Brownian Motion at the Molecular Level in Liquid Solutions of C$_{60}$

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We report the diffusion coefficients of C$_{60}$ in toluene, benzene, and carbon tetrachloride at 303.15 K. These were determined with the Taylor dispersion technique and the results are discussed in terms of the Stokes–Einstein relationship.

Introduction

The discovery of synthetic methods for producing crystalline C$_{60}$[1-4] has opened many investigations on the structural and physical properties of this new molecule.[5-12] Solid C$_{60}$ is characterized as a soft crystal composed of hard pseudosphere molecules with a diameter of 7.1 Å[9] stabilized by the aromatic character of the π-electrons. C$_{60}$ with its unique cage structure will interact in solution with solvents in interesting ways that can provide new information on the mechanisms of solute–solvent interactions. In solution C$_{60}$ has a rigid, well-defined geometry, in contrast with other solutes whose shapes undergo conformational changes and whose intramolecular vibrations may undergo large and solvent-dependent changes.

In this paper, we report the diffusion coefficients of C$_{60}$ in toluene, benzene, and carbon tetrachloride at 303.15 K. These were determined with the Taylor dispersion technique and the results are discussed in terms of the Stokes–Einstein relationship.

Brownian motion theory[13,14] shows that for the case where there is no correlation of molecular motion, the diffusion coefficient of a large and massive tracer particle immersed in a fluid medium is related to a frictional coefficient ζ by the equation

$$D = kT/\zeta \qquad (1)$$

where T is the temperature and k is Boltzmann's constant. ζ can be calculated for a sphere of radius R moving in a fluid medium of viscosity η. Since the time of Stokes, there were recognized two limits defined by the coefficient of sliding friction between the diffusion particle and its surroundings, i.e. the boundary conditions on the surface of the particle:

(a) $\zeta = 6\pi\eta R$, "stick". In this case sticking boundary conditions are used. There is no slip between the moving sphere and the fluid in contact with it. This is supposed to be the case for a sphere in a continuum or for a large spherical particle in a solvent of low relative molecular mass. This is the commonly called Stokes–Einstein equation.

(b) $\zeta = 4\pi\eta R$, "slip". This is the limit when slipping boundary conditions are used between the moving sphere and the fluid in contact with it. It is believed to be approached when a molecule diffuses through a medium consisting of molecules of comparable size.

Further research in the hydrodynamic friction on moving spheres[15,16] has developed attractive methods for calculating the drag on a sphere in a flowing fluid, eliminating the need for boundary conditions by treating the sphere as a center of force in a continuum obeying the hydrodynamic equations. In particular, for step potentials, the "stick" and "slip" behaviors can be recovered.

Experimental evidence for the "stick" behavior is widespread in the literature,[17] mainly related to the diffusion of large particles (polystyrene latex spheres or very big molecules), and it has

generated a way for measuring viscosities with dynamic light scattering.[18,19] If the size of the diffusing particle is not large compared to that of the solvent molecules, as in molecular solutions, the Stokes–Einstein relationship is not expected to remain valid. The diffusion of a tracer molecule is well described by (1) only in special cases, for instance, when the diffusing molecule is still large in comparison with the molecules of the medium in which it moves, when the medium in which the diffusing molecule moves has a very low viscosity, and when there is no solute–solvent interaction. There are outstanding examples such as the system tetramethylsilane/benzene[20] where the Stokes–Einstein relation is obeyed with the "slip" condition, in wide ranges of temperature and pressure. As the tracer becomes smaller than the solvent molecules, a large body of experimental evidence[21] shows that (1) is violated. There are other classes of liquids for which the Stokes–Einstein relation fails, namely, superfluid helium, which has a vanishing viscosity but a finite tracer diffusion constant, and fragile glass-forming liquids.[22] In general, the relation between the viscosity, molecular radius, and diffusion coefficient, if indeed a unique relation does exist, is by no means clear.[23]

Simulations give another side of the story, although not more illuminating. The most important examples come from molecular dynamics of pure fluids made up of hard spheres[24] and of particles interacting through the Lennard-Jones potential.[25-27] In particular, for the case of the hard-sphere fluid molecular dynamics calculations have shown that (1) is obeyed when the "slip" condition is used. On the other hand, simulations performed by Bearman and Jolly[25] for self-diffusion coefficients in binary isotopic Lennard-Jones solutions in the limit of infinite dilution have shown an intrinsic mass dependence, suggesting that eq 1 cannot be completely applicable for these systems. Ould-Kaddour and Barrat[26] on the basis of their simulations for truncated Lennard-Jones fluids suggested that for particles of the same size, the Stokes–Einstein relationship is essentially independent of the mass ratio when the mass of the tracer particle is smaller than those of the solvent. It is important to mention that neither the work of Bearman and Jolly[25] nor the work of Ould-Kaddour and Barrat[26] are direct tests of the Stokes–Einstein relationship, since they do not evaluate the shear viscosity of the fluid in their simulations. Heyes[27] has studied the self-diffusion and the shear viscosity in Lennard-Jones fluids in order to test the Stokes–Einstein relationship with the "slip" condition. He has shown that at high liquid densities the estimated diameters given by (1) are close to the Lennard-Jones length parameter, σ. On the average, for densities greater than $\rho\sigma^3 = 0.65$ the estimated diameters are 1.22 times the σ. When the "stick" condition is used on the data of Heyes[27] at those densities, the estimated diameters are 0.82 times the σ on the average. Heyes[27] also found that as the density decreases the estimated diameter grows to several molecular diameters, suggesting an increase of collective motion.

Roughly, the size of C$_{60}$ (7.1 Å diameter) is of the same order

TABLE 1: Diffusion Coefficient of C$_{60}$ (m^2/s) in Liquids at 303.15 K

solvent	D (10^{-9})	error (%)	X_{nom} $(10^{-7})^a$
toluene	0.97	3.7	16.2
benzene	2.38	1.3	2.73
CCl$_4$	0.802	15.2	4.67

^{a} Mole fraction.

TABLE 2: Characteristic Lengths Obtained with Equation 1

system	d_{stick} (Å)	d_{slip} (Å)
C$_{60}$/toluene	8.72 ± 0.32	13.08 ± 0.48
C$_{60}$/benzene	3.30 ± 0.04	4.96 ± 0.06
C$_{60}$/CCl$_4$	6.56 ± 1.02	9.86 ± 1.53

Characteristic Diameters Reported for C$_{60}$ (Å)	
7.1	from X-ray studies in C$_{60}$[9]
11.2	from pressure/area isotherms[10]
9.10	Lennard-Jones σ[30]
7.08	from X-ray studies in K$_3$C$_{60}$[31]

of the molecules of the viscous fluids used here (Lennard-Jones σ's: 5.698, 5.349, and 5.947 Å for toluene, benzene, and carbon tetrachloride, respectively), and its molecular weight is by far larger than the molecular weight of the molecules of those fluids. Therefore, the main question addressed in this paper is as follows: Does the Stokes–Einstein relationship describe the diffusion of C$_{60}$ in the liquids of interest here? In particular, the diffusion of other tracers in those fluids usually does not follow the Stokes–Einstein relationship, as we will show below.

Experimental Section

The Taylor dispersion technique is based on the dispersion of an injected binary-mixture pulse in a laminar flowing stream of the same mixture at slightly different composition, by the joint action of convection and molecular diffusion. Under proper conditions, the pulse concentration profile will eventually become normal, and the center of gravity of the profile will move with the mean velocity of laminar flow. The theory for the development of ideal equipment to measure diffusion coefficients with this method was reviewed by Alizadeh et al.[28] Furthermore, they presented detailed criteria for the design of a practical instrument, and the details of our instrument were presented in ref 29.

The values for the moments of the distributions obtained in the experiment were determined with a nonlinear fitting program of the digitized values corresponding to the analog signal of a differential refractometer (Waters 402), in the region where it has a linear response to the concentration difference between the cells. The acquisition of data was performed with a data acquisition board (PC-LabCard, Advantech, Co.), and a Print-aform PC.

Toluene and benzene of 99.9% and 99% purity, respectively, were supplied by J. T. Baker Co., carbon tetrachloride of 99.8% purity was supplied by Merck, and C$_{60}$ of 99.9% purity was supplied by Mer Corp. The binary mixtures for the δ-peaks were prepared with an estimated error in the quoted mole fractions to be less than 1 × 10^{-4}.

Our measurements were performed at almost infinite dilution. Hence, following the principle of the Taylor dispersion technique, we had pure solvents flowing through the capillary tubing, and injected the C$_{60}$ mixture pulses (δ-peaks) at a specified but very dilute concentration of about half of the maximum solubility of C$_{60}$ in the selected solvent. The diffusion coefficient obtained corresponds to a reference concentration given by

$$X_{1r} = X_{1f} + \delta X_1 \qquad (2)$$

where X_{1f} is the flowing-stream composition (zero in our case) and δX_1 is a small correction described in refs 28 and 29.
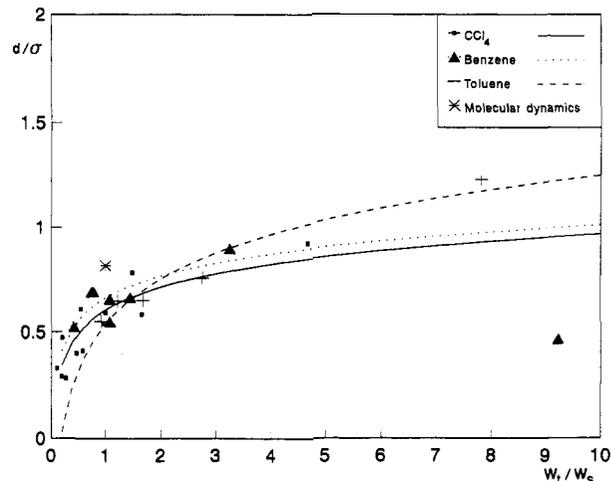

Figure 1. Ratio of the diameter of the tracers (d) obtained with the Stokes–Einstein equation ("stick" boundary conditions) in three solvents to the size of the tracer molecules (σ) as a function of the ratio of the molecular weight of the tracer molecules (W_t) to the molecular weight of the solvent molecules (W_s). The tracers used in this figure are as follows: for the case of carbon tetrachloride, Ar, N$_2$, CH$_4$, Cl$_2$, C$_2$H$_6$, CF$_4$, CCl$_4$, C$_6$H$_{12}$, SF$_6$, I$_2$, C$_{16}$H$_{34}$, and C$_{60}$; for toluene C$_6$H$_{14}$, CCl$_4$, chlorobenzene, I$_2$, and C$_{60}$; for benzene, CH$_3$NO$_2$, CH$_3$OH, acetone, C$_6$H$_{12}$, C$_6$D$_6$, chlorobenzene, I$_2$, and C$_{60}$. A point coming from molecular simulations for the Lennard-Jones fluid using the "stick" condition is included, which is an average value for liquid densities. Lines are guides to the eye.

Results and Discussion

The diffusion coefficients at infinite dilution obtained in our experiments are presented in Table 1. Surprisingly, the experiments devoted to obtaining the diffusion coefficients of C$_{60}$ in the solvents reported here were not so simple as expected. Solubilization of C$_{60}$ to prepare the δ-peaks was difficult. The concentrations at which the diffusion data are reported here must be considered as an upper bound, and for our purpose the better, since they are closer to infinite dilution. The actual concentrations are below of those quoted in Table 1, since it was necessary that the δ-peak samples were centrifuged several times in order to prevent shoulders in the normal distribution of the concentration profile at the end of the experiment. The appearance of these shoulders was associated with small clusters of C$_{60}$ not well dissolved in the injected pulses and which spoiled many of the determinations. This was particularly true when CCl$_4$ was used, since in this solvent the solubility of C$_{60}$ is lower.[12]

The diffusion coefficients and the viscosity values for the liquids used here allowed us to obtain characteristic lengths, R, using eq 1, for the "stick" and "slip" cases. In Table 2, we present the corresponding C$_{60}$ diameters ($d = 2R$) obtained in each of the studied systems. Moreover, in this table some cage diameters for the C$_{60}$ molecule obtained by other very different techniques are shown for comparison. Surprisingly, our data are very close to those obtained by X-ray for the cage diameter. In particular, when the "stick" condition is used the C$_{60}$/toluene and the C$_{60}$/CCl$_4$ systems show predicted diameters for C$_{60}$ which deviate from the 7.1 Å value by 22.8% and −7.7%. The C$_{60}$/benzene system presents a deviation of −30.1% when the "slip" condition is used. The better result was obtained with the most spherical solvent. Our sizes are closer to the calculated radius coming from X-ray than those obtained from pressure–area isotherms[10] at the air–water interface.

It is difficult to explain our results, since neither theory nor experimental data give a clear picture for diffusion in molecular solutions. Nevertheless, it is a curious finding that for the case of benzene, which does not have a dipolar moment, the diffusion coefficient of C$_{60}$ gives a cage diameter closer to the 7.1 Å value when the "slip" condition is used. In the case of toluene, which

has a low dipolar moment, we are closer to the 7.1 Å when the "stick" condition is used. This kind of reasoning cannot be extended to the case where carbon tetrachloride is used as a solvent. Here, the results are closer to the "slip" condition, although the solvent does not present a dipolar moment.

An interesting comparison between our measurements and measurements performed for other tracers in toluene, benzene, and carbon tetrachloride can be done. Since the bare numbers are not very helpful, we followed a different approach. In Figure 1, for several tracer molecules including C_{60}, we present the ratio of the diameter of the tracers obtained from diffusion coefficients given in the literature using the Stokes–Einstein equation (with stick boundary conditions) to the size of the tracer molecules as a function of the ratio of the molecular weight of the tracer molecules to the molecular weight of the solvent molecules. Several kinds of sizes can be used to estimate the size of the tracers; for simplicity we have chosen the Lennard-Jones length parameter,[32] except for C_{60}. In this case the 7.1-Å value was used. The tracers used in Figure 1, for the case of carbon tetrachloride were Ar,[33] N_2,[33] CH_4,[33] Cl_2,[33] C_2H_6,[33] CF_4,[33] CCl_4,[33] C_6H_{12},[34] SF_6,[33] I_2,[33] $C_{16}H_{34}$,[14] and C_{60}; for toluene C_6H_{14},[35] CCl_4[35] chlorobenzene,[34] I_2[36] and C_{60}, and for benzene CH_3NO_2,[37] CH_3OH,[38] acetone,[38] C_6H_{12},[14] C_6D_6,[14] chlorobenzene,[14] I_2,[36] and C_{60}. In addition, a point coming from the molecular dynamics simulations study of Heyes[27] for the Lennard-Jones fluids was included in Figure 1, which is an average value for liquid densities.

Only main trends can be obtained from Figure 1, since experimental data for tracers are limited and the way in which the actual size of the tracers was estimated, through the σ's to obtain the d/σ ratio, can be questioned. Probably, the most important feature that can be obtained from this figure is that as the molecular weight of the tracer particle increases with respect to the solvent molecules, the diameters obtained for those tracers with the Stokes–Einstein equation are closer to our common estimation of molecular diameters, i.e. the σ's. This agrees with the assumptions underlying the Stokes–Einstein equation. An exception is the C_{60} in benzene. Here, as mentioned above, our results are closer to the slip condition.

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