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Self-Diffusion Coefficients of Some Hydrocarbons in Water: Measurements and Scaling Relations

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We present values of the self-diffusion coefficients at 25 °C of four hydrocarbons (*n*-pentane, *n*-hexane, cyclohexane, and *o*-xylene) at saturation concentrations in (heavy) water. To calculate the corresponding values for the series of *n*-alkanes, we suggest two alternative scaling relations for the dependence of the self-diffusion coefficients on the molecular weights of the *n*-alkanes. The scaling relations are "calibrated" using the value presented for *n*-pentane.

Introduction

The translational motion as quantified by the value of the self-diffusion coefficients (D) of hydrocarbons in water is an important parameter in the theory of Ostwald ripening.[1−3] Experimentally derived self-diffusion coefficients are also important experimental data in the context of molecular dynamics simulations, as they can be used to calibrate the potentials used in the simulations.[4]

Tracer data for water diffusion is available for a number of different water/hydrocarbon pairs.[5] However, due to the low solubility of hydrocarbons in water, very few self-diffusion coefficients of hydrocarbons in water have been reported in the literature. As far as we have been able to ascertain, only values for methane[6] and benzene[4] are available. Both of these values were obtained by means of the NMR pulsed gradient spin−echo (PGSE) method.[7]

To improve the situation we present in this paper data for the self-diffusion at 25 °C of 4 hydrocarbons at saturation concentration in D_2O: *o*-xylene, cyclohexane, *n*-pentane, and *n*-hexane. The data were obtained using the PGSE NMR method at 300 and 500 MHz. Based on the data obtained, we suggest values for the self-diffusion coefficients of *n*-alkanes in water using scaling relations for the dependence on D on the hydrocarbon molecular weight.

Experimental Section

Materials. The hydrocarbons used were obtained from Nacolai Tesque (Kyoto) (cyclohexane and *n*-pentane) and Sigma (St. Louis, MO) (*o*-xylene and *n*-hexane). They were all of the highest quality available. D_2O was from Isotec Inc. (Miamisburg, OH).

Methods. The samples were made as follows. D_2O (7.5 g) was transferred to a 20 mL glass vial containing a magnetic stirring bar. Next, 0.5 mL of the hydrocarbon was added, and the vial was tightly sealed. The mixture was stirred for 24 h, and allowed to separate for 48 h. A laser beam (635 nm) was shone through the samples. No scattering of the beam was observed, indicating that there were no large droplets of hydrocarbons dispersed in the aqueous hydrocarbon solutions. Finally, 200 μL of the solutions were carefully transferred to susceptibility matched NMR tubes (BMS-005, Shigemi, Tokyo), by means of a syringe. The samples were taken from close to the bottom of the glass vials.

All of the experiments were carried out at 25 °C on 300 (for cyclohexane and *o*-xylene) and 500 (for *n*-pentane and *n*-hexane) MHz Bruker DRX 300 and DMX 500 spectrometers, respectively. Inverse detection probes with *z*-gradient coils were used. The gradient strengths were 0.05 T (mA)$^{-1}$ at 300 MHz and 0.07 T (mA)$^{-1}$ at 500 MHz, respectively.

Hahn-echo diffusion experiments were used,[7] using typically 2 ms rectangular gradient pulses and 70 ms between the leading edges of the gradient pulses. The gradient amplitude was varied and typically 15 values were used in one determination. To avoid saturation of the receiver by the high intensity of the water peak (from HOD), the water resonance was presaturated by means of soft pulses prefixed to the Hahn sequence. The waiting time between successive accumulations was set to 10 T_1. The low solubility of the hydrocarbons in water made it necessary to use extensive signal accumulation. For the compound with the lowest solubility, *n*-hexane, approximately 30 h of signal averaging was used.

The values of the diffusion coefficients were obtained by least-squares fits of eq 1 to the data

$$E_\Delta(k) = e^{-kD} \tag{1}$$

Here $E_\Delta(k)$ is the (normalized) NMR signal intensity and $k = (\gamma\delta g)^2(\Delta - \delta/3)$ where γ is the gyromagnetic ratio, δ the length of the gradient pulses, Δ is the distance (from leading edge to leading edge) between the gradient pulses, g the gradient amplitude, and D, is the diffusion coefficient. In writing eq 1 it is assumed that the signal intensity of the data-point with zero gradient is unity.

Error analysis was performed using the Monte Carlo technique as outlined in ref 8. All quoted errors correspond to an 80% confidence interval, taking only random errors into account.

Results and Discussion

The results obtained for the diffusion coefficients are given in Table 1, where we also give some relevant physical properties

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TABLE 1: Obtained Values for the Diffusion Coefficients for Four Hydrocarbons in Water and Some Relevant Physical Properties of the Studied Molecules

molecule	solubility[a] (10^{-3} moles (kg water)$^{-1}$)	η[b] (10^{-3} kg (ms)$^{-1}$)	D_{bulk}[c] (10^{-9} m^2 s^{-1})	V (Å^3)/R (Å)[d]	D_w[e] (10^{-9} m^2 s^{-1})	R (Å) from eq 2, with $C = 4$
n-pentane	0.535 ± 0.052	0.225	5.72	192.8/3.6	0.86 ± 0.10	3.5
n-hexane	0.110 ± 0.016	0.294	4.26	218.5/3.7	0.85 ± 0.33	3.5
c-hexane	0.655 ± 0.107	0.95	1.42	180.5/3.5	0.77 ± 0.06	3.9
o-xylene	1.651 ± 0.075	0.764	1.45	201.3/3.6	0.70 ± 0.06	4.3

[a] Solubilities from ref. 11 [b] Viscosities from ref. 14 [c] Values of the diffusion coefficients for the pure liquids. Data from refs. 15 and 16 and this work (*o*-xylene). [d] Molecular volumes from ref. 17 and radii from $R = (3V/4\pi)^{1/3}$. [e] Diffusion coefficients of the hydrocarbons in (heavy) water.

of the studied molecules. It is interesting to note that the diffusion coefficients in water are relatively similar for the studied molecules, while the corresponding bulk values vary considerably. This is due to fact that the viscosities of the bulk liquids vary (cf. Table 1). The relation between the effective hydrodynamic (or Stokes) radius of a diffusing molecule, R (N.B. this is not necessarily equal to the molecular radius), the viscosity, η, and the diffusion coefficient is given by the Stokes−Einstein equation:

$$D = \frac{kT}{C\pi\eta R} \tag{2}$$

where C is a constant that takes the value 4 or 6 for slip or stick boundary conditions, respectively.[9] Since the molecular volumes of the studied molecules are reasonably similar, it follows that their diffusion in water should be similar. We recall that for moderate deviations from spherical shape, the translational diffusion coefficient is mainly determined by molecular volume.[10] It should be noted that the Stokes−Einstein equation applies for spherical molecules diffusing in a continuum. This condition is somewhat violated in the present context, since the size of a water molecule is roughly half of the size of the hydrocarbons studied. However, eq 2 is often used successfully even in the description of diffusion of one-component liquids (such as water molecules diffusing in water).

Unfortunately, it was not possible to obtain the diffusion coefficient for *n*-heptane, the next member in the series of *n*-alkanes, since its solubility is a factor of 40 lower than for *n*-hexane.[11] However, using the data for *n*-pentane and *n*-hexane we can produce a reasonable estimate for the values of the diffusion coefficients for the series of *n*-alkanes. We proceed in the following way. While eq 2 is expressed in terms of the radius of the diffusing species, the relation between the (known) molecular volume, V, and R is not obvious, as it depends on the molecular shape and intermolecular interactions. It should be noted though that the radii calculated from eq 2 with $C = 4$ are reasonably close to the values obtained from the molecular volumes assuming spheres, cf. Table 1. If the molecules are indeed modeled as spheres then R should be proportional to $V^{(1/3)}$ and thus to the molecular weight as $\mathrm{MW}^{(1/3)}$ (this follows since the molecular volumes of *n*-alkanes depend linearly on the MW). For such a situation D would scale with the molecular weight as $\mathrm{MW}^{(-1/3)}$.

A different scenario holds for a random coil polymer in a solvent under Θ conditions. Here D scales with $\mathrm{MW}^{(-1/2)}$. This scaling relation has been shown to be valid for oligomers containing just a few monomers.[12]

In Figure 1 we present diffusion coefficients for *n*-alkanes starting with butane and ending with *n*-hexadecane. The values have been obtained using the two scaling relations presented above. The unknown parameters of the scaling relations have been determined using our data for *n*-pentane (for which the data point has considerably less error than that of *n*-hexane). It should also be mentioned that the data corresponds to that for water as we have multiplied the experimental data by the ratio of the viscosity for water and heavy water ($\eta_{D_2O}/\eta_{H_2O} = 1.23$).[13]

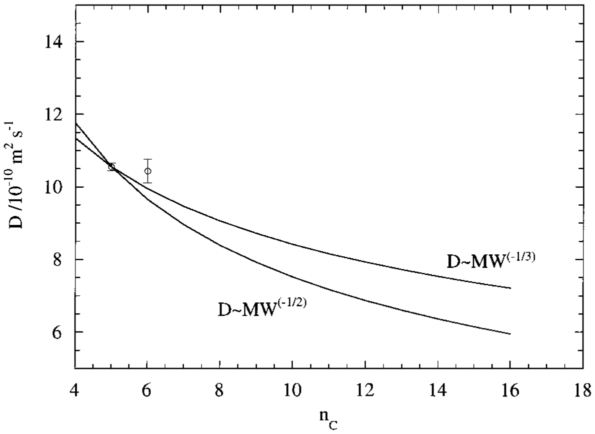

Figure 1. The predicted values of the self-diffusion coefficients for *n*-alkanes (n_C denotes the number of carbons in the alkanes) using two scaling relations between D and the molecular weight (see text for details). Also included are experimental data for *n*-pentane and *n*-hexane.

Although the experimental data set needed to “calibrate” the scaling relations is limited, we feel that the values of the diffusion coefficients for *n*-alkanes in water should be found within the boundaries set by the two scaling relations. We note that if the scaling relations are used to compute the value of the self-diffusion coefficient for methane we obtain 1.7×10^{-9} m^{2}s^{-1} (from $D \sim \mathrm{MW}^{(-1/3)}$) and 2.2×10^{-9} m^{2}s^{-1} (from $D \sim \mathrm{MW}^{(-1/2)}$), respectively. Laaksonen and Stilbs have presented values for the diffusion of methane in water.[6] The value they present at 25 °C is $(2.2 \pm 0.2) \times 10^{-9}$ m^{2}s^{-1}, a value which lends support for the conjecture underlying the data in Figure 1.

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