A General Free Volume Based Theory for the Diffusion of Large Molecules in Amorphous Polymers above T_g. 3. Theoretical Conformational Analysis of Molecular Shape

Christopher S. Coughlin, Kenneth A. Mauritz,* and Robson F. Storey

Department of Polymer Science, University of Southern Mississippi,
Southern Station Box 10076, Hattiesburg, Mississippi 39406-0076

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ABSTRACT: Mauritz and Storey have advanced a free volume theory for the above-T_g diffusion, in amorphous polymers, of molecules that are large in relation to the size of the dynamic chain segments of the host polymer. This theory has been favorably evaluated in general terms against experimental evidence for plasticizer-in-PVC diffusion while utilizing somewhat crude estimates of the requisite sizes and shapes of the penetrant molecules. In this work, the actual atomic-level structures of these complex molecules are theoretically determined by an energetics-based conformational analysis. The diffusion theory, in its most general form, requires the values of the penetrant's maximum cross sectional areas that are perpendicular to the three principal axes that pass through the molecular center of gravity. We have developed numerical methods for evaluating these irregular areas for the intrinsically complex structures predicted by the theoretical conformational analyses, and the resultant diffusion coefficients for di-*n*-alkyl phthalates in rubbery PVC are in reasonable agreement with available experimental data.

Introduction

The diffusion of large molecules within polymers is a subject of great technological importance from the standpoint of both processing and useful properties. In the present context, a penetrant molecule is considered to be "large" if its size exceeds that of a chain segment of the host polymer by a reasonable amount. A broadly applicable model for the diffusion of large molecules in rubbery amorphous polymers would be of great utility in consideration of the controlled transport of plasticizers, surfactants, lubricants, or biologically active molecules through polymeric materials.

An excellent summary of earlier models of diffusion in macromolecular systems is given by Kumins and Kwei in the volume by Crank and Park.[1] The pioneering works of Barrer,[2,3] Meares,[4] Bueche,[5] Brandt,[6] and DiBenedetto and Paul[7-9] are of special prominence.

Several recent theories have been developed to model the diffusion of particularly large molecules in polymer systems. Notably, the work of Vrentas and Duda has been shown to be generally valid within its intended realm of application.[10-13] However, it does suffer from a serious limitation of its utility as a predictive tool as it requires a rather large body of experimental data. Similarly, Pace and Datyner have presented a rather elaborate statistical mechanical model for the diffusion of both simple and "complex" penetrants in polymers.[14] While this theoretical formulation is impressive in both breadth and depth, its utility in the optimization of a diffusion process for a practical situation appears quite limited.

In order to address the need for a reasonable and straightforward model that uses readily available or easily determined physical parameters, we have initiated the development of a penetrant shape dependent, largely free volume based diffusion model that utilizes theoretical conformational analysis to generate specific low-energy penetrant molecular shapes and predict diffusion coefficients (D) for large diffusants within amorphous polymers, which can also be either cross-linked or semicrystalline, above their glass transition temperatures. The underlying theory has been presented in earlier reports by Mauritz and Storey.[15,16] In this paper, we will apply the general equations developed in our model, as well as the technique of theoretical conformational analysis, to calculate, a priori, values of the diffusion coefficient for selected members of a homologous series of di-*n*-alkyl phthalate plasticizers, given in Table I, and then compare these results with our previously reported experimental diffusion data for these systems.[17]

Table I
Phthalate Plasticizers Investigated

di-*n*-pentyl phthalate (DNPP)
di-*n*-hexyl phthalate (DNHxP)
di-*n*-heptyl phthalate (DNHP)
di-*n*-octyl phthalate (DNOP)
di-*n*-nonyl phthalate (DNNP)
di-*n*-decyl phthalate (DNDP)

The molecular shape dependence of our diffusion model was demonstrated in a general way by noting the sensitivity of D to the relative characteristic dimensions of hypothetical simple figures of high symmetry such as ellipsoids.[16] It was predicted that, for a given fixed molecular volume, compact structures migrate slower than extended ones, all other factors being equal. While the simplifying geometrical assumption that a molecule can be represented as a spheroid is a time-honored practice, an inspection of space-filling models of large molecules, such as plasticizers, reveals rather irregular shapes. Molecules of this complexity are better thought of as being rather bumpy and convoluted so as to leave a large amount of empty space in any sphere or ellipsoid that is forced to enclose them. This realistic consideration has led to the further development of the model to consider the "true" shape, in this sense structural granularity, and effective size of the diffusing penetrant molecules. The determination of the "true" shape of a penetrant molecule is most accurately performed by using a molecular mechanics procedure based on theoretical conformational analysis. This technique utilizes nonbonded pairwise atomic potential energy functions and bond torsional energy functions to locate the minimum energy conformation of a molecule, through bond rotations by minimizing the ener-

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getic sum. The molecular mechanics technique has been used with great success[18] in the conformational analysis of large molecules and will be employed in this study.

Penetrant molecular shape dependence was factored into the theory by demonstrating that the three-dimensional diffusion coefficient is the simple arithmetic average of three one-dimensional diffusion coefficients, D_i, $i = 1$–3, each of which corresponds to unit hopping in the instantaneous directions of the three principal axes that pass through the penetrant molecular center-of-mass. The degree to which $D_1 \neq D_2 \neq D_3$ depends on specific molecular shape, i.e., the distribution of constituent atoms, having characteristic van der Waals radii, about the center-of-mass. It is a very distinctive feature of this model that the elementary molecular displacement along a given principal axis is but a fraction, f_i, of its characteristic dimension along that direction, l_i. The resulting equations are as follows:

$$\bar{D}_i(w_1,T) = F/2l_iA_i^2; \quad i = 1\text{–}3 \tag{1}$$

$$\bar{D}(w_1,T) = F/6(1/l_1A_1^2 + 1/l_2A_2^2 + 1/l_3A_3^2) \tag{2}$$

where the bar over D_i indicates that this quantity represents an average over possible hopping displacements from zero up to the entire molecular dimension l_i along axis i and F is given by

$$F = (M_0/\rho N[0.025 + \alpha_f(T - T_g + kw_1)])^2(eRT/M_p)^{0.5} \tag{3}$$

where w_1 is the weight fraction of penetrant, T the Kelvin temperature, A_i the penetrant maximum cross sectional area in a plane perpendicular to the direction i, M_0 the molecular weight per chemical repeat unit of the polymer, ρ the mass density of the dry polymer at the temperature of interest, N Avogadro's number, α_f the temperature coefficient of free volume expansion, T_g is the glass transition temperature of the unplasticized polymer, k the experimental plasticizer efficiency parameter, R the gas constant, and M_p the molecular weight of penetrant. Thus, with a knowledge of these simple quantities as well as results from the molecular size and shape analysis via theoretical conformational analysis, the diffusion coefficient of the penetrant within the polymer can be calculated for any given weight fraction of penetrant and temperature above the glass transition of the polymer. The remainder of this paper will essentially report the results of the analysis of the most favored conformations of a homologous series of di-*n*-alkyl phthalate plasticizers and the comparison of their calculated diffusivities in PVC with our experimental data for the same systems.

Conformational Analysis

The conformational analyses of the selected di-*n*-alkyl phthalate plasticizer molecules were carried out by using the molecular mechanics method of the CHEMLAB-II software system[19] running on a MicroVax-II computer. Starting molecules were constructed from standard geometry template molecules, and all calculations were done by using a fixed valence geometry. The total internal energy of the molecule is obtained by summing all the possible pairwise nonbonded interatomic interaction energies. These empirical potential energy functions, described in detail by Hopfinger,[18] included the Lennard-Jones 6–12 potential, accounting for van der Waals attractive as well as repulsive (steric) energies, and electrostatic potential energy in the form of Coulomb's law wherein the partial atomic charges were calculated by the CNDO/2 quantum mechanical approximation. The general form of the bond–torsional potential energy function is[20]

$$E = A[B + C\cos^M(N\Theta - \Psi)] + D[1 - \cos(F\Theta - \Psi)] \tag{4}$$

where the constants A, B, C, D, F, M, N, and Ψ depend on the atomic groups in the vicinity of the bond around which a rotation of Θ takes place. The constants used were either preexisting CHEMLAB-II constants or were created by using the molecular mechanics parameterization option of CHEMLAB-II. The rotation sense is defined to be clockwise, sighting along the specified bond so that the least number of atoms is away from the viewer.

All molecules were set into standard reference conformations before conformational analysis. In general, the bond rotations were scanned, up to six bonds at a time, in 30° increments to coarsely identify regions of low energy. The molecules were then set into their observed low-energy conformations, and the energy was further minimized by using the MINMZ option of CHEMLAB-II, which conducts a fixed valence geometry conformational energy minimization by using the aforementioned scanning minima as starting points. Obviously, each of these complex molecules has more than six rotatable bonds. Accordingly, some bonds were held fixed during the conformational analysis. The interior bonds, i.e., those close to the ring, were energy-minimized first and then fixed in their lowest energy conformation while the bonds further out from the ring, in the alkyl chains, were energy-minimized. Since these were ethane-type bonds, they were only scanned in 120° increments, and the energy minimization was then performed. Reminimization was then performed with the interior bonds, with their previous low-energy conformations as starting points, but now scanning with smaller torsional angle increments for the minimizing routine to fine-tune the lowest energy conformation. Of course, these molecules are rather flexible, and more than one conformation may exist near to that corresponding to the lowest energy. In general, the structures resulting from these other minima are seen to be quite close in overall character to that for the chosen global minimum.

The resulting lowest energy conformations were fixed so that their calculated principal axes were aligned with the X, Y, and Z axes of the CHEMLAB-II workspace, and their centers-of-mass were translated to the origin. The alignment of the molecule may have some effect on the cross sectional area calculation and, hence, the predicted diffusion coefficient. Therefore, some standard alignment technique had to be selected. Since diffusion is a mass transport process, this alignment (with center-of-mass at the origin and principal axes aligned with the Cartesian axes) is a logical procedure because in mechanics the translational trajectory of a particle is defined by the path of its center-of-mass. The molecules were thusly aligned prior to the cross sectional area calculation, which is described in the next section, by using the PRINMOMNT option of CHEMLAB-II.

Calculation of Penetrant Molecular Cross Sectional Areas

The effective molecular cross sectional areas in the planes perpendicular to the principal axes were determined by two different numerical statistical methods. These algorithms were coded in Fortran and interfaced transparently with the CHEMLAB-II software. The scanning method, shown in Figure 1, overlays the plane projection or shadow of the molecule with a grid having a user-selectable mesh size. Each square of the grid is scanned to determine whether or not it lies within the molecule. The number

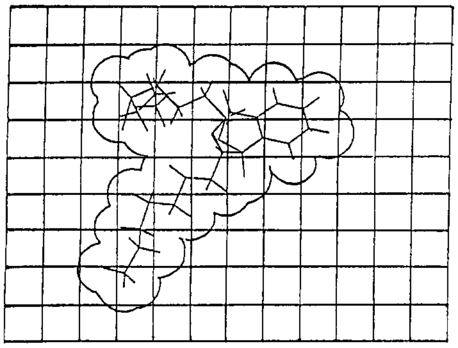

Figure 1. Exaggerated superimposed mesh size in scanning method of penetrant molecular cross sectional area determination.

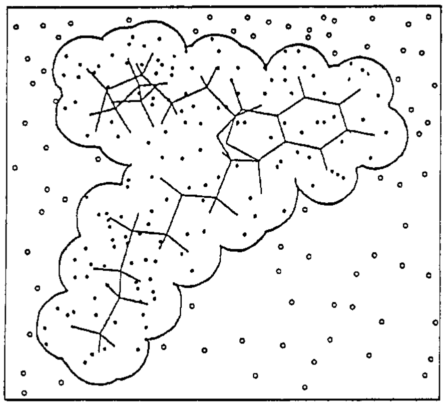

Figure 2. Monte Carlo integration method of penetrant molecular cross sectional area determination wherein the number of randomly selected points is kept low for illustration.

of squares within the molecule multiplied by the area of a square gives an approximation of the effective molecular cross sectional area. Typically, about 1000 points/Å^2 were scanned, corresponding to an individual square size of 10^{-3} Å^2.

The method depicted in Figure 2, on the other hand, uses the technique of Monte Carlo integration.[21] A box that barely encloses the molecular projection is drawn around it. Pairs of random numbers are generated with a distribution equivalent to the dimensions of the box. Each pair is mapped onto the box and tested to determine whether or not it lies within the projected perimeter of the molecule. The area of the box multiplied by the proportion of points lying within the molecule then gives an approximation of the area. Again, a typical point density of 1000/Å^2 was employed. Higher point densities, say greater than 2000/Å^2, could be employed, but generally the accuracy gained is not worth the CPU effort.

Calculation of Plasticizer Diffusion Coefficients

The three-dimensional diffusion coefficients for the selected di-*n*-alkyl phthalate molecules were then calculated by using eqs 2 and 3. The effective molecular cross sectional areas used in this case were derived from Monte Carlo integration. A value of 353 K was used for the T_g of pure PVC,[22] and 62.5 was used for the molecular weight per PVC repeat unit. The value of α_f was taken as the "universal" value of 4.8×10^{-4}. Plasticizer efficiencies were experimentally obtained in our laboratory by using the DSC module of a Du Pont 9900 thermal analyzer system.

In the following section, commentary on the specific plasticizer molecular conformations that give rise to the required values of A_i and l_i is made in detail.

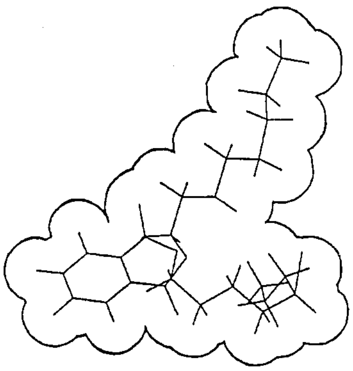

Figure 3. Projection, in the *XY* plane, of the di-*n*-octyl phthalate molecule in its calculated minimum energy conformation.

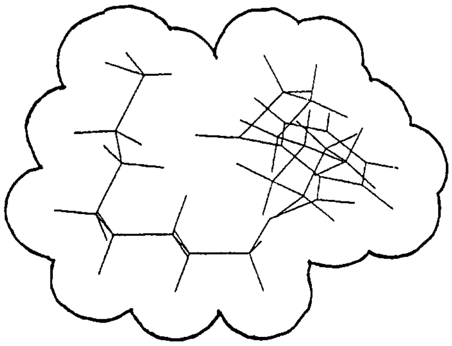

Figure 4. Projection, in the *YZ* plane, of the di-*n*-octyl phthalate molecule in its calculated minimum energy conformation.

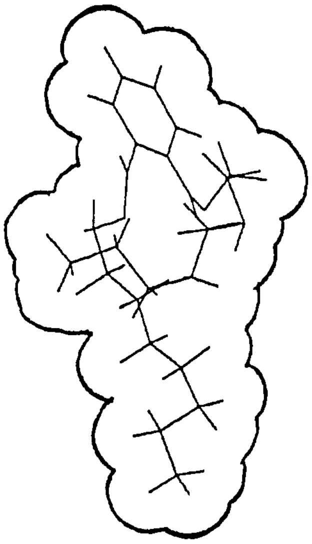

Figure 5. Projection, in the *XZ* plane, of the di-*n*-octyl phthalate molecule in its calculated minimum energy conformation.

Theoretical Conformational Analysis Results

Figures 3, 4, and 5 show the *XY*, *YZ*, and *XZ* plane projections of di-*n*-octyl phthalate in its calculated minimum energy conformation. The molecular perimeters consist of piecewise-continuous series of arcs of circles with radii equal to the van der Waals radii of the outer atoms. Similar views for the other di-*n*-alkyl phthalates used in this study also showed, in general, similar lumpy irregular shapes with varying degrees of elliptical character and protrusions of the alkyl chains. The phthalates with longer chain lengths tend to be more elongated, particularly when viewed in the *XY* plane. The chains did not prefer to fold back on themselves. Table II shows specific results of the cross sectional area calculations for the minimum energy conformations for the di-*n*-butyl phthalate through di-*n*-decyl phthalate series.

Table II
Molecular Dimensions and Cross Sectional Area Calculations for Minimum Energy Conformations

	molecular dimension, Å			molecular cross sectional area, Å^2		
plasticizer	l_X	l_Y	l_Z	A_{XY}	A_{YZ}	A_{XZ}
DNPP	13.47	12.21	9.10	79.06	57.46	66.08
DNHxP	13.70	10.63	10.92	83.16	57.18	71.61
DNHP	15.67	11.26	8.99	97.97	57.74	75.42
DNOP	17.21	12.37	10.05	98.27	71.06	84.76
DNNP	17.00	10.86	10.86	104.4	68.89	98.81
DNDP	19.14	13.31	11.80	108.3	84.00	103.3

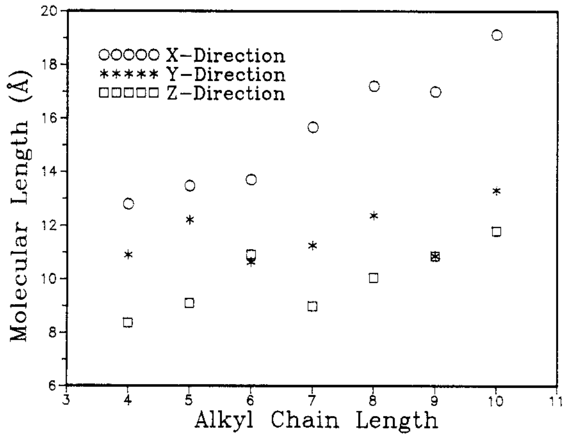

Figure 6. Molecular dimension (l_i; $i = x, y, z$) vs number of carbons in the alkyl chains of di-*n*-alkyl phthalates in their minimum energy conformations.

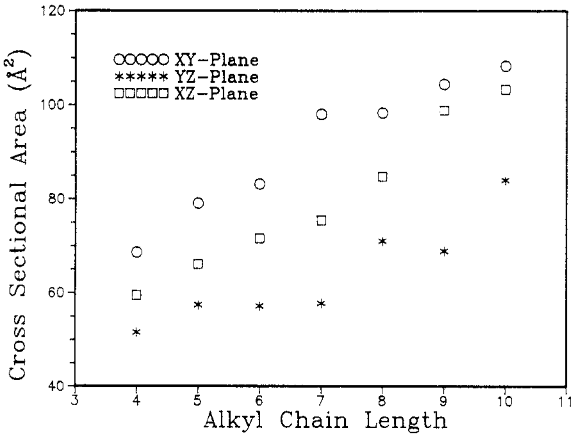

Figure 7. Effective molecular cross sectional area (A_i; $i = x, y, z$) vs number of carbons in the alkyl chain of di-*n*-alkyl phthalates in their minimum energy conformations.

These results are also graphically depicted in Figures 6 and 7.

Note in Figure 6 that the molecular length stays relatively constant in both the *Y* and *Z* directions through the whole range of carbon numbers while the length in the *X* direction seems to take an upswing at about a carbon number of 7. This indicates that as the chain length reaches a lower limit of around seven carbons, the low-energy conformations promote molecular elongation considerably more so in the *X* direction while maintaining roughly the same *Y* and *Z* dimensions. Graphical examination of the space-filling structure of the higher carbon number phthalates bears out this observation. As the side-chain length increases, the low-energy conformations of the alkyl chains are more likely to be straighter and extended outward, rather than folded back onto themselves or against the ring. This results in a molecule that is less round (more elongated) in the *X* direction while still relatively "round" in the *Y* and *Z* directions, as depicted in Figures 3–5.

An examination of Figure 7 shows that, while all of the cross sectional areas increase with increasing alkyl chain length, the area in the *YZ* plane, which is roughly perpendicular to the overall chain extension direction, stays relatively much lower than do the areas in either of the *XY* or the *XZ* planes. This, of course, is in accord with the major growth in the *X*-direction as discussed above. The *YZ* plane area does not increase considerably because the molecule is increasing in size primarily in the *X*-direction.

For this homologous series of di-*n*-alkyl phthalate plasticizers, the apparent preferential lengthening of the molecules in the *X*-direction with increasing carbon number, without much change in the *YZ* cross sectional area, is a physically satisfying observation in light of the basic concept embodied in our diffusion model. As we had cited earlier,[15] experimental studies of the pressure dependence of the diffusion coefficient for a homologous series of *n*-alkanes in polyethylene show that, over the homologues, *n*-hexane, *n*-octane, and *n*-decane, the volume of activation for diffusion is practically constant and equal to that of about two chain segments.[23,24] The addition of methyl side groups, however, increases this volume. While the volume of activation for benzene was found to be equal to its molar volume, the volumes of activation for linear paraffins are clearly less than their molar volumes. The interpretation is that *n*-paraffin molecules diffuse by motion along their chain contours while they are in general alignment with the polymer chains. The hole size required for unit flow, as well as the jump length, would seem to be independent of penetrant molecular length. Our own experimental diffusion studies of straight-chain phthalate plasticizers suggest a similar longitudinal mode of diffusion.[17] Physically, the relatively smaller area of the *YZ* plane would seem to imply that diffusion along the *X* direction should be easier than along either of the *Y* or *Z* directions since less of the polymer medium would be required to be swept aside to accommodate a molecular jump. This is in fact predicted by our general diffusion theory and is in general agreement with the familiar diffusion behavior of a penetrant migrating preferentially along its length. It is not seen, however, that above a certain number the *YZ* area stays constant for the homologous series of straight-chain phthalate plasticizers. Our model in fact depicts a more complex situation, taking into account other variables such as the molecular weight of the penetrant and its efficiency as a plasticizing agent. While the exact details of the mode of diffusion for a given large molecule may never be understood with absolute certainty, we believe the results of our conformational analysis and cross sectional area calculations are physically reasonable and in general harmony with the interpretation of limited experimental studies.

Plasticizer Diffusion Coefficient Calculations

Table III shows the experimentally determined plasticizer efficiency values for three di-*n*-alkyl phthalates: di-*n*-pentyl, di-*n*-octyl, and di-*n*-decyl phthalate, or DNPP,

Table III
Plasticizer Efficiencies for PVC Containing Indicated Di-*n*-alkyl Phthalates

plasticizer	k, K
DNPP	213
DNOP	337
DNDP	282

Table IV
Diffusion Coefficients in PVC at 363 K and 0 wt % Plasticizer

plasticizer	exptl D, $\times 10^9$ cm^2/s	calcd D, $\times 10^9$ cm^2/s
DNPP	81.3	8.29
DNHxP	29.6	7.27
DNHP	16.8	6.00
DNOP	5.54	4.13
DNNP	4.23	3.65
DNDP	0.576	2.53

DNOP, and DNDP, respectively. While one might, at first, expect these values to vary in somewhat monotonic fashion, with perhaps smaller plasticizer molecules giving higher values of k than the larger molecules, this was not found to be the case, with DNPP in fact having the lowest of the three values. Interestingly, we also note that Doty and Zable found that the Flory–Huggins polymer–solvent interaction parameter, χ, did not vary monotonically but in fact showed a singular dip when χ was plotted versus molecular weight for a homologous series of di-*n*-alkyl phthalate plasticizers in PVC.[25] Of course, our data are currently too sparse to confirm a similar related trend in k values. k values for the entire series of di-*n*-alkyl phthalates are currently being determined and will be reported in a future communication.

Listed in Table IV are diffusion coefficients for these three plasticizer-in-PVC systems, as well as for three additional di-*n*-alkyl phthalate plasticizers in PVC, di-*n*-hexyl, di-*n*-heptyl, and di-*n*-nonyl phthalate (DNHxP, DNHP, and DNNP, respectively), for which k values have not been determined. The first column shows D values experimentally determined in our laboratory,[17] while the second column shows values calculated via the conformational analyses detailed above and via eqs 2 and 3. Actually, all of the experimental values of D listed in Table IV correspond to very low plasticizer levels[17] so that kw_1 is effectively zero in all cases. In this way, one is evaluating trends in diffusivity that are rather exclusively due to penetrant molecular size and shape in equivalent dynamic environments without having to sort out the additional complication of variable T_g shifting by different plasticizers. The theoretical D values, then, reflect an essentially unplasticized polymer. As can be seen, the agreement between the experimentally determined diffusion coefficients and those calculated by using our model is reasonable at 90 °C. Certainly, the theoretical values are of the proper order of magnitude and vary with the proper general trend with respect to molecular size. It is of significant note that there are no adjustable parameters in the model, and no fitting of the experimental data has taken place. The calculated diffusion coefficients are, however, less sensitive to molecular size than are the experimental values. This may, in part, be a result of the conformational analysis technique, which presently does not account for polymer–penetrant interactions explicitly other than through the parameter k. We are currently addressing this problem with the development of a "reverse solvation" model which tries to take into account the "solvation" of a large plasticizer molecule by the surrounding smaller fluid polymer chain segments and its subsequent effect on plasticizer molecular conformation. In addition, we are examining the possibility of including the effect of higher energy conformations on the calculation of diffusion coefficient, as it is possible that a higher energy, but still feasible, conformation may exist with a much smaller effective molecular cross sectional area and hence be more favorable for a net diffusive jump. On the other hand, one might rationalize that once the polymer–penetrant nearest-neighbor interactions are "broken" as the cavity enclosing the penetrant enlarges (through random thermal fluctuations), the stereochemical constraints on the penetrant's conformation are temporarily relieved, at least to some extent. Thus, *if* the minimum energy penetrant conformation can be attained within the lifetime of the enlarged cavity, the equilibrium conformation might then be viewed as realistic.

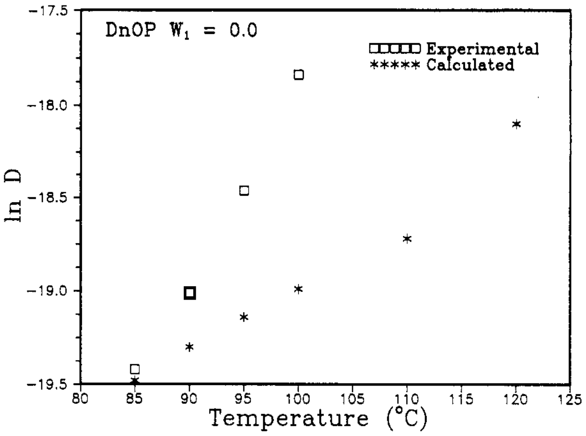

Figure 8. ln D (cm^2/s) vs T for di-*n*-octyl phthalate at low levels in rubbery PVC: (O) experimental; (*) calculated points.

A plot of ln D versus temperature is shown in Figure 8 for DNOP in the range 85–100 °C for both experiment and theory. The experimental data seem to be more sensitive to temperature than predicted from our model. Again, at least part of the shortfall might be attributed to the conformational analysis. As the temperature increases, higher energy conformations will occur with greater probability over an ensemble of molecules. Also, one might expect changes in the magnitude of polymer–penetrant interactions. These factors, in turn, will affect the calculated diffusion coefficient. A consideration of the conformational *entropy* as well as internal energy of the molecule will be helpful in identifying the effect of temperature on conformation.

Conclusions

In our earlier version of the theory for the diffusion of extraordinarily large molecules in rubbery polymers, intrinsically irregular and complex penetrant shapes, such as those possessed by commercial plasticizer molecules, would of necessity be fitted to prescribed geometries of high symmetry. In this work, however, we have considerably refined the model by generating the "exact" space-filling molecular shape by use of energetics-based theoretical conformational analysis and by computing, for the minimum energy structures, the maximum penetrant cross sectional areas in the planes that are perpendicular to the three principal molecular axes. These areas, along with the corresponding molecular dimensions along the principal axes, are then substituted in the most general expression for the diffusion coefficient. In short, the model has been rendered considerably more versatile in being applicable to diffusant molecules of *any* shape, however complex or irregular.

The results presented in this paper have shown that our model yields reasonable values for the diffusion coefficients of di-*n*-alkyl phthalate plasticizer molecules in rubbery PVC, considering that no adjustable parameters were employed. The predicted diffusion coefficients show the proper general trends with molecular size and temperature, though their variation is not as wide as seen in our earlier experimental data. The theoretical conformational analyses of the selected members of the homologous series of di-*n*-alkyl phthalate plasticizers have shown an interesting leveling-off of YZ cross sectional areas, which are roughly perpendicular to the general alkyl chain directions, and a greater increase in molecular length along the X axis than along either of the other two axes, as the side-chain carbon number increases. However, these calculations would conceivably be improved and rendered even more useful by incorporating explicit polymer–penetrant interactions as well as the effect of temperature on penetrant conformation. The inclusion of higher energy conformations and the minimization of the effective molecular cross sectional area for a given conformation could also be employed to generate a more realistic molecular picture. In addition to implementing these fundamental model improvements, future work will include relaxing the assumption of rigid penetrant conformation, thus explicitly considering the flexibility of the penetrant molecules, the formulation of a concentration-averaged D that is appropriate for use within the context of penetrant uptake kinetics, an accounting for penetrant molecular pooling at high concentrations, polymer molecular weight, crystallinity or cross-linking, and a theoretical energetics-based method of determining the penetrant plasticizing efficiency parameter, k.

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