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Diffusion of Various Dialkyl Phthalate Plasticizers in PVC

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ABSTRACT: Diffusion coefficients of several *n*-alkyl phthalates and several commercial phthalate plasticizers in PVC were measured over the temperature range $60 \leq T \leq 100$ (°C) by using a mass uptake technique. The values were observed to be in the range 2×10^{-10} to 8×10^{-7} cm^2/s. With other conditions held constant, diffusion coefficients were found to increase with temperature, decrease with increase in alkyl group length, and decrease with increase in alkyl group branchiness. Diffusion temperature dependence was observed to follow an Arrhenius relationship over the temperature range studied, but with a change in slope at the glass transition of PVC. The activation energy for diffusion of di-*n*-hexyl phthalate was found to be 22 kcal/mol above the PVC glass transition and 7.9 kcal/mol below it. Among the *n*-alkyl phthalate series, ln (diffusion coefficient) was found to be approximately linear with respect to the number of carbons in the *n*-alkyl chain.

Introduction

The diffusion of large penetrant molecules within polymers is an important process which directly impacts such technologies as the processing of various additives into polymers, membrane liquid/liquid separations, the transport of biologically active molecules through polymer matrices in controlled-release applications, and many others. We are currently developing a penetrant shape-dependent, largely free volume based diffusion model that utilizes theoretical conformational analysis[1,2] to predict diffusion coefficients (D) for large penetrant molecules within amorphous, cross-linked, or semicrystalline polymers above their glass transition temperatures (T_g).

An important application for this model, and one which concerns us presently, is the diffusion of plasticizer molecules into and out of poly(vinyl chloride) (PVC). PVC is one of the most important commodity industrial polymers, and in most applications its properties are modified by compounding with a compatible plasticizer. Introduction of the plasticizer into PVC usually takes place in a dry blending operation in which suspension-polymerized PVC particles are heated and rapidly sheared with plasticizer and other compounding ingredients in a mixer. It has been suggested that the rate of dry blending is in fact diffusion controlled;[3,4] thus the rate of diffusion of a particular plasticizer into PVC determines the required dry blending time, which directly affects processing costs.

Plasticizer diffusion also affects the longevity of plasticized PVC goods. Just as plasticizer diffusion into PVC affects the ease of processing, plasticizer diffusion out of the processed vinyl compound determines to a great extent the useful lifetime of the article.

There exists a great volume of literature dealing with the thermodynamics and kinetics of the uptake of various commercial plasticizers in PVC resin particles as well as in solvent-cast and hot-pressed PVC films. While it is quite impossible to enumerate all of the studies performed in this vast general area, we will summarize only those we feel most closely relate to the work reported herein.

In an early study, Knappe determined diffusion coefficients of DOP in PVC films by measuring index of refraction as a function of time.[5] At 80 °C, for example, D steadily increased from 6.1×10^{-11} to 6.7×10^{-8} cm^2/s as the plasticizer concentration increased from 10 to 80 wt %. At 100 °C, D increased from 5.6×10^{-10} to 1.4×10^{-7} cm^2/s over the same concentration range. Furthermore, ln D vs T^{-1} curves were quite linear, and the energies of activation for diffusion decreased from 30.1 to 8.7 kcal/mol from 10 to 80 wt % DOP.

Using a procedure similar to that reported in this work, Grotz determined D values from the slopes of plasticizer uptake vs (time)$^{1/2}$ lines obtained by using disks of suspension-polymerized PVC immersed in excess DOP in the temperature range 65–85 °C.[6] D increased, in Arrhenius fashion, from 9.6×10^{-11} to 3.0×10^{-8} cm^2/s from 65 to 85 °C, respectively, after an initial induction period, with an activation energy of 60 kcal/mol. In contrast with Knappe's results, Grotz's activation energy was somewhat high and appeared to be independent of incorporated plasticizer concentration.

It is necessary for us, at this time, to point out that the equation used by Grotz is in fact based on a solution to the diffusion equation derived from boundary conditions that are inappropriate for the situation of a disk immersed

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in an "infinite" reservoir of the liquid. The correct solution, presented in this work, can show that Grotz's analysis leads to diffusion coefficients that are too large by a factor of 4 when the sample contains no initial diffusant. If diffusion begins with a nonzero concentration of plasticizer, an additional correction upon the Grotz equation must be applied. On the other hand, activation energies will remain the same. We are compelled to note this discrepancy for two important reasons: (1) Our methodology and system are very much alike those of Grotz, and meaningful comparison of results must be based on the same correct diffusion equation solutions. (2) Grotz's results have been cited to a significant extent in the body of literature dealing with the science and technology of PVC plasticization.

More recently, Griffiths, Krikor, and Park reported the self-diffusion coefficients of di-*n*-butyl, hexyl, and decyl phthalates in PVC films, obtained by a radiotracer method.[7] D values were obtained from 25 to 55 °C at plasticizer concentrations in the range 28–50 wt %. D was observed to steadily increase with increasing penetrant concentration, by a factor of about 50 over this range, and it increased by about 20-fold for the 30 °C increase in temperature. In proceeding from 28 to 50 wt %, the energies of activation decreased from 20 to 12 kcal/mol for the hexyl and from 18 to 12 kcal/mol for the decyl forms. For 50 wt % plasticizer at 55 °C, D was measured to be 4.8×10^{-8} and 4.6×10^{-8} cm^2/s for the hexyl and decyl forms, respectively. In comparing diffusion coefficients from their study against those determined under kinetic conditions, two important facts should be noted. First, the measurements of Griffiths et al. were performed at temperatures below the unplasticized T_g for PVC, although these temperatures were above the plasticized T_g. Second, during the experiments, the plasticizer–polymer system was already in chemical equilibrium, and neither plasticizer concentration gradients nor phase heterogeneity (glassy + rubbery) existed within the sample.

Storey, Mauritz, and Bui[8] monitored the kinetics of absorption of di-*n*-decyl phthalate into PVC resin particles in the temperature range 70–100 °C using optical microscopy. As also noted in similar swelling studies by Davidson,[3] we have observed three distinct stages of plasticizer uptake by PVC: (1) an initial induction period during which the polymer is evolving from a glassy to a rubbery material with progressive solvation; (2) a period of rapid uptake by a rubbery, dynamic polymer matrix; (3) an asymptotic approach to the equilibrium resin swelling capacity, controlled in large measure by the restraining action of very small crystallites that act as cross-links.[9] The decrease in induction time with increase in temperature exhibited Arrhenius-like behavior with an activation energy of 61 kcal/mol. We have interpreted this number as the cumulative energy of solvation that is required to loosen all the polymer chains to attain the long-range segmental mobility characteristic of the rubbery state. During the induction period, plasticizer diffusion is non-Fickian.

To guide the development of our mathematical model, we have generated a broad data base of experimentally-measured D values for various commercial and model phthalate plasticizers in PVC films. We have employed a modification of the earlier cited mass uptake experiment reported by Grotz.[6] Our general goal was to establish diffusion trends for a large collection of dialkyl phthalates with varying chain lengths and chain branching by using a uniform, reproducible method.

Experimental Section

Materials. All phthalate plasticizers and compounded PVC films were generously supplied by Exxon Chemical Co. Table I lists each phthalate and its acronym used herein.

Table I
Phthalate Plasticizers Investigated

Model *n*-Alkyl Phthalates	Commercial Phthalates
di-*n*-pentyl phthalate (DNPP)	bis(2-ethylhexyl) phthalate (DOP)
di-*n*-hexyl phthalate (DNHxP)	diisodecyl phthalate (DIDP)
di-*n*-heptyl phthalate (DNHP)	diundecyl phthalate (DUP)
di-*n*-octyl phthalate (DNOP)	undecyl dodecyl phthalate (UDP)
di-*n*-nonyl phthalate (DNNP)	
di-*n*-decyl phthalate (DNDP)	

Model di-*n*-alkyl phthalate plasticizers (pentyl, hexyl, heptyl, octyl, nonyl, decyl) were provided as essentially pure compounds. Diisodecyl phthalate (DIDP) is a C_{10} phthalate carrying between two and four randomly placed methyl branches per alkyl moiety. Undecyl dodecyl phthalate (UDP) is a mixed ester composed of C_{11}, C_{12}, and C_{13} alkyl moieties (average C_{12}) carrying two to four randomly placed methyl branches each. Diundecyl phthalate (DUP) is a C_{11} phthalate of nearly linear structure (<0.5 methyl branches per alkyl moiety).

Unplasticized PVC films for the mass uptake experiments were compression molded from a commercial suspension-polymerized PVC resin (Exxon Chemical Co., grade 369) which was described in detail in a previous publication.[8] The PVC resin was compounded with 2.0 phr (parts per hundred parts resin) Mark 7101 stabilizer and 0.2 phr stearic acid. Films were also provided which contained initially 10 and 20 phr (8.9 and 16 wt %) of each commercial plasticizer.

Density Measurements. Measurement of D by the mass uptake technique requires knowledge of the plasticizer density at the temperature of the experiment. Densities of all the plasticizers were determined dilatometrically by using a constant-temperature oil bath. An accurately determined mass of plasticizer was charged to the dilatometer (Ace Glass cat. no. 6282), and the volume of the plasticizer was determined at a number of temperatures in the range 30–80 °C. The data were fitted to a linear volume expansion equation of the form:

$$1/\rho_T = (1/\rho_{25})(1 + \alpha\Delta T) \quad (1)$$

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).

Diffusion Measurements. Circular disks (diameter 2.54 cm) were stamped from a PVC film (thickness 0.050 cm) with a machined die. The disks (six to eight per run) were individually weighed and placed together in a beaker of plasticizer held in a constant-temperature oil bath. The temperature of the plasticizer was controlled to ±0.5 °C, and the inside bottom of the beaker was lined with glass mesh to allow free contact of the plasticizer with both sides of the disk. After 3 min, the first disk was removed, wiped clean of adhering plasticizer, reweighed, and discarded. After 3 min more, a second disk was removed, and so on. The change in weight due to imbibed plasticizer was recorded for each disk as a function of contact time with the plasticizer.

Theory, Results, and Discussion

We chose to measure diffusion of plasticizer into PVC disks, since these are of convenient geometry and are readily produced from compression-molded films. The appropriate solution of the time-dependent diffusion equation subject to the boundary conditions of this problem is given by Crank.[10] The solution is shown schematically in Figure 1 for the case of a constant surface concentration of plasticizer, c_0, maintained at one end of a cylinder whose axis is in the x-direction and throughout which the initial plasticizer concentration is c'. For the situation depicted, the plasticizer concentration at any point x along the cylinder axis at any time t is given by

$$[c(x,t) - c'] = (c_0 - c')[1 - \mathrm{erf}(x/2D^{1/2}t^{1/2})] \quad (2)$$

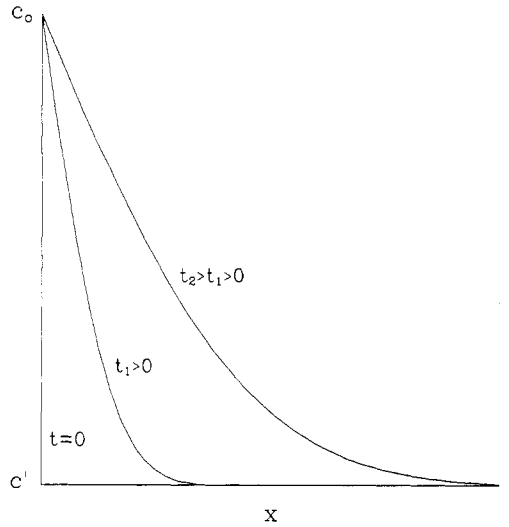

Figure 1. Solution of the time-dependent diffusion equation for the case of a constant surface concentration of plasticizer, c_0, maintained at one end of a cylinder whose axis is in the x-direction and throughout which the initial plasticizer concentration is c'.

In practice, it is much easier to measure the total mass of penetrant, s, which has entered the cylinder up to a given time rather than determine the actual concentration profile at a given instant. Differentiation of eq 2 with respect to x and applying Fick's first law yield for the penetrant diffusion flux at the surface

$$J = -D\frac{\partial c}{\partial x}\bigg|_{x=0} = (c_0 - c')(D/4\pi t)^{1/2} \qquad (3)$$

Integration of the flow of entering penetrant with respect to time yields the accumulation of penetrant within the cylinder of cross section q, at any time t:

$$s = q\int_0^t J\,dt = 2q(c_0 - c')(Dt/\pi)^{1/2} \qquad (4)$$

Rearrangement of eq 4 yields an explicit expression for D.

These equations can be reasonably applied to flattened cylinders (disks) of finite thickness as long as concentration changes near the boundaries are negligible. Thus if the uptake experiment is shortened such that the penetrant concentration profile vanishes short of the opposite face of the disk, the equations listed are applicable. Additionally, the use of a thin disk minimizes the effect of lateral flow of penetrant into the exposed edge of the cylinder.

Since we experimentally have a cylinder that is exposed to bulk plasticizer at *both* ends, the problem can be viewed as having two semiinfinite cylinders, back to back as shown in Figure 2, with the condition that experimental times be sufficiently short that penetrant concentrations effectively vanish short of the center of the disk, x_m= 0.025 cm. Without this restriction, one can imagine that when the counterdiffusion fronts intercept each other, advancing penetrant molecules no longer experience a "fresh" environment but one that is already plasticized to some degree. To retain the simplicity of eq 2 and avoid the use of a cumbersome infinite series solution that would rigorously apply at *all* experimental times,[11] let us define "sufficiently short times" as those which satisfy the condition $\mathrm{erf}(x_m/2D^{1/2}t^{1/2}) = 1.0$, which is essentially true for $t < x_m^2/16D \cong 4 \times 10^{-5}/D$. Such condition did hold for all D values measured, except the four largest; however, in these cases no systematic departure from linearity was observed at longer times, which we feel indicates the possible error is not significant.

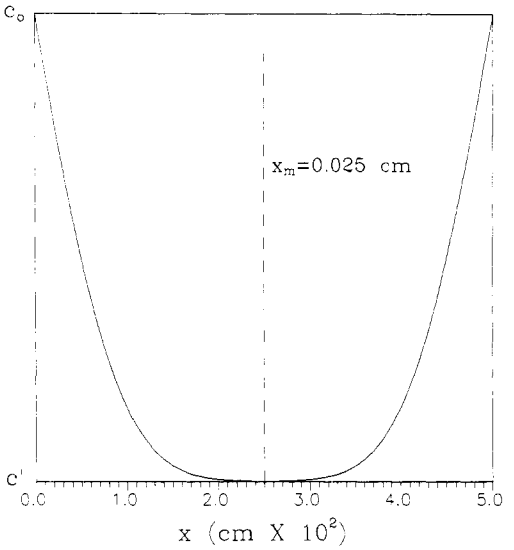

Figure 2. Theoretical concentration profiles, at t = 2500 s, for diffusion ($D = 10^{-8}$ cm^2/s) into both sides of a disk of thickness 0.050 cm.

Table II
Densities and Expansion Coefficients for Various Dialkyl Phthalates

phthalate	$\sigma_{25°C}$, g/mL	expansion coef $\alpha \times 10^4$, °C^{-1}
di-*n*-pentyl (DNPP)	1.027	6.82
di-*n*-hexyl (DNHxP)	1.006	6.93
di-*n*-heptyl (DNHP)	0.994	6.71
di-*n*-octyl (DNOP)	0.982	6.65
di-*n*-nonyl (DNNP)	0.971	6.52
di-*n*-decyl (DNDP)	0.962	6.45
bis(2-ethylhexyl) (DOP)	0.986	6.64
diisodecyl (DIDP)	0.970	6.18
diundecyl (DUP)	0.956	6.29
undecyl dodecyl (UDP)	0.944[a]	6.0[b]

[a] Reported by manufacturer. [b] Estimated.

Thus, for diffusion into both ends of the cylinder, we simply introduce a factor of 2 in eq 4, which yields the following expression for D:

$$D = \frac{\pi s^2}{16q^2(c_0 - c')^2 t} \qquad (5)$$

If plasticizer mass uptake is plotted vs $t^{1/2}$, a linear relationship should result for constant D, from which we may extract D as follows:

$$D = \frac{\pi(\mathrm{slope})^2}{16q^2(c_0 - c')^2} \qquad (6)$$

The external plasticizer concentration, c_0, is its bulk liquid density, which must be measured or calculated for the temperature of the diffusion experiment. The initial plasticizer concentration within the sample, c', if nonzero, is readily calculated, assuming no volume change upon mixing (weak polymer–plasticizer interactions), from the initial weight fraction of plasticizer, w_1, and c_0, and the density of PVC, which was taken to be 1.36 g/mL at 90 °C. Densities of all the plasticizers were measured dilatometrically in the range 30–80 °C. Specific volume vs T – 25 °C plots were quite linear, yielding expansion coefficients (α) that are listed along with room temperature densities for each plasticizer in Table II. As expected, phthalate density goes down as the length of the alkyl chain increases. Surprisingly, we found that branching in the alkyl chain caused a slight increase in density when

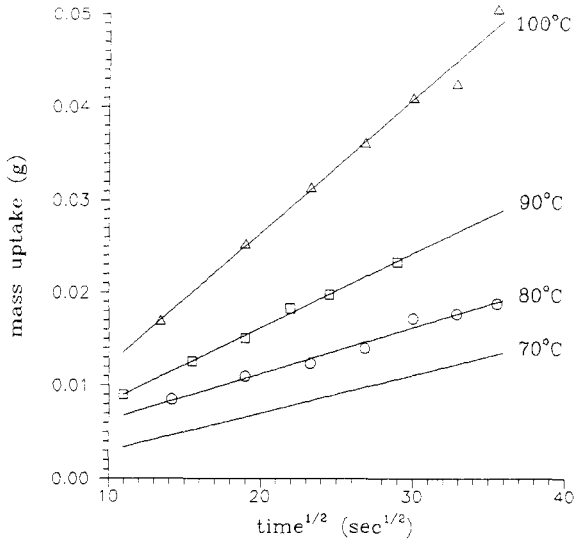

Figure 3. Mass uptake plots for diffusion of di-*n*-octyl phthalate (DNOP) at 70 °C (solid line) and at several temperatures above the glass transition of PVC: (○) 80, (□) 90, (△) 100 °C.

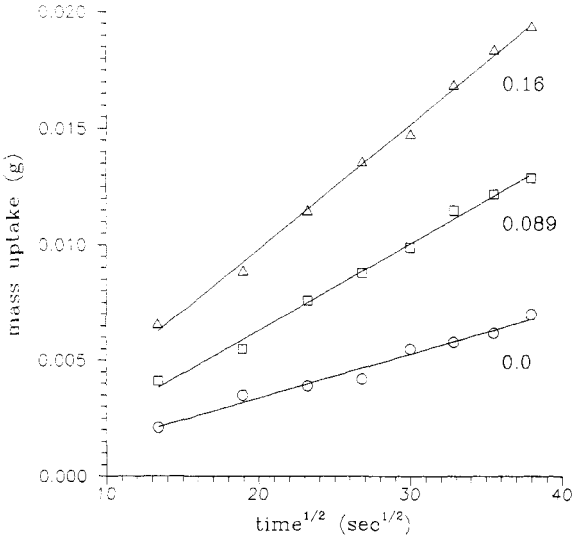

Figure 4. Mass uptake plots for diffusion of diundecyl phthalate (DUP) at 90 °C for several initial plasticizer contents (w_1): (○) 0, (□) 0.089, (△) 0.16.

compared to a normal phthalate of equal carbon number e.g., DIDP (branched) vs DNDP (normal) and DOP (branched) vs DNOP (normal). Expansion coefficients were found to fall in the range (6–7) × 10^{-4} °C^{-1} for all the plasticizers, and with the exception of DNPP, they tended to decrease with increasing alkyl chain length.

Figures 3 and 4 depict representative mass uptake plots for a model straight-chain alkyl phthalate at various temperatures and a commercial phthalate plasticizer at different initial plasticizer concentrations, respectively. It should first be noted that the plots are quite linear with respect to (time)$^{1/2}$, indicating Fickian diffusion with "constant" D. Also, Figure 3 illustrates the monotonic increase in D which was always observed with increasing temperature. The sub-T_g (70 °C) plot pictured with no data points is actually a back-extrapolation from much longer times; accurately measurable mass increases were observed much later owing to slow uptake. In Figure 3, the increased scatter in the data at long times for the highest temperature measured is representative of a general trend observed under conditions of high solvation, i.e., long times, high temperatures, and/or low molecular weight phthalates. Under these conditions the solvating

Table III
Diffusion Coefficients of Di-*n*-alkyl Phthalates into Initially Unplasticized PVC

n-alkyl group	T, °C	D, cm^2/s
pentyl	80	2.45×10^{-8}
pentyl	90	8.13×10^{-8}
pentyl	100	7.84×10^{-7}
hexyl	60	7.63×10^{-9}
hexyl	70	9.79×10^{-9}
hexyl	80	1.50×10^{-8}
hexyl	85	2.19×10^{-8}
hexyl	90	2.96×10^{-8}
hexyl	95	5.26×10^{-8}
hexyl	100	8.09×10^{-8}
heptyl	80	5.54×10^{-9}
heptyl	90	1.68×10^{-8}
heptyl	100	5.97×10^{-8}
octyl	70	1.39×10^{-9}
octyl	80	2.10×10^{-9}
octyl	85	3.68×10^{-9}
octyl	90	5.54×10^{-9}
octyl	95	9.60×10^{-9}
octyl	100	1.79×10^{-8}
nonyl	80	1.34×10^{-9}
nonyl	90	4.23×10^{-9}
nonyl	100	6.88×10^{-9}
decyl	80	1.93×10^{-10}
decyl	90	5.76×10^{-10}
decyl	100	2.67×10^{-9}

power of the plasticizer is highest, which leads to softening of the PVC surface, and it becomes difficult to remove excess plasticizer from the surface of the disk prior to weighing.

In Figure 4, mass-uptake slopes are shown to increase with increasing initial plasticizer concentration in the PVC disk. The enhanced diffusion rates result from the increase in free volume brought about by preincorporation of penetrant molecules into the polymer structure.[12] It is important to note in this regard that the state of dynamic equilibrium of polymer chains in such a sample that has been preblended with a given quantity of plasticizer is not the same as the state of chains in a sample incorporating the same quantity but at a given instant in a kinetic uptake situation. An increase in free volume, brought about by plasticization, is usually quantified in terms of the T_g of the PVC/plasticizer blend:[13]

$$V_f = V[0.025 + \alpha_f(T - T_g)] \quad (7)$$

where V_f is the average free volume in polymer, V the total sample volume (steric + free), and α_f the temperature expansion coefficient of free volume.

The blend T_g, furthermore, can be predicted from the weight fraction of plasticizer, w_1. We have found the following linear relationship[12] to hold quite well for a number of phthalate ester/PVC mixtures at $w_1 \leq 0.35$:[2]

$$T_g = T_{g2} - kw_1 \quad (8)$$

where T_{g2} is the T_g of pure unplasticized PVC (ca. 354 K), k the plasticizer efficiency parameter (K), and w_1 the weight fraction of incorporated plasticizer. A blend T_g which conceivably evolves to lower values during plasticizer uptake over long times implies that actual s vs $t^{1/2}$ curves would exhibit a slowly increasing derivative. The linear region for which we obtain a slope is in fact the initial portion of such a curve.

Diffusion coefficients for all the phthalates investigated are listed in Tables III and IV. The following trends may be noted: Diffusion coefficients (1) increase with increasing temperature, (2) decrease with increasing alkyl chain length, and (3) decrease with increasing degree of alkyl chain branching.

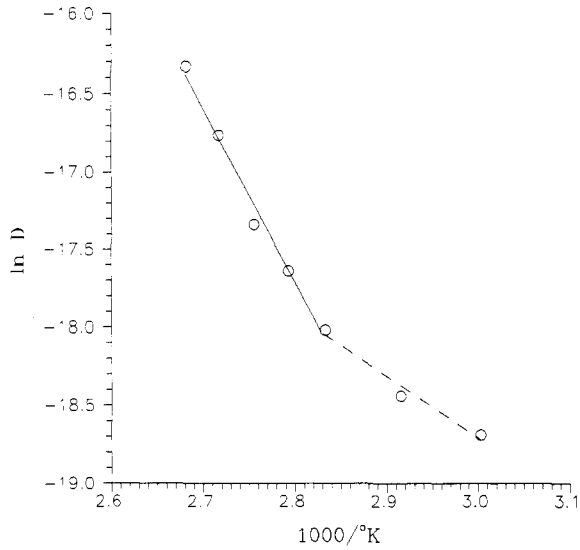

Figure 5. ln D vs $1/T$ for di-*n*-hexyl phthalate (DNHxP).

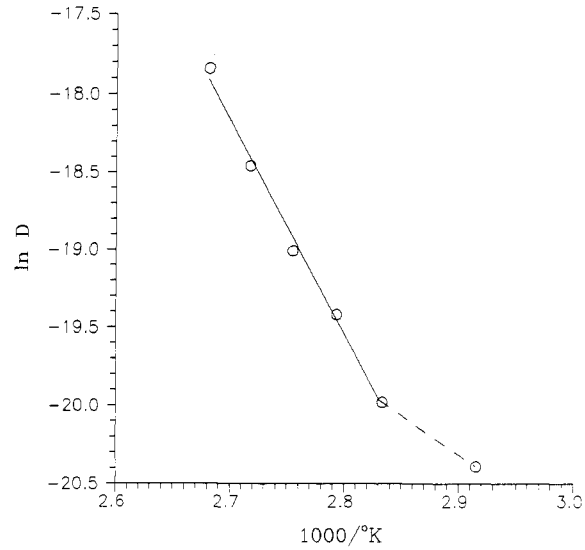

Figure 6. ln D vs $1/T$ for di-*n*-octyl phthalate (DNOP).

Table IV
Diffusion Coefficients of Several Commercial Phthalates in PVC

phthalate	T, °C	w_1	c'	D, cm^2/s
DOP	80	0	0	1.26×10^{-9}
DOP	90	0	0	3.74×10^{-9}
DOP	100	0	0	1.02×10^{-8}
DIDP	90	0	0	4.58×10^{-10}
DIDP	90	0.089	0.116	1.49×10^{-9}
DIDP	90	0.16	0.207	5.55×10^{-9}
DUP	90	0	0	3.29×10^{-10}
DUP	90	0.089	0.116	1.70×10^{-9}
DUP	90	0.16	0.206	4.36×10^{-9}
UDP	90	0	0	2.60×10^{-10}
UDP	90	0.089	0.116	7.53×10^{-10}
UDP	90	0.16	0.206	9.65×10^{-9}

The effect of temperature on plasticizer diffusion is depicted by ln D vs $1/T$ plots in Figures 5 and 6 for DNHxP and DNOP, respectively. The linearity of these plots for $T \geq 80$ °C suggests that diffusion above the T_g of PVC (ca. 81 °C) follows an Arrhenius expression:

$$\ln D = \ln A - E_{act}/RT \quad (9)$$

where A is the entropy–frequency prefactor and E_{act} is the activation energy for diffusion. It may be noted that the smaller penetrant molecule has a lower E_{act} above T_g than the larger penetrant molecule. The E_{act} for DNHxP is 22 kcal/mol, while for DNOP it is 27 kcal/mol. Further examination of these plots, in particular Figure 5, reveals a similarly linear relationship below T_g with an abrupt change in slope at the T_g of PVC (ca. 81 °C). It is significant and reasonable that the activation energy for diffusion is lower below T_g than above. For DNHxP (Figure 5), the activation energy above T_g is 22 kcal/mol, while below T_g it is 7.9 kcal/mol. From an energetics standpoint, the cooperative motion of a greater number of consecutive chain segments is possible above T_g; hence the E_{act} is greater. The greater temperature sensitivity of D above the T_g might also be thought of in terms of a greater thermal expansion coefficient of the fractional free volume; below T_g the fractional free volume stays relatively constant, and only localized in-chain motions are active. It is the onset of expansion of available free volume with temperature above the T_g that leads to the change in slope observed in Figure 5.

This behavior, of course, suggests that the mechanism for plasticizer diffusion in PVC is different above and below T_g. Because of the relative constancy of unrelaxed free volume below T_g, it is reasonable that diffusion is accompanied by the local solvation of a handful of consecutive chain segments rather than through a long-range reordering of free volume as in the α-relaxation. In other words, the mobility of polymer chain segments is initially low but is enhanced within the immediate vicinity of the penetrant through polymer–solvent interactions. Diffusion by continuing solvation, implying as it does a more or less diffuse penetrant front uniformly progressing through the sample, would connote behavior that is non-Fickian, as implied by our earlier work on the kinetics of plasticizer swelling of PVC particles.[8] However, the 60 and 70 °C s vs $t^{1/2}$ plots for DNHxP are in fact quite linear, which suggests Fickian behavior in these cases, at least. On the other hand, DNDP, the largest, most poorly solvating model phthalate in this study, yielded nonlinear s vs $t^{1/2}$ plots at 70 °C.

The data in Tables III and IV clearly reveal that D significantly decreases with increasing molecular size of the phthalate penetrant. For example, at 100 °C D is observed to decrease by a factor of ~300 as one moves up from the 5-carbon to the 10-carbon normal phthalate. The qualitative direction of this trend is obvious for the following reasons: A large, massive penetrant molecule has a thermal kinetic velocity during an activated displacement that is inversely proportional to the square root of its mass. Furthermore, and of greater importance, the probability for free volume redistribution to form a hole of sufficient size to accommodate all or a portion of the molecule goes down exponentially with increasing size of the penetrant according to the free volume theory.[14] As shown in Figure 7, ln D vs number of carbons in the *n*-alkyl phthalate chain is approximately linear for several temperatures above the T_g of PVC. Since classical diffusion theory predicts that $-\ln D$ is directly proportional to the free volume requirement for penetrant hopping,[14] this result implies that diffusion occurs in the direction of the long axis of the plasticizer molecule and that the alkyl chains assume extended conformations. In other words, increasing the phthalate ester alkyl chain length serves only to lengthen the molecule without significantly altering its effective lateral dimensions. Thus, the horizontal axis of Figure 7 may be regarded as the increasing steric volume of the penetrant molecule, in increments of pairs of methylene units. The vertical intercept of such a plot is the diffusion coefficient defined for a hypothetical phthalate "core" of the *n*-alkyl phthalate homologous series. The solid points

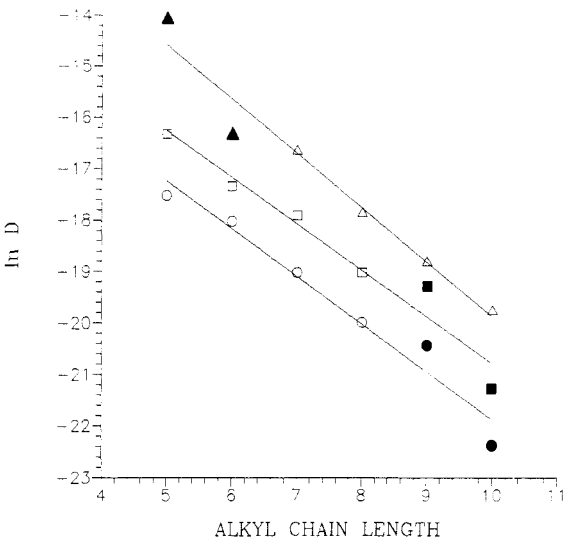

Figure 7. Dependence of D on number of carbons in the alkyl chain of di-*n*-alkyl phthalates at several temperatures above the glass transition of PVC: (○) 80, (□) 90, (△) 100 °C. Solid symbols represent data taken at opposite extremes of experimental conditions, which border the useful limits of the mass uptake technique.

in Figure 7, which deviate from the linear portion of the plots, are D values taken at two opposite extremes of experimental conditions, which in fact define the useful limits of the mass uptake technique, which are the combination of high temperature and relatively strongly solvating plasticizer (solid triangles) and the combination of low temperature and poorly solvating plasticizer (solid squares and solid circles). Diffusion measurements made under strongly solvating conditions are difficult because of degradation through partial solvation of the disk surface; measurements made at low temperatures and/or with large, marginally compatible plasticizers are difficult because of very slow diffusion.

A final comparison which may be made from the data in Tables III and IV is the difference in diffusion between branched and unbranched phthalates of the same molecular weight. Commercial DOP is the branched analogue of DNOP, and commercial DIDP is likewise the branched analogue of DNDP. In both cases, diffusion rate was observed to decrease with branching. This result was expected and is, in fact, a prediction of our molecular shape-dependent theoretical model.[1] In general terms, for penetrants of equal volumes, compacted structures are predicted to diffuse slower than extended ones.

Conclusions

The mass uptake technique used in this work is a straightforward and reproducible method for determination of the diffusion coefficients of plasticizers into rubbery polymers within certain limits of temperature and penetrant solvating activity. When diffusion of a series of *n*-alkyl phthalates and several commercial branched phthalate plasticizers into PVC was measured, it was determined that in all cases diffusion coefficients increased with increasing temperature and decreased with increasing plasticizer size and branchiness.

For DNHxP and DNOP it was found that the temperature dependence of diffusion above the glass transition could be well-fitted to an Arrhenius-type relationship yielding activation energies of 22 and 27 kcal/mol, respectively. For sub-T_g temperatures, diffusion of DNHxP was also observed to follow an Arrhenius-type equation, but with lower activation energy. The change in slope was observed to be sharp and centered precisely at the T_g of PVC.

Finally, it was found that ln D decreased approximately linearly with increasing alkyl chain length within the series of *n*-alkyl phthalates. Within the framework of the free volume theory, wherein $-\ln D$ is directly proportional to the free volume requirement for penetrant hopping, this result suggests a longitudinal molecular displacement, i.e., along the direction of elongated alkyl chains.

We were unable to collect, from the existing literature, a data base of D values as broad as that reported in this work for comparison. While caution should be exercised in comparing diffusion coefficients derived from different methodologies, we note the following.

The orders-of-magnitude of our D values for DOP at 80 and 100 °C are around those of Knappe[5] at his concentration midrange. We do not feel we have sufficient temperature data for the DOP case to ascertain an accurate E_{act} to compare with values obtained by either Knappe or Grotz,[6] although it is seen that the values reported by these investigators, in fact, do not agree well with each other. Grotz's value of $D = 3.0 \times 10^{-8}$ cm^2/s at 85 °C, when corrected by dividing by 4 (for the reasons cited in the Introduction), agrees rather well with our values at 80 and 90 °C listed in Table IV.

A reasonably meaningful comparison can be made between our results for DNHxP at 60 °C and that of Griffiths et al.[7] for this plasticizer at 55 °C. These authors report $D \sim 3 \times 10^{-8}$ cm^2/s at 45 wt %, which is approximately 4 times our result at 60 °C and at 0 wt %, as seen in Table III. We also feel that, considering the difference in experimental methods, our above/below T_g activation energies of 22/8 kcal/mol, respectively, for DNHxP are roughly comparable to the values of 20 and 12 kcal/mol obtained by Griffiths et al. at the lower and upper ends, respectively, of their investigated plasticizer concentration range. On the other hand, these authors list slightly lower activation energies for DNDP than for DNHxP, which is contrary to our results.

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Registry No. DNPP, 131-18-0; DNHxP, 84-75-3; DNHP, 3648-21-3; DNOP, 117-84-0; DNNP, 84-76-4; DNDP, 84-77-5; DOP, 117-81-7; DIDP, 26761-40-0; DUP, 3648-20-2; UDP, 116998-09-5; PVC, 9002-86-2.

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