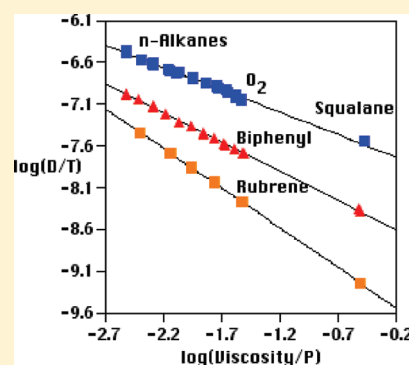


Diffusion of Organic Solutes in Squalane

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ABSTRACT: The translational diffusion constants, D , of 26 hydrocarbons have been determined in squalane (2,6,10,15,19,23-hexamethyltetracosane) at room temperature using capillary flow techniques. These new data and previously published room-temperature D values for the same solutes in some (or all) of the n -alkanes n -C₆– n -C₁₆ constitute a study of solute diffusion in media spanning a 100-fold change in viscosity; at 23 °C, $\eta = 0.31$ cP for n -C₆, 3.2 cP for n -C₁₆, and 30 cP for squalane. The D values in the n -alkanes and squalane show deviations from the Stokes–Einstein relation, $D = k_B T / (6\pi\eta r)$; the values of r , a solute's hydrodynamic radius, decrease as the viscosity increases. The deviations increase as the solute size decreases and are analyzed by fitting the diffusion constants to the modified Stokes–Einstein equation, $D/T = A_{SE}/\eta^p$. Fits involving the n -alkane-only and combined n -alkane-squalane D values give comparable results with values of $p < 1$ that increase as the solute size increases; $p = 1$ for the Stokes–Einstein limit. The deviations from Stokes–Einstein behavior also are discussed in terms of the relative sizes of the solutes, the n -alkanes, and squalane.



1. INTRODUCTION

The translational diffusion constants, D , of several types of nonpolar solutes in the n -alkanes have been shown to depend on the relative sizes of the solution components and the interactions between them.^{1–8} The solutes included alkenes, aromatic hydrocarbons, and O₂; their D values were determined in some or all of the n -alkanes n -C₆– n -C₁₆ using capillary flow techniques;^{1,2} the initial analyses used the Stokes–Einstein relation^{9,10}

$$D = k_B T / (f_t \pi \eta r) \quad (1)$$

where η is the viscosity, T is the absolute temperature, k_B is Boltzmann's constant, r is the solute's hydrodynamic radius, and $f_t = 6$ and 4 for the stick and slip limits, respectively. We found that the stick limit r values for a given solute decreased as the n -alkane chain length and viscosity increased;^{1–7} a common r value would be expected if eq 1 holds. These deviations from Stokes–Einstein behavior are a consequence of the solutes having sizes comparable to or smaller than those of the solvents; eq 1 is valid only if the solute is much larger than the solvent.¹⁰

The D values were then fitted to the modified Stokes–Einstein equation^{11–13}

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

where p and A_{SE} are constants for a given solute; $p = 1$ for the Stokes–Einstein limit. The values of $p(n-C_i)$ and $\log A_{SE}(n-C_i)$ for the solutes in the n -alkanes are given in Table 1. The values of $p(n-C_i)$ are <1 and increase as the solute size increases;^{1–7} they are consistent with molecular dynamics simulations that showed the gauche–trans isomerization rates were essentially independent of chain length for n -C₈, n -C₁₂, n -C₁₆, and n -C₂₀.¹⁴ Solute, particularly the smaller ones, should experience similar interactions with the shorter and longer chains, making their translational motion less dependent on the bulk viscosity.¹⁴

The diffusion rate in the n -alkanes was varied by changing the solvent because our experiments were limited to room temperature. Representative viscosities¹⁵ ranged from 0.309 cP for n -C₆ at 22.0 °C¹ to 3.00 cP for n -C₁₆ at 25.5 °C¹ (1 cP = 1 mPa s); longer, more viscous n -alkanes could not be used because of their higher freezing points.¹⁶ It was possible, however, to determine the D value for O₂ in squalane² (2,6,10,15,19,23-hexamethyltetracosane, Figure 1), a room temperature liquid with a 24-carbon backbone and six symmetrically placed methyl groups. Our squalane result at 21.0 °C² ($\eta = 33.3$ cP¹⁷) gave O₂ data spanning a ≈ 100 -fold change in viscosity.

We now have used capillary flow techniques to measure the diffusion constants in squalane for the 26 hydrocarbons listed in the Experimental Methods section. The method used to determine the D values was checked by studying six of the solutes in n -C₁₆; agreement with our earlier results was found. The D values in squalane are used to test and extend the n -alkane fits to eq 2; they also may be useful in other areas. There is interest in molecular dynamics simulations of diffusion in alkanes with 20 or more carbon atoms;^{18,19} results such as ours can be used to check and calibrate the computer codes' force fields. Diffusion constants for polynuclear aromatic hydrocarbons are input parameters for simulations of aquatic oil weathering;²⁰ several of our solutes (biphenyl, pyrene, and chrysene) have been found in unweathered petroleum samples.²¹ The D values of neutral hydrocarbon solutes in viscous (and nonviscous) alkanes have been used to determine the mobilities of the solutes' anions and cations;²² the differences in the mobilities of the oppositely charged ions have been explained in terms of differences in their solvation shells. With its six methyl groups, squalane might be viewed as an idealized oligomer of hyperbranched polyethylene.^{23,24} The

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Table 1. Values of p and A_{SE} Obtained from Fits to eq 2^a

solute	$p(n-C_i)$	$p(\text{all})$	$-\log A_{SE}(n-C_i)$	$-\log A_{SE}(\text{all})$	$D(\text{expt})/D(n-C_i)^b$
O ₂ ^c	0.553 ± 0.009	0.537 ± 0.012	7.878 ± 0.018	7.844 ± 0.026	1.15
biphenyl ^d	0.718 ± 0.004	0.701 ± 0.013	8.782 ± 0.008	8.749 ± 0.026	1.09
diphenylacetylene ^d	0.752 ± 0.011	0.730 ± 0.017	8.929 ± 0.021	8.883 ± 0.033	1.10
diphenylbutadiene ^d	0.797 ± 0.009	0.773 ± 0.016	9.085 ± 0.020	9.038 ± 0.033	1.10
pyrene ^d	0.805 ± 0.006	0.787 ± 0.013	9.060 ± 0.012	9.022 ± 0.026	1.11
perylene ^d	0.822 ± 0.007	0.803 ± 0.014	9.162 ± 0.013	9.122 ± 0.028	1.10
coronene ^d	0.858 ± 0.009	0.851 ± 0.019	9.300 ± 0.018	9.284 ± 0.040	1.04
rubrene ^d	0.943 ± 0.014	0.953 ± 0.020	9.710 ± 0.030	9.731 ± 0.040	0.95
C ₆₀ ^e	0.903 ± 0.006	0.924 ± 0.010	9.604 ± 0.012	9.649 ± 0.020	0.85
<i>trans</i> -stilbene ^f	0.726 ± 0.003	0.713 ± 0.016	8.862 ± 0.064	8.835 ± 0.034	1.06
diphenylbutadiene ^f	0.793 ± 0.022	0.750 ± 0.017	9.053 ± 0.047	8.963 ± 0.034	1.20
tetraphenylbutadiene ^f	0.942 ± 0.031	0.908 ± 0.018	9.612 ± 0.064	9.541 ± 0.035	1.15
diphenylhexatriene ^f	0.833 ± 0.018	0.790 ± 0.017	9.169 ± 0.037	9.080 ± 0.034	1.19
tetraphenylethylene ^f	0.825 ± 0.020	0.854 ± 0.016	9.324 ± 0.042	9.385 ± 0.032	0.88
diphenylanthracene ^f	0.899 ± 0.019	0.893 ± 0.014	9.510 ± 0.035	9.498 ± 0.027	1.03
<i>p</i> -terphenyl ^f	0.712 ± 0.033	0.705 ± 0.019	8.915 ± 0.065	8.899 ± 0.040	1.04
<i>p</i> -cyclophane ^f	0.836 ± 0.013	0.836 ± 0.018	9.176 ± 0.025	9.176 ± 0.034	1.00
tritycene ^f	0.873 ± 0.021	0.861 ± 0.017	9.368 ± 0.041	9.345 ± 0.034	1.08
DDHTP ^g	0.777 ± 0.029	0.836 ± 0.023	9.124 ± 0.058	9.250 ± 0.046	0.77
bibenzyl ^f	0.759 ± 0.015	0.712 ± 0.015	8.955 ± 0.015	8.857 ± 0.030	1.25
C ₆ H ₆ /C ₆ D ₆ ^f	0.716 ± 0.001	0.680 ± 0.009	8.614 ± 0.002	8.534 ± 0.022	1.19
toluene ^h	0.727 ± 0.011	0.689 ± 0.015	8.685 ± 0.025	8.598 ± 0.034	1.19
1-hexene ⁱ	0.637 ± 0.027	0.656 ± 0.017	8.503 ± 0.052	8.542 ± 0.034	0.93
1-tetradecene ⁱ	0.725 ± 0.017	0.679 ± 0.014	8.935 ± 0.035	8.839 ± 0.029	1.20
cyclohexene ⁱ	0.786 ± 0.015	0.743 ± 0.018	8.845 ± 0.030	8.760 ± 0.036	1.18
tetracene ^j	0.804 ± 0.022	0.753 ± 0.018	9.077 ± 0.046	8.975 ± 0.036	1.21
chrysene ^j	0.790 ± 0.009	0.767 ± 0.020	9.050 ± 0.018	9.002 ± 0.041	1.12

^a The values of $p(n-C_i)$ and $\log A_{SE}(n-C_i)$ are from the refs in footnotes c–f and h–j and refer to the fits involving only the n -alkane data; $p(\text{all})$ and $\log A_{SE}(\text{all})$ are from fits involving the combined n -alkane-squalane data. The fit parameters were obtained using the D values in cm² s^{−1} and η in P. ^b The average of the values of $D(\text{expt})/D(n-C_i)$ given in Tables 2 and 3. ^c From ref 2. ^d From ref 3. ^e From ref 4. ^f From ref 5. ^g Dodecahydrotriphenylene; the uncertainty reported for $p(n-C_i)$ in ref 5, ±0.003, is incorrect; the correct value is given here. ^h The fit parameters were obtained using the D values in the $n-C_i$ from refs 33 and 37 ($i = 6, 7, 8, 10, 12$, and 14). ⁱ From ref 6. ^j From ref 7.

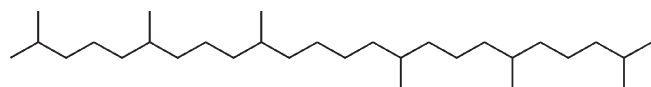


Figure 1. Structure of squalane.

results presented here could provide baseline information pertaining to plasticizer (solute) diffusion in this type of polymer.

2. EXPERIMENTAL METHODS

2.1. Chemicals and Sample Preparation. Squalane (99%) and $n-C_{16}$ (99%) were obtained from Aldrich as were the solutes biphenyl (99%), *trans*-stilbene (96%), *p*-terphenyl (99.5+%), diphenylacetylene (98%), 1,4-diphenylbutadiene (99%), triptycene (98%), coronene (99%), pyrene (98%), perylene (99+%), 1,4-diphenyl-1,3-butadiene (98%), 1,1,4,4-tetraphenyl-1,3-butadiene (99+%), 1,6-diphenyl-1,3,5-hexatriene (98%), tetraphenylethylene (98%), tetracene (98%), chrysene (98%), rubrene (98%), 9,10-diphenylanthracene (97%), C₆₀ (99.5%), 1-hexene (97%), cyclohexene (99+%), C₆D₆ (99.6% D), toluene (99.8%), bibenzyl (99%), and dodecahydrotriphenylene (99%); 1-tetradecene (99+) and *p*-cyclophane (99%) were purchased from

Lancaster and Sigma, respectively. All substances were used as received. Solutions were prepared by adding 0.2–0.3 mg of the solid solutes (Table 2) and 0.050 mL of the liquid solutes (Table 3) to 8.0 mL of solvent.

2.2. Profile Acquisition and Analysis. The elution profiles used to determine the D values in squalane were obtained by first drawing the solvent through a fused silica microcapillary (Polymicro Technology, 76.5 μm i.d.) for several hours via reduced pressure. We then broke the pressure, transferred the capillary to a solution with solute concentration C_0 , reset the pressure, and started the data acquisition. The sigmoidal profiles (Figures 2 and 3) were collected using Chrom Perfect software (Justice Innovations) and a Thermo Separation Products SC100 variable wavelength detector; the solute wavelengths (or references for them) are given in Tables 2 and 3.

An initial estimate of D for a given solute, $D(n-C_i)$, was obtained using the solute's values of $p(n-C_i)$ and $A_{SE}(n-C_i)$,^{2–7,25–29} η for the temperature of interest,¹⁷ and eq 2. A profile calculated using $D(n-C_i)$ and^{30,31}

$$C(t)/C_0 = (1/2)(1 - \text{erf}\{x_1/[2(kt)^{1/2}]\}) \quad (3)$$

$$x_1 = x - Ut \quad (4)$$

$$k = a^2 U^2 / 48D \quad (5)$$

was compared with experiment and adjustments were made to attain agreement. In eqs 3–5, the relative profile intensity ratio, $C(t)/C_0$, increases from 0 to 1 as the solution moves past the detector; t is the time, U is the solution's flow speed through the capillary, a is the

Table 2. Diffusion Constants of O₂ and Solid Solutes in Squalane

solute ^a	<i>T</i> , °C	10 ⁷ <i>D</i> (expt), cm ² s ^{−1}	<i>r</i> , Å ^b	<i>D</i> (expt)/ <i>D</i> (<i>n</i> -C ₁₆) ^c
O ₂ ^d	21.0	82.3	0.0786	1.15 ± 0.11
biphenyl	23.25	13.0	0.557	1.12 ± 0.10
biphenyl	22.75	12.1	0.583	1.06 ± 0.10
<i>trans</i> -stilbene	24.25	10.7	0.713	1.06 ± 0.19
diphenylacetylene	24.0	9.80	0.769	1.10 ± 0.11
<i>p</i> -terphenyl	23.5	8.95	0.821	1.04 ± 0.19 _s
diphenylbutadiene	23.5	8.28	0.887	1.20 ± 0.15
tetracene	23.5	8.01	0.917	1.21 ± 0.15
pyrene	24.0	7.79	0.968	1.11 ± 0.10
chrysene	24.0	7.91	0.952	1.12 ± 0.11
diphenylbutadiyne	24.0	7.23	1.04	1.10 ± 0.11
diphenylhexatriene	23.5	6.63	1.11	1.19 ± 0.14
coronene	23.0	4.30	1.67	1.04 ± 0.11
tritycene	24.5	4.16	1.86	1.08 ± 0.14
tetraphenylethylene	23.0	3.31	2.16	0.88 ± 0.14 _s
tetraphenylethylene	23.25	3.31	2.19	0.87 ± 0.14 _s
diphenylanthracene	23.0	2.75	2.61	1.03 ± 0.13
tetraphenylbutadiene	23.0	2.57	2.79	1.15 ± 0.19
C ₆₀	24.5	1.97	3.92	0.85 ± 0.10
<i>p</i> -cyclophane	24.5	5.72	1.35	1.00 ± 0.12
DDHTP ^e	21.5	4.06	1.63	0.77 ± 0.18
bibenzyl	21.0	9.43	0.686	1.25 ± 0.11
bibenzyl	20.25	9.13	0.679	1.25 ± 0.11
perylene	22.75	5.93	1.19	1.10 ± 0.10 _s
rubrene	22.75	1.67	4.22	0.95 ± 0.12

^a The detection wavelengths are given in refs 2–5 and 7. ^b Calculated using eq 1 and the stick limit. ^c The values of $D(n-C_{16})$ were calculated from eq 2 using $p(n-C_{16})$ and $\log A_{SE}(n-C_{16})$ from Table 1. ^d From ref 2. ^e Dodecahydrotriphenylene.

Table 3. Liquid Solute Diffusion Constants in Squalane

solute ^a	<i>T</i> , °C	[solute], mM	10 ⁷ <i>D</i> (expt), cm ² s ^{−1}	<i>r</i> , Å ^b	<i>D</i> (expt)/ <i>D</i> (<i>n</i> -C ₁₆) ^c
C ₆ D ₆	23.0	70.6	20.1	0.358	1.18 ± 0.10
C ₆ D ₆	22.25	8.31	19.6	0.352	1.19 ± 0.10
C ₆ D ₆	22.25	4.41	19.9	0.346	1.21 ± 0.10
cyclohexene	22.25	12.3 ^d	12.4	0.556	1.18 ± 0.12
cyclohexene	22.5	6.17 ^d	12.4	0.564	1.17 ± 0.12
1-tetradecene	22.25	24.7	9.85	0.699	1.24 ± 0.13
1-tetradecene	24.0	24.7	10.3	0.733	1.21 ± 0.13
1-tetradecene	23.25	6.18	9.48	0.763	1.15 ± 0.13
1-hexene	23.0	50.4	18.5	0.389	0.93 ± 0.17
toluene	23.0	58.7	16.8	0.427	1.15 ± 0.12
toluene	22.75	58.7	17.8	0.397	1.23 ± 0.12
squalane	23.0	self-diffusion	3.00 ^e	2.39	

^a The detection wavelengths for 1-hexene, 1-tetradecene, and cyclohexene are given in ref 6; the others are 198 nm for C₆D₆ and 260 nm for toluene. ^b Calculated using eq 1 and the stick limit. ^c The values of $D(n-C_{16})$ were calculated from eq 2 using $p(n-C_{16})$ and $\log A_{SE}(n-C_{16})$ from Table 1. ^d The original solution for cyclohexene (61.7 mM) gave asymmetric profile shapes; the profiles for the diluted solutions listed here had acceptable shapes. ^e Calculated from a fit to the self-diffusion data given in ref 42.

capillary radius, and x is the distance between the capillary tip and the detector.

Figure 2a compares an experimental profile for cyclohexene in squalane with one calculated using $D(n-C_{16}) = 1.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Differences are seen near the onsets and plateaus of the profiles; agreement is obtained (Figure 2b) for a value of $D(\text{expt}) = 1.17D(n-C_{16})$. In Figure 3a, the value of $D(n-C_{16}) = 2.32 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for C₆₀ in squalane does not produce agreement with experiment; $D(\text{expt}) = 0.85D(n-C_{16})$ is needed (Figure 3b). The values of $D(\text{expt})$ and $D(\text{expt})/D(n-C_{16})$ for the solid solutes and O₂ are given in Table 2; the results for the liquid solutes are shown in Table 3. The uncertainties in $D(\text{expt})/D(n-C_{16})$ are one standard deviation ($\pm\sigma$) and include the $\pm 10\%$ uncertainties in $D(\text{expt})$ and the uncertainties in $D(n-C_{16})$ due to the uncertainties in $p(n-C_{16})$ and $\log A_{SE}(n-C_{16})$.

A different method of data acquisition gave Gaussian-shaped profiles in $n-C_6-n-C_{16}$.^{1–7} For those experiments, the pure solvent was drawn through the capillary by reduced pressure, the pressure was broken, and the capillary was dipped in a solute-containing solution. We then returned the capillary to the pure solvent, reset the reduced pressure, and started the data acquisition. The profiles' retention times and widths were used to determine the D values; see refs 1 and 2 for more details and ref 4 for representative profiles. This procedure was not used for squalane because its relatively high viscosity led to broad profile widths and weak profile intensities.

To check the consistency of the two profile acquisition methods, we used the one employed for squalane to determine $D(\text{expt})$ for several of the solutes in $n-C_{16}$; the values of $D(n-C_{16})$ were calculated using $p(n-C_{16})$, $A_{SE}(n-C_{16})$, and the viscosity of $n-C_{16}$.¹⁵ As seen in Table 4, the agreement with the predictions of eq 2 is good ($1.05 \geq D(\text{expt})/D(n-C_{16}) \geq 0.96$) and corroborates the results obtained in squalane; a similar check was made for O₂ in $n-C_{15}$.² Figure 4 shows the agreement between an experimental profile for pyrene in $n-C_{16}$ and one calculated using $D(\text{expt}) = 4.42 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} = 1.04D(n-C_{16})$.

2.3. Experimental Results and Comparisons. We are aware of one result with which our D values in squalane can be compared. Temperature-dependent data for pyrene³² ($-5 \leq T \leq 40^\circ \text{C}$) can be fitted to $\log D = -1645/T - 0.6627$ and give $10^7 D = 6.34 \text{ cm}^2 \text{ s}^{-1}$ at 24.0°C ; our value is 23% larger (Table 5).

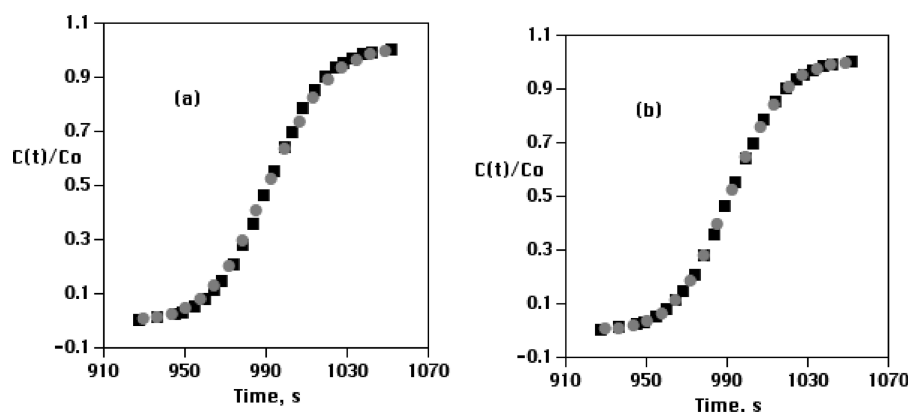


Figure 2. Experimental (squares) and calculated (circles) profiles for cyclohexene in squalane at 22.5 °C. The D values for the calculated profiles in (a) and (b) are $D(n-C_i) = 1.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D(\text{expt}) = 1.24 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.

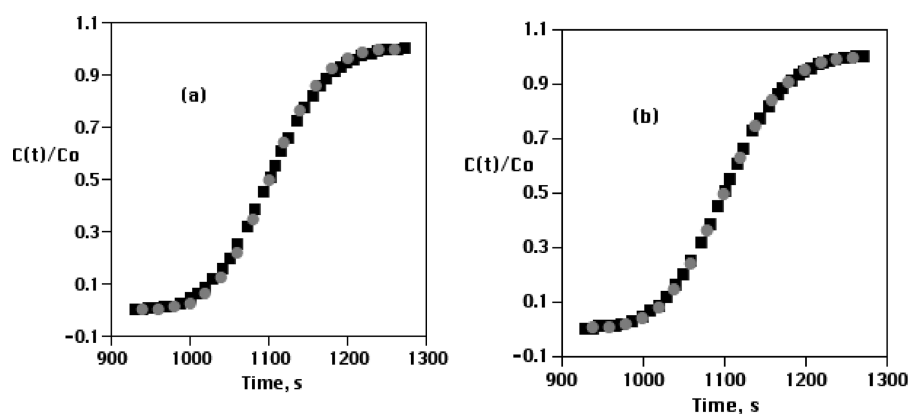


Figure 3. Experimental (squares) and calculated (circles) profiles for C_{60} in squalane at 24.5 °C. The D values for the calculated profiles in (a) and (b) are $D(n-C_i) = 2.32 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $D(\text{expt}) = 1.97 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively.

Table 4. Solute Diffusion Constants in $n\text{-C}_{16}$

solute ^a	$T, ^\circ\text{C}$	$10^6 D(\text{expt}), \text{cm}^2 \text{ s}^{-1}$	$r, \text{\AA}^b$	$D(\text{expt})/D(n-C_i)^c$
C_6D_6	23.0	8.38	0.819	0.98 ± 0.10
C_6D_6	22.5	8.89	0.762	1.05 ± 0.10
biphenyl	24.0	5.96	1.18	1.00 ± 0.10
<i>p</i> -terphenyl	22.25	3.99	1.69	0.96 ± 0.23
pyrene	24.0	4.42	1.59	1.04 ± 0.11
<i>p</i> -cyclophane	22.0	3.58	1.87	$1.03 \pm 0.12_5$
diphenylanthracene	22.25	2.09	3.22	1.04 ± 0.15
diphenylanthracene	22.75	2.03	3.36	1.00 ± 0.15
O_2^d	23.0	2.99	0.297	1.02 ± 0.11

^a The detection wavelengths are the same as those used in squalane.

^b Calculated using eq 1 and the stick limit. ^c The values of $D(n-C_i)$ were calculated using eq 2 and $p(n-C_i)$ and $\log A_{SE}(n-C_i)$ from Table 1.

^d From ref 2 in $n\text{-C}_{15}$.

Reference 32 also reported D values for pyrene in several n -alkanes at 20 °C. As seen in Table 5, our values calculated using $p(n-C_i)$, $A_{SE}(n-C_i)$, and eq 2 are again 20–45% larger but are in agreement with those from several other sources.^{33–35} This agreement leads us to favor our result for pyrene in squalane. Also lending support is the D value determined for pyrene in

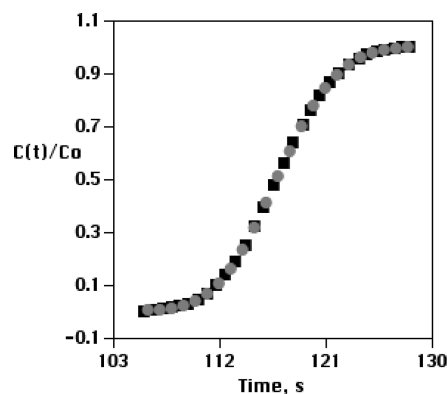


Figure 4. Experimental (squares) and calculated (circles) profiles for pyrene in $n\text{-C}_{16}$ at 24.0 °C. For the calculated profile, $D(\text{expt}) = 4.42 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} = 1.04D(n-C_i)$.

$n\text{-C}_{16}$ (Figure 4 and Table 4); it was obtained using the method employed for squalane and agrees with our earlier work.³ Additional examples of agreement between our D values in the n -alkanes and literature values are given in ref 36.³⁷ In the next section, fits of the combined n -alkane-squalane data to eq 2 are discussed; they do not affect the conclusions reached here. The D values calculated for pyrene in the n -alkanes using the combined

Table 5. Comparison of Diffusion Constants for Pyrene in *n*-Alkanes and Squalane

solvent	<i>T</i> , °C	$10^5 D$, cm ² s ⁻¹		$D(\text{ours})/D(\text{lit})$	ref
		$D(\text{ours})^a$	$D(\text{lit})^b$		
<i>n</i> -C ₇	20.0	2.14	1.48	1.45	32
<i>n</i> -C ₈	20.0	1.71	1.18	1.45	32
<i>n</i> -C ₁₀	20.0	1.12	0.87	1.29	32
<i>n</i> -C ₁₂	20.0	0.743	0.62	1.20	32
<i>n</i> -C ₁₆	20.0	0.389	0.31	1.25	32
squalane	24.0	0.0779	0.0634	1.23	32
<i>n</i> -C ₆	25.0	2.80	2.93	0.96	34
<i>n</i> -C ₆	25.0	2.80	2.58	1.08 ₅	33, 35
<i>n</i> -C ₇	25.0	2.28	2.16	1.06	33, 35
<i>n</i> -C ₈	25.0	1.82	1.81	1.01	33, 35
<i>n</i> -C ₁₀	25.0	1.21	1.23	0.98	33, 35

^a The values of $D(\text{ours}) = D(n\text{-}C_i)$ for the *n*-alkanes are calculated from eq 2 using $p(n\text{-}C_i)$ and $\log A_{SE}(n\text{-}C_i)$ from Table 1; for squalane, $D(\text{ours}) = D(\text{expt})$ from Table 2. ^b The values of $D(\text{lit})$ for the *n*-alkanes are from the indicated references; the value for squalane is calculated from a fit to the temperature-dependent data in ref 32.

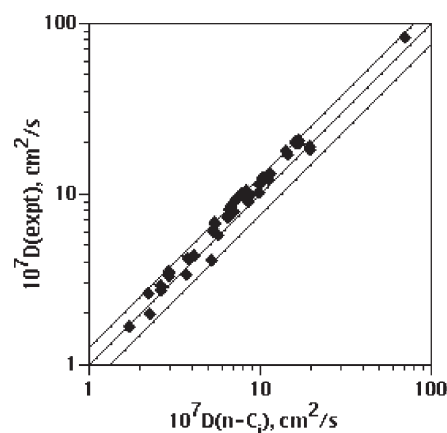
Table 6. Calculated *D* Values for the *n*-Alkane-Only and Combined Fits

solute	solvent	<i>T</i> , °C	$10^5 D$, cm ² s ⁻¹		$D(n\text{-}C_i)/D(\text{all})$
			$D(n\text{-}C_i)^a$	$D(\text{all})^b$	
pyrene ^c	<i>n</i> -C ₇	20.0	2.14	2.12	1.01
pyrene	<i>n</i> -C ₈	20.0	1.71	1.69	1.01
pyrene	<i>n</i> -C ₁₀	20.0	1.12	1.13	0.99
pyrene	<i>n</i> -C ₁₂	20.0	0.743	0.752	0.99
pyrene	<i>n</i> -C ₁₆	20.0	0.389	0.400	0.97
pyrene	squalane	24.0	0.0703 ^d	0.0751 ^d	0.94
toluene	<i>n</i> -C ₇	20.0	3.31	3.28	1.01
toluene	<i>n</i> -C ₈	20.0	2.71	2.71	1.00
toluene	<i>n</i> -C ₁₀	20.0	1.85	1.89	0.98
toluene	<i>n</i> -C ₁₂	20.0	1.27	1.32	0.96
toluene	<i>n</i> -C ₁₆	20.0	0.710	0.762	0.93
toluene	squalane	22.75	0.144 ^e	0.168 ^e	0.86

^a The values of $D(n\text{-}C_i)$ for the *n*-alkanes and squalane are calculated from eq 2 using $p(n\text{-}C_i)$ and $\log A_{SE}(n\text{-}C_i)$ from Table 1. ^b The values of $D(\text{all})$ for the *n*-alkanes and squalane are calculated from eq 2 using $p(\text{all})$ and $\log A_{SE}(\text{all})$ from Table 1. ^c The *n*-alkanes and temperatures used for pyrene are from ref 32. ^d At 24.0 °C, $10^5 D(\text{expt}) = 0.0779$ cm²/s for pyrene in squalane; $D(\text{expt})/D(n\text{-}C_i) = 1.11$, $D(\text{expt})/D(\text{all}) = 1.04$. ^e At 22.75 °C, $10^5 D(\text{expt}) = 0.178$ cm²/s for toluene in squalane; $D(\text{expt})/D(n\text{-}C_i) = 1.24$, $D(\text{expt})/D(\text{all}) = 1.06$.

fit (Table 6) differ from those for the *n*-alkane-only fit by an average of only 1.4%. The *D* values calculated using the two fits for the solutes and solvents in ref 36 differ by an average of only 1.2%.

The *D* values for several of the liquid solutes were determined as a function of dilution (Table 3) because the original samples had values of $D(\text{expt})/D(n\text{-}C_i)$ marginally larger than $1 + \sigma$. This could be indicative of diffusion faster than predicted by eq 2 due to a decrease in the solution viscosity; the liquid solutes do have lower viscosities than squalane. However, no real differences were found; the values of $D(\text{expt})/D(n\text{-}C_i)$ for $[C_6D_6] = 70.6 - 4.41$ mM vary

**Figure 5.** $D(\text{expt})$ vs $D(n\text{-}C_i)$ for solutes in squalane. The unit slope line is shown as are those for $D(\text{expt})/D(n\text{-}C_i) = 1 \pm 0.25$.

by only 3%, those for cyclohexene and 1-tetradecene vary by only 8%, and the *D* values are considered to be those for solutes in an essentially neat solvent (as are those for the solid solutes because of their low concentrations, 0.035–0.24 mM).

3. DISCUSSION

3.1. Modified Stokes–Einstein Analysis. One of our objectives was to use the diffusion constants in squalane to test the *n*-alkane fits to eq 2. Tables 2 and 3 show that 14 of the 26 hydrocarbon solutes have average values of $D(\text{expt})/D(n\text{-}C_i)$ within $1 \pm \sigma$, several others are barely outside this range, and only bibenzyl, with $D(\text{expt})/D(n\text{-}C_i) = 1.25$, is beyond $1 \pm 2\sigma$. Figure 5 shows a plot of $D(\text{expt})$ versus $D(n\text{-}C_i)$. All 26 of the solutes have average values of $D(\text{expt})$ within $\pm 25\%$ of $D(n\text{-}C_i)$, 23 are within $\pm 20\%$, 17 are within $\pm 15\%$, and 12 are within $\pm 10\%$; O₂ has $D(\text{expt})/D(n\text{-}C_i) = 1.15 \pm 0.11$.

We also were interested in the possibility of estimating *D* values in solvents more viscous than squalane. Squalane extended the viscosity range of our *n*-alkane studies an order of magnitude beyond that of *n*-C₁₆ and if uncertainties of ± 20 – 25% were acceptable, it would seem that fits based on the combined *n*-alkane-squalane data might be employed for solvents an order of magnitude more viscous than squalane. The work of Hiss and Cussler³⁸ supports this conjecture. They determined the diffusion constants for naphthalene at 25 °C over a range of viscosities much wider than ours and found good agreement with eq 2; the solvents were 2,2,4-trimethylpentane ($\eta = 0.484$ cP) and a series of hydrocarbon oils with $3.093 \leq \eta \leq 5137$ cP. The *D* values gave³⁸ $p = 0.688 \pm 0.007$, $-\log A_{SE} = 8.733 \pm 0.010$, and a linear correlation coefficient³⁹ $R = 0.999$.

Consequently, the *D* values for our solutes in squalane and the *n*-alkanes have been fitted to eq 2. Figure 6 shows plots of $\log(D/T)$ versus $\log \eta$ (in P) for the combined data of cyclohexene, pyrene, and C₆₀. The fits are reasonably good; all have values of $R > 0.999$. The combined fits for the other solutes are good as well; with the exception of bibenzyl (0.998) and O₂ (0.997), they too have $R \geq 0.999$. The values of $p(\text{all})$ and $\log A_{SE}(\text{all})$ for the combined fits are given in Table 1. The fits to the *n*-alkane-only data have essentially the same values of *R* as those for the combined fits; only those for toluene (0.998), triptycene (0.998), *p*-terphenyl (0.998), and O₂ (0.997) are < 0.999 .

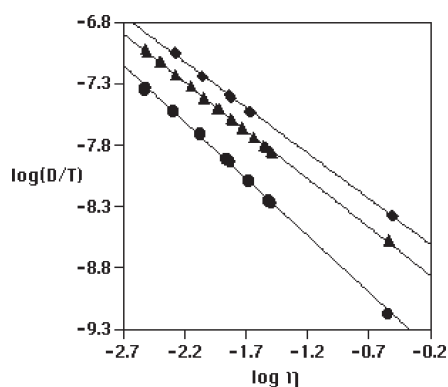


Figure 6. Fits of the diffusion constants in the *n*-alkanes and squalane for cyclohexene (diamonds, $R = 0.999$), pyrene (triangles, 0.999), and C_{60} (circles, 0.999) to $D/T = A_{SE}/\eta^p$ with D in $\text{cm}^2 \text{s}^{-1}$ and η in P.

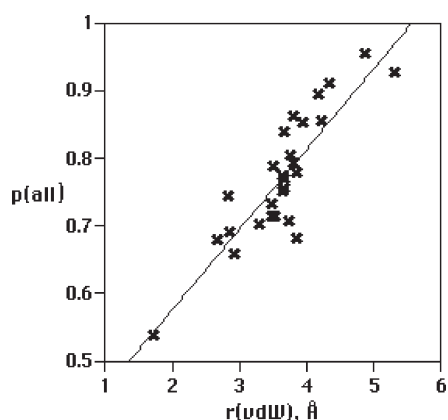


Figure 7. Values of $p(\text{all})$ for the fits to eq 2 for the combined *n*-alkane–squalane D values vs $r(\text{vdW})$.

There is general agreement between the values of p and $\log A_{SE}$ for the two fits, but as seen in Table 1, there are differences that increase as the values of $|D(\text{expt})/D(n-C_i) - 1|$ increase. The differences between the D values predicted by the two sets of fit parameters have the same dependence on $D(\text{expt})/D(n-C_i)$. For example, toluene and pyrene have values of $D(\text{expt})/D(n-C_i) = 1.19$ and 1.11, respectively; as shown in Table 6, the differences in the *n*-alkanes are larger for toluene than for pyrene (an average of 2.8% and 1.4%, respectively). The combined fits give calculated D values for toluene and pyrene in squalane within 6% and 4% of the experimental values, respectively.

3.2. Values of r and p . The values of $p(n-C_i) < 1$ were a consequence of a given solute's r values decreasing with increasing *n*-alkane chain length and viscosity.^{1–7} The similar values of $p(n-C_i)$ and $p(\text{all})$ are the result of the r values in squalane following that trend; they are smaller than the values in *n*- C_{16} (compare Table 4 with Tables 2 and 3) and for several solutes are smaller than 1.70 Å, the van der Waals radius of a carbon atom.⁴⁰

The solutes' interactions with the *n*-alkanes' isomerizations, mentioned above as a possible explanation for the values of $p(n-C_i) < 1$, are facilitated by the solvents' relatively extended conformations. Medium length alkanes (8–20 carbons) tend to be more rodlike than spherical;⁴¹ for example, a simulated rms end-to-end distance^{14,41} of 14.5 Å indicated such was the case for *n*- C_{16} . Figure 4 of ref 42 shows that squalane also has a

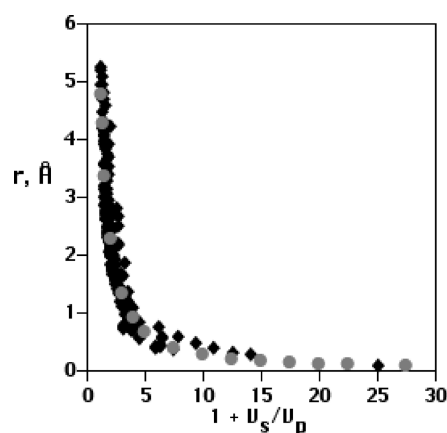


Figure 8. Solute stick limit r values in the *n*-alkanes and squalane (diamonds) vs $1 + V_s/V_p$. The circles are from a fit of the r values to eq 6.

fair degree of extension; its time-averaged end-to-end distance is 19.06 Å.

As seen in Figure 7, the values of $p(\text{all})$ show a general increase as the van der Waals radii of the solutes increase; the radii, $r(\text{vdW})$, are calculated using $r(\text{vdW}) = (3V_p/4\pi)^{1/3}$, where V_p , the van der Waals volume of a solute probe, is determined from the Bondi–Edward increments.^{40,43} There is scatter, but the correlation is apparent and comparable to that in the plot of $p(n-C_i)$ versus $r(\text{vdW})$ in Figure 2 of ref 5.

3.3. Volume-Dependent Analysis. The deviations from Stokes–Einstein behavior, i.e., the solvent-dependent values of r for a given solute, also can be discussed using^{5–7}

$$r = R_0 / (1 + V_s/V_p)^m \quad (6)$$

where R_0 is an effective radius, $m \approx 1$ is a fit parameter, and V_s is the van der Waals volume of a solvent molecule (also estimated using the Bondi–Edward increments^{40,43}). Equation 6 follows from the work of Zwanzig and Harrison,⁴⁴ who argued that the viscosity dependence of D should be given by eq 1 and characterized r as an effective hydrodynamic radius that measures the coupling of the solute motion to the solvent flow; it was suggested that the deviations from eq 1 be explained in terms of properties of the solution components. Equation 6 predicts, as we have found, that r for a given solute decreases as V_s increases; it also approaches the Stokes–Einstein limit; i.e., r is independent of V_s , when $V_p \gg V_s$. The conditions under which the Stokes–Einstein relation holds (and the corresponding values of r) have been the focus of kinetic theory and molecular dynamics calculations carried out by a number of authors. The strength of the solute–solvent interaction potential as well as the sizes and masses of the solute and solvent have been varied; representative results (and references to other studies) are given in ref 45.

Figure 8 shows a plot (versus $1 + V_s/V_p$) of the stick limit r values for the solutes in squalane and the even *n*- C_i with $i = 6–16$; the latter were obtained from D values calculated using eq 2 and the *n*-alkane-only fits at 25 °C. Also included is the stick limit r value calculated from the self-diffusion constant of squalane (Table 3),⁴² which has $V_s/V_p = 1$. The fit of the data to eq 6 is reasonably good, giving $R_0 = 5.735$ Å and $m = 1.334$. Squalane's value of $V_s = 521.4$ Å³ extended the range over which eq 6 could be studied; in the *n*-alkanes, 113.4 Å³ ($n-C_6$) $\leq V_s \leq 283.4$ Å³ ($n-C_{16}$).

4. SUMMARY AND CONCLUSIONS

Capillary flow techniques have been used to measure the translational diffusion constants for 26 solutes in squalane, a C₃₀ alkane with a room temperature viscosity approximately 10 times that of *n*-C₁₆ and 100 times that of *n*-C₆. In previous work, we determined the *D* values for the solutes in some (or all) of the *n*-alkanes *n*-C₆–*n*-C₁₆. Fits of the diffusion constants in the *n*-alkanes to eq 2, a modification of the Stokes–Einstein relation, were used to predict the solutes' *D* values in squalane; 12 were within $\pm 10\%$ of the predicted value, 23 were within $\pm 20\%$, and all 26 were within $\pm 25\%$. It is suggested that if uncertainties of ± 20 – 25% are acceptable, fits of the combined *n*-alkane–squalane data to the modified Stokes–Einstein relation might be used for even more viscous solutions. Equation 2 was used because the viscosity dependence of the *D* values in the *n*-alkanes and squalane is weaker than predicted by the Stokes–Einstein relation. These deviations are found because the solutes are the same size or smaller than the solvents and are discussed in terms of the van der Waals volumes of the solutes and solvents.

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