Diffusion of Bis(2-ethylhexyl) Phthalate above and below the Glass Transition Temperature of Poly(vinyl chloride)

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Received March 23, 1990; Revised Manuscript Received July 3, 1990

ABSTRACT: Diffusion coefficients of bis(2-ethylhexyl) phthalate in PVC were measured over the temperature range $60 \leq T \leq 100$ °C by using a mass-uptake technique. Near and above the unplasticized T_g of PVC (ca. 81 °C), the values were observed to be in the range 1.29×10^{-9}–1.10×10^{-8} cm^2/s and to follow approximately an Arrhenius relationship with an activation energy for diffusion of 29 kcal/mol. Within this temperature range, mass uptake vs time$^{1/2}$ plots were observed to be curves with a slowly increasing derivative; the initial, approximately linear region yielded the diffusion coefficient in pure (unplasticized) PVC. Below the unplasticized T_g of PVC, mass uptake vs time$^{1/2}$ plots recorded three stages of diffusion: (1) non-Fickian initial behavior constituting essentially an induction period; (2) a brief, approximately Fickian diffusion of plasticizer into glassy PVC; and (3) linear, Fickian diffusion into the plasticized, rubbery polymer. The transition between stages 2 and 3 was characterized by a discontinuity in the mass-uptake plot. Stage 3 diffusion coefficients were calculated to be in the range 3.44×10^{-10}–1.00×10^{-9} cm^2/s from 65 to 78 °C, respectively, and the activation energy for diffusion within this temperature range was 19 kcal/mol. The value for D at 60 °C was found to be 1.68×10^{-10} cm^2/s, and this value was significantly lower than that predicted by the Arrhenius relation for stage 3 diffusion.

Introduction

In a recent series of papers,[1-3] we have introduced a penetrant shape-dependent, largely free-volume-based theory that utilizes theoretical conformational analysis[4] to predict diffusion coefficients (D) for large penetrant molecules within amorphous polymers above their glass transition temperatures (T_g). An important application for this model is the diffusion of plasticizer molecules in poly(vinyl chloride) (PVC).

To aid development of the theory and to test its predictive capabilities, we have employed a simple but effective mass-uptake technique for the experimental determination of D's for a variety of plasticizers in PVC within certain limits of temperature and plasticizer solvating activity. The method is a refinement of an earlier procedure published by Grotz[5] and involves measurement of the time-dependent cumulative plasticizer absorption of molded PVC disks exposed to a given plasticizer under isothermal conditions. While D is calculated simply from the slope of a plot of cumulative mass uptake vs time$^{1/2}$, the defining mathematical expressions are more complex and derive by integrating with respect to time the flow of penetrant entering the disk surface, which in turn derives by the application of Fick's first law to the differentiated form of the appropriate solution of the time-dependent diffusion equation subject to the boundary conditions of our experiment. For a more detailed discussion of the underlying mathematical development, the reader is referred to an earlier manuscript published recently by us.[6]

We have found our experimental method to be reproducible and sufficiently sensitive to distinguish among subtle differences in plasticizer structure such as, for example, alkyl chain length and degree of branchiness of phthalate esters. In ref 6 we presented a broad survey of experimentally measured D values for both commercial and model n-alkyl phthalate plasticizers in pure and plasticized PVC films. In all cases, with other conditions held constant, D's were found to increase with temperature, decrease with an increase in alkyl group length, and decrease with an increase in alkyl group branchiness. Above the T_g of pure, unplasticized PVC (ca. 81 °C), the temperature dependence of diffusion was observed to follow an Arrhenius-type relationship, and although the data exists for only two or three plasticizers, it appears that the activation energy for diffusion increases with increasing alkyl chain length within the homologous series of n-alkyl phthalate plasticizers. It was also found that, at constant temperature, ln D increased approximately linearly with increasing alkyl chain length within the series of n-alkyl phthalates. This suggests a predominantly longitudinal molecular displacement during diffusion, i.e., along the direction of least resistance for an elongated molecule, which is a concept embraced by our theory.

Below the T_g of pure PVC, diffusion is more complex, since accumulating plasticizer causes an evolution of the T_g to ever lower values. If, during the diffusion experiment, the system is allowed to traverse the particular plasticizer concentration, denoted $C_g(T)$ by Berens,[7] which depresses the blend T_g to exactly the temperature of the experiment, then any number of complex diffusion behaviors can result, e.g., case II diffusion[8] or penetrant crazing.[9] However, if the temperature or activity of the penetrant is low enough that the system remains glassy throughout the experiment, Fickian diffusion is observed.[7] Likewise, if the concentration of plasticizer is extended beyond $C_g(T)$, Fickian diffusion is again observed in the now rubbery matrix. Our preliminary data reported in ref 6 suggested that here too diffusion follows an Arrhenius-type relationship, but with a lower activation energy. In the present manuscript, we present a detailed examination of the diffusion behavior of just one plasticizer, bis(2-ethylhexyl) phthalate (DOP), with particular attention paid to the characteristic diffusion behavior below and near the T_g of pure PVC.

Experimental Section

Materials. DOP and compounded PVC films were generously supplied by Exxon Chemical Co.

Unplasticized PVC films were compression molded from a commercial suspension-polymerized PVC resin (Exxon Chemical Co., grade 369), which was described in detail in a previous publication.[10] The PVC resin was compounded with 2.0 phr (parts per hundred parts resin) Mark 7101 stabilizer and 0.2 phr stearic acid.

0024-9297/91/2224-0450$02.50/0

Diffusion Measurements. Circular disks (diameter 2.54 cm) were stamped from a PVC film (nominal thickness 0.050 cm) using a machined die. A group of disks (usually four to six) were individually tared and placed together in a beaker of plasticizer held in a constant-temperature bath. The temperature of the plasticizer was controlled to ±0.5 °C, and the disks were placed in a low-mass, tin basket fashioned to minimize plasticizer temperature perturbation and to facilitate nearly total contact of the plasticizer with both sides of the disk. After a specified time (different for each temperature), all of the disks were removed and wiped clean of adhering plasticizer, and the increase in weight of each disk was recorded. Utilization of a number of disks simultaneously enabled a reasonable average mass uptake to be determined as a function of contact time with the plasticizer. The procedure for determining mass uptake for time intervals subsequent to this initial measurement differed between samples taken above and below the T_g of PVC as follows.

Below T_g (60–78 °C). After the initial measurement, the same disks were again immersed in the plasticizer for approximately the same time interval as before. After this time they were again wiped clean, reweighed, and the average increase in weight was recorded as a function of the cumulative immersion time. This procedure was repeated until the desired number of data points had been collected.

Above T_g (80–100 °C). The rapidity of DOP diffusion within this temperature range dictated short time intervals between mass-uptake measurements. This made it impractical to utilize the above-described method since temperature control suffered from frequent removal and reintroduction of disks to the plasticizer. Thus the disks used for the initial measurement were discarded subsequent to weighing, and new disks were individually tared and immersed in the plasticizer. These disks were allowed to remain in the plasticizer for approximately twice as long as the initial group, thereby providing an average mass-uptake measurement for a second data point. This procedure was repeated for longer and longer times until the desired number of data points had been collected.

Calculation of the Diffusion Coefficient. For diffusion into both ends of a right circular cylinder of cross-sectional area, q, and height, h, the following expression of D is valid for immersion time, t, short enough that $\mathrm{erf}(h/4D^{1/2}t^{1/2}) = 1.0$, which is essentially true for $t < h^2/64D \approx 4 \times 10^{-5}/D$:

$$D = \frac{\pi s^2}{16q^2(c_0 - c')^2 t} \qquad (1)$$

Here, s is the mass of imbibed plasticizer, c_0 is the external plasticizer concentration (its bulk liquid density), and c' is the initial plasticizer concentration within the sample. The latter, if nonzero, is readily calculated, assuming no volume change upon mixing (weak polymer–plasticizer interactions), from the initial weight fraction of plasticizer, w_1, c_0, and the density of PVC.

The bulk liquid density of DOP at various temperatures is calculated by using a linear volume expansion equation of the form

$$\frac{1}{\rho_T} = \frac{1}{\rho_{25}}(1 + \alpha\Delta T) \qquad (2)$$

where ρ_T is the density (g/mL) at a given temperature, ρ_{25} the density at 25 °C, α the temperature coefficient of volume expansion, and ΔT the temperature difference (T − 25 °C). Our measured values of ρ_{25} and α for DOP are 0.986 g/mL and 6.64 × 10^{-4} °C^{-1}, respectively.

When plasticizer mass uptake is plotted vs $t^{1/2}$, a linear relationship with slope, m, should result for constant D, from which D is extracted by using the following equation:

$$D = \frac{\pi m^2}{16q^2(c_0 - c')^2} \qquad (3)$$

Results and Discussion

Diffusion above the T_g of PVC. Figure 1 shows representative mass-uptake plots for DOP diffusion at several temperatures above the T_g of PVC. Although the plots do not pass directly through the origin, indicating a slight induction period, it is clear that the plots assume linearity with respect to $t^{1/2}$, indicating Fickian diffusion with nearly constant D. Since the average tare mass of a disk is about 0.4 g, these data, which encompass s values of no more than about 5% of the original mass of the disk ($w_1 \leq 0.05$), represent diffusion essentially into pure, unplasticized PVC. However, as the concentration of plasticizer rises within the sample due to diffusion, two opposing effects must be considered. The first, which is of lesser importance at low to moderate plasticizer loadings, is the decrease in the quantity $c_0 - c'$, which represents the concentration difference or the driving force for diffusion. The second effect, which is overwhelmingly more important, is the increase in free volume within the sample brought about by the incorporation of small penetrant molecules.[11] This increase is conveniently quantified in terms of the T_g of the PVC/plasticizer blend

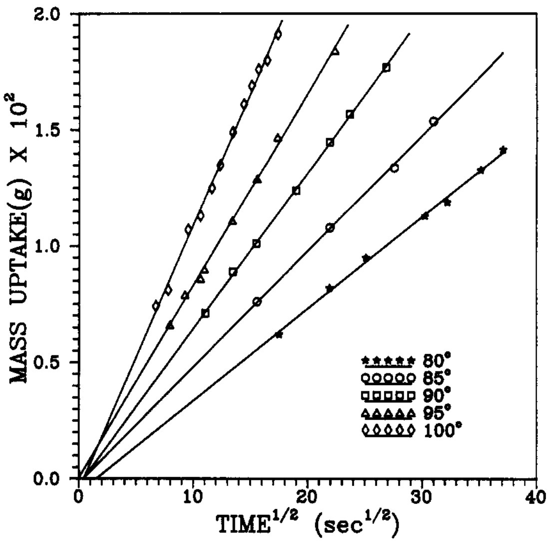

Figure 1. Mass-uptake plots for DOP diffusion at several temperatures above the T_g of PVC; $w_1 \leq 0.05$.

$$V_f = V[0.025 + \alpha_f(T - T_g)] \qquad (4)$$

where V_f is the free volume in the blend, V the total sample volume (steric + free), and α_f the temperature coefficient for expansion of free volume. The T_g of a plasticizer/polymer blend, furthermore, has been shown by us[1,12] and others[13,14] to be related to the glass transition temperature of the pure polymer, T_{g2}, and w_1, in the following linear fashion for many plasticizer/polymer mixtures at $w_1 \leq 0.35$

$$T_g = T_{g2} - kw_1 \qquad (5)$$

where k is the plasticizer efficiency parameter, which for DOP in PVC has been measured to be 323 K.[13] Combining eqs 4 and 5 yields eq 6, which was used earlier by Fujita and Kishimoto[15] and which is used in the Mauritz–Storey diffusion theory[1-3] to quantify V_f in terms of w_1.

$$V_f = V[0.025 + \alpha_f(T - T_{g2} + kw_1)] \qquad (6)$$

In light of eq 6 it is apparent that the very act of measuring diffusion as we do under nonequilibrium, kinetic conditions must cause the T_g of the sample to evolve to lower values, causing the V_f and hence the D to slowly rise as plasticizer enters the disk. When the mass-uptake experiments pictured in Figure 1 were extended under the same conditions to higher degrees of swelling, as shown in Figure 2, the initial linear regions were found, as expected, to be portions of curves with slowly increasing derivatives. These results serve to emphasize the impor-

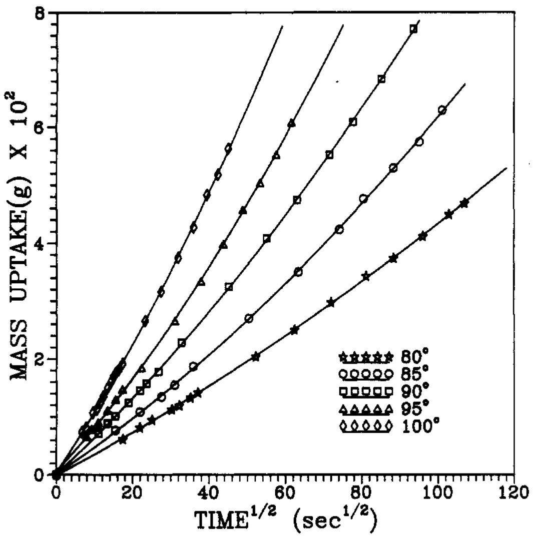

Figure 2. Mass-uptake plots of DOP diffusion at several temperatures above the T_g of PVC, extended to higher degrees of swelling.

Table I
Diffusion Coefficients of DOP at Various Temperatures above the T_g of PVC

temp, °C	diffusion coefficient (D), cm^2/s	temp, °C	diffusion coefficient (D), cm^2/s
80	1.29×10^{-9}	93	5.49×10^{-9}
83	1.65×10^{-9}	95	6.84×10^{-9}
85	2.19×10^{-9}	98	9.14×10^{-9}
88	2.90×10^{-9}	100	1.10×10^{-8}
90	3.95×10^{-9}		

tance of calculating D only from data taken at low s values, if the D is to be representative of diffusion into unplasticized PVC. It should also be noted that *all* of the data points pictured in Figure 2 satisfy the condition, $t < 4 \times 10^{-5}/D$, which ensures that advancing penetrant molecules from either side of the disk do not overlap at the center of the disk.

The D values for diffusion of DOP in pure PVC, calculated as described above, are listed in Table I for a number of temperatures above the T_g of pure PVC. It can be seen that the D's increase steadily from a value of 1.29×10^{-9} cm^2/s at 80 °C to a value of 1.10×10^{-8} cm^2/s at 100 °C, and it will be shown later than these fit reasonably well an Arrhenius-type relationship. It is also noteworthy that for a relatively fast-diffusing and compatible plasticizer like DOP, 100 °C represents the practical upper temperature limit for this particular experimental technique. Above this temperature, not only does the rapidity of diffusion present experimental difficulties, but the enhanced solvating power of DOP causes erosion of the disk surfaces.

Diffusion below the T_g of PVC. When mass-uptake plots were obtained within the temperature range $60 \leq T \leq 78$ °C, complex behavior was observed caused by a glassy to rubbery transition of the matrix during the course of the kinetic diffusion experiment. Representative data are shown in Figure 3. It was found that diffusion under these conditions proceeded through three stages: (1) an induction period characterized by an initial upward curvature of the plot; (2) a brief period of apparently Fickian diffusion into a partially plasticized but still glassy matrix; and (3) an extended period of Fickian diffusion in a plasticized, rubbery matrix. The transition between stages 2 and 3, which represents the point at which the evolving T_g of the PVC/plasticizer blend falls through the temperature of the experiment, was associated with a discontinuity in the mass-uptake plot, which might be characterized best as a "pause" in the process of diffusion. An even more interesting phenomenon, associated with the pause, is the observation, best seen in the data at 70 °C, that the final rate of diffusion before the pause may actually be greater than the rate of stage 3 rubbery diffusion.

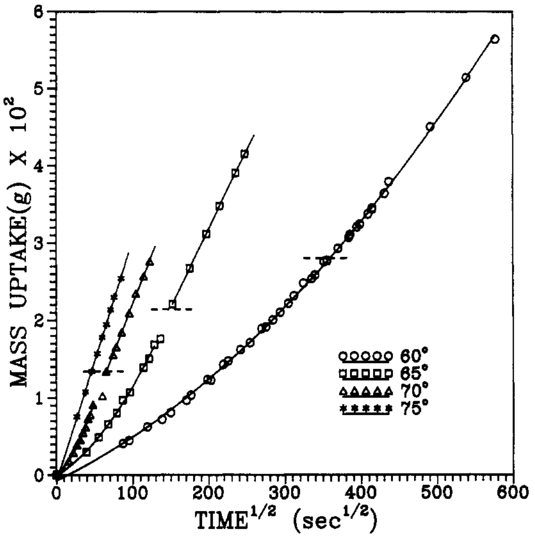

Figure 3. Mass-uptake plots for DOP diffusion at several temperatures below the T_g of PVC. Dashed lines predict the mass-uptake necessary to depress the T_g of PVC to the temperature of the experiment.

Only for temperatures near the midpoint of the studied range were all three stages distinctly observed. For example, data obtained at 60, 65, and 70 °C clearly display the stage 1 induction period characterized by an initial upward curvature of the plot. However, no induction period was observed at 75 or 78 °C simply because it was too short to detect. Furthermore, at the lowest temperature, i.e., 60 °C, the relatively long induction period led directly into stage 3 rubbery diffusion with no indication of the transitional pause.

Through the use of eq 5 we can calculate the w_1 necessary to depress the T_g of PVC to exactly the temperature T of the diffusion experiment. Then, the following relationship can be applied to estimate the mass uptake, s, necessary to achieve that particular composition in the disks of average tare mass, m_0:

$$s = \frac{m_0(T_{g2} - T)}{k - (T_{g2} - T)} \qquad (7)$$

This was done for the plots of 60, 65, and 70 °C, and the resulting values of s are indicated by the dotted lines in Figure 3, which intersect the respective curves. It is remarkable how closely these calculated values predict the onset of stage 3 diffusion, and it confirms that the discontinuous pause is a manifestation of the behavior of the system at the glass transition. More detailed examination of the system in the vicinity of the pause was difficult due to the kinetic, transient nature of the experiment. Plots of the mass-uptake data vs t^1 did not suggest type II diffusion[8] in the vicinity of the pause or elsewhere.

Stage 3 diffusion coefficients are listed in Table II. It must be emphasized that these values were measured at temperatures below the T_g of unplastized PVC, but they actually describe diffusion in a plasticized, rubbery matrix. Thus, these D's are not representative of the diffusion of DOP in pure PVC because a certain degree of "preplas-

Table II
Diffusion Coefficients of DOP at Various Temperatures below the T_g of PVC

temp, °C	diffusion coefficient (D), cm^2/s	temp, °C	diffusion coefficient (D), cm^2/s
60	1.68×10^{-10}	75	8.21×10^{-10}
65	3.44×10^{-10}	78	1.00×10^{-9}
70	5.29×10^{-10}		

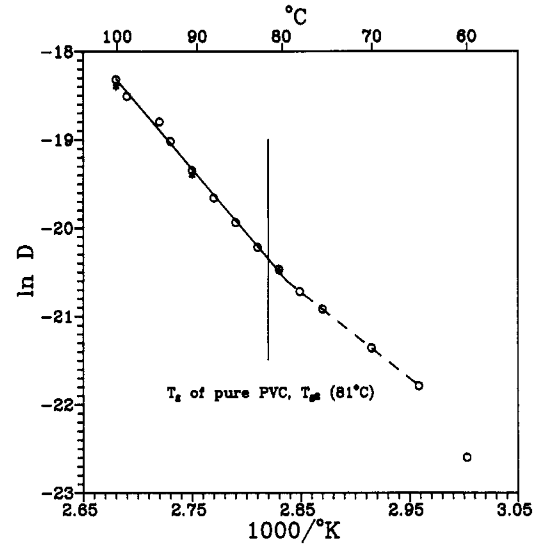

Figure 4. ln D vs T^{-1} for DOP diffusion in PVC. Solid and dotted lines represent best linear fits for supra-T_{g2} and sub-T_{g2} data, respectively. Asterisks are earlier data from ref 6.

ticization" necessarily took place in order to achieve a rubbery composition. For example, at 65 °C, rubbery diffusion began only after an average $w_1 = 0.050$ had been reached. Furthermore, the concentration profile at this stage most likely is not entirely consistent with the solution of the time-dependent diffusion equation upon which the experiment is ultimately based, since non-Fickian diffusion has occurred previously to this time. Thus, there is no obvious way to account for this possible error and still retain the simplicity of the method, and in any case, the error would be small since the levels of preplasticization under consideration are very low.

Temperature Dependency of Diffusion. Storey, Mauritz, and Cox[6] demonstrated earlier that phthalate plasticizer-in-PVC, mass-uptake diffusion data for temperatures above the T_g of pure PVC, T_{g2}, could be fitted reasonably well to an Arrhenius expression

$$\ln D = \ln A - E_{\mathrm{act}}/RT \tag{8}$$

where A is the preexponential frequency factor and E_{act} is the apparent activation energy for diffusion. It was also suggested that diffusion data below T_{g2} might also follow such a relationship but with lower activation energy. However, in this earlier manuscript, insufficient data were gathered to define with confidence the sub-T_{g2} E_{act}.

The temperature dependency of DOP diffusion is shown in Arrhenius fashion in Figure 4. The lines represent the best fits to eq 8 for supra-T_{g2} (solid line) and sub-T_{g2} (dotted line) data. From the slopes of these lines the activation energies for diffusion above and below T_{g2} were calculated to be 29 and 19 kcal/mol, respectively. The difference between these two values is significant, and it is reasonable that the presence of a small fraction of plasticizer molecules, whose motions do not require the same degree of long-range cooperativeness as do polymer chain segments, would contribute to an overall lower energy requirement for diffusion. This same effect has been shown clearly by Griffiths, Krikor, and Park,[16] who reported the activation energy for diffusion of di-n-hexyl phthalate in PVC decreased from 20 to 12 kcal/mol in proceeding from 28 to 50 wt % plasticizer.

Several aspects of the data presented in Figure 4 are particularly noteworthy. It is satisfying that the activation energy for above-T_{g2} diffusion of DOP, 29 kcal/mol, is very close to our earlier reported[6] value of 27 kcal/mol measured for di-n-octyl phthalate (DNOP). Given the close structural similarity between these two plasticizers, it would be expected that their diffusion behaviors would also be alike. The data points denoted by asterisks in Figure 4 are data gathered 1 year earlier by a different experimenter; these were included to demonstrate the high degree of precision and reproducibility attained with our method.

It may also be noted in Figure 4 that the D value at 60 °C does not fall on the sub-T_{g2} Arrhenius line but is in fact much too low. We believe this represents real behavior and is not an artifact of the experiment. In fact, this particular temperature was run several times with the same result; the 60 °C data in Figure 3 represent data from two different runs made on two separate occasions, and the precision is obviously excellent. It is probable that this point locates the beginning of a downward curvature in the sub-T_{g2} Arrhenius plot, which represents a breakdown in the validity of the mass-uptake method at these low temperatures. Very likely the degree of preplasticization that occurs prior to stage 3 diffusion becomes sufficient at this temperature to cause the plasticizer concentration profile within the disk to be inconsistent with the solution of the diffusion equation upon which the method is based. Thus, when Figure 4 is viewed in its entirety, one observes a relatively steep slope within the region above T_{g2}, a transitional region of lower slope, centered just below T_{g2}, and finally another region of steep slope, perhaps curving downward, at temperatures well below T_{g2}. Obviously, diffusion behavior within the latter region is difficult to adequately characterize by using our present method.

Conclusions

Using a simple mass-uptake technique, the detailed analysis of the diffusion of DOP in PVC has been carried out, with particular attention paid to the characteristic behavior at and near the glass transition. By its very nature, the technique measures diffusion under kinetic rather than equilibrium conditions, and hence the T_g of the sample is constantly evolving during the experiment. In this sense, the D values so generated are concentration-averaged; however, in many instances the cumulative uptake of plasticizer is sufficiently low than the diffusion coefficient can be considered reflective of diffusion in pure PVC.

At 80 °C, the lowest temperature for which pure PVC is essentially rubbery, D was measured to be 1.29×10^{-9} cm^2/s. D was observed to increase uniformly with increasing temperature to reach a value of 1.10×10^{-8} cm^2/s at 100 °C. The most directly comparable literature values available are those given by Grotz,[5] who reported for DOP diffusion at 85 °C, $D = 3.0 \times 10^{-8}$ cm^2/s. It can be shown, as outlined elsewhere,[6] that due to his use of an incorrect diffusion equation, Grotz's values should be reduced by a factor of 4, which when done leads to a value that agrees quite well with ours.

When diffusion was measured in the range $60 \leq T \leq 78$ °C, characteristic mass-uptake curves were obtained, which consisted of (1) an induction period, (2) a period of glassy diffusion leading to a pause, which signified passage of the plasticized T_g through the temperature of the experiment, and (3) a prolonged period of rubbery diffusion for which a meaningful D value could be extracted. Diffusion coefficients measured in this manner ranged from 1.68×10^{-10} cm^2/s at 60 °C to 1.02×10^{-9} cm^2/s at 75 °C. It is significant that, at the midrange temperatures 65 and 70 °C, the above-described pause occurred at an average degree of plasticization, which was entirely consistent with the known plasticization efficiency of DOP.

It was found that the temperature dependency of diffusion could be well-fitted, within a relatively narrow range of temperatures, to an Arrhenius expression both above and below the T_g of pure PVC, T_{g2}. The activation energy for diffusion was found to be 29 kcal/mol above T_{g2} and 19 kcal/mol below it, and when the $\ln D$ vs T^{-1} data were plotted over the entire temperature range studied, the sub-T_{g2} region was observed to be actually a brief transition with shallow slope leading to a more steeply downwardly curving region at even lower temperatures. The overall shape of the $\ln D$ vs T^{-1} plot is nearly identical with similar plots reported by Meares[17] for the diffusion of simple gases in poly(vinyl acetate) over the temperature range 10–45 °C. The difference, of course, is that Meares' data below the transition are presumably truly glassy diffusion, whereas ours is plasticized, rubbery diffusion.

The above-T_{g2} activation energy for DOP of 29 kcal/mol compares closely to our earlier reported value[6] of 27 kcal/mol for the structurally similar DNOP. It is difficult to say whether the difference of 2 kcal/mol is significant and, consequently, whether this could be indicative of a general effect brought about by differences in branchiness among phthalate alkyl chains. From our general experience, including some as yet unpublished work, we can state with reasonable confidence that within a homologous series of plasticizers such as the di-n-alkyl phthalates, activation energies for diffusion tend downward with decreasing carbon number, at least within the C_6–C_{10} range.

Acknowledgment. We gratefully acknowledge the consistent and generous support of this work by the Performance Products Group of the Exxon Chemical Co. and the valuable interactions with L. G. Krauskopf and J. R. Hooton.

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Registry No. PVC, 9002-86-2; DOP, 117-81-7.