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Diffusion of Buckminsterfullerene in *n*-Alkanes

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The translational diffusion constant, *D*, of C_{60} has been determined in the even *n*-alkanes n-C_6H_{14} to n-$C_{16}H_{34}$ using microcapillary techniques and Taylor-Aris dispersion theory. Experiments were conducted over extended periods of time to ensure that the solute was not associated with itself or with solvent. The *D* values show deviations from the Stokes−Einstein (SE) relation ($D = kT/6\pi\eta r$); the values of the solute's hydrodynamic radius *r* decrease as the solvent viscosity η increases. The data can be fitted to $D/T = A_{SE}/\eta^p$ with $p = 0.903 \pm 0.006$ ($p = 1$ for the SE relation).

Introduction

There has been considerable interest in the liquid-phase chemistry and physics of C_{60} because of its near-spherical shape (Figure 1) and primal position in the fullerene hierarchy. C_{60} is a large target, offering thirty electron-rich double bonds across [6−6]-ring junctions as potential sites for chemical reactions.[1,2] Its photophysical properties (as well as those of other fullerenes)[2] have been studied because of potential applications as acceptors in electron and energy transfer reactions. The relative importance of diffusion, size, and electronic structure is integral to the understanding of these and related processes in solution. This paper focuses on *D*, the translational diffusion constant[3,4] of C_{60}.

It would be desirable to study C_{60} in a series of homologous liquids whose properties are well-known and can be correlated with the *D* values. Here we report the first such set of experiments using the *n*-alkanes C_6, C_8, C_{10}, C_{12}, C_{14}, and C_{16} (C_i is used for n-C_iH_{2i+2}). The *D* values were calculated from solute dispersions obtained when dilute solutions were drawn through microcapillaries.

These solutions, with a large nonpolar solute in nonpolar solvents, are good systems for testing the dependence of *D* on the solution viscosity η, the absolute temperature *T*, the size of the diffusing probe, and the solute−solvent interactions. The Stokes−Einstein (SE) relation, a commonly used hydrodynamic model, gives[3−7]

$$D = k_B T/(f_T \pi \eta r) \tag{1}$$

where k_B is Boltzmann's constant and $f_T = 6$ and 4 for the stick and slip limits, respectively; *r* is the radius of a sphere or a length determined by a nonspherical solute's shape and dimensions. Our earlier results for O_2 and a series of aromatic solutes[5−7] in the *n*-alkanes showed deviations from the SE relation; the *r* values for a given solute decreased as the solvent chain length and viscosity increased. The deviations were attributed to the relative sizes of the solutes and solvents. The SE relation holds when the solute size is much greater than that of the solvent, a condition not generally met by our systems.[5−7] The *D* values were fitted to[4−10]

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

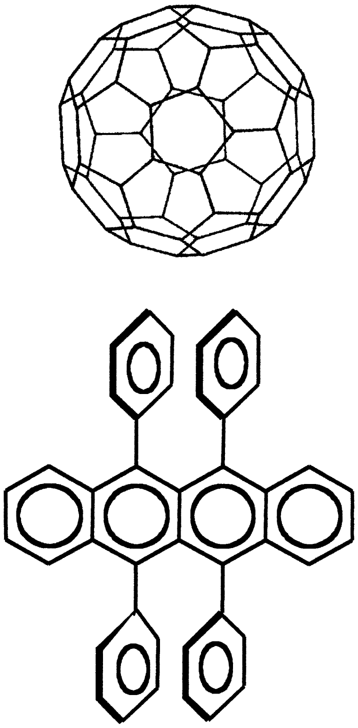

Figure 1. C_{60} (top) and rubrene (bottom).

where *p* and A_{SE} are constants; $p = 1$ for the SE limit. SE behavior was approached as the solute size increased.[7] The smallest solute, O_2, had the smallest value of $p = 0.553 \pm 0.009$.[6] Rubrene (Figure 1) had the largest *p* value (0.943 ± 0.014) with those for the other aromatic hydrocarbons decreasing in the order coronene (0.858 ± 0.014) > perylene (0.822 ± 0.007) > pyrene (0.805 ± 0.006) > diphenylbutadiyne (0.797 ± 0.009) > diphenylacetylene (0.752 ± 0.011) > anthracene (0.749 ± 0.011) > biphenyl (0.718 ± 0.004).[7] C_{60}, a relatively large molecule, would seem to be a candidate for SE behavior but its *r* values also decrease as the *n*-alkane chain length increases; the stick limit values of *r* vary from 5.34 ± 0.18 Å in C_6 to 4.31 ± 0.13 Å in C_{16}. While the resulting *p* value is relatively large (0.903 ± 0.006), the shape of C_{60} appears to prevent it from attaining the SE limit; unlike the tetraphenyl-substituted rubrene, there are no protruding substituents to engage the *n*-alkanes and give more complete coupling to their viscosities.

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TABLE 1: Concentrations for C_{60} Solutions

solvent	soln.	time[a]	C_{orig}, μM[b]	C_{estd}, μM[c]
C_6	1	2	50.0	27.8
C_6	2	81	13.9	
C_6	3	2	20.0	
C_8	1	59	50.0	27.8
C_{10}	1	1	50.0	38.9
C_{12}	1	56	50.0	44.4
C_{12}	2	12	22.2	16.7
C_{12}	3	5	25.0	22.2
C_{14}	1	98	55.5	50.0
C_{16}	1	102	55.5	

[a] The number of days after preparation that the final determination of *D* was made for the solution. [b] Concentration based on the amount of C_{60} used for sample preparation. [c] Estimated concentration if not all of the C_{60} used for sample preparation dissolved.

Our *r* values are discussed in terms of solute−solvent interactions and molecular structure data. Possible aggregation and solvation of C_{60} also are considered. These effects have been observed in some solutions[11−13] but do not appear to be taking place in our systems; data taken over a period of months indicate that the diffusing species is neither aggregated nor solvated. Reasons for favoring this interpretation are discussed.

Experimental Section

Solutions and Procedures. The solvents and C_{60} (Aldrich, 99.5%) were used as received. C_{10}, C_{12}, C_{14}, and C_{16} (all 99+%) were obtained from Aldrich; C_8 (99+%) and C_6 (Optima) were obtained from Sigma and Fisher, respectively. The viscosities are from ref 14.

Single solutions of C_{60} were prepared in C_8, C_{10}, C_{14}, and C_{16} while three solutions were prepared in both C_6 and C_{12}; their concentrations are given in Table 1. In several cases, not all of the C_{60} weighed for sample preparation dissolved (even though sonication was used to facilitate dissolution). These solutions were filtered before elution profiles were obtained; their concentrations are based on filter paper residues (which had estimated uncertainties of 10−20%). Small amounts of solute would occasionally precipitate out of solution during the lengthy intervals between determinations; these solutions would be filtered before more data were taken. The concentrations in Table 1 refer to the initial solution preparation. The maximum [C_{60}] in a given *n*-alkane increases as the *n*-alkane chain length increases. This pattern of concentration variation, the same as that for the molar solubilities,[15,16] will play a role in our discussion of the solution chemistry of C_{60}. Also given in Table 1 is the number of days after preparation that the final determination of *D* was made for each solution. This time is seen to be the order of two to three months for several of the solutions.

The solutions retained their light purple (magenta)[17] color for the entire period of time the experiments were conducted. The UV−visible spectrum of C_{60} in C_6 was in agreement with that of Leach et al.[18] The peak at 419.7 nm characteristic of the [6−6]-closed fullerene derivative $C_{60}O$[19] was not observed in any of the *n*-alkanes (including spectra taken over a year after solution preparation). $C_{120}O$ also has received attention as a component of air-exposed C_{60} samples.[20−22] We believe it is not a problem in our experiments because the maximum impurity level of $C_{120}O$ is estimated to be only 1%,[20] its solubility in C_6 is extremely low (although no quantitative data have been given),[20] and the absorption of $C_{120}O$ appears to be less intense[23,24] at 258 nm, the UV wavelength we used to detect C_{60}.[17,18] The significant presence of oxygen−C_{60} complexes in solution also has been noted as being unlikely.[25,26]

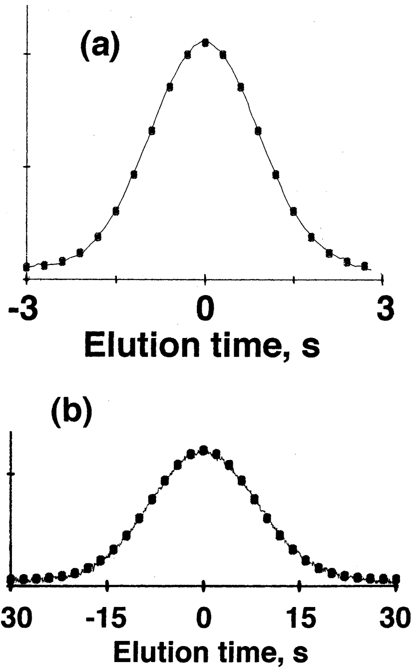

Figure 2. (a) Elution profile for C_{60} in C_6 (solution 3, acquired on the day of preparation) at 297.2 K and a Gaussian profile (●) calculated using the experimental profile's full width at half-height, $w_{1/2} = 2.13$ s. (b) Elution profile for C_{60} in C_{16} (solution 1, acquired 102 days after preparation) at 298.2 K and a Gaussian profile (●) calculated using $w_{1/2} = 19.3$ s. The center of the calculated profiles, $t = 0$ s, corresponds to the C_{60} retention time t_R for the experimental profiles; $t_R = 17.76$ and 181.9 s for (a) and (b), respectively.

TABLE 2: Typical Diffusion Constants and Hydrodynamic Radii for C_{60} Solutions

solvent[a]	soln.	*T*, K[b]	$10^5 D$, cm^2 s^{-1}	η, cP	r_{stick}, Å[c]
C_6 (81)	2	297.7	1.37 ± 0.07	0.301	5.29 ± 0.26
C_6				average value (8)[d]	5.34 ± 0.18
C_8 (8)	1	298.2	0.886 ± 0.026	0.508	4.85 ± 0.14
C_8				average value (7)	4.84 ± 0.14
C_{10} (1)	1	298.2	0.570 ± 0.007	0.838	4.57 ± 0.08
C_{10}				average value (3)	4.55 ± 0.13
C_{12} (56)	1	298.7	0.365 ± 0.011	1.37	4.37 ± 0.13
C_{12}				average value (14)	4.35 ± 0.12
C_{14} (98)	1	298.2	0.242 ± 0.010	2.09	4.32 ± 0.19
C_{14}				average value (4)	4.31 ± 0.17
C_{16} (102)	1	297.7	0.166 ± 0.004	3.06	4.29 ± 0.11
C_{16}				average value (6)	4.31 ± 0.13

[a] The number is parentheses is the number of days after solution preparation that a given determination was made. [b] The constant or average temperature (±0.5 K) for the determination. [c] $r_{slip} = 3r_{stick}/2$. [d] The total number of determinations of *D* for all of the solutions for the indicated solvent.

Taylor-Aris dispersion theory[27,28] 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,[5−7] which predicts the Gaussian-shaped profiles[3,27,28] found experimentally for C_{60} (Figure 2), gave diffusion constants in good agreement with literature values for the aromatic hydrocarbons in the *n*-alkanes.[7] The profiles were obtained at room temperature, which was measured repeatedly and varied by at most ±0.5 °C during the ≈2 h needed for a given determination of *D*. The UV detector, data acquisition system, and other aspects of the experimental procedure have been described previously.[5−7] The uncertainties in *D* and *r* (given below and in Table 2) as well as those for the eq 2 fit parameters correspond to ± one standard deviation.

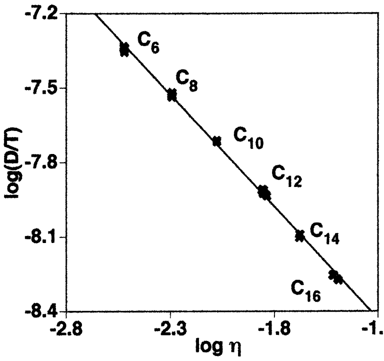

Figure 3. Fit of diffusion constants for C_{60} in the *n*-alkanes to $D/T = A_{SE}/\eta^p$; $p = 0.903 \pm 0.006$, $\log A_{SE} = -9.604 \pm 0.012$.

Results and Discussions

SE Comparison and Modification. Representative D values for C_{60} in the even *n*-alkanes are given in Table 2. Figure 3 shows a plot of log(D/T) vs log η for the 42 C_{60} data points in the *n*-alkanes (including eight in C_6 and 14 in C_{12}). The small scatter of data for the individual solvents over the appreciable lengths of time the measurements were made is consistent with the diffusion of a single species, as are the Gaussian profile shapes in Figure 2. As discussed below, it seems reasonable to assume that the single species is monomeric C_{60}. The fit to eq 2 gives $p = 0.903 \pm 0.006$, $\log A_{SE} = -9.604 \pm 0.012$.

Stick limit r values (from eq 1) for C_{60} in the even *n*-alkanes also are given in Table 2. In keeping with $p < 1$, they decrease as the chain length increases; the average value in C_{16} (4.31 ± 0.13 Å) is 19% smaller than the average value in C_6 (5.34 ± 0.18 Å). In ref 7 we used stick limit values of r in C_7 and C_{15} at 25 °C to illustrate that the relative change in r decreases as p increases; O_2 ($p = 0.553$) had $\Delta r_{7,15} = 100[r(C_7) - r(C_{15})]/r(C_7) = 57\%$ while rubrene ($p = 0.943$) had $\Delta r_{7,15} = 10\%$.[5-7] Similar calculations using D values from eq 2 for C_{60} give $\Delta r_{7,15} = 17\%$. As pointed out by Zwanzig and Harrison,[10] the r values are a measure of the coupling of the solute motion to the solvent flow. The decrease in r with increasing *n*-alkane chain length for a given solute is indicative of increasingly weaker coupling to the viscosity. Additionally, the increase in $\Delta r_{7,15}$ as the solute size decreases shows that the solute−solvent interactions become weaker as the solute size decreases.

The value of $p = 0.903$ for C_{60} does indicate a reasonable degree of solute−solvent coupling. In the *n*-alkanes, only one of our aromatic hydrocarbons,[7] rubrene (Figure 1), has a larger p value (0.943); its four phenyl rings clearly have strong interactions with the solvent. It may be that the relatively smooth surface of C_{60} prevents it from transferring momentum and energy to the solvent more effectively[10] and reaching the SE limit.

Experimental Sizes of C_{60}. Our solvent-dependent r values are at odds with the simple model (the SE relation) used to obtain them. However, the majority of sizes determined by other techniques are in agreement with our average stick limit value of r in C_6; this solvent, our smallest, would be expected to be closest to the SE limit.

X-ray diffraction[29] showed the distance between adjacent molecular centers in C_{60} to be 10.02 Å, giving a “hard sphere” radius of 5.01 Å. Our value of $r = 5.34 \pm 0.18$ Å in C_6 is a bit larger than this “size” in crystalline C_{60} but is in general agreement with several other “structural” values of r. Pressure−area isotherms of Langmuir−Blodgett (LB) films gave $r = 5.6 \pm 0.7$ Å[30] and $r = 5.2 \pm 0.3$ Å.[26] Scanning tunnel microscopy (STM) gave $d = 2r = 10.5 \pm 0.5$ Å[31] for LB films while $d = 11.0 \pm 0.5$ Å was found from STM studies of hexagonal arrays of C_{60} on a Au(111) surface.[32] Atomic force microscopy gave a nearest neighbor distance of $d = 10.7 \pm 1.3$ Å on crystalline C_{60}.[33] An outer diameter of 10.44 Å ($r = 5.22$ Å) has been suggested[1] for C_{60} using $d_g = 3.35$ Å, the interplanar separation in graphite, and a nucleus-to-nucleus diameter of 7.09 Å calculated from the C−C and C=C bond lengths. Electron diffraction (ED) showed the free molecule’s icosahedral diameter to be $2r_{ED} = 7.113$ Å,[34] giving $r = 5.23$ and 5.33 Å if $d_g/2$ and the van der Waals radius of the benzene C atom, $r_C(C_6H_6) = 1.77$ Å, respectively, are added to r_{ED}. Small-angle neutron scattering (SANS) has been used to determine R_g, the radius of gyration of C_{60} in CS_2.[25] In those studies (discussed below), R_g for *unsolvated* C_{60} is 3.48 Å; the addition of $r_C(C_6H_6)$ and $d_g/2$ gives $r = 5.25$ and 5.16 Å, respectively.

TABLE 3: Values of *r* for C_{60} from Partial Molar Volume Data at 25 °C

solvent	$V^m(C_{60})$, cm^3 mol$^{-1,a}$	r_{V_m}, Å^b	V_m, cm^3 mol$^{-1\,c}$
n-$C_{16}H_{34}$	437.6 ± 272.5^d	5.58	292.95
cis-decalin	401.6 ± 10.4	5.42	154.12
1-MN^e	389.4 ± 8.2	5.36	142.06
o-xylene	379.0 ± 7.8	5.32	122.03
1,2,4-TMB^f	370.9 ± 5.6	5.28	135.21
toluene	363.5 ± 11.0	5.24	106.52
benzene	358.2 ± 11.0	5.22	89.37
CS_2	351.4 ± 5.6	5.18	60.14
C_{60}(s)	429	5.54	

[a] The values of $V^m(C_{60})$ and their uncertainties are the averages of the values for each solvent in Table 3 of ref 35. [b] Calculated from the average values of $V^m(C_{60})$ and $r_{V_m} = [3V^m(C_{60})/4\pi]^{1/3}$. [c] From ref 36. [d] The uncertainties for *n*-$C_{16}H_{34}$ are in fact very much larger than those of the other solutes, see ref 35. [e] 1-Methylnaphthalene. [f] 1,2,4-Trimethylbenzene.

The size of C_{60} in solution also can be discussed in terms of its partial molar volume, $V^m(C_{60})$. Ruelle et al.[35] determined $V^m(C_{60})$ at infinite dilution and 25 °C in twelve organic solvents; the average values for the seven hydrocarbons and CS_2 are given in Table 3 as are the solvent molar volumes at 25 °C,[36] V_m. With the exception of C_{16} (for which the uncertainties are very large; see Table 3 and ref 35), the values of $V^m(C_{60})$ are smaller than the molar volume of pure C_{60}. This is not typical; the partial molar volume for a solute in solution is usually much closer to that of the pure solute.[35] The data show that progressively smaller solvent molecules appear to occupy the inter-fullerene regions more efficiently and give smaller values of $V^m(C_{60})$. The values of $r_{V_m} = [3V^m(C_{60})/4\pi N_A]^{1/3}$ in the hydrocarbons and CS_2 also are given in Table 3 (N_A is the Avogadro constant). Only the value of $r_{V_m} = 5.58$ Å in C_{16} is outside the uncertainties for $r = 5.34 \pm 0.18$ Å in C_6. In particular, the values of r_{V_m} for toluene, benzene, and CS_2 (the smallest of the solvents) are 5.24, 5.22, and 5.18 Å, respectively, possibly indicating that a limiting value is being approached.[37] While $V^m(C_{60})$ does contain free space as well as the actual volume of the solute, these values of r_{V_m} as well as the structural sizes mentioned above do seem to suggest that our value r for C_{60} in C_6 is reasonable.

Possible Aggregation and Solvation of C_{60}. The discussion to this point has been in terms of the stick limit values of r; the slip limit values are 50% larger than the stick values, ranging from $r = 8.01 \pm 0.27$ Å in C_6 to 6.46 ± 0.20 Å in C_{16}. While this would seem to raise the question of a diffusing particle larger than a single C_{60} molecule, i.e., solute association either with itself or with solvent, experimental results and a recent review article[15] argue against these phenomena (and the slip limit r values) in the *n*-alkanes.

Room-temperature light scattering studies by Chu et al.[11,12] indicated a slow aggregation of C_{60} in concentrated C_6H_6 solutions[15] ($[C_{60}] \geq 1$ mM) with radii of over 100 Å after more than a month. Subsequent UV absorption and light-scattering investigations by Sapre and co-workers[13] showed no tendency for C_{60} to aggregate in C_6H_6 and a cycloalkane (decalin) for $[C_{60}] \leq 500$ μM (our concentrations were 13.9−55.5 μM). Aggregation of C_{60} has been found in benzonitrile, PhCN, for $[C_{60}] > 100$ μM,[13] in PhCN−C_6H_6 and PhCN−decalin mixed solvents with $[C_{60}] \approx 400$ μM,[13] and in mixed solvents consisting of two components (such as acetonitrile and toluene)[15] in which the fullerene has widely differing solubilities. A series of UV studies directly relevant to our systems showed that C_{60} aggregation was not occurring in either C_6 or cyclohexane but did take place in liposomes and films.[38] Solute aggregation was mentioned as a possible contributor to the large values of r (11.1−25.0 Å) found in electrochemical studies in polar solvents.[39]

In our solutions, the maximum C_{60} concentration in a given *n*-alkane increases as the chain length increases; the *decrease* in r as the solute concentration increases is not consistent with aggregation. Also, aggregation has been shown to be time-dependent[11,12,40] and the constancy of the r values over the relatively long periods of time during which data were taken argues against this scenario. The variation in the sizes obtained from the D values for C_{60} in non-*n*-alkane hydrocarbons[41−47] and CS_2[25,48−50] was one of the reasons for our multiple determinations of D over extended periods of time.

The possibility of C_{60}−solvent association has been mentioned in several electrochemical studies.[39,51] Changes in the electronic spectra accompanying the dissolution of C_{60} in tertiary amines and substituted anilines have been interpreted in terms of charge-transfer complexes.[15,52,53] The diffusion constants of C_{60} in two N-heterocycles[40] decreased with time and were explained in terms of fullerene−solvent aggregates. Interactions between C_{60} and aromatic molecules also have been discussed,[11,12,15,38,54,55] but the *n*-alkanes are considered to be inert.[56] This appears to be consistent with our results; the stick limit value of r in C_6 (5.34 ± 0.18 Å) is in approximate agreement with the size of C_{60} and the *decrease* in r as the chain length increases argues against the solute "dragging" progressively larger solvent molecules through solution.

Summary and Conclusions

The translational diffusion constants of C_{60} were determined in the even *n*-alkanes C_6 to C_{16} using capillary flow techniques and Taylor−Aris dispersion theory. The initial analysis of the data showed deviations from the SE relation, eq 1; the solute size decreased as the solvent viscosity increased. The data were then fitted to eq 2 in which p, the exponent of the viscosity, is a measure of the deviations from SE behavior ($p = 1$). The near-spherical C_{60} has a smaller p value (0.903 ± 0.006) than might be expected considering its relatively large size. The solute's shape also appears to play a role in determining p; it may be that the smoothness of C_{60}'s surface diminishes the degree of interaction between the solute and solvent. Precautions were taken to ensure that the diffusion constants were those of C_{60} molecules that were not in clusters or associated with solvent molecules.

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orientation of adjacent C_{60} molecules showed that r_C varied from r_{min} = 1.47 Å to r_{max} = 1.76 Å (which is close to $r_C(C_6H_6)$ = 1.77 Å). The calculated volumes give $r_{vdW} = (3V_{vdW}/4\pi)^{1/3}$ = 4.75 and 5.08 Å for r_{min} and r_{max}, respectively.

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