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A General Free Volume Based Theory for the Diffusion of Large Molecules in Amorphous Polymers above T_g. 5. Application to Dialkyl Adipate Plasticizers in Poly(vinyl chloride)

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We have in a series of recent papers reported the progressive development of a hybrid free volume energetics based, penetrant molecular shape dependent theory for the diffusion of large molecules in rubbery polymers.[1-4] With regard to molecular geometry, the theory evolved from using simple symmetric shapes to a rather sophisticated accounting for the conformationally dependent irregular shapes of large penetrant molecules. Initially, our model did not incorporate polymer–penetrant intermolecular interactions. Throughout its development, our model was critically evaluated against our extensive experimental data for the diffusion of linear and branched dialkyl phthalate plasticizers in rubbery poly(vinyl chloride) (PVC).[3] While the agreement between predicted and experimentally determined diffusion coefficients was somewhat reasonable for this initial model, the theoretical values were not adequately sensitive to either penetrant molecular size or temperature. Recently, however, we have explicitly factored nonbonded penetrant–polymer intermolecular interactions into the model via a "reverse solvation" concept.[4] The amended model yields diffusion coefficients for dialkyl phthalate plasticizers in rubbery PVC that are in considerably better agreement with the corresponding experimental values with respect to accuracy and molecular size and temperature trends.

The general expression we have derived for the diffusion coefficient (D) of a large penetrant molecule in a rubbery polymer, accounting for polymer–penetrant interactions, is

$$D = \frac{V_f^2}{6}\left(\frac{eRT}{M}\right)^{1/2}\left(\frac{1}{l_1A_1^2} + \frac{1}{l_2A_2^2} + \frac{1}{l_3A_3^2}\right)\exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

where e is the base of the natural logarithm, R is the gas constant, T is the absolute temperature, M is the molecular weight of the penetrant molecule, l_i is the length of the penetrant molecule along a given direction i, and A_i is the effective molecular cross-sectional area perpendicular to the direction i. These mutually orthogonal directions are along the three principal axes of inertia of the molecule, which are determined knowing the coordinates and masses of all the constituent atoms in the minimum energy conformation. We have developed three accurate means of determining the A_i for any penetrant molecule in any fixed conformation, namely, the grid-scanning, Monte Carlo, and geometric waveform integration methods.[3,5] E_a is the effective activation energy for an elementary diffusional jump. Equation 1 applies to a penetrant that executes fundamental molecular displacements that are but small fractions of the l_i. Owing to the severe entropy penalty for free volume redistribution, the adjacent hole that is spontaneously created by random thermal density fluctuation in the liquidlike medium is not nearly the size of the entire penetrant molecule. However, given short-ranged interactions, the energy penalty for hopping, i.e., E_a, is independent of the created hole size and requires all polymer–penetrant energetic contacts to be broken regardless of the subsequent net displacement that occurs due to the thermal kinetic energy associated with a newly liberated translational degree of freedom.

A "large" penetrant molecule, within the context of this theory, is one for which $V_f/V_s \ll 1$, where V_s is the effective steric volume of the penetrant molecule and V_f is the average free volume per polymer chain segment. Equation 1 is strictly applicable to molecules that are large enough to satisfy this general size criterion. The penetrant molecular shape dependence is partly and quite explicitly represented by the three-termed expression within the parentheses of eq 1, although E_a also depends on molecular shape, being directly proportional to the surface area. It should be stressed that this equation applies to *any molecular shape* regardless of its complexity. A detailed discussion and mathematical description of these physical concepts are beyond the scope of this Note and are provided in our earlier papers.[1-4] V_f depends on the penetrant concentration and is given by the Fujita and Kishimoto equation[6]

$$V_f = V[0.025 + \alpha_f(T - T_{g2} + kw_1)] \quad (2)$$

where V is the total volume per polymer repeat unit, α_f is the temperature coefficient of free-volume expansion, T_{g2} is the glass transition temperature of the unplasticized polymer, k is the plasticizing efficiency, and w_1 is the weight fraction of the penetrant. Our initial, purely free volume based expression for D consisted of eq 1 minus the E_a-containing exponential factor.[2] We have recently added this energetic factor to the former expression in the spirit of absolute, temperature-activated rate theory[7] in the same fashion as done by Macedo and Litovitz, who were earlier concerned with a simple model for diffusion in simple low molecular weight liquids.[8] Not only was it logical to assume that this energetic-exponential factor would impart a greater and much-needed temperature dependence to our diffusion model, but a detailed computation of E_a using specific interactions for a given polymer–penetrant system would render the model rather sensitive to *chemical identity* and hence extend its predictive utility.

Since we are considering the rubbery state of the polymer, it is reasonable to picture the penetrant molecules as being "solvated" by the liquidlike nearest-neighbor polymer chain segments. Our motivation for this view derives not only from the fact that polymer chains are in a dynamic, liquid state above T_g but also from the fact that the penetrant molecular size greatly exceeds the size of the individual surrounding polymer chain segments for the diffusants of interest. We therefore term this concept as "reverse solvation", the energetics of which gives rise to E_a. We then define E_a in terms of the equation

$$E_a = \sigma a \quad (3)$$

σ is the polymer–penetrant interaction energy per unit area, and a is the solvent-accessible surface area of the penetrant molecule in its minimum-energy conformation, as defined by the computational procedure of Connoly.[9] The choice to employ a surface rather than a volume free energy, that is, to neglect interactions beyond the first nearest-neighbor (reverse) solvation shell about the penetrant molecule, was essentially motivated by the following considerations. Foremost, the predominant atomic-pairwise potential energy acting within the polymer–penetrant systems of interest is of the weak and short-ranged Len-

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nard-Jones 6–12 type. In this case, one might reasonably speak in terms of "contact forces". Also, from a practical standpoint, polymer–penetrant energetic computations are greatly simplified if only those polymer chain segments that are in immediate contact with the van der Waals surface of the penetrant molecule are considered. Finally, the energy expense in creating the *surface* of an adjacent hole that is just large enough for a penetrant to jump into is already a familiar device in the analysis of small molecule diffusion through rubbery polymers.[10,11]

E_a according to eq 3, being directly proportional to the effective surface area of the penetrant molecule, is consequently dependent on the molecular conformation and therefore on the molecular *shape*. In addition to increasing the sensitivity of predicted D to temperature, the reverse solvation feature added to the model enhances the sensitivity of D to penetrant molecular size and shape in this way.

It is beyond the scope of this Note to repeat the numerous details of the calculation of σ, and the reader is referred to ref 4. In general, the statistical mechanical method involves the calculation of the interaction free energies of the natural atomic groupings within the penetrant molecule with a defined model polymer chain segment, termed a "probe molecule". Then the number-average (over the composition of chemical groups in the penetrant molecule) free energy of interaction was obtained to define a single "effective group". These energies, in turn, were scaled according to the accessible surface areas of the groups as they are incorporated into a complete penetrant molecule.

In this Note, we will apply the model to predict diffusion coefficients for dialkyl adipate plasticizers in rubbery PVC. While these plasticizers are of commercial significance, we are unaware of any extensive experimental diffusion data against which the results of our calculations can be compared.

Calculations

Theoretical conformational analyses were executed by using the molecular mechanics method of the CHEMLAB II software system on a series of dialkyl adipate plasticizer molecules. In summary, all calculations were performed with fixed valence bond geometry, and the total intramolecular energy was the sum of all pairwise nonbonded interatomic energies, i.e., dispersive, repulsive, Coulombic, and bond-rotational potential energies. The minimum energy conformations were identified by sampling a large number of rotations about the chemical bonds in the adipate molecules.

The minimum energy penetrant conformations were then fixed with their centers of mass at the local origin and their principal axes of inertia aligned with the X, Y, and Z axes of the coordinate system. The maximum penetrant molecular cross-sectional areas formed by the projections of each molecule on each of the three mutually orthogonal planes that are perpendicular to the three principal axes of inertia were determined via the techniques described earlier.[3,5]

The calculation of solvent-accessible molecular surface area, given the conformation, bond lengths, bond angles, and van der Waals radii of the constituent atoms, was performed by the method of Connoly.[9] The computational procedure solves for the area of the surface of the molecule experienced by a contacting "probe" of a prescribed radius, which for the present case was taken as 1.0 Å.

All of the penetrant groupwise energetic parameters for the PVC probe molecule that are necessary to calculate σ for the adipates were previously determined in the course of our computations involving dialkyl phthalates.[4] The resulting effective group–PVC probe energies for *linear* dialkyl adipates are given by the following general formula:

$$\bar{A}_{\text{total}} = \frac{C_1 - nC_2 - TC_3 - nTC_4}{8 + 2(n-1)} \tag{4}$$

where n is the number of carbon atoms in each alkyl side chain. (C_1, C_2) and (C_3, C_4) are the sums of Boltzmann-averaged energy terms and the corresponding sums of entropy terms, respectively, for all of the penetrant group–PVC probe interactions. Each of the individual terms has been multiplied by the appropriate accessible surface area scaling factor for that group when it is bonded into the entire penetrant molecule. All of the area scaling factors for the groups in this work were previously calculated and are listed in ref 4. The energy/entropy sums are $C_1 = -3.685$ kcal mol^{-1}, $C_2 = 0.401$ (kcal mol^{-1})/n, $C_3 = 0.041$ kcal mol^{-1} K^{-1}, and $C_4 = 0.024$ (kcal mol^{-1})/n K^{-1}. Branched-chain structures require a slightly different form of eq 4. Methyl- or ethyl-branched dialkyl adipates can be described in general by

$$\bar{A}_{\text{total}} = \frac{C_1 - TC_2 - mC_3 - mTC_4 - nC_5 - nTC_6}{6 + 2n} \tag{5}$$

where n is the number of carbons in each alkyl side chain, m is the number of methyl or ethyl branches on each side chain, and $C_1 = -3.685$ kcal mol^{-1}, $C_2 = 0.081$ kcal mol^{-1} K^{-1}, $C_3 = 0.172$ (kcal mol^{-1})/m, $C_4 = -0.002$ (kcal mol^{-1})/m K^{-1}, $C_5 = 0.401$ (kcal mol^{-1})/n, and $C_6 = 0.024$ (kcal mol^{-1} K^{-1})/n. To yield the values of σ for use in eq 1, adjusted $\bar{A}_{\text{total}}$ values were divided by the surface area of the PVC dimer test molecule, obtained by the method of Connoly,[9] to give values of the free energy of interaction on a kcal per mol *per unit area* basis. The "adjustment" applied to $\bar{A}_{\text{total}}$, being an energy baseline shift, will be described shortly. In like fashion, the effective stereochemical surface area of the complete penetrant molecule (a) was determined to yield a surface area representing that of the polymer chain segment "cage" surrounding the penetrant molecule, assuming an optimal packing of the segments.

When $\sigma = 0$ eq 1 would seem to portray a situation wherein polymer–penetrant interactions are *apparently* not required. Consequently, as in our preceding work,[4] we define the "zero interaction point" for a given polymer–penetrant combination as the point of intersection of the experimental D vs T curve with the theoretical D vs T curve as derived from eq 1 where $E_a = 0$. At the temperature corresponding to that point, as no explicit consideration of polymer–penetrant interactions is *apparently* necessary, $\sigma = 0$. We consider this energetic situation to define a convenient reference state.

Equation 1 is formally reconciled with the experimental diffusion data for the linear nine-carbon adipate plasticizer in PVC if $E_a = 0$, i.e., $\bar{A}_{\text{total}} = 0$, at 375 K. E_a calculated at this temperature using eq 4 was systematically subtracted from the E_a values directly computed at all the other temperatures. This is the energetic "adjustment", or baseline shift, referred to above. As no experimental D vs T data are currently available for other linear adipates, this same point of "zero interaction" was utilized to shift the energies for all of the linear adipate plasticizers studied in this work. Of course, the temperature at the point of D-curve intersection for $n = 9$ and the associated value of E_a will not be the same for other values of n. This procedure is somewhat arbitrary but still meaningful if one is comparing the diffusion of penetrants within a family of molecules with very close chemical structures as is

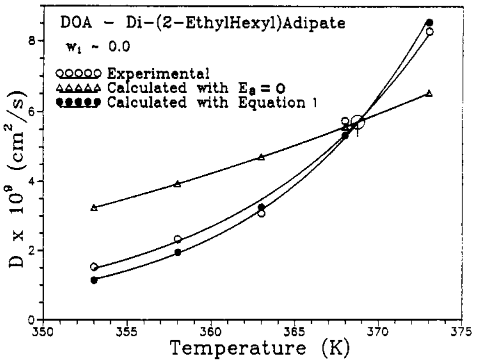

Figure 1. Theoretical and experimental D vs T curves for bis(2-ethylhexyl) adipate at very low concentrations in rubbery PVC. The triangular points refer to calculations made with the earlier diffusion model version in which $E_a = 0$ and the point of "zero interaction" is at the center of the large circle.

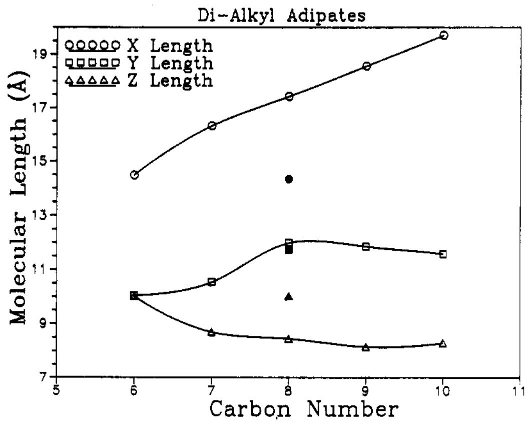

Figure 2. Molecular dimensions along the three principal axes of inertia (l_i, $i = x, y, z$) vs number of carbons in each of the two alkyl chains of the indicated di-n-alkyl adipates when in their minimum-energy conformations. The filled points represent the branched eight-carbon isomer bis(2-ethylhexyl) adipate.

certainly the case here.

Figure 1 shows experimental D vs T data obtained in our laboratory for the branched plasticizer bis(2-ethylhexyl) adipate (DOA) in PVC above the unplasticized T_g, as well as D calculated for this system with the condition $E_a = 0$ in eq 1. The theoretical D vs T graph (for $E_a = 0$) intersects the corresponding experimental graph at T = 369 K.

Diffusion coefficients were finally calculated with E_a and a determined by the procedures outlined above using eq 1 and then compared to the limited experimental diffusion data determined in our laboratory.

Results and Discussion

Figure 2 shows the molecular dimensions (l_i, i = 1–3) along the three principal axes of inertia for the minimum-energy conformations determined for five di-n-alkyl adipate plasticizers. The empty points represent results for the following linear adipates: di-n-hexyl (DnHxA), di-n-heptyl (DnHpA), di-n-octyl (DnOA), di-n-nonyl (DnNA), and di-n-decyl (DnDA). The three filled points entered at a carbon number of 8 represent the l_i values calculated for bis(2-ethylhexyl) adipate (DOA), a *branched* isomer of DnOA, for comparison. In general, on visual inspection of the space-filling structures, the linear adipates show a folded conformation with the two alkyl side chains packing more or less alongside one another.[5] Obviously, Figure 2 shows that the X dimension of the linear adipates increases quite monotonically with increasing chain length while the other two orthogonal dimensions remain somewhat constant; i.e., as more methylene units are added to each chain, the molecule enlarges in only one direction. Additionally, the values of the three molecular dimensions for DOA (branched) are spread considerably less than those for DnOA, its linear counterpart. Our theory, in general, would predict that the more compact branched isomers would exhibit lower D's than the linear isomer, all other factors being equal.[2] This general theoretical prediction is also in harmony with our experimental diffusion data that show that branched, more "spherical" or compact, penetrant structures diffuse more slowly than the corresponding linear structures.[1-3,12]

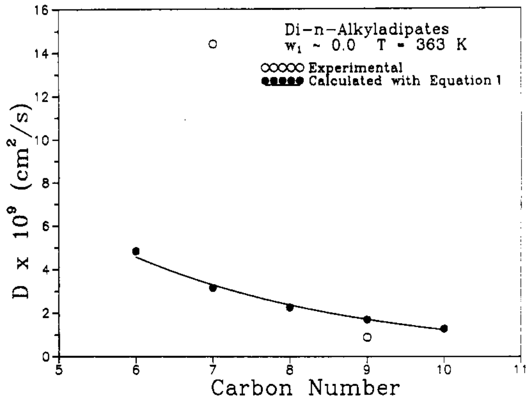

Figure 3. Theoretical diffusion coefficient (D) vs number of carbons in each of the two alkyl chains of di-n-alkyl adipate plasticizers at 363 K and at very low plasticizer concentrations in PVC. The open circles correspond to experimentally determined D values.

Figure 3 shows theoretical D values versus alkyl chain length for this series of di-n-alkyl adipates in rubbery PVC at 363 K. The two experimental data points seen in this figure (open circles) were determined in our laboratory by a gravimetric technique that we have previously described.[12] These limited experimental points should be viewed as preliminary at this time, and complete diffusion data for this series of adipates will be reported later. The theoretical D value is seen to fit rather well with experimental D for the nine-carbon adipate. On the other hand, there is a significant difference between the experimental and predicted D values for the seven-carbon adipate. Perhaps this considerable discrepancy is at least partially due to the procedure of E_a baseline-shifting, which in this case employs the DnNA, rather than DnHpA energy at the temperature of "zero interaction". It is also possible that the seven-carbon adipate, in reality, adopts a more chain-extended conformation than that which we have predicted to give a considerably smaller A_i along the x direction, which would consequently yield a larger D that would then lie closer to the experimental D in Figure 3.

Returning to Figure 1, we see the theoretical vs experimental temperature dependence of D for DOA in a temperature range just above the unplasticized T_g of PVC. The compliance of the experimental and calculated values is excellent over this entire temperature range, with respect to both the absolute magnitude of D and the general shape of the D vs T curve. As mentioned earlier, the curve passing through the triangular points is based on our earlier equation in which E_a = 0. In this figure it is again dramatically demonstrated that the addition of the explicit polymer–penetrant interaction term ($\exp(-E_a/RT)$) to the expression for D is critical in reproducing the proper shape of the D vs T curve. This computational exercise also illustrates the applicability of our diffusion model to rather complex branched structures and therefore underscores its generality.

Conclusions

In our earlier work, we developed a largely free volume based theory for the diffusion of rather large penetrant molecules in amorphous polymers above T_g and we have recently extended its systems applicability, as well as greatly improved its precision, by explicitly incorporating polymer–penetrant interactions. The theory had previously been demonstrated to predict very good diffusion coefficients for various dialkyl phthalate plasticizers in rubbery PVC. In the work reported herein, we applied our upgraded diffusion model to analyze a somewhat different class of plasticizers in rubbery PVC, namely, the dialkyl adipates, considering both branched and linear structures. It appears that our theory also compares well with experimental results when applied to these systems in predicting diffusion coefficients as a function of temperature in the region just above the unplasticized T_g of PVC. These results serve to reinforce our claim that the model is of general applicability. To be sure, the theory needs to be challenged against other penetrants having structures that are considerably different than those of dialkyl phthalates and adipates, as well as using polymeric media other than rubbery PVC.

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