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ARTICLES

Diffusion of Water in Liquid and Supercritical Carbon Dioxide: An NMR Study

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Tracer diffusion coefficients have been measured for water in liquid and supercritical carbon dioxide (CO_2) from 10 to 35 °C in the pressure range from 130 to 300 bar. The measurements were performed by means of pulsed field gradient NMR (PFG-NMR) methods incorporating compensation for electrical eddy currents and mass convection. In the NMR active volume, the sample was contained in a 1.4 mm i.d. PEEK tube with provisions for recirculation and external sample loading. The diffusion coefficients are consistent with the Stokes−Einstein equation with "slip" boundary conditions and a hydrodynamic radius of 1.7 Å for water in the high temperature and low density region. In the low temperature and high density region, the diffusion coefficients indicate either a trend toward "stick" boundary conditions or the dynamic clustering of water molecules.

Introduction

Liquid and supercritical carbon dioxide (CO_2) have received considerable attention as environmentally benign solvents. The primary limitation to the widespread use of this solvent is its inability to dissolve both polar and hydrophobic solutes. This has led to the search for surfactants that can help dissolve materials of interest. Recently, surfactants with the ability to stabilize water-in-CO_2 (W/C) microemulsions have been reported.[1,2] However, it has been noted that the analysis of W/C microemulsions requires that the behavior of water molecularly dissolved in CO_2 be taken into account.[3] The solubility of water in CO_2 at various temperatures and pressures has been available since the classic work of Wiebe,[4] but the diffusion coefficient of water in CO_2 has apparently not been reported.

In this article we report tracer diffusion coefficient measurements of water in CO_2 from 10 to 35 °C in the pressure range 130 to 300 bar by means of pulsed field gradient NMR (PFG-NMR) methods. These measurements are possible because of the availability of a high pressure cell with sufficient volume to permit NMR signals to be acquired with high signal-to-noise ratios and a CO_2 handling system that permits the injection of appropriate volumes of water. The temperature range is limited at the low end by deviations from simple diffusion behavior that complicate the analysis of data and at the high end by mass convection effects. Even so, the range presented is very useful for the study of microemulsions and many other applications.

Experimental Section

SFC/SFE grade CO_2 (Air Products, >99.9999%) and distilled water were used throughout. At room temperature (~20 °C) distilled water (15 μL) was loaded into a variable volume cell and then CO_2 (~12 mL) was injected into the system at 138 bar. The pressure and volume of injected CO_2 were controlled by an automatic syringe pump (Model 260D, Isco, Inc.). The high pressure NMR setup has previously been described;[3] however, for this work the fused silica capillary bunch was replaced with a PEEK sample cell that is illustrated in Figure 1. The variable volume mixing cell and the stainless steel

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TABLE 1

T (°C)	pressure (bar)	diffusion coeff (10^{-8} m^2 s^{-1})	T (°C)	pressure (bar)	diffusion coeff (10^{-8} m^2 s^{-1})	T (°C)	pressure (bar)	diffusion coeff (10^{-8} m^2 s^{-1})
10	132.0	1.32	25	133.3	2.07	35	134.7	2.81
	148.3	1.27		148.3	1.88		149.0	2.63
	162.6	1.24		164.6	1.72		163.3	2.31
	189.8	1.16		189.1	1.61		189.1	2.20
	217.7	1.11		217.7	1.57		214.3	2.02
	244.9	1.07		241.5	1.52		242.8	1.94
	268.7	1.01		272.8	1.41		268.7	1.89
	298.0	0.96		297.3	1.36		298.0	1.82

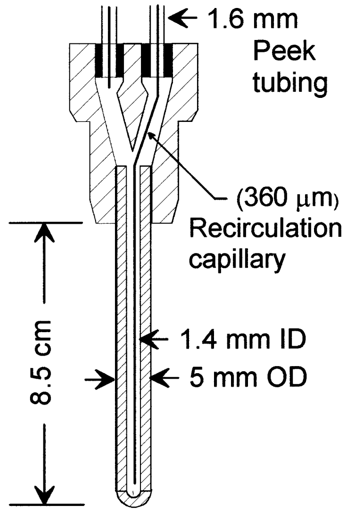

Figure 1. PEEK sample cell (see text).

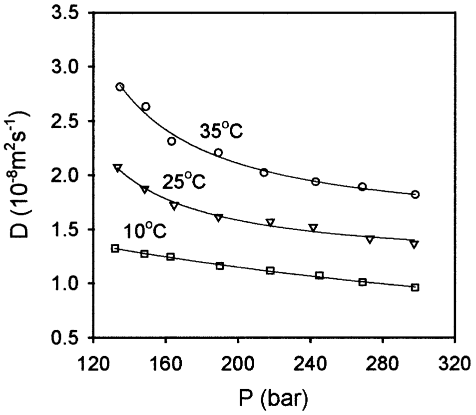

Figure 2. Tracer diffusion coefficient (D) versus pressure (P) for water in carbon dioxide.

transfer tubing were maintained at room temperature (~21 °C). The stainless tubing was connected to the PEEK sample cell with PEEK capillary tubing. The temperature of the PEEK sample cell was controlled to ±0.1 °C with a Bruker BVT 3000 variable temperature unit. The heating/cooling gas was nitrogen and the flow rate was 670 L/h.

In contrast to the PEEK cells previously reported,[5] we used a precision bore tube (i.d. = 1.4 mm) that was prepared with a Drill Masters water-cooled gun drill. The cap on the PEEK cell contains two ports for input and output of samples. From these ports PEEK tubing connects the sample cell with the high pressure system. A PEEK capillary tube (o.d. = 360 μm, i.d. = 150 μm) extends from the input port to the bottom of the sample tube, and another PEEK capillary tube extends from the output valve into the upper part of the sample tube. The placement of these two capillaries permits convenient recirculation of the sample.

The larger sample volume relative to the folded capillary cells yields about a 10-fold increase in the signal intensity and decreases the problems related to adsorption on the walls. Also, the removal of the folded and crimped capillary bundle greatly reduces shear forces that can disrupt structures in some samples, e.g., microemulsions. Unfortunately, the samples in the larger cell are more susceptible to Rayeigh-Benard instabilities and the resulting mass convection.[6]

^{1}H NMR measurements were performed with a Bruker Avance 500 spectrometer equipped with a 5 mm Nalorac diffusion probe. Typically, 16k data points were acquired for a 10 ppm (5000 Hz) spectral width and 16 transients were accumulated to achieve satisfactory signal-to-noise ratios. The free induction decays were zero-filled to 32k after exponential multiplication to give a line-broadening of 5 Hz. The diffusion measurements for H_2O in CO_2 required the use of a convection-compensated pulse sequence.[7] In the notation of Jerschow and Müller[7] the parameters were as follows: gradient duration $\delta/2 = 1$ ms, gradient amplitude $g = 0.0206-0.206$ T/m; gradient spacing $\tau_1/2 = \tau_2/2 = 1$ ms, the first storage period $T/2 = 4.67$ ms; corrected diffusion time $\Delta_r = T + 4\delta/3 + 5\tau_1/4 + \tau_2/4 = 15$ ms, eddy-current delay $T_e = 5$ ms, repetition time = 5 s. Finally, 32 transients were acquired after 8 dummy scans to achieve steady-state conditions.

The diffusion coefficients were then obtained by nonlinear regression with the following equation:

$$S(q) = S(0)\exp(-Dq^2\Delta_r) \quad (1)$$

where $S(q)$ is the signal intensity, $q = \gamma g\delta$, γ is the gyromagnetic ratio, and g is the gradient amplitude, and with the parameters listed above the experimental variable $x = \Delta_r q^2$ took on 16 exponentially spaced values[8] ranging from 2.35×10^2 to 2.35×10^4 s/cm^2. The data at all temperatures could be fit by the single-exponential function in eq 1; however, the 10 °C data show positive deviations for the three data points with $x < 5.88 \times 10^2$ s/cm^2. These deviations do not significantly affect the analysis and represent only about 5% of the signal at $x = 0$, but they are reproducible.

Results and Discussion

The tracer diffusion coefficients for H_2O were measured at 10, 25 and 35 °C and at pressures varying from 130 to 300 bar. The results are tabulated in Table 1 and plotted in Figure 2. In an attempt to understand the magnitudes of the diffusion coefficients we have turned to the Stokes−Einstein equation:

$$D = \frac{k}{c\pi R_h}\left(\frac{T}{\eta}\right) \quad (2)$$

Here D is the tracer diffusion coefficient, k is the Boltzmann constant, R_h is the hydrodynamic radius of the solute, T is the temperature, η is the viscosity of the solvent, and c is a parameter that takes on the values 4 and 6 for “slip” and “stick”

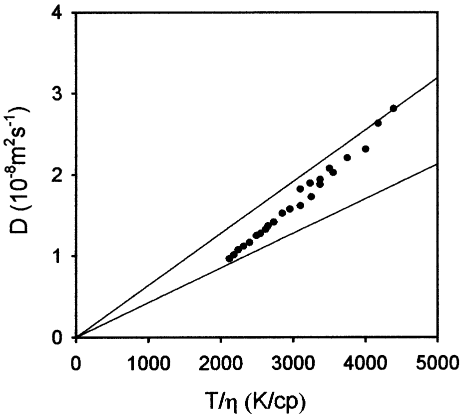

Figure 3. Tracer diffusion coefficient (D) versus T/η.

boundary conditions, respectively. It is difficult, if not impossible, to justify this equation at the molecular level;[9] however, its success in relating experimental diffusion coefficients to molecular radii is well-known.[10] Indeed, a plot of D versus T/η (Figure 3) supports the form of eq 2.

In situations where the solute molecules have similar or smaller sizes than the solvent molecules, "slip" boundary conditions are likely to apply.[11] With the additional assumption that high temperatures and low viscosities favor "slip" conditions, we have used the point having the largest value of T/η with $c = 4$ in eq 2 to obtain $R_h = 1.72$ Å. A model of water built with covalent radii and van der Waals' radii for the atoms yields an all inclusive radius of approximately 2 Å whereas a simple computation based on the volume occupied by a molecule in liquid water gives about 1.5 Å. The upper and lower straight lines from the origin in Figure 3 were calculated with eq 2 assuming a constant value of R_h with c equal to 3 and 6, respectively. One interpretation of the data in Figure 3 is that the c varies from 4–6 as T/η is decreased, showing that "stick" conditions are favored at the lower values. Another possibility, that cannot be ruled out, is that water molecules are involved in dynamic aggregation processes. Lower temperatures and higher viscosities may favor larger water clusters and slower exchange between molecularly dissolved water and associated water molecules. We hope to resolve this problem with detailed studies at temperatures below 10 °C.

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