Size-Dependent Diffusion in the *n*-Alkanes

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The translational diffusion constants, D, of *trans*-stilbene, 1,4-dipheny-1,3-butadiene, 1,6-dipheny-1,3,5-hexatriene, 1,1,4,4,-tetraphenyl-1,3-butadiene, tetraphenylethylene, 9,10-diphenylanthracene, *p*-terphenyl, bibenzyl, 1,1′-binaphthyl, [2.2]paracyclophane, triptycene, and dodecahydrotriphenylene have been determined in the *n*-alkanes using capillary flow techniques. The solutes showed deviations from the Stokes−Einstein (SE) relation ($D = k_BT/(6\pi\eta r)$); the values of the hydrodynamic radius, r, decrease as the viscosity, η, increases. The data can be fitted to $D/T = A_{SE}/\eta^p$ with $p < 1$ ($p = 1$ for the SE relation). The values of p increase as the solute size increases; they range from $p = 0.712$ for *p*-terphenyl to $p = 0.942$ for 1,1,4,4,-tetraphenyl-1,3-butadiene. The deviations from SE behavior are discussed in terms of the ratio V_s/V_p, where V_s and V_p are the van der Waals volumes of a solvent and diffusing probe, respectively. The diffusion constants also are discussed in terms of the Wilke−Chang equation. The values of D^{-1} for several of the solutes are compared with their rotational correlation times, τ_θ, in the *n*-alkanes. The values of τ_θ, which showed deviations from the Stokes−Einstein−Debye expression ($\tau_\theta = 4\pi r^3\eta/(3k_BT)$), have the same general dependence on viscosity as D^{-1}.

Introduction

The translational diffusion constants, D, of solutes in dilute solutions are of central importance in the study of motion in liquids.[1,2] They have been measured by a number of methods and provide checks of diffusion theories and molecular dynamics calculations.[1] The diffusion constants depend on the shape, size, and polarity of the solute and solvent, as well as the interactions between them. The analysis and discussion of the experimental D values usually starts with the well-known Stokes−Einstein (SE) relation[1,2]

$$D = k_BT/(f_t\pi\eta r) \qquad (1)$$

where η is the solution viscosity, T is the absolute temperature, and r is the solute's hydrodynamic radius; $f_t = 6$ and 4 for the stick and slip limits, respectively.

The SE relation holds when the solute's volume is much larger than that of the solvent, a requirement that many solutions do not meet. We (and others)[3−7] have found deviations from eq 1 when the solute size is smaller than or comparable to some, if not all, of the *n*-alkanes, C_6 through C_{16} (C_i is used for n-C_iH_{2i+2}). At constant temperature, the r values obtained from eq 1 for a given solute decreased as the *n*-alkane chain length and viscosity increased; if eq 1 holds, one would expect to find a common solute size as the chain length is varied. Also, in ref 5, we used values of r in C_7 and C_{15} at 25 °C to show that the relative change in r decreased as the solute's size increased; O_2 had $\Delta r_{7,15} = 100[r(C_7) - r(C_{15})]/r(C_7) = 57\%$, anthracene had $\Delta r_{7,15} = 38\%$, while rubrene had $\Delta r_{7,15} = 10\%$.

The diffusion data were then analyzed using the modified Stokes−Einstein (MSE) expression[3−7]

$$D/T = A_{SE}/\eta^p \qquad (2)$$

where p and A_{SE} are constants; $p = 1$ for the SE limit. Our studies of O_2 showed clear deviations from the SE relation,[4] that is, $p = 0.553$ in C_6 through C_{16}. We also studied several aromatic hydrocarbons in the *n*-alkanes; their p values[5] ranged from 0.718 for biphenyl to 0.943 for rubrene. The latter clearly has strong solute−solvent interactions; the four phenyl groups attached to its tetracene nucleus cause it to experience close to the full viscous drag of the *n*-alkane chains.

The use of eq 2 does not necessarily imply that the SE relation is incorrect. Zwanzig and Harrison[8] noted that the experimental data could be analyzed using eq 1 with r becoming an environment-dependent effective hydrodynamic radius (EHR) that measures the strength of the coupling between the solute and solvent motions. They mentioned the need to look for the dependence of D on properties that could be used to understand the relation between the EHR and intermolecular forces. Following this approach, we examine the deviations from SE behavior in terms of the ratio V_s/V_p, where V_s and V_p are the van der Waals volumes of a solvent and diffusing probe, respectively. We replace the radius r in eq 1 by

$$r = R_0/(1 + V_s/V_p)^m \qquad (3)$$

where R_0 is an effective radius; m and V_s/V_p are measures of the deviation from the SE relation, which is recovered when $V_p \gg V_s$ or $m = 0$ (our data fits show that $m \approx 1$). Equation 3 also is consistent with the observed decrease in r for a given probe as the solvent size increases.

In this paper, eq 3 is applied to the r values of more than 50 molecules in the *n*-alkanes. The data include (a) our previous results for O_2[4] and a series of aromatic hydrocarbons,[5] (b) literature results for more than 20 other solutes, (c) literature results for the self-diffusion of the *n*-alkanes, and (d) new results for 12 solutes that we have studied using capillary flow techniques. The new solutes are *trans*-stilbene (TSB), 1,4-dipheny-1,3-butadiene (DPBD), 1,6-dipheny-1,3,5-hexatriene

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TABLE 1: Detection Wavelengths and Fit Parameters for Equation 2

solute	solvents[a]	λ_{max}	p	$-\log A_{SE}$
p-terphenyl	6, 8, 10, 12, 16	280	0.712 ± 0.033	8.915 ± 0.065
trans-stilbene	6−14 (even)	292	0.726 ± 0.003	8.862 ± 0.064
bibenzyl	6−16 (even)	219	0.759 ± 0.015	8.955 ± 0.015
DDHTP	7−13 (odd)	195	0.777 ± 0.003	9.124 ± 0.058
DPBD	7−13 (odd)	327	0.793 ± 0.022	9.053 ± 0.047
TPHE	6−14 (even)	240	0.825 ± 0.020	9.324 ± 0.042
DPHT	7−13 (odd)	352	0.833 ± 0.018	9.169 ± 0.037
PCPH	8−16 (even)	224	0.836 ± 0.013	9.176 ± 0.025
BNP	6−16 (even)	220	0.848 ± 0.011	9.273 ± 0.022
triptycene	7−15 (odd)	212	0.873 ± 0.021	9.368 ± 0.041
DPA	6−16 (even)	260	0.899 ± 0.019	9.510 ± 0.035
TPBD	8−14 (even)	344	0.942 ± 0.031	9.612 ± 0.064

[a] The numbers refer to *i*, the number of C atoms for the C_i; "even" and "odd" mean only C_i with even and odd numbers of C atoms, respectively, were used.

(DPHT), 1,1,4,4,-tetraphenyl-1,3-butadiene (TPBD), tetraphenylethylene (TPHE), 9,10-diphenylanthracene (DPA), *p*-terphenyl, bibenzyl, triptycene, 1,1′-binaphthyl (BNP), [2.2]paracyclophane (PCPH), and dodecahydrotriphenylene (DDHTP). They too show deviations from the SE relation that decrease as the solute size increases. The *D* values for the solutes also are compared with the predictions of the Wilke−Chang equation (WCE),[9] an oft-used relation in chromatographic analyses.

Deviations from simple hydrodynamic theories also are found for the rotational motion of several of our solutes in the *n*-alkanes;[10−16] as the solvent chain length is varied for a given probe at constant *T*, the reorientational correlation time τ_θ is not linear in η as predicted by the Stokes−Einstein−Debye (SED) relation[16−19]

$$\tau_\theta = (V/k_B)(\eta/T) \tag{4}$$

where *V* is the effective hydrodynamic volume of the solute (which is often written as $4\pi r^3/3$ but is understood to include frictional and shape effects as well as solute−solvent interactions[16−19]). A comparison of our values of D^{-1} and the τ_θ data for several solutes shows them to have a similar dependence on viscosity.

Experimental Section

All of the solutes except binaphthyl (Acros Organics) were from Aldrich Chemical. They, as well as the solvents, were used as received. The *n*-alkanes were obtained from Aldrich (C_9−C_{16}, all 99+%), Fisher (C_6, Optima; C_7, HPLC grade), and Sigma (C_8, 99+%). The viscosities for the *n*-alkanes are from ref 20. The solutions used to determine *D* values were prepared by dissolving 1 mg of solute in 25 mL of an *n*-alkane; the concentrations ranged from 5.6×10^{-5} M for TPBD to 1.1×10^{-4} M for TSB and bibenzyl.

Taylor−Aris dispersion theory[21,22] was used to calculate the *D* values from solute dispersions (elution profiles) obtained by introducing a small amount of solution into a stream of the pure solvent being drawn through a microcapillary by reduced pressure. This approach[3−5] gave diffusion constants in good agreement with literature values for the aromatic hydrocarbons in the *n*-alkanes.[5] The elution profiles were obtained using UV detection at room temperature, which varied by at most ±0.5 °C during the ~2 h needed for a given determination of *D*. The detector, data acquisition system, and other aspects of the experimental procedure have been described previously.[3−5] The UV wavelengths used for the solutes are given in Table 1.

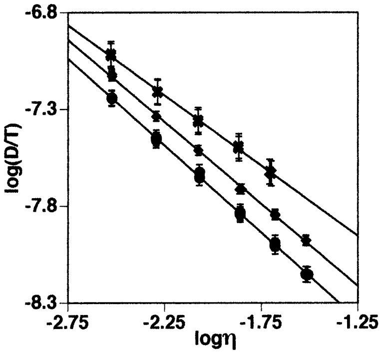

Figure 1. Fits of the diffusion constants in the *n*-alkanes for (×) TSB, (◆) BNP, and (●) DPA to $D/T = A_{SE}/\eta^p$ (η in P).

Results and Discussions

SE Comparison and Modification. The *D* values for our solutes in the *n*-alkanes were fitted to eq 2. Plots of log(*D*/*T*) vs log η for TSB, BNP, and DPA are shown in Figure 1. The uncertainties for the *D* values are ±3.5% for TSB, ±2.5% for BNP, and ±4.2% for DPA; the average uncertainty in all of our *D* values is ±4%. The uncertainties for log(*D*/*T*) in Figure 1, which include the uncertainties in both log A_{SE} and *p*, show that the experimental data are well described by eq 2.

All of the solutes have values of $p < 1$ that tend to increase as the solute size increases. This is the same trend seen in ref 5, where in an effort to relate *p* to solute size, the half-lengths of their molecular axes, R_j ($j = x, y, z$), were determined from structural data and van der Waals radii. The values of *p* in the *n*-alkanes showed an approximately linear correlation with $R = (R_xR_yR_z)^{1/3}$. *R* is proportional to the cube root of the molecular volume for an ellipsoid, but most of our solutes are more irregularly shaped. In this paper, we have adopted a different approach to size determination. The van der Waals volumes of both solutes and solvents were calculated from Bondi's increments;[23−26] a single length was then obtained from $r_{eff} = (3V_i/(4\pi))^{1/3}$, where i = p and s. There are other measures of molecular size that might be used, but Bondi's commonly employed procedures can be applied in a straightforward manner to all of our systems. We have calculated r_{eff} for 41 solutes with a considerable range of shapes, sizes, and chemical composition. They include the 12 new probes from this paper, as well as O_2,[4] C_{60},[26] and the eight probes considered in ref 5 (biphenyl, diphenylacetylene, diphenylbutadiyne, anthracene, pyrene, rubrene, perylene, and coronene). The data in refs 7, 27, and 28 were used to obtain the *p* values for CCl_4, CH_4, Xe, Kr, Ar, $Sn(Me)_4$, $Sn(Et)_4$, $Sn(Pr)_4$, and $Sn(Bu)_4$, while ref 29 was used for benzoquinone (BZQ), tetramethylbenzoquinone (TMBZQ), tetrachlorobenzoquinone (TCBZQ), and tetraphenylporphine (TPPH). Data from the literature also were used to obtain the *p* values for I_2,[30] CO_2,[31,32] ethane,[31] propane,[33] benzene,[34−37] and cyclohexane.[38] The values of *p* and log A_{SE} for C_{60} and the solutes not studied in our laboratory are given in Table 2 and, like our own, show that *p* increases as the solute size increases. For example, the tetraalkyltin compounds, SnX_4, show that *p* increases from 0.764 to 0.853 for X = Me and Bu, respectively; *p* also increases from 0.715 for BZQ to 0.959 for the much larger TPHP. Figure 2 shows some scatter but indicates that the value of *p* is correlated with the solute size in the *n*-alkanes.

Volume-Dependent Modification of the SE Relation. The literature, particularly that of chemical engineering, contains a number of empirical relations used to estimate solute diffusion constants. Some of these equations have the same dependence

TABLE 2: Fit Parameters for Equation 2[a]

solute	solvents[b]	p[c]	$-\log A_{SE}$[c]
C_{60}[d]	6−16 (even)	0.903 ± 0.006	9.604 ± 0.012
CH_4	6, 7, 8, 10, 12, 14, 16	0.533 ± 0.010	7.893 ± 0.022
CCl_4	6, 8, 10, 14	0.755 ± 0.005	8.798 ± 0.009
Xe	6, 8, 10, 14	0.598 ± 0.004	8.248 ± 0.009
Kr	6, 8, 10, 14	0.514 ± 0.012	7.972 ± 0.023
Ar	6, 8, 10, 14	0.478 ±0.014	7.756 ± 0.031
$Sn(Me)_4$	6, 8, 10, 14	0.764 ± 0.007	8.856 ± 0.016
$Sn(Et)_4$	6, 8, 10, 14	0.804 ± 0.004	9.048 ± 0.009
$Sn(Pr)_4$	6, 8, 10, 14	0.827 ± 0.006	9.197 ± 0.016
$Sn(Bu)_4$	6, 8, 10, 14	0.853 ± 0.008	9.327 ± 0.018
I_2	6, 7, 8, 14	0.752[e]	8.755[e]
CO_2	7, 16	0.497[e]	7.881[e]
ethane	6, 7, 8, 12, 16	0.485 ± 0.008	7.926 ± 0.018
propane	6, 7, 8, 16	0.519 ± 0.012	8.084 ± 0.023
benzene	6, 7, 8, 12, 16	0.716 ± 0.001	8.614 ± 0.002
cyclohexane	6, 7, 8, 12	0.779 ± 0.022	8.869 ± 0.047
BZQ	6, 10, 14, 16	0.715 ± 0009	8.651 ± 0.016
TMBZQ	6, 10, 14, 16	0.779 ± 0.022	8.962 ± 0.038
TCBZQ	6, 10, 14, 16	0.748 ± 0.007	8.916 ± 0.015
TPHP	6, 10, 14, 16	0.959 ± 0.007	9.805 ± 0.013

[a] The data used to obtain p and log A_{SE} were all at 25 °C; the references are given in the text. [b] The numbers refer to i, the number of C atoms for the C_i; "even" and "odd" mean only C_i with even and odd numbers of C atoms, respectively, were used. [c] The uncertainties include uncertainties in the experimental D values. [d] From ref 26. [e] No experimental uncertainties were given for individual D values of these solutes.

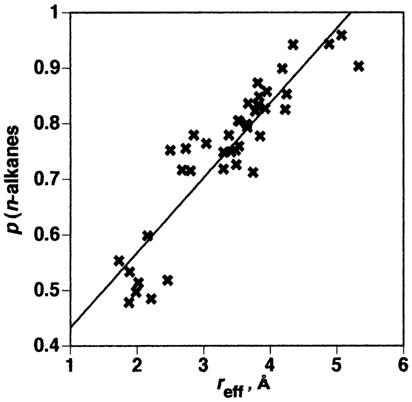

Figure 2. Values of p in the n-alkanes vs r_{eff}. The solutes are listed in the text; the fit line is $p = 0.1347r_{eff} + 0.2983$.

on temperature and viscosity as the SE relation but do not reduce to eq 1 for $V_p \gg V_s$; they are reviewed in refs 39 and 40. Equation 3, which does not appear to have been used previously, was chosen because of its simple dependence on the solvent/solute volume ratio and because it does give eq 1 as $V_s/V_p \rightarrow 0$. It has been applied to data in the n-alkanes at 25 °C in Figures 3 and 4. The stick limit solute r values were calculated from literature D values or from D values obtained using eq 2 for the even C_6 through C_{16} (C_6, C_8, C_{10}, C_{12}, C_{14}, and C_{16}). Figure 3 shows a plot of r vs $1 + V_s/V_p$ for (a) the 41 solutes from Figure 2 in the even C_6 through C_{16}, (b) the self-diffusion of the n-alkanes C_6 through C_{14},[41] and (c) the crown ethers s-trioxane, 12-crown-4, 15-crown-5, 18-crown-6, dicyclohexano-18-crown-6, and dicyclohexano-24-crown-8 in C_{10} and C_{14}.[42] The decrease in r as $1 + V_s/V_p$ increases is obvious; a fit of the 267 data points to eq 3 gave $R_0 = 5.396$ Å and $m = 1.203$.

To isolate the dependence of r on solute size in a given solvent, r was plotted vs $1 + V_s/V_p$ for 57 solutes in C_6 and 45 solutes in C_{16}. The solutes in C_6 included the 41 used for Figure 2, the self-diffusion of C_6,[41] seven n-alkanes (C_5, C_7, C_8, C_{10}, C_{12}, C_{16}, and C_{18}),[43] 2-methylbutane,[44] 2,2-dimethylbutane,[44] 2,2,4-trimethylpentane,[44] tetralin,[44] phenanthrene,[44] toluene,[45] benzo(a)pyrene,[45] and CS_2.[45] The solutes in C_{16} were the 41 used for Figure 2 and four n-alkanes (C_6, C_7, C_8, and C_{12});[43] the C_{16} data is shown in Figure 4. The fits to eq 3 gave $R_0 = 4.752$ Å and $m = 1.109$ for C_6 and $R_0 = 5.783$ Å and $m = 1.281$ for C_{16}. The R_0 values indicate that the SE limit ($V_s/V_p = 0$) is achieved for a smaller solute size in C_6 (4.752 Å) than in C_{16} (5.783 Å); this is reasonable because C_6 is the smaller solvent. The larger value of m in C_{16} (1.281 vs 1.109 for C_6) also indicates larger deviations from SE behavior in the larger solvent.

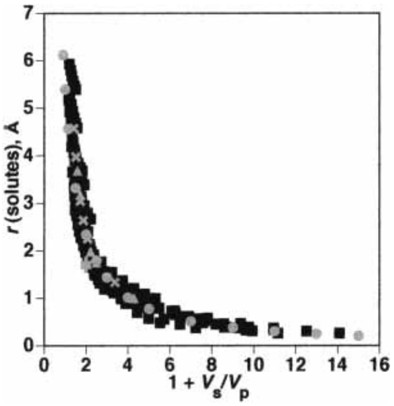

Figure 3. Solute stick limit r values in the n-alkanes vs $1 + V_s/V_p$ at 25 °C. Specific systems (with the gray data points) are the self-diffusion of (+) C6 through C14 and crown ethers in (×) C_{10} and (▲) C_{14}; the other solutes and solvents (■) are listed in the text. The gray circles are from the fit to eq 3.

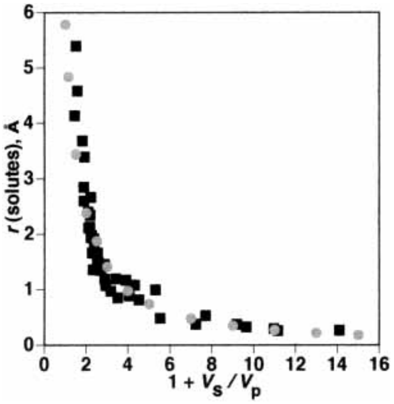

Figure 4. Solute stick limit r values in C_{16} (■) vs $1 + V_s/V_p$ at 25 °C; the solutes are listed in the text. The gray circles are from the fit to eq 3.

Comparison with Other Approaches. Equation 3 has been introduced in the spirit of the Zwanzig−Harrison suggestion[8] that correlations between r and properties of the solution components be sought when deviations from the SE relation are found. It was chosen because of its relative simplicity and because it, like the experimental data, approaches the SE limit as the ratio V_s/V_p decreases. We have tested eq 3 by combining it with eq 2 to give

$$D/T = A_V(1 + V_s/V_p)/\eta^{p(V)} \qquad (5)$$

where $p(V)$ is a fit parameter, R_0 has been incorporated into A_V, and $m = 1$ was assumed to avoid introducing a second fit parameter. A value of $p(V) = 1$ would support the use of eq 1 with the EHR accounting for the deviations previously attributed to p.[8] For the solutes in Table 3, plots of $\log(D/T) - \log(1 + V_s/V_p)$ vs $\log \eta$ were linear; the slopes for all solutes gave values of $p(V)$ that were closer to 1 than the value of p from eq 2. The

TABLE 3: Values of *p* and *f* for Translational and Rotational Motions in the *n*-Alkanes

solute	p^a	$p(V)^b$	$p(\mathrm{rot})^c$	$10^{-16}f$, cm^{-2} ^{d}
p-terphenyl	0.712	0.891	0.817^e	0.199
trans-stilbene	0.726	0.927	0.793^f	0.238
bibenzyl	0.759	0.952		
DDHTP	0.777	0.936		
DPBD	0.793	0.962	0.858^g	0.126
TPHE	0.825	0.968		
DPHT	0.833	0.989		
PCPH	0.836	1.014		
BNP	0.848	1.017	0.668^h	
triptycene	0.873	1.037		
DPA	0.899	1.044	0.902^i	0.205
TPBD	0.942	1.069		
O_2	0.553	0.899		
biphenyl	0.718	0.930	0.635^j	0.554
anthracene	0.749	0.941		
diphenylacetylene	0.752	0.941		
diphenylbutadiyne	0.797	0.974		
pyrene	0.805	0.993		
perylene	0.822	0.989	0.581^k	
coronene	0.858	1.013		
rubrene	0.943	1.043		

[a] From eq 2. [b] From eq 5. [c] From eq 7. [d] From eq 8. [e] In C_6 through C_{16} (even) at 20 °C from ref 10. [f] In C_6 through C_{16} (even) at 25 °C from ref 11. [g] In C_6 and C_{14} at 25 °C from refs 12 and 13. [h] In C_8 through C_{16} (even) at 20 °C from ref 15. [i] In C_{10} through C_{16} (even) at 22 °C from ref 14. [j] In C_6 through C_{16} at 20 °C from ref 10. [k] In C_6, C_7, C_8, C_9, C_{10}, C_{12}, and C_{16} at 27 °C from ref 16.

only solutes with values of $p(V) < 0.927$ (the value for TSB) were O_2 (0.899) and *p*-terphenyl (0.891).

Equation 3 also can be compared with the WCE, probably the most widely used correlation for estimating *D* values in liquid chromatography,[46] which is given by[9,39,40]

$$D_{\mathrm{ps}} = 7.4 \times 10^{-8} T(\phi M_{\mathrm{s}})^{1/2}/(\eta V_{\mathrm{bp}}{}^{0.6}) \qquad (6)$$

where D_{ps} is the diffusion constant of probe p in solvent s, ϕ is the association factor for the solvent (= 1 for the nonassociated *n*-alkanes), and M_{s} is the molecular weight of the solvent (in g mol^{-1}); V_{bp}, the molar volume of the solute at its normal boiling point (in cm^3 mol^{-1}), is usually estimated using the Le Bas group contribution method.[39,40,47]

We have found that the WCE does give reliable estimates for some of the solutes in the *n*-alkanes but deviations are found as well. The data have been divided into two groups based on a visual inspection of the degree of agreement between the experimental *D* values and eq 6 at 25 °C. Figure 5a shows that the experimental and predicted *D* values for the "good" WCE solutes are tightly clustered about the unit-slope line; they are TSB, biphenyl, bibenzyl, perylene, coronene, DPBD, DPHT, TPHE, *p*-terphenyl, PCPH, BNP, DDHTP, benzene, cyclohexane, BZQ, TMBZQ, TCBZQ, CCl_4, $Sn(Me)_4$, $Sn(Et)_4$, $Sn(Pr)_4$, and $Sn(Bu)_4$ in the even-numbered C_6 through C_{16}; also included are the crown ethers in C_{14}. The difference in agreement for the "bad" WCE solutes (Figure 5b) is obvious. This group, which contains some of the larger and smaller solutes, is comprised of O_2, CH_4, ethane, propane, CO_2, iodine, Xe, Kr, Ar, TPPH, TPBD, DPA, rubrene, triptycene, and C_{60} in the even-numbered C_6 through C_{16}; also included are the crown ethers in C_{10} and the self-diffusion of the *n*-alkanes. Li and Carr[46] have discussed other systems for which deviations from the WCE predictions have been found. The regression coefficient for all of the *D* values in panels a and b of Figure 5 is $R^2 = 0.934$.

The same trends follow when eq 3 is tested. We have done this by calculating *r* values using eq 3 (with $R_0 = 5.396$ Å and $m = 1.203$) and comparing them with the values obtained from eq 1 and the experimental *D* values used for the WCE comparison. Figure 6a shows that the agreement between the experimental and calculated *r* values for the "good" WCE solutes is reasonably good, while that for the "bad" WCE solutes in Figure 6b is less satisfactory. The regression coefficient for all of the *r* values in panels a and b of Figure 6 is $R^2 = 0.871$, which is slightly less than R^2 for the WCE correlation.

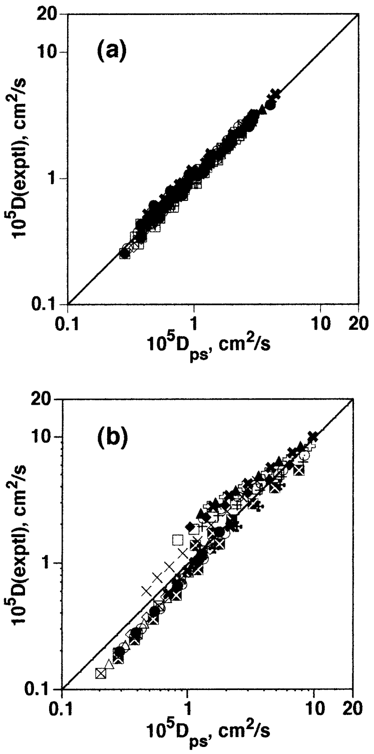

Figure 5. Plots of 10^5D(exptl) vs 10^5D_{ps} from eq 6 in C_6 through C_{16} (even) at 25 °C for (a) the "good" and (b) the "bad" WCE solutes including the *n*-alkanes' self-diffusion (×). The solutes are listed in the text.

Some of the same systems, such as the *n*-alkanes' self-diffusion,[41] present challenges for both approaches. Because $V_{\mathrm{s}} = V_{\mathrm{p}}$, eq 3 predicts their size ($r = R_0/2^m$) to be independent of chain length. As seen in Table 4, the *r* values are essentially constant for C_6 through C_{14}, with an average value of 1.70 ± 0.03 Å. The quantitative agreement with eq 3, which gives $r = 2.29$ Å, is less satisfactory; these data are near the bottom of the band of data points in Figure 3 and below the unit slope line in Figure 6. The *n*-alkanes also were noted to be "bad" WCE solutes; eq 6 predicts *D* values 20% lower than the experimental values (Table 4 and Figure 5). Additionally, the solutes and *n*-alkane solvents that we have considered are generally nonpolar; it would be interesting to see whether changes in eq 3 are needed to accommodate data for polar solutes and solvents. We note, however, that the crown ethers, solutes of which the heterocyclic structures are different from those of the other solutes, are in the middle of the band of solutes in Figure 3. The overall correlation between *r* and $1 + V_{\mathrm{s}}/V_{\mathrm{p}}$ in Figure 3 and the values of $p(V) \approx 1$ in Table 3 are considered to justify the use of eq 3 and its further study. Eu and co-workers[48] have proposed a correlation that depends on the masses, as well as the sizes, of the solutes and solvents; our data will be compared with their results in a future publication.

Comparison of Translational and Rotational Motions. Laser spectroscopy has been used to obtain solvent-dependent reorientational correlation times, τ_θ, for biphenyl,[10] *p*-terphenyl,[10]

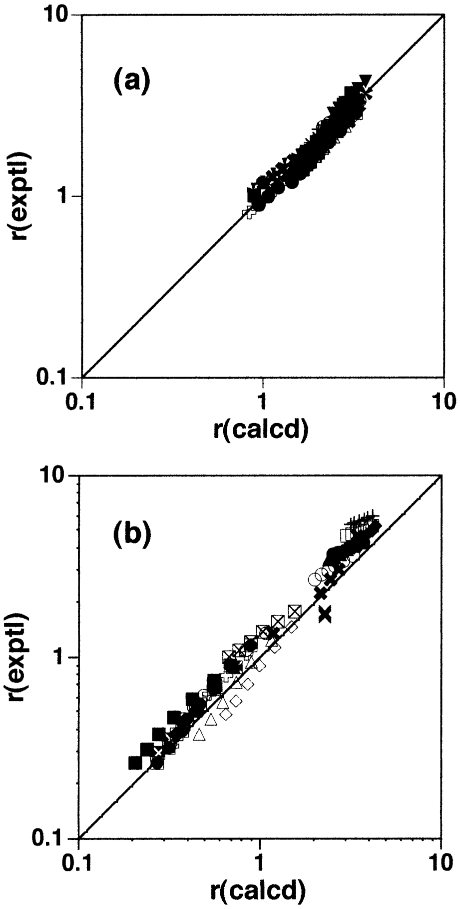

Figure 6. Plots of *r*(exptl) vs *r* calculated from the fit to eq 3 in C_6 through C_{16} (even) at 25 °C for (a) the "good" and (b) the "bad" WCE solutes including the *n*-alkanes' self-diffusion (×). The solutes are listed in the text.

TABLE 4: Stick-Limit *r* Values for Self-Diffusion in C_6 through C_{14} at 25 °C

solvent	10^5D(exptl), $cm^2\ s^{-1}$ [a]	$r(C_i)$, Å [b]	10^5D_{ps}, $cm^2\ s^{-1}$ [c]
C_6	4.44	1.64	3.52
C_7	3.32	1.71	2.71
C_8	2.55	1.69	2.03
C_9	1.96	1.68	1.53
C_{10}	1.48	1.76	1.20
C_{11}	1.17	1.70	0.912
C_{12}	0.93	1.7_0	0.718
C_{13}	0.75	1.6_9	0.572
C_{14}	0.60	1.7_4	0.468

[a] The *D*(exptl) values are from ref 41. [b] Calculated using *D*(exptl) and eq 1. [c] Calculated using eq 6.

TSB,[11] DPBD,[12,13] DPA,[14] BNP,[15] and perylene[16] in the *n*-alkanes. The data show deviations from the SED expression, eq 4; τ_θ for a given probe is not linear in the viscosities of the *n*-alkanes at constant temperature.

Deviations from the SE relation for translational motion are described by *p* in eq 2. The rotational deviations from the SED expression can be taken into account by writing

$$\tau_\theta = A_{\text{rot}}\eta^{p(\text{rot})}/T \qquad (7)$$

We found plots of log τ_θ vs log η to be linear at constant temperature; the slopes gave the values of *p*(rot) in Table 3, all of which are less than unity (the SED limit). A comparison with the translational results shows that, with two exceptions, $\Delta p =$ *p*(rot) − *p* is relatively small ($|\Delta p| = 0.1$ or less). τ_θ has a slightly stronger dependence on η than *D* has, that is, *p*(rot) > *p*, for *p*-terphenyl ($\Delta p = 0.105$), TSB ($\Delta p = 0.067$), and DPBD ($\Delta p = 0.065$). *D* has the stronger dependence on η, that is, *p*(rot) < *p*, for biphenyl ($\Delta p = -0.083$), BNP ($\Delta p = -0.180$), and perylene ($\Delta p = -0.241$); the two *p* values are virtually the same for DPA ($\Delta p = 0.003$).

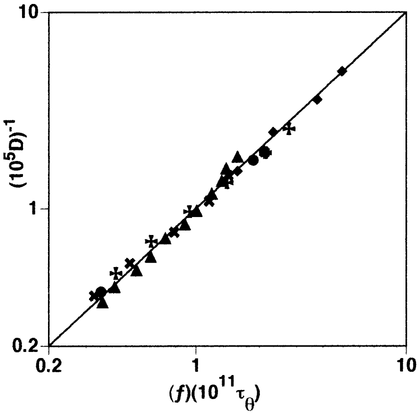

Figure 7. Plot of 1/*D* vs $f\tau_\theta$ in the *n*-alkanes for (×) *trans*-stilbene, (●) DPBD, (◆) DPA, (+) *p*-terphenyl, and (▲) biphenyl.

If $\Delta p = 0$, eqs 2 and 7 give

$$1/D = f\tau_\theta \qquad (8)$$

where $f = (A_{\text{rot}}A_{\text{SE}})^{-1}$ is solute-dependent. Analyses of rotational and translational data gave the values of *f* in Table 3; the *D* values for each solute were calculated (using eq 2) for the constant temperature of each set of rotational data. If eq 8 holds, a plot of 1/*D* vs $f\tau_\theta$ should have unit slope. Figure 7 shows that the data are in reasonable agreement with this prediction for *p*-terphenyl, TSB, DPBD, biphenyl, and DPA; BNP and perylene were not considered because of their large values of $|\Delta p|$. Possible reasons for the differences in the dependence of τ_θ and 1/*D* on η have been discussed in ref 5, in which we also discussed the viscosity dependence of the translational and rotational motions of biphenyl and perylene but did not determine *p*(rot) as we have done here.

To this point, the discussion and comparison of rotational and translational diffusion rates have been made at (or near) constant temperature; the viscosity was varied by varying the solvent. However, varying the temperature for a given solvent also changes the diffusion rate. Kim and Fleming[11] found that the SED equation, written as $\tau_\theta = S(\eta/T)$, holds for TSB in the individual C_i, that is, τ_θ is linear in η/T when the temperature is varied. In addition, *S* (i.e., r^3) decreases for TSB as the solvent chain length increases. A similar decrease in *r* (from *D*) was observed when the chain length increased. Therefore, the solute−solvent interactions may be independent of temperature in a given *n*-alkane, but may vary from one to another.

Summary and Conclusions

The translational diffusion constants of 12 solutes in the *n*-alkanes have been determined using capillary flow techniques. Deviations from the SE relation, eq 1, have been found for all solute−solvent systems; for a given solute, the radius *r* from eq 1 decreases as the *n*-alkane chain length and viscosity increase. The data were fitted to the modified SE relation, eq 2, giving values of *p* < 1, which also indicate deviations from SE behavior. The values of *p* increase as the solute size increases. The deviations from SE behavior for more than 50 solutes were discussed in terms of the van der Waals volumes of the solvents, V_s, and solute probes, V_p, and $r = R_0/(1 + V_s/V_p)^m$, where R_0 is an effective radius and $m \approx 1$ is a fit parameter. The diffusion constants also are discussed in terms of the Wilke−Chang equation, which is reasonably accurate for our intermediate-sized solutes but is less successful for the relatively small and large solutes. The D values for several of the solutes were compared with their rotational correlation times, which showed deviations from the SED expression, eq 4; D^{-1} and τ_θ had the same general dependence on viscosity for five of the seven solutes considered.

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