Incremental Vapor Sorption in a Phase-Segregated Polyurethane Elastomer

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Synopsis

Incremental vapor sorption and desorption runs have been carried out with o-dichlorobenzene (ODCB) a strongly swelling solvent, in 2, 6, and 10 mil polyether polyurethane films. Two-stage sorption behavior occurs at intermediate and higher concentrations but is generally absent in the desorption runs. Analysis of the two-stage curves, using the Berens–Hopfenberg model of independent Fickian diffusion and first-order relaxation processes, leads to apparent diffusion coefficients which increase with thickness and show a pronounced maximum with concentration, whereas the relaxation rate constant decreases with concentration. Correction for the pressure drift during the runs, due to the low vapor pressure of ODCB, reduces the thickness dependence. The negative concentration dependence of the relaxation rate constant is related to the distribution of microdomain stabilities. Calculated values of the self-diffusion coefficient show that the maximum in the apparent diffusion constant with concentration can be accounted for largely, but not entirely, by the thermodynamic contributions. It is proposed that the additional factor is relaxation-controlled swelling which arises from the strong coupling between the matrix and hard-segment responses.

INTRODUCTION

The segmented polyurethane elastomers are heterophase polymers containing glassy or semicrystalline microdomains dispersed in a rubbery matrix. A large body of work has shown that the properties of these materials are the direct consequence of the phase-segregated structure and are dependent on the details of the microdomain morphology. However, the influence of the heterophase structure on small molecule transport behavior has received only limited attention. Most of the reported work, with the exception of water as permeant, has involved studies of gas diffusion. Ziegel,[1] in a study using a gas flow method, observed two-step transient behavior with the larger gas molecule penetrants, Ar and N_2. Although this indicated some influence of the heterophase structure on the diffusion behavior, a qualitative model was not successful in classifying the origin of the effect. McBride et al.[2] studied gas diffusion as a function of temperature in several polyurethanes. They noted a discontinuity in the Arrhenius plots, similar in certain respects to the behavior reported by Odani et al.[3] in a styrene-butadiene-styrene (SBS) block

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copolymer. The effect was correlated with the onset of the glass transition temperature in the hard segment domains.

Studies of solvent diffusion in a heterophase polymer have been reported by Odani et al.[4] and later by Chiang and Sefton.[5] They investigated the diffusion of n-hexane in SBS block copolymers and observed non-Fickian behavior both in the lack of superposition of sorption curves for samples of different thicknesses when plotted as a function of $(t/l^2)^{1/2}$, where t is the time and l the thickness, and in the anomalous shape of some sorption curves. The behavior was attributed to solvent-induced relaxation in the interfacial region between the polybutadiene matrix and polystyrene domains. Similar effects might be produced in polyurethanes with a solvent capable of interacting with the hard segment, as well as with the soft segment regions.

The sorption and desorption of heptane and the immersion sorption behavior of a series of chloroalkane liquids in a diphenyl methyl diisocyanate-based polyether polyurethane were reported in a previous paper.[6] The behavior of heptane, which is sorbed to a limited extent, appeared nominally Fickian. The sorption rate was generally much faster then desorption, which was also true with the chloroalkane liquids in keeping with Fickian behavior. Various non-Fickian anomalies were observed in the chloroalkane studies, the most striking being the "S"-shaped appearance of the desorption curves. Solubility parameter calculations suggested that the different chloroalkanes could interact in varying degrees with the hard-segment as well as the soft-segment phase. However, it was not possible to explain the specific effects which occurred. The purpose of the present work is to examine the detailed sorption and diffusion behavior of a highly swelling solvent in the same polyurethane sample. In this work the sorption process is measured over limited concentration intervals using the incremental vapor sorption method. It was hoped that the results would give a clearer picture of the behavior which occurs as a function of concentration leading to some definition of the contributing processes.

EXPERIMENTAL

The sample used in this study was an Estane polyurethane manufactured by B. F. Goodrich. The soft segment consists of a 1000 molecular weight poly(tetramethylene oxide) (PTMO), and the urethane segment was prepared from 4,4'-diphenyl methyl diisocyanate (MDI) extended with butanediol (BD). The molar composition is MDI/BD/PTMO = 2 : 1 : 1, which corresponds to approximately 38 wt.% urethane hard segment. The composition of this sample was incorrectly reported as MDI/BD/PTMO = 3 : 2 : 1 in the prior publication. Film samples were prepared by casting on a glass plate from a 20% solution in tetrahydrofuran and were brought to dryness in a vacuum oven at 50°C to complete solvent removal.

Incremental sorption measurements were carried out in a vacuum system using a thermostated quartz spring balance with a sensitivity (in milligrams/millimeter) appropriate to the sample weight. Sample films of 2, 6, and 10 mil thickness were used with dimensions of approximately 1 in.^{2} to eliminate any error resulting from edge effects. The displacement of the spring was determined within 0.02 mm using a Gaertner cathetometer. Sorption and

desorption experiments were conducted at 24°C using *o*-dichlorobenzene (ODCB) which has a saturation vapor pressure $p_o = 1.4$ mmHg at this temperature. Beginning with the dry film sample, the procedure involved equilibrating the film with solvent at some vapor activity (p_i/p_o), exposing the film to a step change in activity [$(p_f - p_i)/p_o)$] and recording the weight change as a function of time until equilibrium corresponding to this new activity was achieved. The procedure was repeated in activity increments of about 0.1 until the full range was covered. Because of the slow approach to equilibrium in the initial sorption cycle, each such determination usually required 1 day or more. After completing the set of sorption measurements, the procedure was reversed and desorption experiments were performed beginning with the film equilibrated at high activity. Once again, the full activity range was traversed by exposing the film to step decreases in activity and recording the weight loss as a function of time.

RESULTS

Comparison of Heptane and *o*-Dichlorobenzene Sorption Behavior

Sorption studies were reported previously[6] for heptane in the same Estane sample. Heptane, a nonpolar solvent, shows an equilibrium uptake of only 8 wt.% in liquid immersion experiments. The sorption and desorption time behavior are both Fickian in appearance (see the section on analysis), and the sorption curve lies somewhat above the desorption curve, suggesting some positive dependence of the diffusion coefficient D on concentration. Incremental sorption experiments show that the sorption isotherm, relating vapor activity to sorbed concentration, is slightly concave upward. The incremental sorption-time curves were Fickian in shape, and D showed a moderate but linear increase with concentration from 3×10^{-8} cm²/s at $C = 0$ to 12×10^{-8} cm²/s at $C = 6$ wt.% for measurements at 35°C.

In comparison, ODCB is a strong solvent for the Estane sample, with an immersion uptake of 230 wt.%. The sorption isotherm for ODCB, determined by incremental sorption and desorption experiments on the three film thicknesses, is contrasted with that for heptane in Figure 1. The ODCB isotherm shows an initial linear region and then curves sharply upward in a manner typical of a swelling solvent. Departure from the linear Henry's law regime occurs at a concentration of about 20 wt.%. The value extrapolated visually to unit activity is consistent with 230 wt.% immersion uptake. It was shown previously, on the basis of estimated solubility parameters used in conjunction with the Flory–Huggins relation, that ODCB should be a strong solvent for the dispersed hard-segment phase as well as the soft segment matrix.[6] The dramatic increase in the sorption isotherm at high activities can probably be attributed to some swelling in the hard-segment phase, which is absent with heptane. It will be seen in the following discussion that this interaction with the hard-segment phase also has a profound affect on the diffusion behavior.

Sorption and Desorption Time Behavior

At ODCB concentrations in the Henry's law solubility region, all of the sorption-time curves generally appear Fickian, as illustrated by the results for
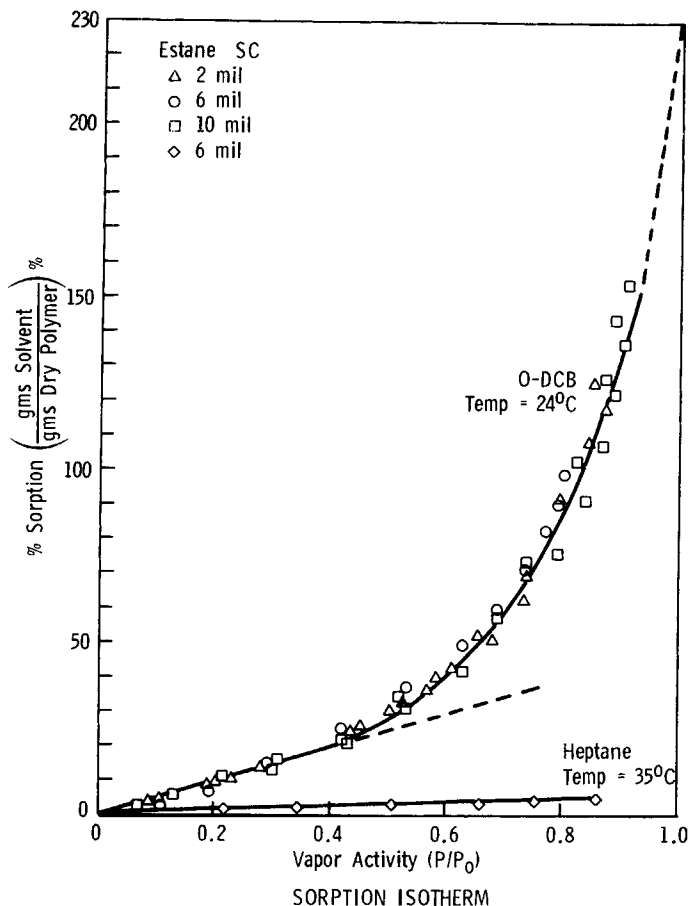
Fig. 1.   Comparison of sorption isotherms for orthodichlorobenzene and heptane.

the 6 mil film in Figure 2. The diffusion coefficient, determined from the sorption curve, when used in the series solution to Fick's law, provides a very close approximation to the experimental data, as illustrated in Figure 2 where the solid curve represents the theoretical calculation. The calculated D values at low concentrations are in the same range as those determined at corresponding heptane concentrations, reported earlier, and display an almost linear increase with concentration (see Fig. 6). However, there are some indications that the behavior is not strictly Fickian. The sorption time for the 2 mil film falls distinctly below that of the 6 and 10 mil films, which are in good agreement. On desorption, curves for the three thicknesses (not shown) almost superimpose, differing only in that the 2 mil film shows a slightly more gradual approach to equilibrium. Another anomaly is that the desorption curves lie slightly above the sorption curves as illustrated in Figure 2. This is the reverse of the behavior expected when D is an increasing function of concentration.

At concentrations above the Henry's law region, the sorption curves are no longer Fickian in shape, as illustrated by the 2 mil film results shown in the
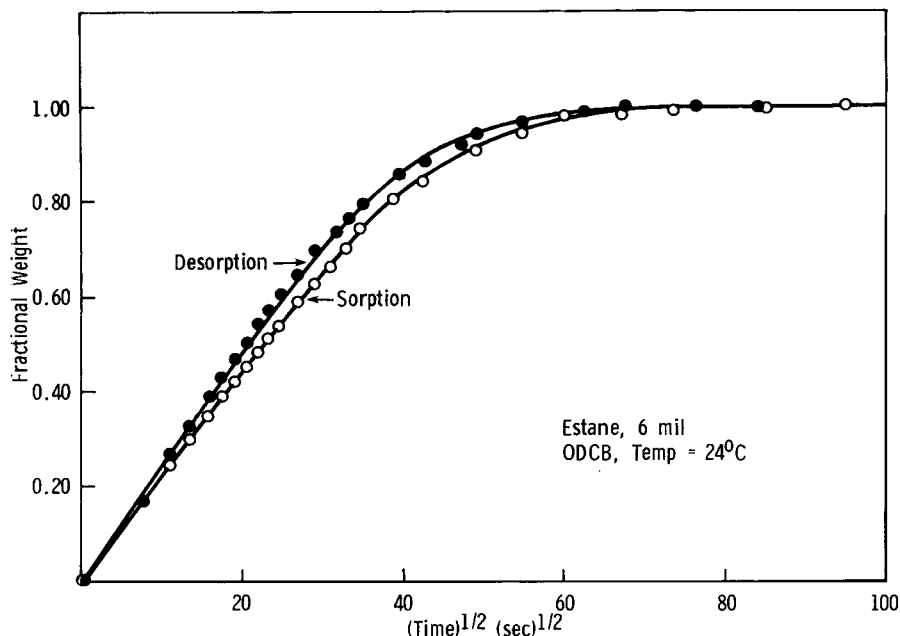
Fig. 2. Sorption and desorption curves at low orthodichlorobenzene concentration in a 6 mil film.

lower curve of Figure 3. All of the sorption curves display an initial steeply sloped region followed by a second nearly linear region of reduced slope which levels off to the final equilibrium. The upper curve in Figure 3 depicts the 2 mil desorption results which are typical for all of the concentration intervals measured. Initially, desorption occurs more rapidly than sorption and shows a small, residual weight loss at later times. In this concentration range, similar anomalies in the sorption behavior are observed in the 6 and 10 mil films, as illustrated in the comparison curves, Figure 4, plotted on a reduced time basis. The severity of the second-stage behavior decreases with increasing sample thickness. However, the sorption curve, even for the 10 mil film, is somewhat non-Fickian, as would be evident in a comparison with the desorption curve, which approaches equilibrium more rapidly and lies above the sorption curve. These anomalies are clear evidence of solvent interaction with the hard-segment phase, which does not occur at lower ODCB concentrations or with heptane.

The contribution of the second-stage behavior at each thickness becomes more pronounced with increasing concentration but is always less apparent in the 10 mil than in the 2 mil film. However, the 6 mil sorption behavior shows an unexpectedly large second stage compared with the 2 mil film in the same concentration range. At concentrations greater than 75 wt.%, more than 40% of the uptake in the 6 mil film occurs during the second stage compared with 25% in the 2 mil film. Even at these concentrations the desorption curves for the 6 mil film remain Fickian in shape, although desorption is more rapid than sorption. In general, the pronounced two-stage curve, typical of many sorption runs, was absent in the desorption results at the various thicknesses.
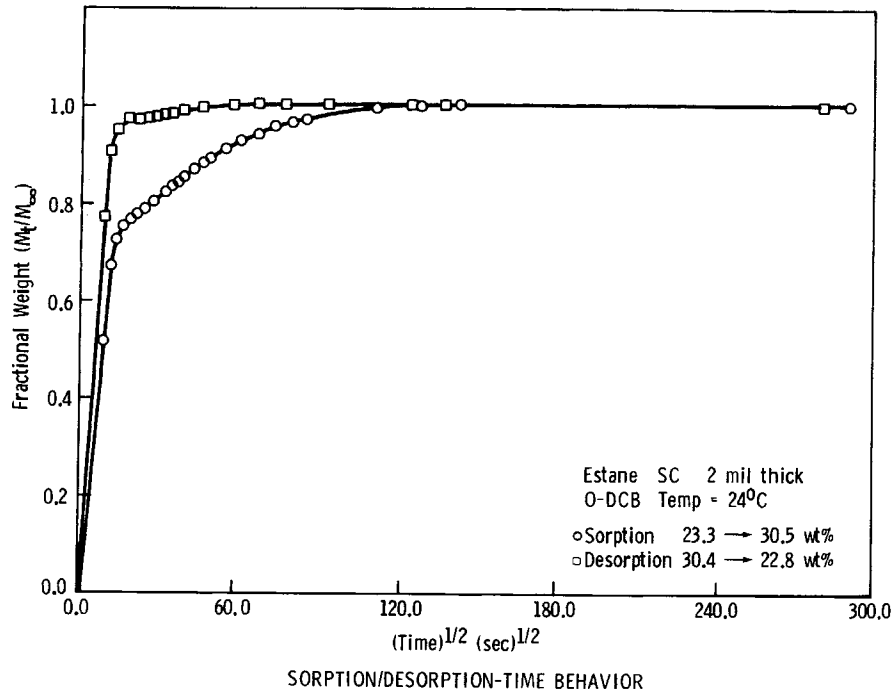
SORPTION/DESORPTION-TIME BEHAVIOR

Fig. 3. Sorption and desorption curves at intermediate orthodichlorobenzene concentration in a 2 mil film.
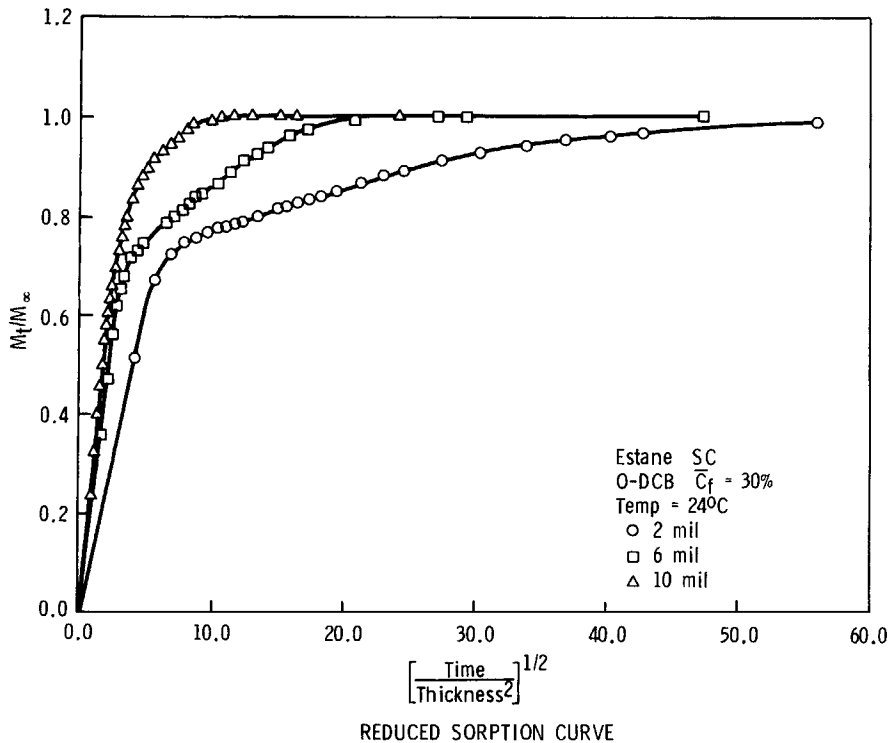

REDUCED SORPTION CURVE

Fig. 4. Comparison of sorption curves at intermediate orthodichlorobenzene concentrations for three film thicknesses.

Analysis of Sorption Time Behavior

It is well established that the diffusion of organic vapors into polymers well above the glass transition temperature generally obeys Fick's law.[7] Some features of Fickian diffusion, detailed in Crank,[8] which are relevant in comparisons with the current data are as follows: a linear curve for the initial 60% of the weight change in sorption or desorption when plotted against the square root of time; sorption curves for different thicknesses, l, which superimpose when plotted as fractional weight gain M_t/M_o against $(t/l^2)^{1/2}$; sorption and desorption curves which coincide for constant D; a sorption curve which lies above the desorption curve for D increasing with C, as commonly observed with organic solvents. For Fickian diffusion, with D constant, the value can be calculated from the initial slope m of a plot of M_t/M_∞ versus $t^{1/2}$ by the relation

$$D = \frac{\pi m^2 l^2}{16} \qquad (1)$$

where l is always the original thickness. This relation can be applied to incremental vapor sorption data, with a concentration dependent diffusion coefficient, by the procedure of Duda et al., where D is plotted at a specified concentration in the interval.[9] In the present work, all results are plotted against the final concentration in the interval, since use of the corrected concentrations produced only a slight shift in the results. A more detailed consideration of the treatment of the diffusion coefficient from the incremental sorption experiment is given in a later section.

As detailed in the preceding section, the sorption behavior with ODCB exhibits various departures from the requirements of Fickian behavior specified above. In the low concentration region, this is limited to a reversal in the expected rates of sorption and desorption. At higher concentration, there is the emergence of an increasingly pronounced two-stage sorption behavior, which is uncommon in an elastomeric material. Formally, the distinct two-stage sorption curves characteristic of the 2 and 6 mil films at the higher ODCB concentrations resemble the behavior reported by Berens and Hopfenberg[10] for diffusion in glassy poly(vinyl chloride) and polystyrene microspheres. They treated the behavior phemonenologically as the sum of independent Fickian and relaxation processes:

$$M(t) = M_F(t) + M_R(t) \qquad (2)$$

where $M(t)$ is the total weight change, $M_F(t)$ is the Fickian contribution, and $M_R(t)$ is the relaxation controlled contribution, described simply by a first-order rate equation:

$$M_R(t) = M_R(\infty)\left[1 - \exp(-k_R t)\right] \qquad (3)$$

Here k_R is the relaxation rate constant, which should be a material property and, therefore, independent of changes in sample dimension. A dimensionally

similar rate constant k_F for the Fickian process in eq. (2) can be defined by

$$k_F = \frac{\pi^2 D}{l^2} \tag{4}$$

and used to characterize the rate of diffusion. It should be noted that the characteristic appearance of the sorption curve will vary with the sample thickness, which affects k_F but not k_R. Because of the very low solvent diffusion coefficient in polystyrene, in order to observe two-stage behavior, Berens and Hopfenberg were compelled to work with submicron diameter spheres. This increased the diffusion rate relative to the rate of polymer relaxation so that sorption was no longer totally controlled by diffusion. In the present work, it appears most likely that the two-stage behavior results from solvent-induced relaxation of the glassy microdomains of the poly-urethane sample. The results of Figure 4, which show a decrease in the relaxation contribution with increasing film thickness, are in accordance with a reduction in k_F, the rate constant for diffusion, which allows more time for the relaxation process to occur.

A simple curve-fitting method was used to resolve the parameters which describe the two-stage behavior according to eqs. (2) and (3). If k_R is much smaller than k_F, the long time behavior is determined by the relaxation process. Equation (2) when plotted in the form

$$\ln[M(\infty) - M(t)] = -k_R t + \ln[M_R(\infty)] \tag{5}$$
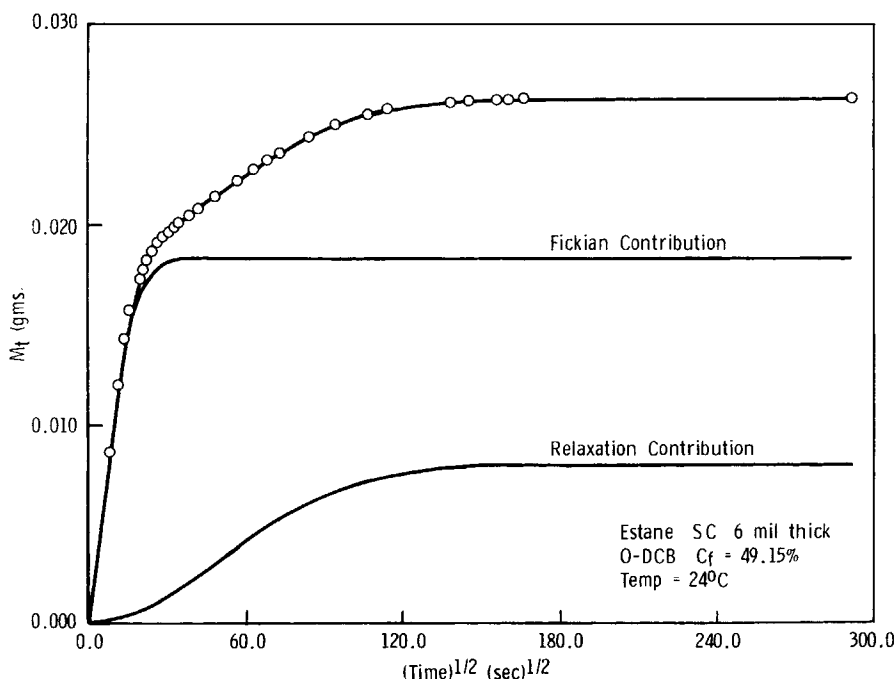

Fig. 5. Two-stage sorption behavior in a 6 mil film at intermediate orthodichlorobenzene concentration; resolution into Fickian and relaxation contributions.

reaches a straight line asymptote from which k_R and $M_R(\infty)$ are determined by a least-squares fit. These values can then be used in a similar asymptotic plot, based on the first series term in the Fick's law series solution:

$$\ln[M(\infty) - M_R(\infty)\exp(-k_R t) - M(t)] = -k_F t + \ln[8M_F(\infty)/\pi^2] \quad (6)$$

to obtain the Fickian parameters k_F and $M_F(\infty)$. Weight uptakes calculated using these four parameters and eq. (2) can produce an excellent fit to the data as shown in Figure 5 for the 6 mil film. Most of the uptake is attributed by the analysis to the diffusion process, as expected from the shape of the curve. However, when applied to an apparently Fickian curve, this method also interprets the approach to equilibrium as a relaxation process and delivers an erroneously high estimate for the relaxation contribution while still producing an excellent fit. A nonlinear, least-squares procedure was developed in an attempt to eliminate this problem. Although this procedure was not any more successful for curves in which the two stages were not well defined, it continued to be used since it sometimes provided an improved fit to curves with two-stage behavior.

Concentration Dependence of the Diffusion Coefficient

The diffusion coefficient, although assumed constant over each increment, is a strong function of concentration when considered over the full range of the sorption experiment. Apparent diffusion coefficients were calculated for each of the sorption and desorption steps on the three film samples. For Fickian curves, the initial slope method, eq. (1), was used. For curves displaying two-stage sorption behavior, the independent diffusion and relaxation contributions were first determined and then the initial-slope analysis was applied to the Fickian portion.

Values of D for the 2, 6, and 10 mil films obtained in desorption, directly from the initial slope of the essentially Fickian curves, are shown in Figure 6. In each case D initially increases with concentration, reaches a maximum, and then drops off with further increases in concentration. At the highest concentrations, where the films contain over 100% ODCB (g solvent/100 g polymer), D values drop off to levels which approach the values measured at low penetrant concentrations. The curves for the sorption results are generally similar, except that there is more scatter in the data. These curves of diffusion constant versus concentration are anomalous in two major respects: the pronounced maximum in D versus C and the strong thickness dependence of D at the various concentrations.

The apparently marked thickness dependence of D is largely an artifact of the low ODCB vapor pressure ($p_o = 1.4$ mm at 24°C) and the high solubility of this solvent in the polyurethane sample. Thus, even working with an 8 L system volume, there is considerable drift in vapor pressure during the run. The analysis of sorption from a limited source is given as a series solution in Crank[8] for concentration-independent solubility and diffusion coefficients. An approximate method of correcting results was derived, based on the early-time approximation to this solution:
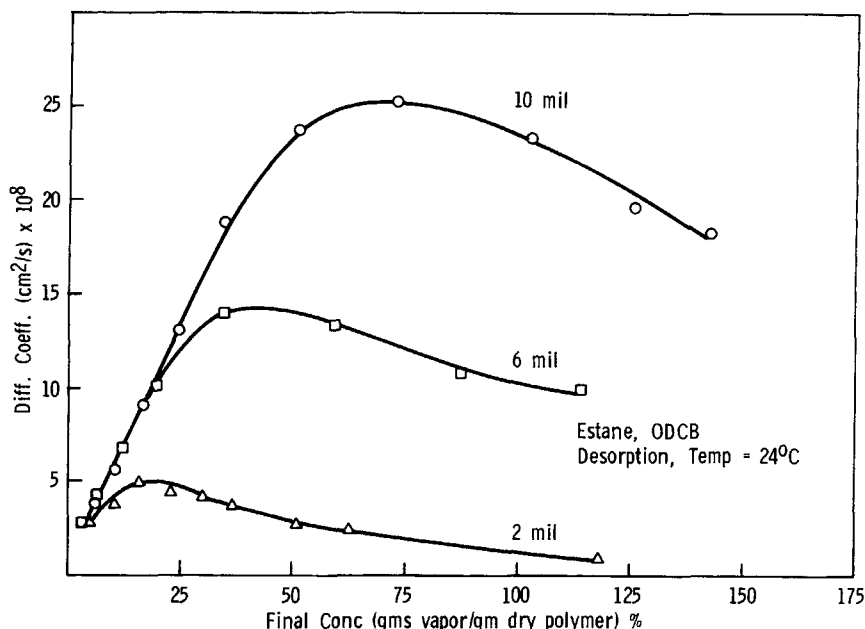
$$D = D_{APP}(1 - F_s)^2 \quad (7)$$

Fig. 6. Curves showing apparent diffusion coefficient versus concentration determined in incremental desorption runs for three film thicknesses.

Here D is the true diffusion coefficient, and D_{APP} is the apparent diffusion coefficient obtained from the initial slope of the sorption curve when a fraction F_s of the solute is sorbed. In the incremental sorption experiments, F_s was calculated as the ratio of the drop in pressure during the run ($p_2 - p_\infty$) and the initial set pressure increment ($p_2 - p_1$). In a similar manner, diffusion coefficients from desorption runs were corrected by calculating the fraction of the solute released as the ratio of the increase in pressure ($p_\infty - p_2$) during the run and the set incremental reduction in pressure ($p_1 - p_2$). There was good agreement between the actual weight changes and the values calculated from the pressure drift over most of the range of measurements, except at the highest concentrations. No meaningful values of F_s could be obtained for the data in this regime, and these few data points at the highest concentrations were not used.

Corrected diffusion coefficient data from the desorption runs are shown in Figure 7. The effect of the correction is to reduce the magnitude of the previously derived data of Figure 6. The change is larger with greater film thickness since the weight of the sample used increased with film thickness. The corrections are also larger at the higher concentrations, reflecting the strong upward curvature of the sorption isotherm and, therefore, the larger concentration change that results from a given incremental pressure change. The curves for the different thickness samples are now more nearly in the same range. In addition, the maximum is accentuated by the steeper decrease in D at the higher concentrations. The effect of applying the corrections to the sorption data is similar, both in reducing the thickness dependence and sharpening the maximum in the D versus concentration curves.
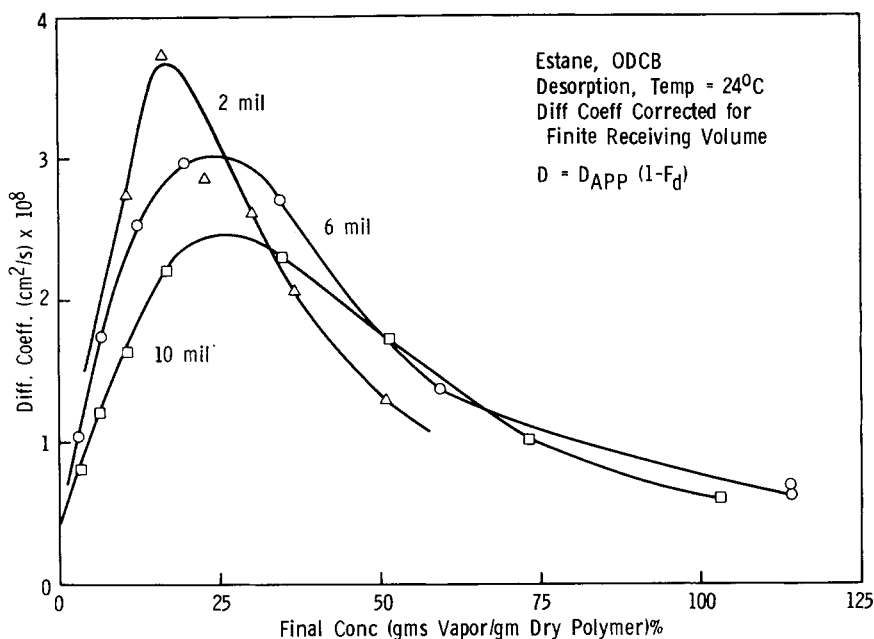
Fig. 7. Curves showing diffusion coefficients determined in incremental desorption runs for three film thicknesses, after correction for pressure drift during the run.

Turning now to consider the concentration dependence of the diffusion constant, the main question is whether the maximum in D versus C arises from specific interactions with the two-phase morphology or can be accounted for by other means. The diffusion constant obtained from the sorption experiment can be expressed as the product of the solvent mobility D_1 and a thermodynamic factor Q;[11]

$$D = D_1Q \qquad (8)$$

where Q expresses the thermodynamic driving force for diffusion, $d \ln a_1/d \ln \phi_1$. The concentration dependence of D_1 can be described in terms of free-volume parameters.[7,12] Since D_1 will generally increase with concentration and Q decreases with concentration, depending on the relative rate of change, D_1 will go through a maximum when the measurements are carried out over a sufficiently large concentration range. Therefore, the maximum in D, in the present case, might be explained by the behavior of Q.

The diffusion coefficient obtained in the incremental sorption, using equation (1), approximates a mean diffusion coefficient $\overline{D\,(C)}$ in the interval. It was shown by Duda et al.[9] that the actual diffusion coefficient, $D(C)$, can be set equal to $\overline{D\,(C)}$, with only a minor error, for some prescribed C in the interval. In a sorption experiment, $C = (C_i + 0.7\Delta C)$ for $\overline{D}$ increasing with C and $C = (C_i + 0.56\Delta C)$ for $\overline{D}$ decreasing with C. The reverse holds for a desorption experiment. If the dry polymer thickness is used in equation (1) then $D(C)$ is the polymer mass-fixed diffusion coefficient. The mutual diffusion coefficient D_{12} may then be calculated from the relation derived by

Crank:[8]

$$D = D_{12}\phi_2^2 \tag{9}$$

The solvent mobility or self diffusion coefficient D_1 is obtained using the relation:

$$D_1 = D_{12}\phi_2\left(\frac{d \ln a_1}{d \ln \phi_1}\right)_{T,P} \tag{10}$$

where all terms are defined for the same concentrations that apply in calculating $D(C)$. The assumptions underlying equation (10) have been discussed critically by Duda et al.[13] who also verified the relation experimentally for one polymer-solvent system.

The preceeding relations were applied to desorption data for the 10 mil Estane film. For simplicity the microdomains were treated as an inert filler and the solvent concentrations were adjusted for the volume fraction of the soft-segment phase. The required values of the thermodynamic correction factor were obtained by graphical differentation of the sorption isotherm. The resulting values of the mutual diffusion coefficient from equation (9) and of the solvent mobility from equation (10) are plotted in Figure 8. The mutual diffusion coefficient goes through a decided maximum. The solvent mobility increases strongly from a zero concentration intercept of about $1.4 \times 10^{-9} \text{cm}^2/\text{sec}$ to a value of 21×10^{-8} at $C = 60\%$ and then follows a downward course. It can be seen that the thermodynamic factor accounts for most, but not all of the decrease in D_1 with concentration.
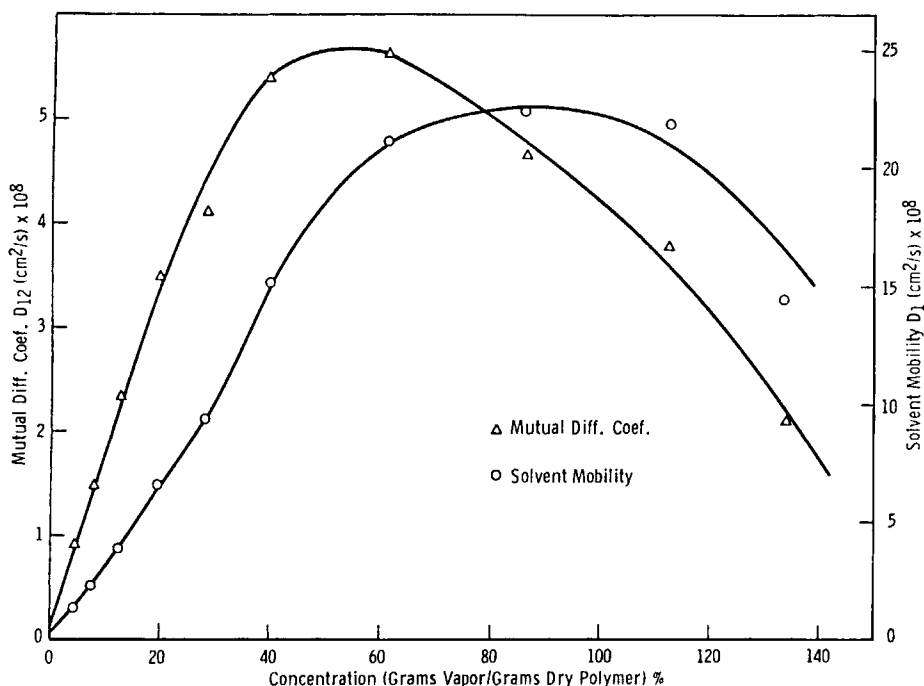

Fig. 8. Curves representing the mutal diffusion coefficient D_{12} and the solvent mobility D_1 as a function of concentration, calculated from desorption results in a 10 mil film.

Relaxation Behavior

The sorption curves for the three polyurethane thicknesses all show discernable two-stage sorption behavior above some concentration. The absence of similar behavior on desorption indicates that two-stage sorption is due to a structural relaxation process and is not just a result of slower diffusion in the dispersed phase. The behavior of the relaxation rate constant k_R, obtained from the Berens–Hopfenberg analysis, is shown in Figure 9 for the three film thicknesses. It is surprising that k_R decreases with increasing concentration, since increased solvent uptake would have been expected to increase segmental mobility and thus k_R. By definition, k_R should be independent of sample thickness. The results in Figure 9 display only mild differences with sample thickness and follow a generally similar trend despite the marked variations in the sorption curves for the different thicknesses (see example in Fig. 4).

There is some concern about the effect which the accelerated uptake due to the finite source will have on the behavior of k_R. To a first approximation it would seem to have very little effect, since k_R should be independent of the overall rate of sorption. The agreement in the behavior of k_R for the various thickness samples, including the 2 mil film for which the finite source corrections are very small, also indicates that the trend in k_R is probably reliable and physically significant.

Nonreversible Effects

In the initial sorption cycle, above about 25% uptake for the 2 and 6 mil films and above about 30% in the 10 mil film, there is distinct two-stage
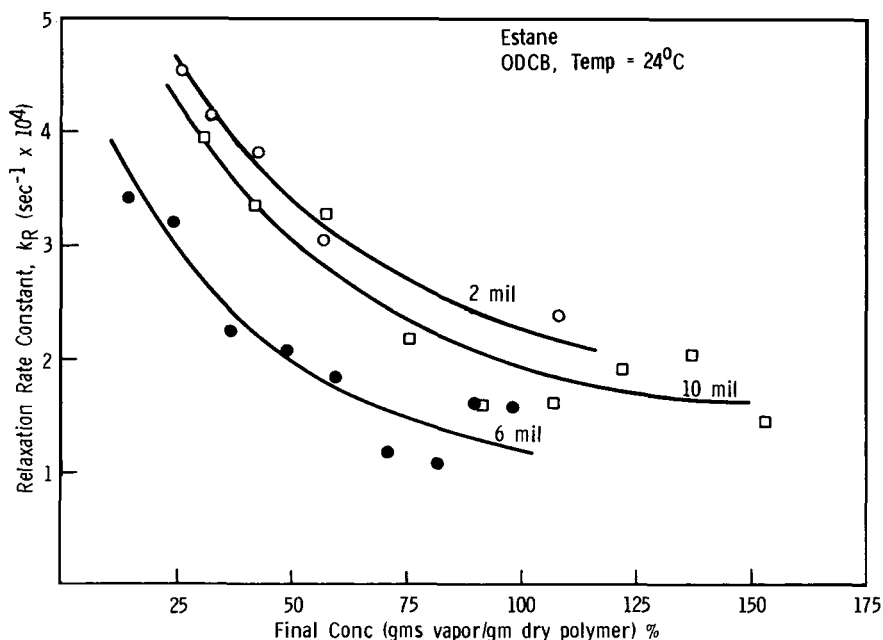

Fig. 9. Behavior of the relaxation rate constant k_R for the three film thicknesses from incremental sorption runs.

behavior which must be associated with swelling and structural relaxation in the hard segment domains. The Fickian shape of the desorption curves suggests that the relaxed structure is retained to a large degree upon solvent removal. Indeed, the repeat sorption occurs more rapidly, approaching the rate observed on the desorption cycle. However, two-stage behavior, although considerably moderated by the previous sorption process, is still observed at sufficiently high concentrations in all three thicknesses. A comparison of the sorption curves for a 10 mil film which was cycled repeatedly in the concentration interval 45–60% is shown in Figure 10. There is a pronounced non-Fickian component in the first sorption cycle, a Fickian desorption curve, and a repeat sorption curve with a larger Fickian component, more nearly like the desorption curve. However, further sorption-desorption cycles traced the same curves and failed to erase the residual relaxation component of the sorption curve. This behavior also occurred after the sample had been kept under vacuum for 1 week, indicating that the alteration of the polyurethane structure is not completely reversible, whereas Berens and Hopfenberg observed reconsolidation of a preswollen glassy polymer only when solvent had been removed.[14] Figure 11 compares the data from a repeat set of sorption runs on a 6 mil film sample. In the second sorption, two-stage curves recurred but showed a reduced Fickian contribution. As shown in Figure 11, the values of D have increased, in comparison to the first sorption cycle, over the entire concentration range above the maximum in the D versus C curve. In this case, the data from repeat sorption and desorption runs almost coincide.
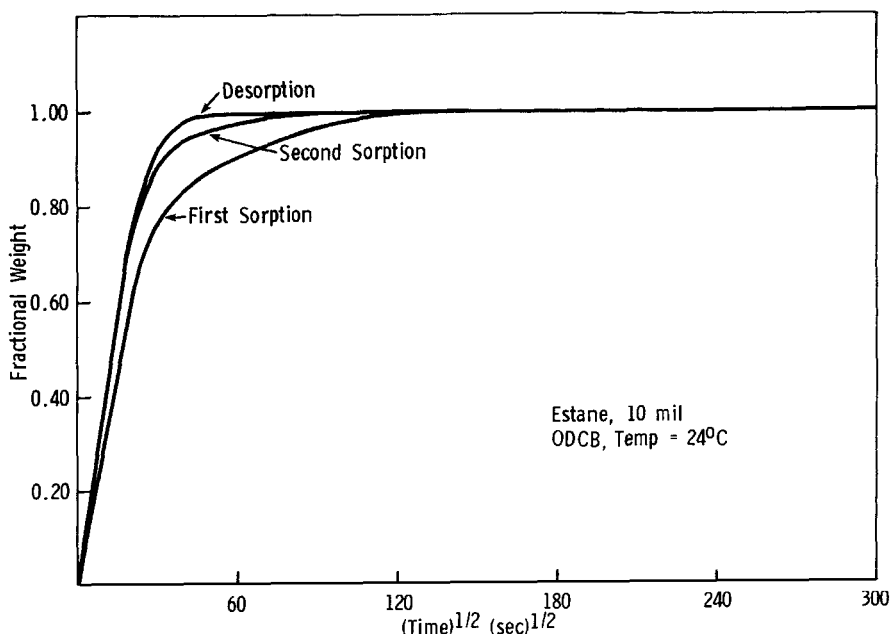

Fig. 10. Comparison of initial and repeat sorption runs, illustrating the reduction of two-stage behavior in the second run on 10 mil film.
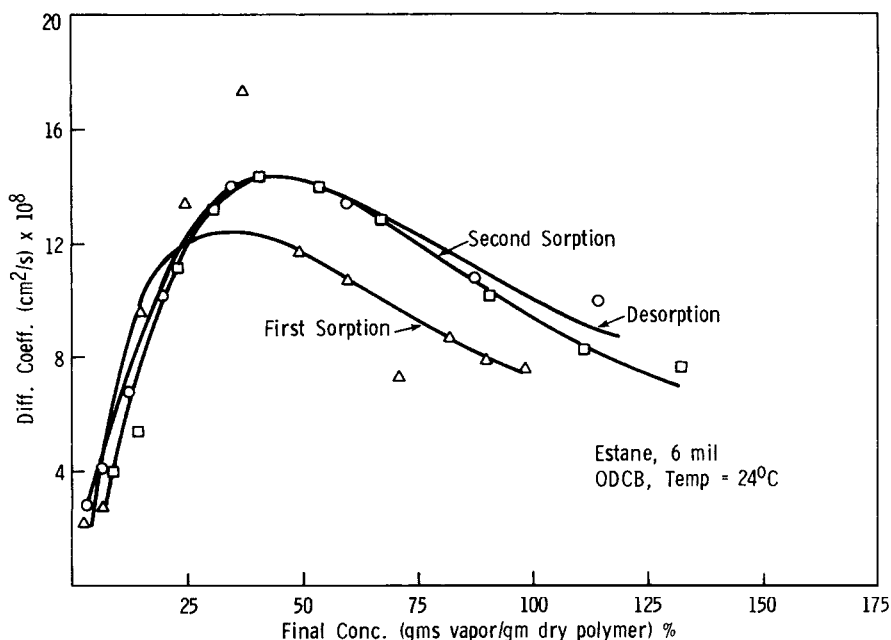
Fig. 11. Comparison of apparent diffusion coefficient in a 6 mil film determined in the initial and repeat sorption, indicating the increase in the second sorption cycle diffusion coefficients and improved agreement with the desorption results.

DISCUSSION AND CONCLUSIONS

Sorption experiments with ODCB demonstrate that the polyurethane sample undergoes extensive swelling with this solvent, characterized by a strongly concave upward sorption isotherm. Prior calculations, based on estimated solubility parameters, indicated that swelling is expected in the hard segment structure as well as the matrix. At low concentrations the incremental sorption curves are Fickian in appearance, but at higher concentration there is increasingly strong two-stage behavior. This two-stage behavior is somewhat reduced in the second sorption cycle and generally absent in the desorption runs. The concentration dependence of the diffusion constant, extracted by application of the Berens–Hopfenberg model where two-stage sorption behavior occurs, exhibits a pronounced maximum. Similar behavior in D versus C obtained on desorption indicates that this unusual concentration dependence is not caused by some difficulty in applying the Berens–Hopfenberg model to the two-stage sorption results. It was shown that the maximum in the concentration dependence of the diffusion coefficient is largely due to the contribution of the thermodynamic factor, reflecting the high level of swelling in the soft segment matrix.

In comparing samples of 2, 6, and 10 mil thicknesses, the two-stage character is observed to decrease from the 2 to the 10 mil film. The 6 mil sample is

somewhat anomalous in showing a stronger second stage contribution than the 2 mil sample, at high concentrations. Although the trend of D versus C is well defined, the large corrections for the pressure drift which occurs on sorption or desorption, due to the low vapor pressure of ODCB, make it difficult to obtain a quantitative measure of the thickness dependence of the D versus C curves.

The main problems which need to be addressed are the unusual behavior of the relaxation rate constant, which decreases with concentration, and the remaining decrease in D_1 with C, after applying thermodynamic corrections to the diffusion data. It might be expected that k_R would increase with penetrant concentration in the glassy microdomains, as in a glassy polymer. An appropriate explanation for the opposite behavior observed here might be offered, based on the recognition that the polyurethane microdomains are not homogeneous but represent a distribution of domain stabilities. Therefore, it is possible that penetrant initially interacts with domains of the lowest stability and, correspondingly, with the fastest relaxation rate. The domains can be distributed in terms of size or degree of organization, depending on the hard-segment length and the annealing history.[15] DSC scans on the present sample showed the presence of a small melting endotherm at 180°C. This small amount of crystallinity could account for the fact that this sample is insoluble in ODCB and could also reduce the extent of swelling of the hard segment structure.

There is little data with which to compare the concentration dependence of D_1. A strong monotonic increase in D_1 with C has been reported for benzene in natural rubber.[16,17] The maximum value of D_1 for ODCB is $2 \times 10^{-7}\,\mathrm{cm^2/s}$, which is about 100-fold lower than the self-diffusion coefficient in the pure liquid, judging by the value of $2 \times 10^{-5}\,\mathrm{cm^2/s}$ reported for benzene.[18] Therefore, it seems reasonable to expect that D_1 should increase continuously with concentration, rather than decreasing or even leveling off above a moderate concentration.

One factor possibly contributing in some measure to the D_1 versus C behavior is an overcorrection for the pressure drift during the sorption or desorption runs. Since the pressure change is larger at higher activities, owing to the larger concentration increments, the error would increase in the same sense. However, even if D_1 were increased by a factor of two at the highest concentration, a marked reduction in slope would still result above the concentration at the maximum in Figure 8. An alternative proposal is that the concentration-dependent behavior of D_1 is influenced by relaxation processes. This assumes that relaxation can influence the diffusion behavior even though the second-stage relaxation contribution has been separated out from the sorption runs and is absent on desorption.

The principal distinction between the polyurethane and a two-phase blend of separate components is that the matrix and hard-segment phases in the polyurethane are not independent. The interactions between the matrix and hard-segment phase are exemplified by the strong dependence of polyurethane mechanical properties on the concentration and structure of the hard-segment domains.[19] If, in a similar manner, the swelling and relaxation of the microdomain structure controls the swelling of the matrix, then the two

coupled processes would progress at comparable rates.

According to this proposal, there must be two relaxation processes in the hard segment. First, there is a slow relaxation process which gives rise to the two-stage sorption behavior and is associated with the largely irreversible structural changes that occur during the initial exposure to the solvent. This process could also affect the diffusion constant on sorption, accounting for the difference between the values from sorption runs calculated by the Berens–Hopfenberg model and the values obtained on the desorption cycle. However, there should also be a shorter time relaxation, which is closely coupled with the matrix swelling. If the matrix swelling is governed by the hard segment relaxation and the relaxation rate decreases with increasing concentration or the relaxation contribution increases with concentration, this would accentuate the decrease in D_1 with C.

There are several difficulties with this proposal. If relaxations of the type proposed are present, then the desorption curves should be pseudo-Fickian. The term pseudo-Fickian is used here to designate Fickian appearing curves which, however, do not superimpose when the fractional weight change is plotted against $(t/l^2)^{1/2}$. The absence of an increase in D with thickness in the present data, after correction for the pressure drift, could indicate that the procedure which was used overcorrects the data, as already noted. A strong thickness dependence has been observed in later studies on the Estane sample[20] using a high vapor pressure liquid to avoid pressure changes during the run. Another problem is the absence of a model for such pseudo-Fickian behavior. An approximate representation can be derived using the generalized treatment of coupled diffusion and relaxation developed by Joshi and Astarita.[21] The theory can predict sorption curves which are only slightly "S" shaped when the diffusion and relaxation time scales are comparable, but it does not predict true Fickian appearing sorption curves which still exhibit a thickness dependence.

Even with these difficulties in formulating a specific model there is reason to believe that coupling between relaxation in the hard segment domains and swelling of the soft segment matrix plays a role in the diffusion behavior. On this basis, extensive swelling of the hard segment structure is not required to account for the increased sorption or for the relaxation effects which occur at high solvent activities. In experiments to be reported later, very strong relaxation effects and a maximum in D versus C have been observed with 1,6-dichlorohexane in the same polyurethane. These results again attest to the strong coupling between the matrix swelling and the hard-segment relaxation, since this solvent has a very low swelling power for the hard-segment structure. Recently, small-angle neutron scattering measurements on a polyurethane sample similar to the present Estane material[22] have shown that the radius of gyration of the polytetramethylene-oxide chains is increased by about 25% over that in the bulk state. This is a further indication that solvent diffusion and relaxation behavior might well be sensitive to the detailed nature of the coupling of hard and soft segments.

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