Diffusion of Dioxygen in Alkanes and Cycloalkanes

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Received: March 28, 2000; In Final Form: June 30, 2000

The translational diffusion constant, *D*, of dioxygen, O_2, has been measured in the odd *n*-alkanes *n*-C_7H_{16} to *n*-$C_{15}H_{32}$, two branched alkanes (isooctane and squalane), and several cycloalkanes (cyclohexane, methylcyclohexane, *n*-butylcyclohexane, dicyclohexyl, *cis*-decalin, and *trans*-decalin). The *D* values were determined using Taylor−Aris dispersion theory in solutions drawn through a microcapillary by reduced pressure. The initial analysis of the data was in terms of the Stokes−Einstein relation ($D = k_BT/6\pi\eta r$). In both the *n*-alkanes and cycloalkanes, the values of the hydrodynamic radius *r* for O_2 are smaller than its known dimensions and decrease as the viscosity η increases, i.e., O_2 is diffusing faster than predicted by a constant solute "size." The data can be fitted to $D/T = A/\eta^p$ with $p < 1$ ($p = 1$ for the Stokes−Einstein relation). When the data for the odd *n*-alkanes are combined with our earlier results for O_2 in the even *n*-alkanes (*n*-C_6H_{14} to *n*-$C_{16}H_{34}$, Kowert, B. A.; Dang, N. C. *J. Phys. Chem.* **1999**, *103*, 779), we find $p = 0.553 \pm 0.009$. For O_2 in the cycloalkanes the fit gives $p = 0.632 \pm 0.017$. The data for isooctane and squalane are in approximate agreement with the *n*-alkane fit. The *D* values are also discussed in terms of computer simulations for small penetrants in hydrocarbons, the molar volumes of the solvents, and free volume approaches. A correlation between the *p* values and results of the free volume analyses is noted and discussed.

Introduction

The determination of the translational diffusion constant, *D*, of O_2 in the *n*-alkanes is of interest for several reasons. The *D* values for small solutes in liquids comprised of progressively larger solvent molecules provide a useful check of theories of diffusion and molecular dynamics calculations. Hydrodynamic results (such as the Stokes−Einstein relation) are not expected to hold for the low (<1) solute/solvent size and mass ratios found in these systems.[1] These studies are also potentially relevant to biological membranes (with interiors containing acyl chains comprised of 16−18 carbon atoms),[2] the design of polymers for gas separations,[3] and the development of protective coatings that are impervious to small penetrants such as O_2.[3]

In a previous study,[4] we determined the *D* values for dioxygen in the even *n*-alkanes C_6−C_{16} using microcapillary techniques and Taylor−Aris dispersion theory.[5,6] (Throughout this paper, C_i is used for *n*-C_iH_{2i+2}). We have now obtained *D* for O_2 in the odd *n*-alkanes C_7−C_{15}, the branched alkanes 2,2,4-trimethylpentane (isooctane) and 2,6,10,15,19,23-hexamethyltetracosane (squalane), and several cycloalkanes (cyclohexane, methylcyclohexane, *n*-butylcyclohexane, dicyclohexyl, and cis-, and *trans*-decalin). We were interested in comparing the *D* values for O_2 in the cycloalkanes and *n*-alkanes, two series of nonpolar solvents with different molecular shapes.

Our results for O_2 in the even *n*-alkanes showed clear deviations from the Stokes−Einstein relation[1]

$$D = k_BT/(f\pi\eta r) \tag{1}$$

where k_B is Boltzmann's constant, *T* is the absolute temperature, η is the viscosity, and *r* is the solute's hydrodynamic radius; $f = 6$ and 4 for the stick and slip limits, respectively. As the chain length (and viscosity) of the *n*-alkanes increased, the value of *r* for O_2 from eq 1 became smaller,[4] i.e., the diffusion of O_2 became progressively faster than predicted by a constant molecular "size." A possible explanation is that the *n*-alkanes, which on average are relatively extended, provide regions of increasing length in which the interactions between O_2 and the hydrocarbon are relatively weak and through which diffusion is relatively rapid. The data were then fitted to[1,7,8]

$$D/T = A/\eta^p \tag{2}$$

where *p* and *A* are constants ($p = 1$ for the Stokes−Einstein relation). A plot of log(*D*/*T*) vs log η gave $p = 0.562 \pm 0.011$ for O_2 in the even *n*-alkanes.[4] When the data in the odd *n*-alkanes are included, the value of $p = 0.553 \pm 0.009$ is essentially unchanged. The *D* values for O_2 in the cycloalkanes give $p = 0.632 \pm 0.017$.

As suggested by molecular dynamics (MD) simulations for small solutes in *n*-alkanes and polymers,[9] our *D* values for O_2 in the *n*-alkanes at 25 °C are approximately linear in n^{-1}. The *D* values for O_2 in polyethylene (PE)[10,11] are faster than predicted by the *n*-alkane data, corresponding to $n \approx 40$ for the polymer. The molar volumes, V_m, of the *n*-alkanes are linear in *n* and we find a reasonable correlation between the O_2 *D* values and V_m^{-1}; no such correlation is found for O_2 in the cycloalkanes. The *D* values for O_2 in the *n*-alkanes can also be fitted using the Doolittle−Cohen−Turnbull[12,13] free volume equation. A correlation between the free volume results and the *p* values is discussed in terms of the sizes of the diffusing species.

Literature data for ^{133}Xe are also discussed. The *D* values for this solute have been determined in a series of the *n*-alkanes at 20 °C[8] and in several of the *n*-alkanes as a function of temperature.[1] While values of *p* were given, free volume analyses were not carried out; we have done so and compared the results with those for O_2.

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10.1021/jp001145v CCC: $19.00

TABLE 1: Diffusion Constants and Hydrodynamic Radii for O_2 in the Odd *n*-Alkanes

solvent (day)	T, K	10^5D, cm^2 s^{-1}	$10^2\eta$, P	r_{stick}, Å[a]
C_7 (1)	292.7	7.89	0.409	0.664
C_7 (2)	291.2	7.66	0.416	0.668
C_9 (1)	294.2	5.98	0.702	0.513
C_9 (2)	293.2	5.76	0.712	0.524
C_{11} (1)	296.2	4.75	1.13	0.403
C_{11} (1)	295.7	4.79	1.14	0.396
C_{13} (1)	294.2	3.50	1.86	0.331
C_{13} (2)	295.2	3.79	1.82	0.313
C_{13} (3)	295.7	3.70	1.81	0.324
C_{15} (1)	296.7	2.81	2.63	0.294
C_{15} (2)	296.2	2.88	2.66	0.283
C_{15} (3)	296.2	2.99	2.66	0.273

[a] $r_{\text{slip}} = 3r_{\text{stick}}/2$.

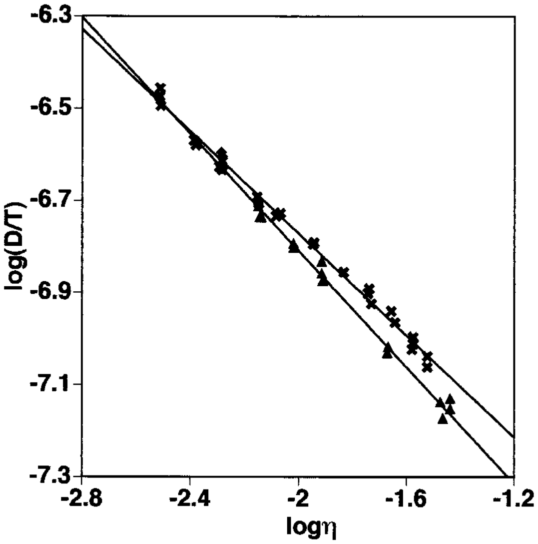

Figure 1. Fits of the diffusion constants for O_2 to $D/T = A/\eta^p$. C_6–C_{16} (×), the cycloalkanes (▲), and isooctane. (◆).

Results and Discussions

Stokes–Einstein Comparison and Modification. The D values for O_2 in the odd *n*-alkanes are shown in Table 1. Also given are the values of r calculated from eq 1 for the stick and slip limits. As was the case in the even *n*-alkanes,[4] the r values are small compared to the van der Waals radius of O (1.50 Å) and the O_2 bond length (1.20 Å);[14] they also decrease as the chain length and solvent viscosity increase. This indicates that the diffusion of O_2 in the *n*-alkanes is progressively faster than predicted by a constant solute "size" and is not in agreement with the Stokes–Einstein relation. This lack of agreement is not surprising since a small nonpolar probe is diffusing in much larger nonpolar solvent molecules. A fit of all of the *n*-alkane data to eq 2 (with η in P) gives $A = (1.32 \pm 0.06) \times 10^{-8}$, $p = 0.553 \pm 0.009$ (Figure 1), essentially unchanged from $A = (1.27 \pm 0.07) \times 10^{-8}$ and $p = 0.562 \pm 0.011$ in the even *n*-alkanes.[4]

TABLE 2: Diffusion Constants and Hydrodynamic Radii for O_2 in the Cycloalkanes and Isooctane

solvent (day)	T, K	10^5D, cm^2 s^{-1}	$10^2\eta$, P	r_{stick}, Å[a]
methylcyclohexane (1)	293.2	5.39	0.727	0.547
methylcyclohexane (2)	294.2	5.43	0.717	0.554
methylcyclohexane (3)	295.2	5.94	0.707	0.515
methylcyclohexane (4)	295.2	5.74	0.707	0.533
cyclohexane (1)	294.2	4.75	0.953	0.476
cyclohexane (2)	294.2	4.65	0.953	0.486
n-butylcyclohexane (1)	297.2	4.13	1.215	0.434
n-butylcyclohexane (2)	296.7	3.97	1.225	0.447
n-butylcyclohexane (3)	297.2	4.38	1.215	0.408
trans-decalin (1)	293.2	2.74	2.128	0.368
trans-decalin (2)	292.7	2.82	2.145	0.355
cis-decalin (1)	292.7	1.97	3.422	0.318
cis-decalin (2)	292.7	1.97	3.422	0.318
dicyclohexyl (1)	297.2	2.10	3.637	0.285
dicyclohexyl (2)	297.2	2.21	3.637	0.271
isooctane (1)	292.2	6.93	0.520	0.593
isooctane (2)	292.2	7.28	0.520	0.565
isooctane (3)	292.7	7.44	0.517	0.557

[a] $r_{\text{slip}} = 3r_{\text{stick}}/2$.

The values of D and r for O_2 in the cycloalkanes are given in Table 2. As was the case in the *n*-alkanes, the r values are smaller than the "sizes" of dioxygen and decrease with increasing viscosity. The fit to eq 2 (Figure 1) gives $A = (8.44 \pm 0.61) \times 10^{-9}$ and $p = 0.632 \pm 0.017$. The more globular shape of the cycloalkanes may be the reason for the increase in p relative to the value in the *n*-alkanes but O_2 is still smaller than the cycloalkanes and its interactions with these nonpolar solvents are also relatively weak. The data for O_2 in isooctane (Table 2, Figure 1) were not included in either of the two fits to eq 2 but are in agreement with the *n*-alkane data. For squalane, the value of $10^6D = 8.23$ cm^2 s^{-1} at 21 °C is in approximate agreement with the value predicted by the *n*-alkane fit ($10^6D = 7.15$ cm^2 s^{-1}) and emphasizes the deviation of the O_2 diffusion constants from the Stokes–Einstein relation. The viscosity of squalane at 21 °C is a factor of 100 larger than that of C_6 at 25 °C (see the Experimental Section). At these temperatures, the D value for O_2 in squalane is only a factor of 12 smaller than that in C_6. The "size" of O_2 in squalane ($r = 0.0786$ Å) is also absurdly small.[15,16]

The results for ^{133}Xe are consistent with those for O_2. Pollack and Enyeart[8] obtained $p = 0.686$ from the D values for ^{133}Xe in C_5–C_{16} at 20 °C. Separate determinations of D for this solute at 10, 20, 30, and 40 °C in C_8, C_{10}, and C_{14} gave $p = 0.708$[1] when combined with data in refs 7 and 8. This p value is larger than that for O_2 in the *n*-alkanes (0.553) and cycloalkanes (0.632). As implied by these p values, the values of r obtained for ^{133}Xe from eq 1 are also larger than those for O_2. Representative stick limit values in C_6 are $r = 0.712$ Å (O_2) and 1.01 Å (^{133}Xe), while in C_{16} one has $r = 0.275$ Å (O_2) and 0.501 Å (^{133}Xe).

Comparison with Molecular Dynamics Results. van der Vegt and co-workers[9] calculated the diffusion constants of a small molecule, methane (CH_4), in *n*-alkane liquids and PE. The dependence of D on n, the number of carbon atoms in the *n*-alkanes, was found to be $D \approx n^{-\alpha}$ with $\alpha = 1.0 \pm 0.1$. Figure 2a shows that at 25 °C our D values for O_2 in the *n*-alkanes are approximately linear in n^{-1} (all of the D values at 25 °C mentioned in this and the following section were calculated using the fits to eq 2). The D value for O_2 in squalane (at 25 °C) is also included in Figure 2a. Squalane contains 30 carbon atoms but has six methyl groups attached to the main chain of 24 carbon atoms. Points are shown for both $n = 24$ and $n = 30$; the latter is in somewhat better agreement with the *n*-alkane fit. The D values for ^{133}Xe in C_5–C_{16} at 20 °C[8] lie below those for O_2 (Figure 2a) and also are approximately linear. Fits of the data to $10^5D = a_n + b_n/n$ gave $a_n = -1.621$, $b_n = 71.02$ for O_2, and $a_n = -1.944$, $b_n = 50.85$ for ^{133}Xe.

The diffusion constants for O_2 in two PE samples at 25 °C are compared with the values in the *n*-alkanes and squalane in Figure 2b. The PE samples[10] have number-average molecular weights of 2.6×10^4 and 4.0×10^4, corresponding to $n = 1857$ and 2857, respectively. It should be noted, however, that PE is a semicrystalline polymer containing crystalline and amorphous

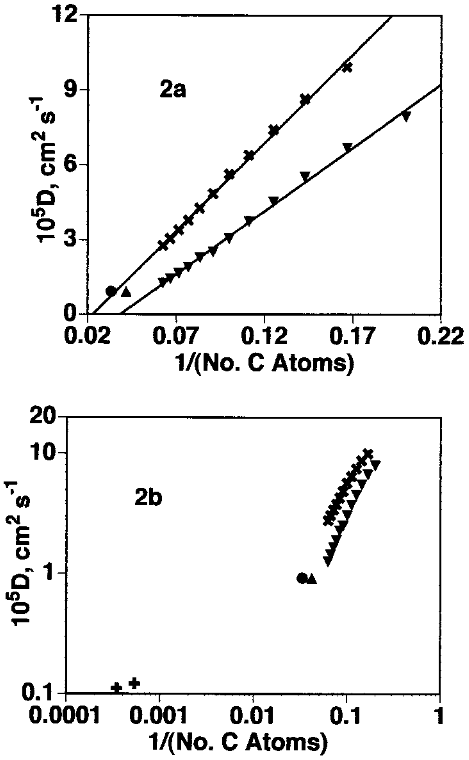

Figure 2. Diffusion constants vs 1/*n*. (a) O_2 in C_6-C_{16} (×) and squalane for $n = 30$ (●) and $n = 24$ (▲) at 25 °C; ^{133}Xe in C_5-C_{16} at 20 °C (▼). (b) O_2 in C_6-C_{16} (×), squalane for $n = 30$ (●) and $n = 24$ (▲), and PE (+) at 25 °C; ^{133}Xe in C_5-C_{16} at 20 °C (▼).

regions. The diffusion constants calculated by van der Vegt et al.[9] for CH_4 in PE assume a homogeneous amorphous material. The data in Figure 2b have been corrected for crystallinity[11] and refer to the amorphous fraction. The *D* values for O_2 in the two PE samples clearly are much larger than predicted by the *n*-alkane data; the experimental O_2 *D* values and the *n*-alkane fit to eq 2 give $n \approx 40$ for the PE chains. It appears that the O_2 diffusion constant becomes a much weaker function of the chain length for large values of *n* (as did the calculated *D* values for CH_4 in PE).[9]

The near-linear correlations between the *D* values and n^{-1} in the *n*-alkanes suggest another possibility. The molar volumes[17] of C_5-C_{16} at 25 °C are given by $V_m(\text{cm}^3\ \text{mol}^{-1}) = 16.2195(n + 2.1029)$. Changing the independent variable to V_m^{-1} corresponds to a plot of *D* versus $(n + 2.1029)^{-1}$; V_m can also be used for the branched alkanes[18] and cycloalkanes.[18] Figure 3 shows plots (vs V_m^{-1}) of the *D* values for O_2 in all of our solvents at 25 °C and ^{133}Xe in C_5-C_{16} at 20 °C. The *D* values for O_2 and ^{133}Xe do not, in general, have a linear dependence on V_m^{-1}. The correlation is best for O_2 in the *n*-alkanes; the *D* values for ^{133}Xe in C_5-C_{11} are linear in V_m^{-1} while those in $C_{12}-C_{16}$ become larger than predicted by the C_5-C_{11} data. Fits to $10^5D = a_v + b_v/V_m$ give $a_v = -3.283$, $b_v = 1.744$ for O_2 in C_6-C_{16}, and $a_v = -4.083$, $b_v = 1.399$ for ^{133}Xe in C_5-C_{11}. The *D* values for O_2 in squalane and isooctane are larger than and in approximate agreement with the *n*-alkane fit, respectively; the *D* values in the cycloalkanes show considerable scatter.

Free Volume Approach. Viscosities, relaxation times, and diffusion constants in liquids and polymers[12,13,19] have been discussed in terms of v_f, the fractional free volume[12]

$$v_f = [V_m - V_o(d)]/V_o(d) \qquad (3)$$

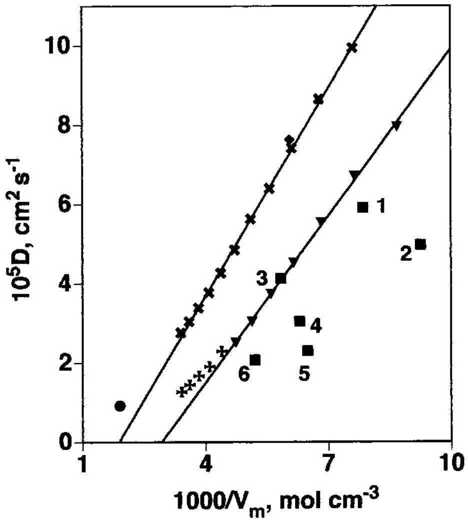

Figure 3. Diffusion constants vs $1/V_m$. (i) O_2 in C_6-C_{16} (×) and squalane (●) at 25 °C; (ii) O_2 in the cycloalkanes at 25 °C (■) with the designations (1) methylcyclohexane, (2) cyclohexane, (3) *n*-butylcyclohexane, (4) *trans*-decalin, (5) *cis*-decalin, and (6) dicyclohexyl; (iii) ^{133}Xe at 20 °C in C_5-C_{11} (▼) and in $C_{12}-C_{16}$ (+).

where $V_o(d)$ is the zero-diffusion volume. The relation between a kinetic property, *X*, and v_f is given by the Doolittle–Cohen–Turnbull equation[12,13]

$$X = F \exp(-B/v_f) \qquad (4)$$

where *F* and *B* are constants with $B \approx 1$. In Cohen and Turnbull's theory,[13] the parameter *B* is the product of a geometric factor *g* ($0.5 \le g \le 1$) and the ratio $v^*/V_o(d)$, where v^* is a critical volume just large enough for diffusion to occur. *B* has also been discussed in terms of the size of groups of molecules that must move cooperatively during the diffusion process.[20–22] In Doolittle's original analysis[12] of the temperature-dependent viscosities of the individual *n*-alkanes, *B* was found to increase as the chain length increased ($B = 0.688$ and 1.00 for C_7 and C_{17}, respectively). Viscosity analyses also have shown that simple molecular liquids such as toluene and isopropyl benzene have smaller *B* values (≤ 1) than associating liquids such as ethers and alcohols ($B = 2-7$).[20]

Equations 3 and 4 have been applied to transport properties of a given material that have been measured over several orders of magnitude by varying pressure as well as temperature.[20] Our situation is different; we have measured the diffusion constant ($X = D$) for a small solute over a narrow range of temperatures as a function of solvent. The *n*-alkanes, with which we will be concerned in this section, have a reasonable range of molar volumes.[17] Our O_2 data as well as those for ^{133}Xe[1,7,8] have been analyzed using $V_o(d) = V_o$, the close-packing volume of the solvent; this is similar to Cohen and Turnbull's assumption[13] that $V_o(d)$ is the van der Waals volume. Formulas from which values of V_o can be calculated for the *n*-alkanes are given in ref 21. Good linear correlations are found for plots of ln *D* versus $(v_f)^{-1}$ for O_2 in C_6-C_{16} at 25 °C and ^{133}Xe in C_5-C_{16} at 20 °C[8] (see Figure 4). The values of *B* and ln *F* for these fits are given in Table 3.

The order of the *B* values (1.259 ± 0.017 for ^{133}Xe, 1.040 ± 0.018 for O_2) roughly parallels the solute size (which would seem to be indicative of the critical volume necessary for diffusion to occur); the *p* values also increase as the solute size increases. In fact, the free volume fit is related to that involving eq 2;[32] the isothermal viscosities of the *n*-alkanes can be fitted

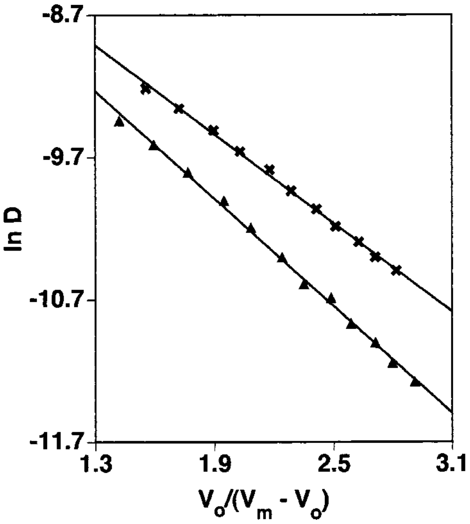

Figure 4. Fits to $\ln D = \ln A - B/v_f$ with $V_o(d) = V_o$. The systems are O_2 in C_6−C_{16} at 25 °C (×) and ^{133}Xe in C_5−C_{16} at 20 °C (▲).

TABLE 3: Free Volume Parameters for O_2 in the *n*-Alkanes and *n*-Alkane Self-Diffusion

diffusant	solvent	B	−ln*A*	*T*, K
O_2[a]	*n*-alkanes[a]	1.040 ± 0.018	7.559 ± 0.040	298.2[a]
^{133}Xe[b]	*n*-alkanes[b]	1.259 ± 0.017	7.596 ± 0.039	293.2[b]
^{133}Xe[c]	C_8	1.493 ± 0.139	7.100 ± 0.265	283.2−313.2
^{133}Xe[c]	C_{10}	1.299 ± 0.016	7.520 ± 0.034	283.2−313.2
^{133}Xe[c]	C_{14}	1.127 ± 0.036	7.993 ± 0.096	283.2−313.2
^{133}Xe[d]	C_8	1.257 ± 0.098	7.598 ± 0.170	283.2−403.2
^{133}Xe[d]	C_{10}	1.313 ± 0.051	7.523 ± 0.100	283.2−433.2
^{133}Xe[d]	C_{14}	1.228 ± 0.014	7.730 ± 0.034	283.2−430.2
^{133}Xe	*n*-alkanes[e]	1.269 ± 0.019	7.595 ± 0.039	283.2−433.2

[a] *D* values from fit to eq 2 in C_6−C_{16} at 25 °C. [b] For the *D* values in C_5−C_{16} at 20 °C from ref 8. [c] Ref 1. [d] Combined analysis using data in refs 1 and 7. [e] Combined analysis using data in refs 1, 7, and 8.

using $\eta = A_\eta \exp(B_\eta/v_f)$ with $B_\eta = 1.881$ ($\ln A_\eta = -8.809$) and 1.826 ($\ln A_\eta = -8.717$) for C_6−C_{16} at 25 °C and C_5−C_{16} at 20 °C, respectively. Combining this equation for η with eq 4 gives $D\eta^p = FA_\eta^p = constant$ with $p = B/B_\eta$; this is the isothermal version of eq 2. We also determined the *D* values for three aromatic hydrocarbons with larger "sizes" than O_2 and ^{133}Xe. They were biphenyl ($p = 0.718 \pm 0.004$, $B = 1.35 \pm 0.02$) and pyrene ($p = 0.805 \pm 0.005$, $B = 1.51 \pm 0.03$) in C_6−C_{16} and rubrene ($p = 0.943 \pm 0.008$, $B = 1.81 \pm 0.03$) in the odd *n*-alkanes C_7−C_{15}.[23] Again, the values of *p* increase as the values of *B* increase, and the experimental values of *p* are very close to those (0.44% or less) calculated using $p = B/B_\eta$. As seen in Figure 5 there is a strong linear correlation between these two parameters for all five of the solutes.

To have confidence in the values of *B* (and *p*), it is important to have a sufficiently large set of diffusion data. For example, the *B* value used for ^{133}Xe in Figure 5 (1.259 ± 0.017) was obtained from the twelve *D* values in C_5−C_{16} at 20 °C.[8] If only the temperature-dependent data from ref 1 for this solute in C_8, C_{10}, and C_{14} are analyzed (four *D* values per solvent), one finds values of *B* that decrease as the chain length increases ($B = 1.493 \pm 0.139$ in C_8, 1.299 ± 0.016 in C_{10}, and 1.127 ± 0.036 in C_{14}). When the temperature-dependent data for C_8, C_{10}, and C_{14} in ref 7 (also four *D* values per solvent) are included with those from ref 1, one finds $B = 1.257 \pm 0.098$ in C_8, 1.313 ± 0.051 in C_{10}, and 1.228 ± 0.014 in C_{14}. These are closer to the value used in Figure 5 or the value when all of the data in refs 1, 7, and 8 are used ($B = 1.269 \pm 0.019$). The values of *B* and ln *F* for these fits are given in Table 3.

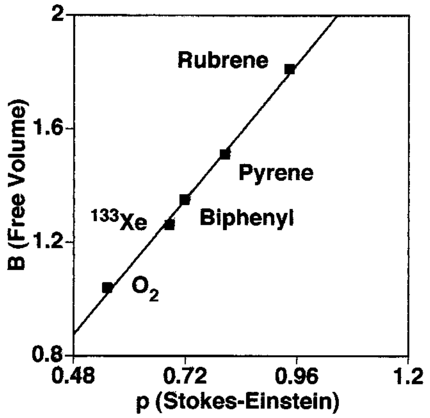

Figure 5. *B* vs *p* in the *n*-alkanes. The data fit gives $B = 1.986p - 0.0774$.

It would be desirable to have data for these and other systems over a wide range of temperatures and pressures. The resulting grid of *B* values might help in establishing a more rigorous interpretation of the physics of *B*[20] as well as determining the extent of its usefulness. Modification of the free volume equations is another possibility. In addition to free volume, explicit dependence on activation energy has been included in the expression for *D*.[24] Weiss and co-workers[25] modified the Cohen−Turnbull[13] theory for application to disklike molecules; in a separate study,[26] they found no relation between molecular shape and the slopes of isochoric free volume plots for self-diffusion data.

Conclusions

The translational diffusion constant, *D*, for dioxygen has been measured in several *n*-alkanes, branched alkanes, and cycloalkanes. The *D* values were determined by drawing oxygenated solutions through a microcapillary using reduced pressure. O_2 is diffusing faster than predicted by the Stokes−Einstein relation and the solvent viscosities. The deviations from Stokes−Einstein behavior in the relatively extended *n*-alkanes are slightly larger than those in the more globular cycloalkanes. The data for the diffusion of O_2 in the branched alkanes are in approximate to good agreement with those for the *n*-alkanes. The *D* values for O_2 in the *n*-alkanes are found to have a linear dependence on n^{-1}, where *n* is the number of carbon atoms in the alkane chain. The diffusion of O_2 in polyethylene (PE)[10,11] is faster than predicted by the *n*-alkane data, corresponding to $n \approx 40$ for PE. In the *n*-alkanes, the O_2 *D* values also have a linear dependence on the inverse of the solvent's molar volume, $(V_m)^{-1}$; there is no correlation between $(V_m)^{-1}$ and *D* in the cycloalkanes.

The *D* values for O_2 in the *n*-alkanes could also be fitted using the Doolittle−Cohen−Turnbull free volume equation[12,13] with the close-packing volume as the zero-diffusion volume. The literature *D* values for ^{133}Xe in a series of the *n*-alkanes[1,8] have been found to be consistent with our results for O_2 with regard to the deviations from Stokes−Einstein behavior, the correlation of *D* with n^{-1}, and the free volume approach. A correlation between the results of the free volume fits and the values of *p* for O_2, ^{133}Xe, and several other solutes has been found. The *p* values and free volume parameters increase as the size of the diffusing species increases.

Experimental Section

Gaseous oxygen and nitrogen were obtained from Acetylene Gas Co. and Gateway Airgas, respectively. With the exception

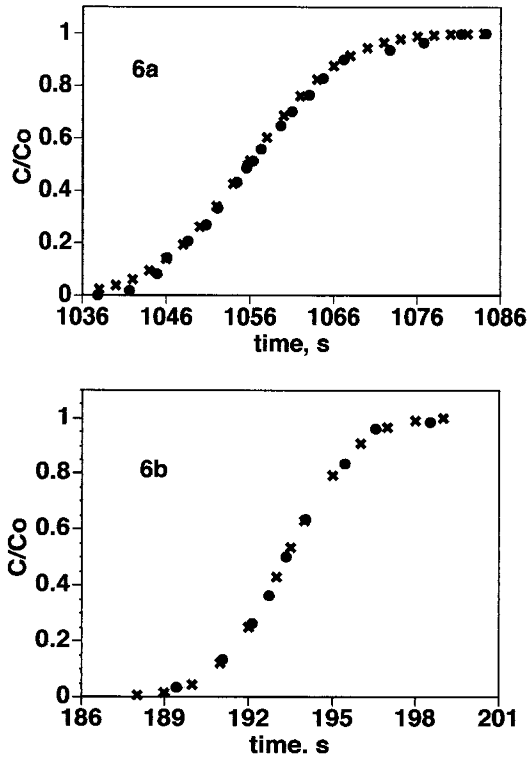

Figure 6. Absorption profiles for O_2. (a) in squalane: experimental (●), calculated (×). (b) in n-$C_{15}H_{32}$: experimental (●), calculated (×).

of squalane (Eastman) and C_7 (Fisher), the solvents as well as biphenyl, pyrene, and rubrene were from Aldrich Chemical Co.; all were used as received. The molar volumes for the *n*-alkanes are from ref 17 while the molar volumes for the branched alkanes and cycloalkanes are from ref 18. The viscosities for the odd *n*-alkanes, cyclohexane, and methylcyclohexane are from ref 27; those for isooctane, *n*-butylcyclohexane, dicyclohexyl, *cis*-decalin, and *trans*-decalin are from ref 28, while those for squalane are from ref 29.

The elution profiles used to calculate D for O_2 were obtained by introducing a plug of oxygenated solvent into a stream of deoxygenated solvent being drawn through a microcapillary (77 μm i.d.[30]) by reduced pressure. The oxygenated and deoxygenated solvents were prepared by bubbling oxygen and nitrogen, respectively, through different containers of the same solvent. The progress of the oxygenated solution through the capillary was followed using UV detection at 190 nm. A more complete discussion of the experimental methods is given in ref 4.

The D values for O_2 in all solvents except squalane (discussed further below) were determined using the widths and elution (retention) times of the profiles, t_R, as discussed in ref 4. The elution profiles were obtained at room temperature (direct temperature control was not possible). The temperature was measured continuously during the 2−4 h needed to acquire profiles. The average daily temperatures, given in Tables 1 and 2, varied by (at most) ±0.5 °C, and ranged from 18.0 to 25.5 °C for the work reported here and in ref 4. "Day" refers to a set of profiles taken for the only solvent studied on that day; the determinations for each solvent were completed before moving on to the next.

When studying squalane the relatively high viscosity (33.3 cP at 21 °C[29]) led to long values of $t_R \approx 1056$ s, broad profile widths, and weak profile intensities. For comparison, O_2 in C_{16} has $t_R \approx 245$ s ($\eta = 3.03$ cP at 25 °C[27]) while $t_R \approx 25$ s in C_6 ($\eta = 0.300$ cP at 25 °C[27]). To determine D for O_2 in squalane, we pulled deoxygenated squalane through the capillary, then broke the reduced pressure, placed the capillary in the oxygenated squalane, reset the pressure, and started the data acquisition. As the oxygenated solution was pulled through the capillary, the boundary between it and the deoxygenated solution in front of it became blurred by diffusion, giving a sigmoid O_2 absorption profile (Figure 6a). A value of $D = 8.23 \times 10^{-6}$ cm^2 s^{-1} (21 °C) was obtained by comparing the experimental profile with profiles calculated using Taylor's equations.[31] As a check, we applied this approach to O_2 in C_{15}. Figure 6b shows the experimental absorption profile taken at 23 °C as well as a profile calculated using the D value (2.99×10^{-5} cm^2 s^{-1}) determined from an analysis of (Gaussian) elution profiles taken on the same day at the same temperature. The agreement between the experimental and calculated profiles is seen to be good.

Acknowledgment. The Department of Chemistry, Saint Louis University, has supported this research. The computer and detector used to obtain the elution profiles were purchased with grants to Dr. Barry Hogan from Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Dr. Mark Conradi (Department of Physics, Washington University) for several helpful questions and comments.

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