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NMR diffusion studies of spherical molecules: Tetramethylsilane and buckyballs

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ABSTRACT

The structural properties and hydrodynamic size of a molecule in solution at infinite dilution are connected to its diffusion coefficient through the Stokes–Einstein–Sutherland equation. In this study, buckyballs (C_{60}) and mixtures of tetramethylsilane and $CDCl_3$ which closely approximate spherical molecules in solution were investigated using nuclear magnetic resonance (NMR) self-diffusion experiments. It was found that the change in diffusion coefficient of mixtures of TMS and $CDCl_3$ was only correlated to the viscosity of the solution. The C_{60} PGSE NMR data was then analysed using various models of obstruction. It was found that the decrease in C_{60} diffusion with increasing concentration can be explained on the basis of aggregation alone, and thus C_{60} self-obstruction must be negligible under these experimental conditions.

1. Introduction

Self-diffusion measurements provide information on the size, shape and interactions of the diffusing molecules [1,2]. Specifically, the diffusion coefficient of a molecule depends on the friction factor which is related to the hydrodynamic size/shape of the molecule and the viscosity of the solvent. In the absence of any external forces acting on the diffusing particle, the infinite-dilution diffusion coefficient of a molecule is related to its effective hydrodynamic radius via the Stokes–Einstein–Sutherland equation [3–5],

$$D_0 = \frac{k_b T}{f_r}, \tag{1}$$

where k_b is the Boltzmann constant, T (K) is temperature and f_r (kg s^{-1}) is the friction coefficient of the diffusing molecule. For a spherical molecule with an effective hydrodynamic radius r_H (m) in a solvent of viscosity η (Pa s), $f_r = c\pi\eta r_H$ where the constant c characterizes the interaction between the solute and the solvent with $c = 4$ or 6 denoting the 'slip' and 'stick' conditions, respectively. The stick condition is more applicable to large solutes or solutes interacting strongly with solvent molecules, whereas the slip condition is applicable to small solutes or less interaction between solute and solvent molecules [6,7].

Many solvents, such as water, dimethyl-sulfoxide, ethanol and methanol, have complex solvent behaviour involving at least transient self-association due to the presence of hydrogen bonds [8–10]. Thus, the presence of H-bonding interactions complicates the interpretation of the diffusion data. Simplistically, from Eq. (1) the hydrodynamic radii of both the internal reference and probe molecules can be related to each other by (e.g., [7,11]),

$$r_{probe} = \frac{D_{ref}}{D_{probe}} r_{ref}, \tag{2}$$

where D_{ref}, r_{ref} and D_{probe}, r_{probe} are the diffusion coefficient and hydrodynamic radius of the reference and probe molecules, respectively. Both the internal reference and probe molecules, being in the same solution, should experience similar viscosity effects from the solvent molecules.

In addition, many diffusing systems are known to undergo self-association with increasing concentration and it can be difficult to determine the size of the different aggregates and their degree of size polydispersity from diffusion data alone [12–14]. In fact, apart from at very low concentration all measured diffusion coefficients include effects of both aggregation and obstruction. Most of the theory used to analyse the experimental diffusion in liquids has been derived on the simple assumption that diffusion is occurring at infinite dilution (i.e., Eq. (1)). Clearly, this is inadequate as almost always these are crowded systems with multiple collisions occurring between solute molecules within the timescale of the measurement. Thus, a diffusion measurement will simultaneously measure true self-diffusion, obstruction and molecular association. The diffusion path and the (time-dependent) coordinates of obstructing particles are very complex due to the presence of obstructing particles of varying shapes and sizes. The

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mathematical complexity of calculating obstruction factors of different sized obstructing particles involves solving the diffusion equation under appropriate boundary conditions. The simple models derived to account for the presence of obstructing particles assume the same shape (mostly spheres) for all obstructing particles and are only valid at very low concentrations [15–23]. The theoretical modelling to account for the combined effects of aggregation and obstruction effects in liquids is still in its infancy. At present, models consider particles as hard spheres [24–26]. The importance of developing cogent models of aggregation that include the effects of obstruction has been highlighted in a number of recent studies [27,28]. TMS is an inert and nonpolar solvent which is widely used as a standard internal chemical shift reference [11]. Since TMS will not be influenced by the complications of H-bonding and because TMS has a pseudo-spherical structure, it is an appropriate choice for our investigation. In this work, the diffusion of two pseudo-spherical molecules, buckyballs (C_{60}) and tetramethylsilane (TMS) [29–31], have been investigated.

The physical and chemical properties of C_{60} are of great interest due to potential applications of C_{60} in biological and chemical systems. A number of studies have used dynamic light scattering (DLS) or fluorescence spectroscopic techniques to investigate the aggregation properties of C_{60} in different solvents [32–36]. Nath et al. [33] have indicated the presence of aggregates at high C_{60} concentrations (i.e., >100 μM) in benzonitrile solutions. Similarly, Chen et al. [32] reported the aggregation and deposition behaviours of C_{60} nanoparticles in toluene solutions with electrolytes and Ying et al. [35,36] have studied the aggregation behaviour of C_{60} in benzene solutions. However, Huo et al. [37,38] have shown that solvent properties of the mixtures have a significant impact on the structure of resultant C_{60} aggregates. All these studies have used the DLS technique to determine the average size distribution near the solubility limit of C_{60} in the respective solvents. If the radii are measurably different, the DLS technique is, in principle, capable of distinguishing between sizes of different aggregates. However, it also depends on concentration fluctuations, as it measures the mutual diffusion coefficient. NMR diffusion spectroscopy is a unique tool for studying the binding of biomolecules, ranging from self-associating systems to ligand–protein associations. Kato et al. [39] and Haselmeier et al. [40] have reported the diffusion coefficient of C_{60} in benzene and carbon disulphide, respectively using ^{13}C NMR. In both studies, C_{60} was ^{13}C enriched (30% [39] and 5% [40]). However, C_{60} aggregation and obstruction properties have never been investigated using NMR diffusion measurements. Concomitant with the improved technical abilities of modern NMR spectrometers to measure diffusion, there has been increased awareness of the experimental limitations and the need for more realistic models to analyse diffusion data of associated systems [6,14,41,42]. A detailed description of the aggregation and obstruction models used to analyse diffusion data of associated/aggregated systems can be found elsewhere [43,44].

In this work, the self-diffusion properties of TMS dissolved in $CDCl_3$ were studied over the entire composition range using ^{1}H NMR and the C_{60} diffusion coefficient was measured at concentrations ranging from 1.65 to 35 mM in 1-chloronapthalene using ^{13}C NMR. This work is organized as follows: In the Results and discussion section, the diffusion coefficient of TMS was measured using ^{1}H NMR at 298 K. Then, NMR self-diffusion measurements of TMS and $CDCl_3$ mixtures are discussed in relation to the hydrodynamic radii (r_H) derived from Eq. (1) [3–5]. Then the NMR diffusion results of C_{60} are discussed in relation to aggregation and obstruction models. Concluding remarks are presented in the final section.

2. Materials and methods

2.1. Materials

TMS (99.9%, NMR grade, Sigma) and $CDCl_3$ (99.8%, Cambridge Isotope Laboratories) were used as supplied. They were mixed together to achieve the desired concentrations and dispensed into 5 mm NMR tubes (Wilmad Lab glass). Then, straight capillary tubes with openings at both ends (1.5 mm, Wilmad Lab glass) were inserted the tubes. Due to the volatility of TMS (boiling point 299 K) and $CDCl_3$, the samples were frozen immediately after preparation using liquid nitrogen and were flame sealed to prevent evaporation.

The C_{60} (99.9%, sublimed, Sigma) solutions were prepared by mixing the desired amount of C_{60} with 1-chloronapthalene (85%, technical grade, Sigma). C_{60} has a maximum solubility of 69 mM in 1-chloronapthalene [45]. A concentrated solution was made by adding C_{60} to 1-chloronapthalene and sonicating. A series of dilutions were performed to achieve the desired concentration solutions. No visible precipitation of the C_{60} was observed in any of the samples.

2.2. Experimental details

^{1}H (TMS) and ^{2}H ($CDCl_3$) pulsed gradient stimulated echo (PGSTE) NMR diffusion experiments were performed at 400 MHz and 61 MHz, respectively at 298 K with a 5 mm BBO probe on a 400 MHz Bruker Avance NMR spectrometer. ^{13}C pulsed gradient spin-echo (PGSE) NMR diffusion experiments (C_{60} and 1-chloronapthalene) were performed at 125 MHz and 298 K with a Micro5 probe and 5 mm ^{13}C/^{1}H rf insert on a 500 MHz Bruker Avance II NMR spectrometer. A standard methanol sample (99.97% MeOH + 0.03% HCl) was used for NMR temperature calibration. The Micro5 probe has a triple axes gradient set with maximum gradient strengths along the x, y and z-axes of 2.92 T m^{-1}, 2.91 T m^{-1} and 2.95 T m^{-1} at 298 K, respectively. The gradient strength along each direction was calibrated by measuring the known diffusion coefficient of residual water (HDO, 1.9×10^{-9} m^2 s^{-1}) in D_2O at 298 K [46].

^{1}H and ^{2}H NMR diffusion experiments were performed with typical acquisition parameters gradient pulse duration (δ) = 1.5 ms, timescale of the diffusion measurement (Δ) = 0.2 s with the gradient amplitude (g) varied from 0.005–0.253 T m^{-1} in increments of 0.017 T m^{-1} to give 16 data points for each echo attenuation curve. Each spectrum was averaged over at least 8 scans depending on the signal-to-noise ratio. The acquisition parameters for the ^{13}C diffusion experiments were $\delta = 5.0$ ms, $\Delta = 0.2$ s with g varying from 0.03 to 0.64 T m^{-1} in increments of 0.09 T m^{-1}. The values δ, g and Δ were selected so that the echo signal was attenuated by at least 80% with the largest value of g. Recycle delays were set to at least five times the spin–lattice relaxation time of the measured species. The ^{13}C spin–lattice relaxation time of C_{60} (34 mM in 1-chloronapthalene) was determined to be 28 s using the inversion recovery pulse sequence.

Unwanted convection effects can easily result from temperature gradients when measurements are performed away from ambient temperature [6,47–49]. Since TMS is very volatile and the diffusion measurements were performed at 298 K (i.e., 1° below boiling), capillaries were added to help minimize convection effects. Undesirable convection effects can also be minimized by using the double-stimulated echo pulse sequence (DSTE) [6,47–49]. Experiments were performed using a sample with capillaries and measurements were made with PGSE, PGSTE and DSTE to eliminate undesirable convection effects.

The NMR diffusion data were analysed by non-linear least squares regression of the appropriate attenuation expression using OriginPro 9 (OriginLab) software [6]. The error values quoted are those obtained from data fitting. However, including factors like temperature fluctuations and other instrumental errors, the true error is likely to be on the order of 1% [50].

3. Results and discussion

3.1. TMS diffusion

A phase change was observed in the TMS diffusion spectra acquired with the magnetic gradient applied along the z-axis using PGSE and