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A General Free Volume Based Theory for the Diffusion of Large Molecules in Amorphous Polymers above T_g. 4. Polymer-Penetrant Interactions

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ABSTRACT: We previously advanced a mainly free volume based, penetrant molecular shape dependent theory for the diffusion of relatively large molecules in amorphous rubbery polymers. When tested against experimental evidence for plasticizer-in-PVC diffusion, our theory predicted diffusion coefficients (D) that were in reasonable agreement, although the trends with penetrant molecular size and temperature did not display adequate sensitivity. In this work, we have refined the theory to include a more realistic and molecular-based accounting of important polymer-penetrant interactions. The general diffusion equation has been appropriately modified to include an explicit activation energy for diffusion. Activation energies were determined by using a new "reverse solvation" model, which employs molecular mechanics based groupwise intermolecular energy calculations. Plasticizer-in-PVC intermolecular energies were calculated in this way for a series of dialkyl phthalate plasticizers and were then employed in the modified diffusion equation to predict diffusion coefficients. The results show a remarkable improvement over our previous calculations in that the calculated D's follow the experimental data more closely and the shapes of the D vs T and D vs molecular size curves are more accurately reproduced.

Introduction

In a recent series of papers we initiated the development of a mainly free volume based, molecular shape dependent theory for the diffusion of large molecules in rubbery amorphous polymers.[1-3] The first two papers in this series were concerned with the basic theoretical framework of the diffusion model and an accounting for the specific conformationally dependent molecular shapes of penetrant molecules. Reference 3 was concerned with the theoretical energetics-based conformational analyses of molecular shapes for a series of dialkyl phthalate plasticizers and the subsequent application of the model to predict the diffusion coefficients for these penetrants in rubbery poly(vinyl chloride) (PVC). The predictions were reasonable, showing the proper order of magnitude and general trends in diffusion coefficient with molecular size and temperature as compared to our experimental data.

These evaluations, however, illustrated inherent weaknesses in our prototype model as applied to these particular systems. For example, while the general trend of calculated diffusion coefficient (D) with molecular size was somewhat reasonable, theoretical D was not nearly as sensitive to molecular size as was experimental D. Furthermore, the theoretical trend of D with temperature also showed a very weak dependence in sharp disagreement with our experimental data.

These facts led to the belief that our model was an oversimplification of the actual diffusion process for these large complex molecules. We had earlier suggested a variety of theoretical improvements including relaxing the assumption of rigid penetrant conformation, a consideration of higher energy, rather than minimum energy penetrant conformations, and an improved representation of polymer-penetrant interactions.[1,2] It is this last point, a more direct consideration of polymer-penetrant interactions, that we will address in this paper.

From ref 3, our expression for the general three-dimensional diffusion coefficient of a large penetrant molecule in an amorphous rubbery polymer is

$$D = \frac{V_f^2}{6}\left(\frac{eRT}{M}\right)^{1/2}\left(\frac{1}{l_1 Ac_1^{\,2}} + \frac{1}{l_2 Ac_2^{\,2}} + \frac{1}{l_3 Ac_3^{\,2}}\right) \qquad (1)$$

where e is the base of the natural logarithm, R the universal gas constant, T the absolute temperature, M the molecular weight of the penetrant molecule, l_i the length of the penetrant molecule along a given direction i (taken as a principal axis of inertia), and Ac_i is the effective molecular cross-sectional area perpendicular to the direction i. V_f is the average free volume per polymer chain segment and is taken to be given by the following often-used equation suggested by Fujita and Kishimoto[4a]

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

where V is the total volume per mole of polymer repeat units, or per polymer chain segment, as in this work, α_f the temperature coefficient of free volume expansion, T the temperature, T_{g2} the glass transition of the pure (unplasticized) polymer, k the plasticizing efficiency of the penetrant for the given polymer, and w_1 the weight fraction of the penetrant in the polymer.

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.[2] Equation 3 is strictly applicable to molecules that are large enough to satisfy this general size criterion. The penetrant molecular shape dependence is represented by the three-termed expression within the parentheses of eq 3. It should be stressed that this equation applies to *any molecular shape* regardless of its complexity. The theory is not restricted to hypothetical penetrants having ideal geometries of high symmetry.

A polymer above its T_g is commonly viewed as being in a dynamic liquidlike state. In a liquid there are random thermal density fluctuations about the mean that can cause relatively large transient pockets of free volume. Of course,

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the local free energy per mole must exceed the average macroscopic value at these locations while energy is conserved overall. Furthermore, if one of these free volume pockets opens up adjacent to the penetrant molecule, the latter, owing to the thermal kinetic energy associated with a liberated translational degree of freedom, will move into the pocket after breaking all of its remaining energetic contacts with its nearest-neighbor polymer chain segments. Excluding the work reported herein, these energetic contacts have not been accounted for in our theory. Depending mainly upon the relative values of the time scales for the thermal motions of the penetrant molecule and of the polymer chain segments, the penetrant molecule could either undergo a net displacement or be trapped at its initial site when the free volume pocket collapses. A discussion and mathematical description of these concepts was provided in our earlier work.[1,2] In this way, the penetrant molecule is envisioned as "swimming" through its liquidlike medium.

Presently, the only accounting for polymer–penetrant interactions in the mixed system is in the value of k, an experimental parameter that is a measure of the ability of a particular penetrant to depress the glass transition of the polymer. While, at this time, an acceptable fundamental, molecular-based theory for predicting k for a given polymer–plasticizer system is not available, we have extracted this parameter from experimental (DSC) T_g vs w_1 graphs for a number of linear and branched dialkyl phthalates in PVC.[4b] These tests were mainly conducted to advance our understanding of the dependence of k on plasticizer size and shape and thereby aid in a future formulation of a molecular-based model for predicting k.

In order to directly account for the specific energetics of polymer–penetrant interactions, we stray somewhat away from the purely free volume based approach to modeling diffusion. Following the lead of other workers who have directly patched the concept of activation energy onto the Cohen–Turnbull formalism in relation to modeling diffusion and viscosity in liquids,[5,6] we will combine both free volume and energy-activated diffusion concepts in a model that is a hybrid of both.

We retain our current free volume based diffusion equation and introduce an exponential factor that contains an activation energy in the usual way to directly account for the changes in polymer–penetrant interactions accompanying site-to-site penetrant hopping. Quite simply, eq 1 is modified to yield

$$D = \frac{V_f^2}{6}\left(\frac{eRT}{M}\right)^{1/2}\left(\frac{1}{l_1Ac_1^2} + \frac{1}{l_2Ac_2^2} + \frac{1}{l_3Ac_3^2}\right)\exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where E_a is the formal activation energy for diffusion.

Now, consider a basic definition of E_a within the context of this system. In temperature-activated rate theory, as applied to self-diffusion within simple low molecular weight liquids as initiated by Eyring,[7] E_a is the energetic barrier height for jumping from one dynamic "equilibrium" site to an adjacent equivalent site. While we wish to preserve the fundamental idea behind this definition, E_a is somewhat more difficult to define for our system as we do not have a simple liquid consisting of small spherical molecules that are distributed over a rough lattice. Since we are considering the rubbery state of the polymer, one imagines that the penetrant molecules are in effect "solvated" by the liquidlike nearest-neighbor polymer chain segments in a manner analogous to the situation in simple liquid–liquid solubility. Our motivation for this view derives from the fact that the polymer chains are known to be in a dynamic, liquid state above T_g as well as from the fact that the penetrant molecular size greatly exceeds the size of the individual surrounding polymer chain segments. On a Flory–Huggins lattice, the penetrant molecule will require a greater number of adjacent sites than will a smaller polymer chain segment for incorporation. We therefore term this concept as "reverse solvation", the energetics of which gives rise to the polymer–penetrant interactions that influence diffusion.

Given, then, a single penetrant molecule, with an "effective" molecular surface area a, which is totally surrounded by liquidlike polymer chain segments, one can define a polymer–penetrant surface free energy of interaction, σ, that is a function of all the pairwise atomic polymer–penetrant interactions and expressed as the energy per mole per unit penetrant molecular surface area. That is, for each unit surface area of interaction between the penetrant molecule and the adjacent polymer chain segments, σ units of energy are contributed to the total energy of interaction between the polymer and penetrant.

In order for a successful diffusion event to take place in this hybrid model, an adjacent hole most open up in the polymer due to a spontaneous redistribution of free volume (entropic process) *and* the penetrant molecule must break *all* of its nonbonded interatomic interactions with the surrounding polymer chain segment "cage" in order to jump into the transient hole. This second step is a local *energy-activated* process. There is a reasonable assumption in this model that only nearest-neighbor interactions are important for the systems under consideration. The penetrant molecule must pass over a high energy-activated state to go from one potential energy well, wherein it is interacting with a full complement of surrounding polymer chain segments in optimal fashion, to the other well. Having jumped, the hole left behind by the penetrant will have collapsed. While there, of course, is no *net* energy change affected in this way, the activation barrier for displacement is the energy cost for the molecule to break all of its polymer–penetrant interactions so that it can translate into the created hole via its thermal kinetic energy and then reestablish all of its former polymer–penetrant interactions in a minimum energy sense. We can then define the activation energy as $E_a = \sigma a$. This activation energy is clearly dependent on the effective surface area of the penetrant molecule, and hence on its conformation, as well as on the polymer–penetrant interaction free energy per unit area. As one might imagine that isomeric penetrants will have different surface/volume ratios, E_a is expected to be strongly dependent on molecular shape.

At this point we recall from our earlier papers[1,2] that the equation for the diffusion coefficient (eq 1 or eq 3) applies to a penetrant that executes fundamental displacements that can be resolved into orthogonal components, along the three principal axes of inertia, which are only *fractions*, usually small, of the penetrant molecular dimensions along these axes. This, in fact, is one of the main features that renders our model applicable to large penetrants. Thus, as the created hole is not nearly as large as the size of the entire penetrant molecule, the entropy penalty for free-volume redistribution is not excessively high. This model, in fact, does not portray an "all or nothing" but a "part of the way" penetrant hopping event. In other words, the penetrant does not hop through a distance that is equal to, but is somewhat less than, its effective molecular diameter. However, in the presence of only short-ranged polymer–penetrant interaction energies, the total hopping energy penalty is in fact independent of the adjacent hole size as it would seem logical that *all* pairwise interatomic energetic contacts of this sort must be broken to set the penetrant molecule in translatory motion *regardless of how far it subsequently moves.*

The precise definition of a and σ remains to be made. The calculation of molecular surface area, given the conformation, bond lengths, bond angles, and van der Waals radii of constituent atoms, while not simple, is basically a solved problem with a variety of computer algorithms available. The method of Connoly[8] is particularly useful from a number of standpoints. The procedure solves for the molecular surface area analytically, not numerically, and allows for the determination of the area of the surface of the molecule experienced by a contacting "probe" of a prescribed radius. This surface, which Connoly refers to as the "solvent accessible surface" more readily approximates the actual molecular surface available for interaction than would be represented by the simple composite, totally accessible van der Waals surface.

The determination of σ for a given polymer–penetrant pair is a more difficult problem to solve. Obviously, the most rigorous modeling approach would be to perform a complete molecular dynamics simulation on a large ensemble of generated polymer chains interacting with each other as well as with a given inserted penetrant molecule. In this way, not only would the energetics of interaction be determined but the actual kinetics of the diffusion process could be derived from following an equation of motion. This approach is in fact being employed by several groups to examine the diffusion of simple gases in polymers,[9] but for large, complex, plasticizing penetrant molecules in polymers, the problem would be greatly magnified, to be sure. In addition, an ambitious approach of this type would certainly limit the predictive usefulness of the theory by virtue of the huge number of calculations required for each given polymer–penetrant pair of interest. It is our goal to create a model that not only is realistic but also is of practical merit with a relatively simple and minimal input experimental structure–properties database.

Another but less-ambitious approach to the calculation of polymer–penetrant interactions would be to employ a model polymer chain segment and sample its interaction with an entire individual penetrant molecule in a large number of intermolecular configurations. The resultant energetics would then be used to generate a statistical mechanical ensemble in the usual way and the free energies scaled up to provide a full shell of chain segments around the penetrant molecule. While this approach is certainly more simple than the molecular dynamics simulation, it still suffers from the need to perform a large number of calculations for a given polymer–penetrant pair. We have developed a simpler but more flexible energetics approach.

Our approach involves the calculation of the interaction energy of all the particular natural atomic groups within the penetrant molecule with a model polymer chain segment. These groupwise contributions are then directly summed to approximate the total intermolecular interaction energy. In this manner, we have reduced a complex problem to a much simpler operational level. Rather than looking at massive ensembles of polymer chains and penetrant molecules, or even at a single whole penetrant molecule with a polymer chain segment, we choose to consider the interaction of each of the constituent atomic groups of the penetrant molecules with a polymer chain segment separately and then assemble the total interaction from this composition.

In the next section we describe how the group interaction calculations are performed and summed to yield σ values for a series of plasticizer molecules in rubbery PVC. The remainder of the paper examines the results of these sample calculations and the effect of accounting for polymer–penetrant interactions on the theoretically predicted diffusion coefficients as compared to established experimental values for these systems.

Calculation of Penetrant Group–Polymer Interaction Energies. Model penetrant molecules were broken down into their natural atomic groupings representative of significant structural features. Representative groups were selected on the basis of their size and lack of internal conformational flexibility. A linear or branched phthalate molecule can be represented by a maximum of five such groups: disubstituted phenyl ring, ester group, and CH_3, CH_2, and CH groups.

The groups were "cleaved" from a representative phthalate molecule, which, as a complete structure, had its partial charge distribution determined by the semiempirical molecular orbital technique CNDO/2. In this way, the charge distribution on the excised group is representative of the distribution over that group when it is incorporated into a complete phthalate molecule. The probe molecule selected to model PVC interactions was an all-trans CH_2CHCl dimer with its partial charge distribution also determined by the CNDO/2 method and oriented so that its center-of-mass was on the origin of its local coordinate system with its chain direction along the Z axis.

In order to calculate the total energy of interaction of a particular penetrant group with the PVC probe segment, the group was fixed so that its center-of-mass was located at the origin of a simple space coordinate system. The probe molecule was then driven around the group and the total interaction energy calculated at a large number of points. There are 6 degrees of freedom in this system, if no intramolecular bond rotations are allowed. The location of the center-of-mass of the probe molecule relative to the origin (i.e., location of the test group's center of mass) is defined by R, its distance from the origin, Z, its translation up or down the z axis, and θ its rotation about the z axis. An additional 3 rotational degrees of freedom are required to define the orientation of the probe molecule relative to its local coordinate system. These rotations around the internal z, y, and x axes are designated α, β, and γ, respectively. These six intermolecular position-orientation parameters are depicted in Figure 1. α, β, and γ rotations take place *without* movement of the probe's center of mass, which is fixed at its local origin.

Table I shows the ranges over which these 6 degrees of freedom were varied for energetic computations. The values of R, Z, and θ show that the entire space out to 10 Å from the sample space origin to the center of mass of the probe molecule was sampled. A total of almost 1400 intermolecular center-of-mass positions were sampled. At each of these points, the local orientation of the probe molecule was varied over 64 possible orientations, resulting in a total of 88 704 intermolecular configurations being sampled. A finer increment in the α, β. and γ variation was actually tested, but the computational results did not differ significantly from those employing the larger 90° increment and the CPU time saving with the larger increment was considerable. At each of the 88 704 intermolecular configurations, the total nonbonded energy

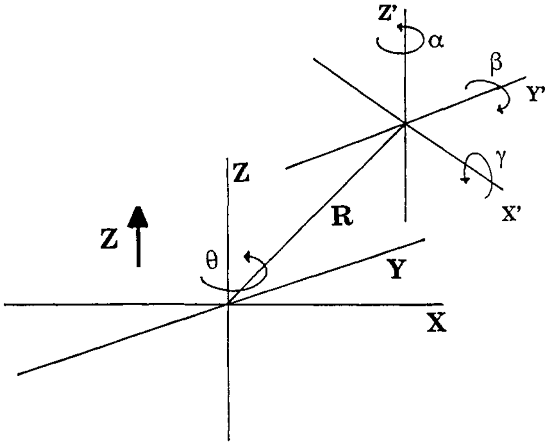

Figure 1. Intermolecular geometric parameters used in the polymer probe–penetrant group interaction energy calculations.

Table I
Ranges over Which the 6 PVC Probe–Penetrant Group Intermolecular Degrees of Freedom Were Varied, as Well as Incremental Values for These Parameters

variable[a]	start	increment	end
R	0	1	10
Z	-10	1	10
θ	0	60	300
α	0	90	270
β	0	90	270
γ	0	90	270

[a] R and Z are in angstroms; θ, α, β, and γ are in degrees.

was calculated and saved using the equation

$$E = \sum_i \sum_j \left(\frac{-A_{ij}}{r_{ij}^{6}} + \frac{B_{ij}}{r_{ij}^{12}} + \frac{kQ_iQ_j}{\epsilon r_{ij}} \right) \tag{4}$$

where the sum is over all of the possible intermolecular atomic pairs i and j, A_{ij}, and B_{ij} are the standard Lennard-Jones 6–12 potential energy constants for a particular nonbonded atomic pair using Hopfinger's Z set,[10] r_{ij} is the interatomic distance, Q_i and Q_j are the partial charges on atoms i and j, k is a unit conversion constant, and ϵ is the dielectric constant of the local medium, which was set equal to 1. The first two terms in eq 4 account for the van der Waals attractions (dispersion forces) and steric repulsions of a given nonbonded atomic pair. The third term is a standard Coulombic potential energy introduced to account for the electrostatic interaction of a given nonbonded atomic pair owing to partial charges.

If the total energy of interaction for a given intermolecular configuration is greater than a designated high cutoff energy, in this case +25 kcal/mol, indicative of a highly unfavorable interaction, that energy was formally removed from the sampled set of energies in the computations. The Boltzmann averaging process detailed below would essentially perform this task automatically, but we apply this procedure beforehand to reduce the number of subsequent computations. Typically, about 13% of the calculated energies were discarded in this manner.

This calculation process was repeated for each individual penetrant group to yield a large number of interaction energies, which were then averaged as described below.

Averaging of Penetrant Group–Polymer Segment Probe Interactions and Free Energy Determination. Boltzmann statistics were used to form an average over the ensemble of computed interaction energies between a given penetrant group and the polymer segment probe.[11a] A partition function, Q, was defined in the usual way for n sampled values of the energy:

$$Q = \sum_{i=1}^{n} \exp\left(\frac{-E_i}{RT}\right) \tag{5}$$

The probability of a given intermolecular configuration can then be calculated in the usual way:

$$p_i \doteq \exp\left(\frac{-E_i}{RT}\right) / Q \tag{6}$$

The more favorable low-energy interactions receive considerably more statistical weight than those of higher energy. The average energy of interaction is then given by

$$\bar{E} = \sum_{i=1}^{n} p_i E_i \tag{7}$$

Of course, intermolecular configurations are not expected to be static in this liquidlike state, and disorder must be factored in by also considering the entropy. The average entropy over the ensemble of intermolecular configurations derives from the expression

$$\bar{S} = -R \sum_{i=1}^{n} p_i \ln p_i \tag{8}$$

Finally, the average *free energy* of interaction, which takes into account both energy and entropy, is

$$\bar{A} = \bar{E} - T\bar{S} \tag{9}$$

Equation 9 relates the Helmholtz free energy to temperature for the interaction of a given penetrant group with a polymer chain segment probe. It is this energetic consideration that renders our diffusion model considerably more sensitive to temperature as it existed previously. Furthermore, additional molecular disorder is factored into the theory in this way, which is satisfying since diffusion is basically considered to be an entropy-driven process.

These energies, however, are overestimated because the calculations are performed with the individual groups isolated in space and not bonded in a complete penetrant molecule and are artificially interactively accessible from all directions. The free energies calculated in this manner therefore need to be scaled by some amount related to the actual accessible surface area of a particular group when it is incorporated into a given complete penetrant molecule.

Energetic Scaling by Group Accessible Surface Area. Accessible molecular surface areas for individual penetrant groups were calculated by the following scheme. All molecular surface areas were calculated by using the earlier mentioned method of Connoly.[8]

Initially, the total surface area of a molecule incorporating the group of interest was determined. The group was then split from the molecule to yield the same fragment on which the energy calculations had taken place. The surface areas of the lone group and of the remaining part of the "mother" molecule were then determined. The sum of these two surface areas is greater than that of the intact mother molecule as they have more exposed surface. The area scaling factor, f, for the group can be calculated from

$$f = \frac{a_{\mathrm{g}} - \frac{1}{2}[a_{\mathrm{g}} + a_{(\mathrm{m-g})} - a_{\mathrm{m}}]}{a_{\mathrm{g}}} \tag{10}$$

where a_{g} is the total surface area of the individual group, a_{m} is the total surface area of the intact molecule, and $a_{(\mathrm{m-g})}$ is the total surface area of the mother molecule with the group of interest removed. The numerator represents the true accessible surface area of the bonded group, which is then divided by the calculated surface area of the totally accessible group to yield the approximate scaling factor.

The scaling factors for the groups of interest in this work are shown in Table II. As can be seen, both the disubstituted phenyl ring and the CH_3 unit have scaling factors quite near to 1, indicating that about 80% of their surface area is still accessible even when bonded. However, the other three units have much less accessible surface area, especially the CH group, most of which is excluded by its being bonded from two directions into a molecule.

$\bar{A}$, given by eq 9, is subsequently multiplied by the appropriate scaling factor to yield an adjusted value for the interaction free energy of a particular group with the dimer probe as a function of temperature.

Average Polymer–Penetrant Interaction Free Energy/Group. The specific Helmholtz free energies of interaction for each penetrant group with the dimer probe, after scaling according to group accessible surface areas via, *f*, are

$$A_P = -6.900(\text{kcal mol}^{-1}) - 0.008(\text{kcal mol}^{-1}\ \text{K}^{-1})T \quad (11a)$$

$$A_E = -1.210(\text{kcal mol}^{-1}) - 0.011(\text{kcal mol}^{-1}\ \text{K}^{-1})T \quad (11b)$$

$$A_3 = -0.432(\text{kcal mol}^{-1}) - 0.017(\text{kcal mol}^{-1}\ \text{K}^{-1})T \quad (11c)$$

$$A_2 = -0.200(\text{kcal mol}^{-1}) - 0.012(\text{kcal mol}^{-1}\ \text{K}^{-1})T \quad (11d)$$

$$A_1 = -0.054(\text{kcal mol}^{-1}) - 0.006(\text{kcal mol}^{-1}\ \text{K}^{-1})T \quad (11e)$$

The subscripts P, E, and 1–3 refer to phenyl, ester, and number of hydrogens on a single carbon atom, respectively.

The number-averaged penetrant group–dimer probe free energy of interaction may then be derived for a given dialkyl phthalate molecule by multiplying each of the above equations by the number of groups of that type in the penetrant molecule, summing the result, and then dividing this by the total number of groups of all types in the molecule. This procedure, in effect, defines a single "effective group". For example, di-*n*-alkyl phthalate plasticizers each contain one phenyl ring, two ester groups, two CH_3 groups, and $2(n-1)$ CH_2 groups, where *n* is the total number of alkyl carbons on one side chain. The effective group free energy, then, is

$$\bar{A}_{\text{total}} = \frac{1A_P + 2A_E + 2A_3 + 2(n-1)A_2}{5 + 2(n-1)} \quad (12)$$

The subscript "total" refers to an average over the total number of chemical groups and not to the total energy. The individual group *A* values can be calculated by using eqs 11a–e at a given temperature and summed via eq 12, or they can be left as a function of temperature to derive a general equation for the effective group intermolecular interaction energy as a function of temperature and side-chain length. The general equation for di-*n*-alkyl phthalates is

$$\bar{A}_{\text{total}} = \frac{C_1 - nC_2 - TC_3 - nTC_4}{3 + 2n} \quad (13)$$

where $C_1 = -9.784$ (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}).

Dialkyl phthalates with branched pendant chains require a slightly different form of eq 12 due to their differing distribution of chemical groups. Methyl- or ethyl-branched dialkyl phthalates can be described by

Table II
Penetrant Group Scaling Factors (*f*) for Accessible Surface Areas

group	*f*	group	*f*
disubstituted phenyl	0.826	CH_2	0.552
ester	0.582	CH	0.270
CH_3	0.800		

$$\bar{A}_{\text{total}} = \frac{1A_P + 2A_E + (2 + 2m)A_3 + 2mA_2 + 2(n - 2m - 1)A_1}{5 + 2(n-1)} \quad (14)$$

where *m* is the number of methyl or ethyl branches on one side chain. A general equation similar to eq 13 can also be derived to express the free energy of interaction of a branched dialkyl phthalate with the PVC dimer probe as

$$\bar{A}_{\text{total}} = \frac{C_1 - TC_2 - mC_3 - mTC_4 - nC_5 - nTC_6}{3 + 2n} \quad (15)$$

where $C_1 = -9.784$ (kcal mol^{-1}), $C_2 = 0.041$ (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*). Of course, similar formulas can be written for other penetrant molecular structures.

Concern might be raised over the construction of penetrant group energetic contributions that are treated as being *additive*. This procedure is most reminiscent of the similar common practice involved in the estimation of solubility parameters as initiated by Hildebrand in his development of the theory of regular solutions.[11b] Our assumption of the additivity of the group contributions to $\bar{A}_{\text{total}}$ should be good in the absence of long-ranged, i.e., strong coulombic, intermolecular forces, which do not exist for the polymer–plasticizer system under consideration in this study.

Scaling of Molecular Interactions. When σ is zero, eq 3 reduces to eq 1, which does not incorporate polymer–penetrant interactions explicitly. Consequently, 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 derived from eq 1. At the temperature corresponding to that point, as no explicit consideration of polymer–penetrant interaction is *apparently* necessary, $\sigma = 0$. We consider this situation to define a reference state.

Figure 2 shows experimental *D* vs *T* data obtained earlier in our laboratory,[12] for di-*n*-octyl phthalate plasticizer in PVC above the unplasticized T_g, as well as *D* calculated for this system with eq 1. In short, the theoretical *D* vs *T* graph for $n = 8$ intersects the corresponding experimental graph at $T = 357$ K. In other words, the earlier version of the diffusion model exactly coincides with experimental reality at this curve-crossover temperature. While the next step to be undertaken, to be sure, deviates from theoretical purity, we also wish to benefit from the availability of the corresponding experimental diffusion data. Equation 3 is formally reconciled with the experimental diffusion data if E_a or $\bar{A}_{\text{total}} = 0$ at 357 K. We have accepted this calibrative assignment in a rather semiempirical sense. As $E_a = -5.10$ kcal mol^{-1} using eq 3 at this temperature, this energy was systematically subtracted from the E_a values directly computed at all the other temperatures. In physical interpretation, $E_a = 0$

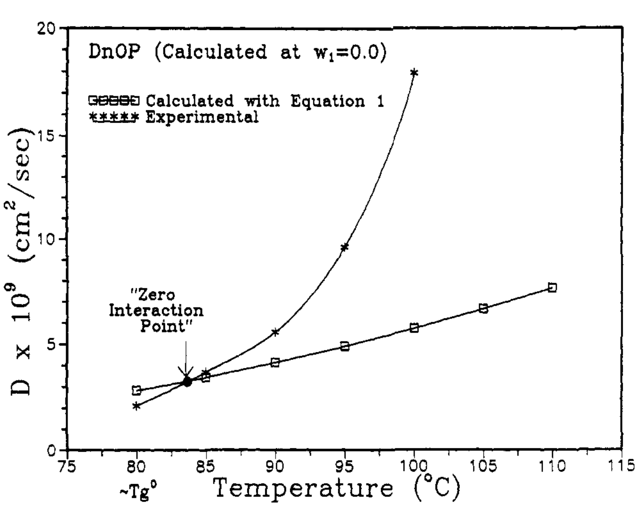

Figure 2. Comparison of experimental D's[12] with those calculated with eq 1 vs temperature for $T > T_g$ for very low D*n*OP concentrations in PVC. The intersection of the two curves defines the point of "zero interaction".

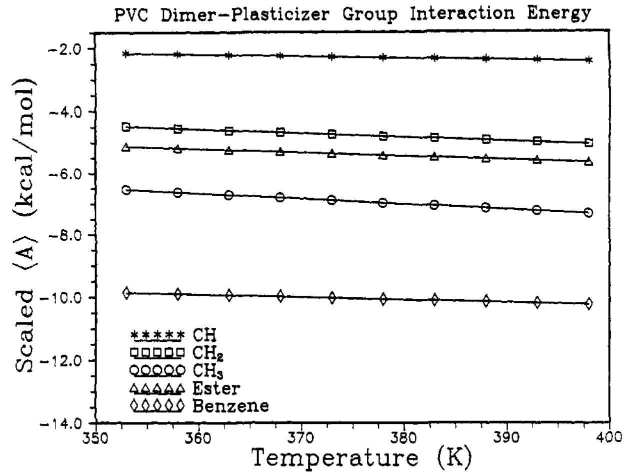

Figure 3. Penetrant group-PVC probe interaction energies vs temperature for the constituent groups of dialkyl phthalate plasticizers. The energies have been scaled according to the solvent-accessible surface areas of the groups when bonded.

Table III
Phthalate Plasticizers Utilized in Computations

di-*n*-hexyl phthalate D*n*HxP	di-*n*-nonyl phthalate D*n*NP
di-*n*-heptyl phthalate D*n*HP	di-*n*-decyl phthalate D*n*DP
di-*n*-octyl phthalate D*n*OP	

at a given temperature does not imply a lack of polymer-solvent intermolecular interactions. Rather, as E_a is a *free energy*, this condition would more reasonably indicate a balance of purely energetic with purely entropic contributions.

Of course, the temperature at the point of curve intersection for $n = 8$, and the associated value of E_a, will not be the same for other values of n. However, to avoid excessive reliance on experimental data, and anticipating that the experimental curves may not actually intersect the theoretical curves within the experimental range of temperatures for some other values of n, we have chosen to shift the zero energy point for all n to be at -5.10 kcal mol^{-1}. The latter 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 certainly the case in this work. This energy-shifting procedure, in effect, scales the values of $\bar{A}_{\mathrm{total}}$ to lie near zero, either positive or negative, with the sign dependent on whether the interaction is "favorable" or "unfavorable" *relative to the* zero interaction point. Also, from a practical computational standpoint, excessively high/low values of the exponents in the Boltzmann factors are avoided in this way. Higher phthalates at lower temperatures are seen to yield the most unfavorable (positive) interaction energies and lower phthalates at higher temperatures yield the most favorable (negative) interaction energies, as is physically reasonable.

Finally, to yield the values of σ for use in eq 3, the adjusted molecular $\bar{A}_{\mathrm{total}}$ values must be divided by the surface area of the PVC dimer test molecule to give values of energy on a kilocalories per mole per unit area basis. The surface area of the PVC dimer was determined, using the method described earlier, to be 155.58 Å^2.

The effective sterochemical surface area of the complete penetrant molecules was determined by using the aforementioned method of Connoly[8] with probe radius of 1 Å (approximately the width of a bonded hydrogen atom) to yield a surface area representing that of the polymer chain segment "cage" surrounding the penetrant molecule, assuming optimal packing of the segments.

Diffusion Coefficient Calculations. Diffusion coefficients were then calculated by using eq 3 for the series of dialkyl phthalate plasticizers in rubbery PVC shown in Table III. The necessary penetrant molecular geometric parameters, i.e., length along each principal axis (l_i, i = 1-3) and the effective maximum cross-sectional area perpendicular to each principal axis (A_{ci}, i = 1-3), were determined for these molecules in our earlier work[3] and were employed in the present computations without modification.

Results and Discussion

Penetrant Group Interaction Free Energies. Figure 3 shows the results of the polymer-penetrant interaction calculations for all the groups present in dialkyl phthalates as a function of temperature. The sampled temperature range was selected to represent the region near to and just above the glass transition temperature of unplasticized PVC.

All of the group contributions appear as being weakly sensitive to temperature in this range so that increasing temperature yields only a slightly more favorable interaction. Recall that these energies involve an interplay between energy and entropy. The most favorable group interaction with PVC is that experienced by the disubstituted, highly polarizable phenyl ring. The groupwise interaction energy for the phenyl ring is in fact much lower than that of any of the other groups over the entire temperature range. This result is in harmony with and helps to reinforce the general belief that it is the phenyl ring and ester group that help to promote the compatibilization of phthalate plasticizers with PVC.[13] The interaction energy for the ester group is quite intrinsically favorable, i.e., as considered in isolation, but it seems to be diminished by virtue of its relatively low accessible surface area as bonded into the complete penetrant molecule. It is obviously the inherent dipole of the ester linkage that renders it quite valuable in compatibilizing the phthalate plasticizers with the reasonably polar PVC structure.

The alkyl groups are inherently less compatible with PVC as they are quite nonpolar. Their less favorable interactions are manifested by the relatively higher values of their group energetics as seen in Figure 3.

Total Polymer-Penetrant Interaction Energies. Figure 4 shows the values of the total intermolecular interaction energies calculated via the groupwise method

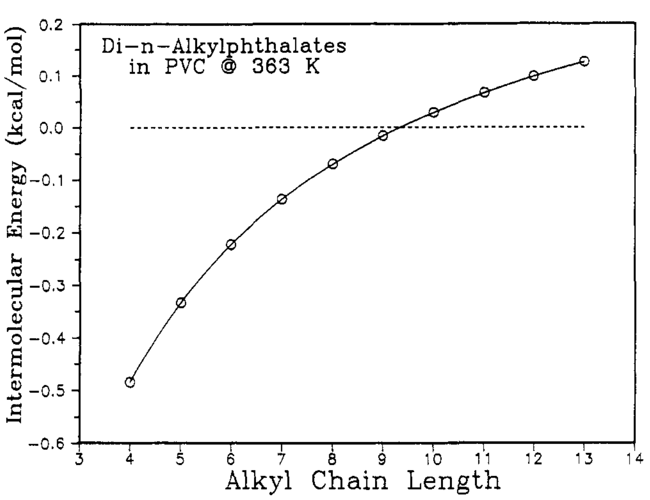

Figure 4. PVC–plasticizer intermolecular energies vs number of carbons in each of the alkyl chains of di-*n*-alkyl phthalate molecules.

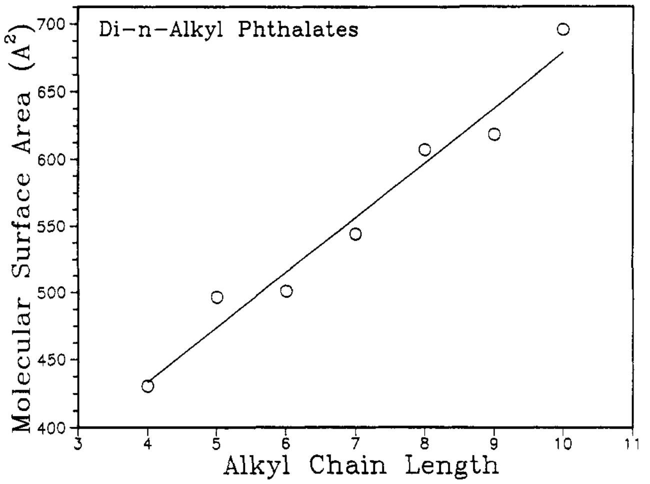

Figure 5. Solvent-accessible molecular surface area, calculated with a probe radius of 1 Å, vs number of carbon atoms in each of the alkyl chains of di-*n*-alkyl phthalate molecules.

and scaled as detailed above for linear dialkyl phthalates in PVC at 363 K, approximately 10 K above the unplasticized T_g of PVC.

As a result of the highly favorable interaction energy calculated for the phenyl ring, the phthalates exhibit a much more favorable interaction energy for the shorter alkyl chain lengths in this range for a given temperature. As more pure hydrocarbon character is added to the molecule by the continued insertion of CH_2 units in each chain, the interaction energy becomes increasingly less favorable. Note that, due to the method of scaling, the value of the energy is about zero for the eight-carbon chain phthalate, negative for lower phthalates, and positive for higher phthalates. It should be recalled, however, that these energies are not absolute but are shifted in relation to the energy at the temperature of zero interaction for $n = 8$.

Molecular Surface Area. Figure 5 shows a plot of molecular stereochemical surface area calculated with a probe radius of 1 Å versus alkyl chain length for the studied series of linear dialkyl phthalates. The data are quite regular and may be reasonably fitted with a straight line. The intercept of this line, having a value of about 270 Å^2, can be viewed as the approximate surface area of the phenyl diester "core" of a dialkyl phthalate molecule, and the slope, being about 41 Å^2/CH_2 unit, can be viewed as the approximate surface area contributed by the addition of a single CH_2 unit to each side chain. These values are also in harmony with those determined previously for use in the calculation of group accessible surface areas.

Table IV
Diffusion Coefficients (*D*) for Di-*n*-alkyl Phthalate Plasticizers in PVC at 363 K and for Very Low Plasticizer Contents (ca. 0 wt %)

plasticizer	exptl D,[a] $\times 10^9$ cm^2/s	calcd D, $\times 10^9$ cm^2/s by eq 3	calcd D, $\times 10^9$ cm^2/s by eq 1
D*n*HxP	29.6	20.0	7.25
D*n*HP	16.8	12.0	5.99
D*n*OP	5.54	6.22	4.13
D*n*NP	4.23	4.10	3.64
D*n*DP	0.576	2.19	2.52

[a] Reference 12.

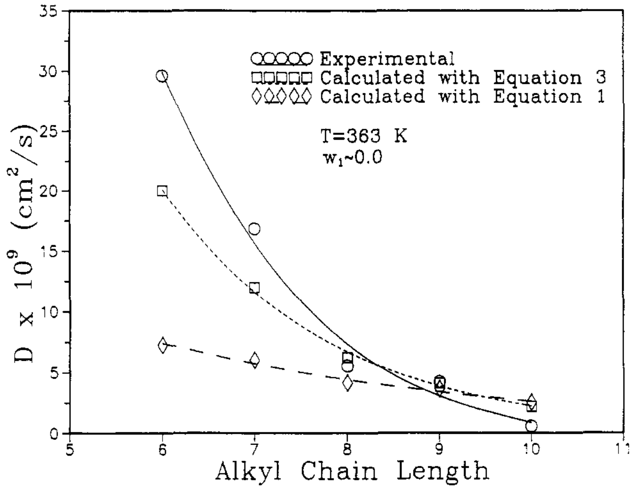

Figure 6. Experimental and theoretical diffusion coefficients vs number of carbon atoms in each of the alkyl chains of di-*n*-alkyl phthalate molecules at 363 K and at very low plasticizer levels in PVC.

Theoretical Diffusion Coefficients. Diffusion coefficients were calculated by using eq 3 with the values of σ and a determined according to the above-explained procedures. Table IV shows the values of D for the series of linear-chained dialkyl phthalate plasticizers at essentially zero weight percent ($w_1 \rightarrow 0$) in rubbery PVC at 363 K. Column 1 shows the experimental D values previously determined in our laboratory.[12] Column 2 shows the values calculated with eq 3 taking into account specific polymer–penetrant interactions, and column 3 shows D values calculated using our earlier equation (eq 1) with no explicit incorporation of polymer–penetrant intractions. Unquestionably, the D values calculated according to eq 3 show considerably better agreement with the experimental data than do the values calculated with eq 1. Figure 6, consisting of plots of these same three data sets, provides a clearer observation of the decreasing trends with increasing chain length. Not only is the magnitude of agreement considerably better with eq 3, but, even more importantly perhaps, the *shape* of the experimental curve is more closely reproduced. Previously, the predicted D values were at the correct order of magnitude for the eight or nine carbon phthalates but were not adequately sensitive to molecular size, the molecular size dependence having been practically linear. The use of eq 3, which explicitly accounts for polymer–penetrant interactions, yields a much stronger dependence on molecular size that more accurately reproduces the experimental data. We cannot offer a meaningful explanation at this time as to why the theoretical D values are sometimes higher and other times lower than the experimental D values. One might imagine

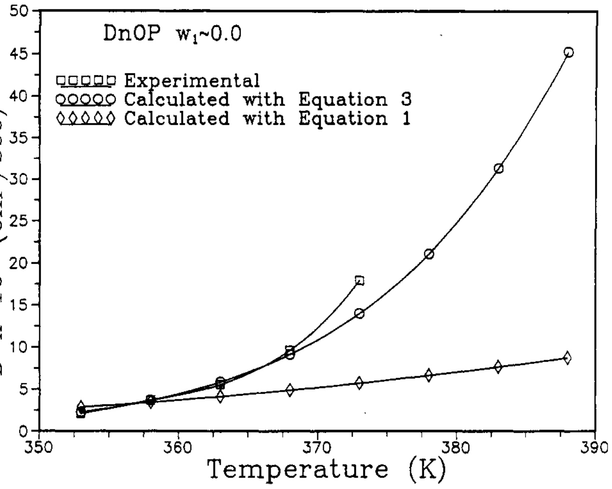

Figure 7. Experimental and theoretical *D* vs *T* curves for di-*n*-octyl phthalate at very low concentrations in rubbery PVC.

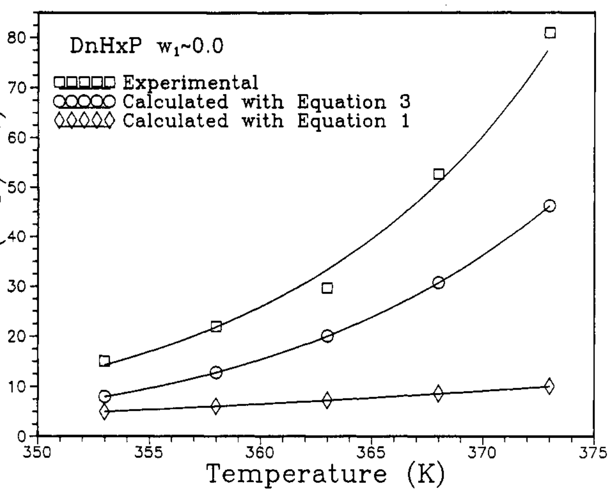

Figure 8. Experimental and theoretical *D* vs *T* curves for di-*n*-hexyl phthalate at very low concentrations in rubbery PVC.

that the experimental values themselves contain a measure of statistical error that causes the order to fluctuate.

Figure 7 depicts the temperature dependence of the experimental and improved calculated diffusion coefficients for D*n*OP. Calculated *D* values are again at effectively zero weight fraction of plasticizer and therefore reflect mainly molecular size and shape effects that were magnified with the inclusion of explicit polymer-penetrent intractions. At very low penetrant concentrations, complications due to polymer plasticization and plasticizer pooling will not be present. Obviously, the values calculated with eq 3 are considerably better fitted to the experimental data. *D*'s calculated without polymer-penetrant interactions show a very weak, nearly linear increase with temperature that deviates increasingly more from the experimental data with increasing temperature. Equation 3 successfully reproduces both the functional shape as well as the absolute numerical values of the experimental data over the entire range for which this diffusion data is available.

Figure 8 shows the temperature dependence of *D* for di-*n*-hexyl phthalate plasticizer. The values calculated by using eq 3 are again more closely related to the experimental data than those calculated with eq 2. *D*'s for D*n*HxP are, however, still somewhat underestimated by eq 3, but the shape of the curve is obviously more closely reproduced than previously. In this regard, we might point out that our theory was developed particularly for "large" molecule diffusion and that its applicability might weaken as the penetrant size becomes as small as that of the D*n*HxP molecule. Also note that the eq 1 derived curve does not intersect the experimental curve within this temperature range. Therefore, a point of "zero interaction" is unavailable for this system, given the scarcity of experimental diffusion data, although this point exists in principle. This case illustrates the practical need to scale E_a values against the E_a at the temperature of "zero interaction" for a single system that displays a well-defined point of curve intersection.

General Conclusions. In our previous version of a theory for the above T_g diffusion of large molecules in amorphous polymers, there was no explicit accounting for polymer-penetrant interactions. Consequently, *D* values that were calculated, while seemingly correct in an order of magnitude sense, lacked adequate sensitivity to penetrant molecular size and temperature for the dialkyl phthalate-PVC systems.

In this work, we modified our approach by the inclusion of a diffusion activation energy in the usual way to represent the breaking of polymer-penetrant intermolecular interactions during the fundamental hopping event. In this modification, the diffusion activation energy is directly related to the solvent-accessible surface area of the penetrant molecule, which is assumed to be in its minimum energy conformation, and to the polymer-penetrant intermolecular energy per unit area.

Using a molecular mechanics technique, we have calculated the polymer-penetrant interaction energy via a simple and flexible groupwise-additive method. Results of the groupwise interaction energy calculations between the consitutent atomic groups of phthalate plasticizer molecules and a PVC chain segment probe indicate that the phenyl ring and ester groups interact more favorably than do the alkyl groups with the PVC environment. It is these particular interactions that compatibilize these plasticizers with the relatively polar PVC structure.

The groupwise contributions were then number-averaged to yield effective penetrant group-polymer interaction energies, which understandably indicate that the longer chain phthalates interact less favorably with PVC by virtue of their higher relative hydrocarbon content.

Finally, the polymer-penetrant free energy and solvent-accessible penetrant surface area calculations were utilized in the improved diffusion equation to produce *D* values for a number of di-*n*-alkyl phthalate plasticizers in PVC and compared with experimental values as well as with values earlier calculated without explicit PVC-plasticizer interactions. The results presented here show that the amended equation gives considerably better agreement with experimental diffusion data in terms of molecular size dependence, and especially with regard to temperature dependence, than before. Although there is still not perfect agreement between theoretical and experimental *D*'s, our revised equation more accurately reproduces the *shape* of the *D* versus temperature and molecular size curves. This fact usually implies a correct molecular-mechanistic representation.

Although we have been able to greatly improve the predictive accuracy of diffusion coefficients by factoring in polymer-penetrant interactions, this procedure presently does require a limited amount of experimental diffusion data. We hope to avoid this encumbrance through future model improvement.

Among future model improvements might be a relaxation of the assumption of rigid, namely low energy, penetrant molecular conformations. Obviously, it is a computational simplification and perhaps even a reasonable assumption that these large molecules will diffuse as a rigid unit. Perhaps higher energy conformations might diffuse with greater facility or perhaps a flexible molecule can better conform to its polymer environment through more efficient packing or be able to move around obstacles (i.e., polymer chains) more readily. In addition, we will be attempting to render the model more structurally realistic by accounting for additional factors such as polymer cross-linking and crystallinity, if present, and the effect of penetrant internal concentration on diffusivity.

Unquestionably, the most significant improvement to the diffusion model by the work reported herein is the strong impartation of *polymer chemical identity*. Therefore, the diffusion model has taken a significant step toward being a useful tool in new polymer material design and process optimization. One might also imagine that these polymer–penetrant energetic calculations can, when combined with similarly determined penetrant–penetrant, as well as polymer–polymer, interaction energies, be directly employed to predict the important Flory–Huggins interaction parameter (χ), which is a useful quantity in ranking polymer–plasticizer compatibility.

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Registry No. PVC, 9002-86-2; D_4HxP, 84-74-2; D_5HxP, 131-18-0; D_6HxP, 84-75-3; D_7HxP, 3648-21-3; D_8HxP, 117-84-0; D_9-HxP, 84-76-4; D_{10}HxP, 84-77-5; D_{11}HxP, 3648-20-2; D_{12}HxP, 2432-90-8; D_{13}HxP, 119-06-2.