy correction is a sine wave which is in phase with the pressure wave, and, hence, it is possible to account for buoyancy in a relatively simple manner in this case also. For the oscillatory experiments carried out in this study, the buoyancy correction was generally less than 3%.

The output from a step-change experiment is a weight pickup or weight loss vs. time t curve for different values of the initial thickness L of the polymer sample. For an absorption experiment these data can be converted to fractional uptake vs. $t^{1/2}/L$ curves for each polymer–solvent system at a given temperature and a specified concentration range. For a Fickian or classical sorption process, the sorption curves for all values of the film thickness L will form a single curve when plotted as fractional uptake vs. $t^{1/2}/L$. This property of Fickian diffusion processes can be used to test for the presence of non-Fickian behavior in the experimental data even when there is a significant concentration dependence of the mutual diffusion coefficient. If there is a negligible concentration dependence of the diffusivity over the concentration interval utilized in a step-change sorption experiment, a value of the mutal diffusion coefficient can be determined for the polymer–solvent system at each value of the sample thickness by using the half-time of the sorption curve.[2] If the diffusion process is Fickian for all values of L, the computed diffusivity should be independent of L since it is a material property of the system being examined. This test for Fickian behavior is of course equivalent to the one described above.

If the concentration dependence of the diffusivity cannot be ignored in the analysis of the step-change experiment, then it is still possible to determine a value of an average diffusivity for the polymer–solvent system at each value of L by again utilizing the half-time of the sorption curve.[2] This measured value of the average diffusion coefficient can then be used to obtain an estimate of the mutual diffusion coefficient at a single concentration in the concentration interval of the sorption experiment. It has been shown elsewhere[19] that the average diffusivity calculated by the initial gradient method of analyzing sorption experiments is approximately equal to the mutual diffusion coefficient at a concentration somewhere between the initial and final concentrations of the sorption experiment. The actual value of this concentration depends on whether the experiment is an absorption or desorption experiment and on whether the diffusivity increases or decreases with increasing solvent concentration. It is reasonable to expect that these results are approximately valid also for average diffusivities determined by using the half-time method. The above procedure is applicable for cases where the diffusivity changes by as much as a factor of 10 over the concentration range of the experiment.

The output from an oscillatory sorption experiment consists of a periodic sequence of sample weight vs. time curves. If there is a sinusoidal variation of the pressure in the gas phase with time, then the periodic variation of the sample weight will also be sinusoidal if the diffusion process is Fickian and if the diffusivity is independent of concentration.[9] The presence of a perfect sine wave for the sample weight–time data when there is a periodic steady state is a necessary condition for the existence of a Fickian diffusion process with a constant diffusivity. Furthermore, for this case, the mutual diffusion coefficient must be independent of frequency. The absence of a frequency dependence for the diffusivity provides a second test for the existence of a Fickian diffusion process with a constant diffusivity.

If the diffusion process is Fickian and if the diffusivity is essentially independent of concentration over the concentration range covered during an oscillation, then the mutual diffusion coefficient can be determined from the phase angle between the sine waves for the pressure and sample weight.[9] The phase angle can conveniently be calculated by appropriate integration of the periodic steady-state data for the pressure and sample weight over a complete cycle. If the variation of the diffusion coefficient over the concentration interval experienced by the sample during the pressure oscillation cannot be ignored, then it is not in general possible to carry out an analysis of the oscillatory output data comparable to that for a constant diffusivity experiment since an analytical solution for the concentration field is not available. However, it has been shown elsewhere[9] that for moderate variations in the diffusivity the oscillatory data are not greatly affected by the concentration dependence of the diffusion coefficient. In such cases, it is still possible to obtain an excellent estimate of the mutual diffusion coefficient at the average concentration in the polymer film by analyzing the periodic steady-state data using the analytical solution for constant diffusivity. Finally, an apparent diffusivity can be calculated in this manner even if the mass-transfer process is non-Fickian, but this quantity will not generally be a meaningful material property of the polymer–solvent system.

Table I
Step-Change Sorption Experiments for PVAc–Solvent Systems

solv	temp, °C	initial solv wt fractn	final solv wt fractn	sample thickness, cm
water	90	0	0.00695	0.0717
	90	0	0.00695	0.186
	90	0	0.00695	0.341
	90	0.00695	0	0.0717
	90	0.00695	0	0.186
	90	0.00695	0	0.341
methanol	60	0.0393	0.0528	0.0139
	60	0.0393	0.0528	0.0469

Table II
Oscillatory Sorption Experiments for PVAc–Solvent Systems

solv	temp, °C	av solv mass fractn	ampl of osciln, solv mass fractn	freq × 10^4, cycle/s
water	90	0.00695	0.00321	0.0868
				0.174
				0.347
				0.694
				1.39
				2.78
				5.56
methanol	60	0.0485	0.0108	0.174
				0.347
				0.694
				1.39
				2.78
				5.56

The water–PVAc system was used in this investigation because it appears that the concentration dependence of the mutual diffusion coefficient near the pure polymer limit is negligible,[20] so that a single value of the diffusivity is sufficient to describe the mass-transfer process for the complete concentration range considered in this study. This of course leads to an unambiguous analysis of the step-change and oscillatory sorption experiments. For the methanol–PVAc system, the concentration dependence of the diffusivity at 60 °C is significant.[21] Even though the amplitude of the oscillatory experiment for this system was kept as small as was consistent with the collection of accurate data, there still was a ±30% variation of the diffusivity about its value at the average film concentration. However, for this diffusivity variation, an excellent estimate of the diffusivity at the average concentration can be determined by using the constant diffusivity analysis. For the step-change experiments, there was a 60% variation of the diffusivity over the concentration interval of the experiments. However, as noted above, the average diffusivity computed from such experiments can be used to estimate the mutual diffusion coefficient at an intermediate concentration, and this can be compared with the value derived from the oscillatory experiment.

Results and Discussion

The step-change and oscillatory sorption experiments carried out in this investigation are summarized in Tables I and II. Reduced sorption curves for the step-change absorption experiments for the two polymer–solvent systems are presented in Figures 2 and 3. Two values of sample thickness were used for the methanol–PVAc system and three for the water–PVAc system. These figures show that all data essentially form a single curve when plotted as fractional uptake vs. $t^{1/2}/L$, so that the diffusion process for the step-change absorption experiments is Fickian for both polymer–solvent systems. The value of the mutual diffusion coefficient D determined from the sorption curve

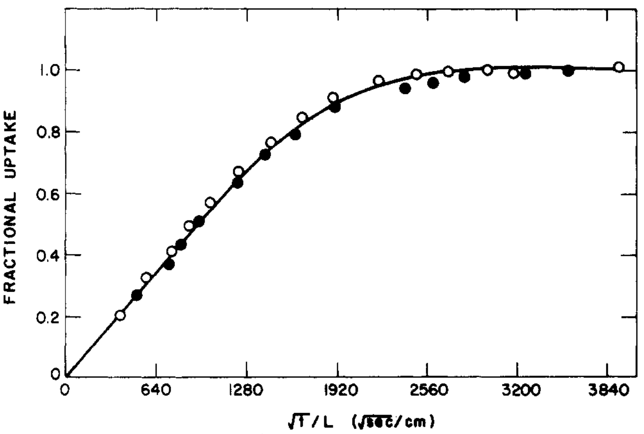

Figure 2. Reduced sorption curve for methanol–PVAc system at 60 °C for two values of the sample thickness L: (●) L = 0.0139 cm; (○) L = 0.0469 cm. The solid line is the theoretical result for Fickian diffusion with $D = 2.2 \times 10^{-7}$ cm^2/s.

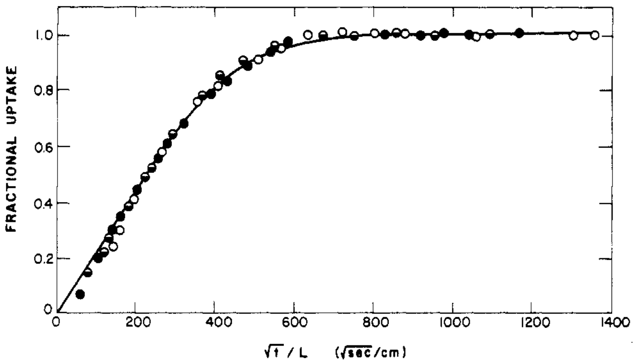

Figure 3. Reduced sorption curve for water–PVAc system at 90 °C for three values of the sample thickness L: (○) L = 0.0717 cm; (◒) L = 0.186 cm; (●) L = 0.341 cm. The solid line is the theoretical result for Fickian diffusion with $D = 3.84 \times 10^{-6}$ cm^2/s.

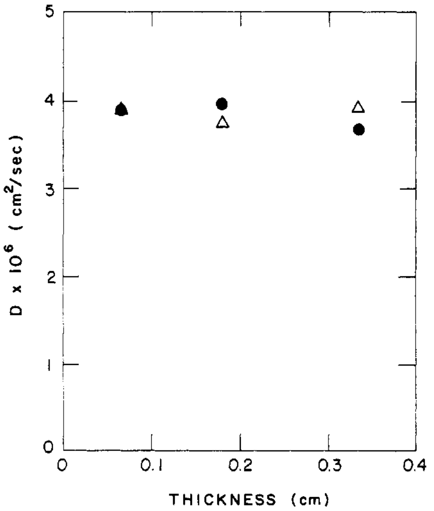

Figure 4. Dependence of D for water–PVAc system on sample thickness at 90 °C: (△) absorption; (●) desorption.

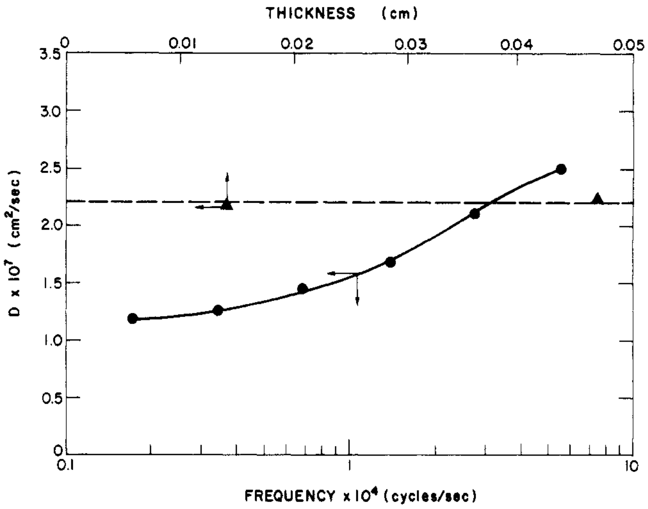

Figure 5. Dependence of D for methanol–PVAc system at 60 °C on sample thickness for step-change experiments and on frequency for oscillatory experiments: (▲) step-change sorption experiments; (●) oscillatory sorption experiments. The dotted line represents the average diffusivity of the step-change experiments, and the solid line is a visual aid.

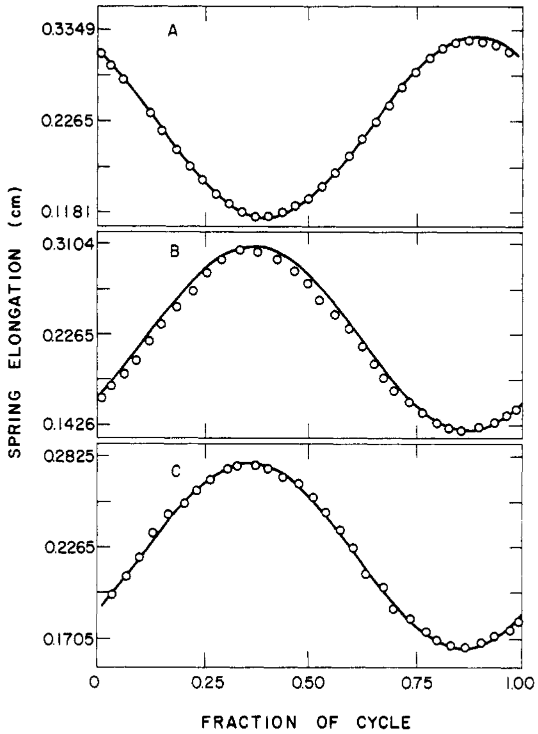

Figure 6. Spring elongation–time curves for water–PVAc system at 90 °C for three frequencies: (A) 32-h cycle time; (B) 4-h cycle time; (C) 0.5-h cycle time. The solid lines represent sine waves.

at each value of the initial sample thickness L is presented in Figure 4 for the water–PVAc system. Within experimental error, the diffusivity D evaluated from step-change absorption experiments appears to be independent of L for nearly a 5-fold change in the sample thickness. Also, values of D determined from step-change desorption experiments are effectively independent of L. Furthermore, as is evident from Figure 4, the diffusivities determined from desorption and absorption experiments are essentially the same. These results are further evidence of the presence of Fickian behavior for this system.

The average diffusivities for the methanol–PVAc system for two values of L are presented in Figure 5. It is evident that the average diffusivity is essentially independent of L for more than a 3-fold change in L. This average diffusivity, which was determined from a step-change absorption experiment ranging from 0.0393 to 0.0528 weight fraction methanol, is approximately equal to the mutual diffusion coefficient at a methanol weight fraction of 0.0488.[19] It appears fair to conclude, from the above evidence, that the step-change sorption experiments for both polymer–solvent systems studied follow the classical theory of diffusion and provide a value of the Fickian diffusion coefficient for a concentration or concentration range near the pure polymer limit.

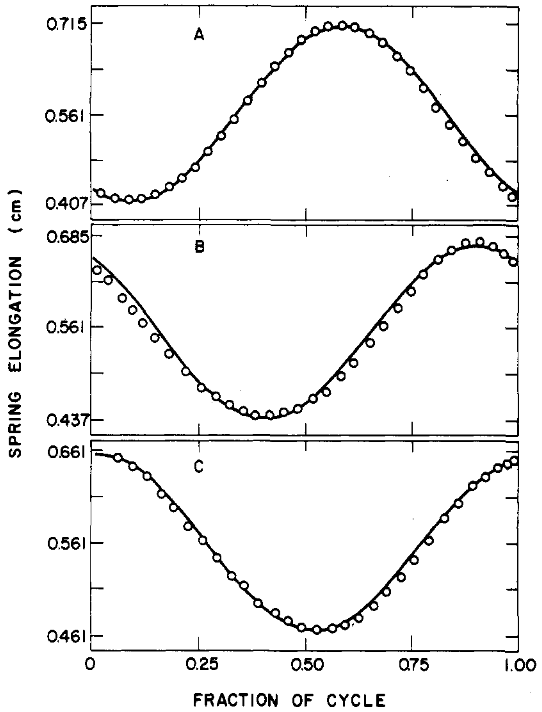

Figure 7. Spring elongation–time curves for methanol–PVAc system at 60 °C for three frequencies: (A) 16-h cycle time; (B) 1-h cycle time; (C) 0.5-h cycle time. The solid lines represent sine waves.

Spring elongation vs. time data are presented for both polymer–solvent systems in Figures 6 and 7. Since the curves in these figures are of course equivalent to sample weight–time curves, a necessary condition for the existence of Fickian diffusion behavior with a constant diffusivity is the presence of a perfect sine wave for the output data for the oscillatory experiment. From Figure 6, it is evident that excellent sine waves are obtained for the shortest (0.5 h) and longest (32 h) cycle times for the water–PVAc system, but there is a definite departure from Fickian behavior at an intermediate frequency (4-h cycle time). Furthermore, even though the diffusivity for the methanol–PVAc system is not effectively constant as it is for the water–PVAc system, similar behavior is observed for this system since the moderate concentration dependence of D appears to have a small influence on the oscillatory data. As is evident from Figure 7, there is again Fickian behavior at the lowest and highest frequencies and nonclassical behavior at an intermediate frequency. Also, as noted above, a second necessary condition for the existence of Fickian behavior with a constant diffusivity is the absence of a frequency dependence for D. Examination of Figures 5 and 8 shows that there are indications that the diffusivity is essentially becoming independent of frequency at low and high frequencies, and it increases by a factor of about 2 as the frequency is increased from the low- to high-frequency Fickian regions. There thus appear to be at least two Fickian regions for polymer–solvent diffusion that can be observed by varying the time scale of the experiment at fixed temperature, concentration, and polymer molecular weight. For both polymer–solvent systems investigated, the high-frequency Fickian region is observed at frequencies about 100 times higher than the frequencies at which the low-frequency Fickian region is found experimentally.

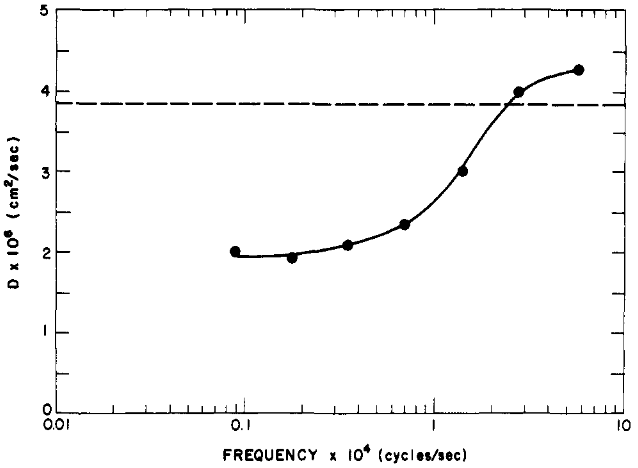

Figure 8. Dependence of D for water–PVAc system at 90 °C on frequency for oscillatory experiments: (●) experimental oscillatory data. The dotted line represents the average diffusivity of the step-change experiments, and the solid line is a visual aid.

Since rheological data were not collected for the two polymer–solvent systems actually studied in the diffusion experiments, it is not possible to construct a diagram similar to Figure 1 and to thus calculate appropriate values of the Deborah number for these systems at the conditions of the experiment. However, approximate Deborah number calculations indicate that the low-frequency region is the viscous diffusion region with the Fickian diffusion process described by a diffusivity D_V, and the high-frequency region is the rubberlike elastic region with a Fickian diffusion process described by a diffusivity D_R. For the two systems studied here, $D_R \approx 2D_V$ at the same temperature, concentration, and polymer molecular weight. Also for both systems studied, $\omega_{RL}/\omega_V \approx 100$. This value is comparable to the data in Figure 1 where $\omega_{RL}/\omega_V \approx 300$. Since both the data in Figure 1 and the diffusivity data for the methanol–PVAc system are representative of transport behavior at 60 °C, a comparison of the corresponding ω_V values is of some interest. The ω_V value for diffusion in the polymer–solvent system is significantly higher than that for the rheological response of the pure polymer, presumably because the presence of solvent has shifted the molecular response to higher frequencies. Any direct comparison of the data in Figure 1 with the present diffusion data is not possible since the polymer sample used to collect the data presented in this figure is significantly different than that used in the diffusion experiments. Plazek[15] used a narrow distribution sample of pure polymer with a weight-average molecular weight of 6.5×10^5, whereas the data here were collected on a broad distribution sample with a molecular weight of 2.3×10^5 in the presence of solvent. Finally, we note that the values of D reported in Figures 5 and 8 for the intermediate-frequency range are not meaningful diffusion coefficients since they were computed by using classical diffusion theory under conditions when there presumably is viscoelastic diffusion.

It is of some interest to compare the mutual diffusion coefficients determined from the step-change sorption experiments with the two Fickian diffusion coefficients measured by using the oscillatory experiment. For the water–PVAc system the mutual diffusion coefficient is effectively independent of concentration for the concentration interval utilized in the present experiments. From Figure 8, it is evident that the diffusivity computed by averaging the results of six absorption and desorption experiments is approxiamtely 10% less than the D_R value determined from the oscillatory experiment. Although the concentration dependence of the diffusivity for the methanol–PVAc system cannot be ignored, the diffusivities determined from the oscillatory and step-change experiments can be directly compared since they are essentially at the same value of the methanol concentration (0.0485 weight fraction methanol for the oscillatory experiment and 0.0488 weight fraction methanol for the step-change experiment). It is evident from Figure 5 that the diffusivity determined from the step-change experiments is approximately 10% less than the diffusivity determined for the high-frequency Fickian region. Consequently, for both systems studied here, the step-change experiment is Fickian with a diffusion coefficient characteristic of rubberlike elastic behavior. As noted previously, it is not possible to accurately characterize a step-change sorption experiment with a single value of the diffusion Deborah number. However, it appears that the small values of charateristic times for particles near the polymer–gas interface lead to relatively high values of the Deborah number for these particles and hence tend to lead to rubberlike elastic diffusion rather than to viscous diffusion for the step-change experiment.

The results of the present experiments are similar in some respects to the results obtained by Adam and Delsanti[10,11] using light-scattering experiments. These investigators used a quasi-elastic light-scattering technique to measure mutual diffusion coefficients for semidilute polystyrene solutions. For good solvent solutions (benzene–polystyrene) they found that the mutual diffusion coefficient measured in a gel regime was approximately 10% larger than that measured in a so-called liquid regime. The gel regime presumably corresponds to the rubberlike elastic Fickian diffusion region studied here, whereas the liquid regime is equivalent to the purely viscous Fickian diffusion region identified in this study. However, for polymer diffusion in a Θ solvent (cyclohexane–polystyrene at 35 °C), the diffusivity in the gel regime was significantly larger (as much as more than twice as large) than that measured in the liquid regime. Adam and Delsanti were able to go from the liquid to the gel regime for a sample with fixed temperature, concentration, and polymer molecular weight by varying the momentum transfer. This is similar to the variation of oscillation frequency in the present experiments. Adam and Delsanti studied semidilute solutions and found substantial differences in liquid and gel diffusivities only for Θ solvent conditions. In this investigation, we have studied very concentrated polymer solutions. It is generally accepted that polymer molecules assume their unperturbed dimensions as the polymer concentration increases so that the 2-fold difference in D_R and D_V values found in this study is consistent with the diffusivity variations reported by Adam and Delsanti for semidilute Θ solutions.

The objective of this paper has been to identify different regions of Fickian diffusion for polymer–solvent systems. The water–PVAc diffusion data presented in Figures 6 and 8 can be regarded as strong evidence for the existence of both low- and high-frequency Fickian regions. This conclusion is supported by the methanol–PVAc data presented in Figure 7 since the data for the shortest and longest cycle times are reasonably good approximations to a sine wave, whereas the data for an intermediate frequency definitely are not. Furthermore, the data in Figure 5 clearly indicate the existence of a low-frequency Fickian region because there is a definite leveling of the diffusivity with frequency in the low-frequency region. However, the evidence for the leveling of the diffusivity with frequency is clearly much weaker in the high-frequency region. More definitive evidence of this leveling could be obtained by collecting data at still higher frequencies, but it was not possible to do this with the present diffusion apparatus. However, the remainder of the evidence for the existence of two Fickian regions is reasonably strong, and observed deviations from Fickian behavior, such as those depicted in Figures 6 and 7, cannot be attributed to experimental error.

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