J. Phys. Chem. A **1999,** *103,* 448−450

Self-Diffusion of Supercooled Water to 238 K Using PGSE NMR Diffusion Measurements

William S. Price,* Hiroyuki Ide, and Yoji Arata

Water Research Institute, Sengen 2-1-6 Tsukuba, Ibaraki 305-0047, Japan

Received: September 29, 1998; In Final Form: December 3, 1998

The translational self-diffusion coefficients of supercooled water at atmospheric pressure were examined using pulsed-gradient spin−echo NMR diffusion measurements down to 238 K. As the temperature decreased, the diffusion behavior became distinctly non-Arrhenius. It was found that the diffusion behavior when plotted in an Arrhenius form was well-described by a Vogel−Tamman−Fulcher-type relationship in the temperature range from 298 to about 242 K. However, a fractional power-law-type equation was found to provide a better fit that extended over the entire measured temperature range. Below this temperature range, the diffusion coefficient decreased rather steeply, and at 238 K, the diffusion coefficient was 1.58×10^{-10} m^2 s^{-1}, the lowest value of the water diffusion coefficient so far determined. At this temperature the activation energy for the diffusion was found to be of the order of 44.4 kJ mol^{-1}. The data presented here should allow theoretical models of water to be more stringently tested.

Introduction

The study of supercooled water has a long history,[1,2] and the anomalous behavior is still not well understood,[3−7] although it is thought to originate from long-ranged structural correlations in the random and transiently hydrogen-bonded network that develops at low temperatures.[8] Despite its fundamental importance, experimental measurements of the diffusion coefficient of supercooled water have attracted surprisingly little attention[9] given the number of theoretical studies in the field. A major impediment to the study of supercooled water is the technical difficulties involved in measuring diffusion while water is in a metastable state.[1] In 1972, Pruppacher[10] measured the water diffusion down to 248 K at ambient pressure using tritium as a tracer. However, the low reliability of the results of Pruppacher at room temperature places some doubt on the accuracy of his measurements at low temperature.[9] Also in 1972, Gillen et al.[11] measured the diffusion coefficient down to 242.5 K using the steady-gradient spin−echo method. Both studies showed that the activation energy increased steeply with decreasing temperature. Gillen et al.[11] reported a value of the activation energy for diffusion, E_A, of 46 kJ mol^{-1} at 242 K. Angell et al.[12] have noted that the values by Gillen et al. obey an equation that predicts that the water diffusion coefficient approaches 0 at 228 K. In later studies, Prielmeier et al.[5,8] studied the pressure dependence of diffusion in supercooled water, which included measurements at atmospheric pressure down to 252 K.

In the current study, translational self-diffusion measurements were performed using the pulsed-gradient spin−echo (PGSE) NMR method. The theoretical and experimental aspects of the PGSE NMR method have recently been reviewed.[13−15] One particular advantage of the PGSE NMR method over the steady-gradient technique is that it allows the simultaneous determination of the diffusion coefficient of more than one species. Further, the temperature dependence of the chemical-shift difference between the methanol methyl and −OH groups was used as an internal temperature standard in the same NMR sample tube (NB the water and methanol compartments were separated).

Materials and Methods

The starting material for the preparation of the water samples was water that had passed through a MilliQ reverse osmosis system (Milli-RX12, Nihon Millipore Ltd, Yonezawa, Japan). Next, this water was passed through a 0.05 μm polycarbonate membrane (Coster Scientific Corp., MA). For the diffusion measurements, a small volume of water (~0.5 μL) was drawn into a fine glass capillary (0.13 mm i.d.; Nihon Rikagaku Kikai Co. Ltd. Tokyo) and sealed. The small volume afforded a very low freezing temperature. For the NMR measurements, a few of these capillaries and a similarly made capillary containing absolute methanol (Sigma, St. Louis, MO) were placed into a 5 mm NMR tube. The methanol was used as supplied, and the sealing of the capillary was accomplished as quickly as possible to minimize moisture absorption.

^{1}H PGSE NMR experiments were performed at 300 MHz using a Bruker DRX 300 (Bruker, Karlsruhe, Germany) equipped with a 5 mm inverse probe with a single (i.e., z) axis shielded magnetic field gradient. The current for the gradient was provided by a Bruker BGPA10 constant current amplifier. The strength of the gradient was first calibrated using the known diffusion coefficient of water of 2.30×10^{-9} m^2 s^{-1} at 298 K.[9,16] The temperature in the NMR probe was calibrated using the temperature-dependent chemical shift of methanol.[17] The actual equations used to relate the chemical shift difference between the methanol methyl and hydroxyl group ($\Delta\delta$ in ppm) were (Bruker)

$$T\,(\mathrm{K}) = 468.1 - 108.6 \times \Delta\delta \text{ for } 265{-}313\ \mathrm{K} \qquad (1)$$

and

$$T\,(\mathrm{K}) = 498.4 - 124.98 \times \Delta\delta \text{ for } 220{-}270\ \mathrm{K} \qquad (2)$$

The cooling rate used between temperatures at which diffusion coefficients were measured was 0.3 K/min for temperatures above 260 K and 0.2 K/min for temperatures below this. Before starting a measurement, more than 10 min was allowed for the temperature to stabilize.

10.1021/jp9839044 CCC: $18.00 © 1999 American Chemical Society
Published on Web 01/12/1999

TABLE 1: Measured Values of the Self-Diffusion Coefficient of Water

T (K)	$D/10^{-9}$ (m^2 s^{-1})	T (K)	$D/10^{-9}$ (m^2 s^{-1})
298.15	2.30	253.1	0.469
297.3	2.16	250.8	0.414
292.6	1.89	249.8	0.385
287.1	1.73	248.6	0.363
286.8	1.67	247.4	0.337
281.2	1.44	246.3	0.320
275.8	1.21	245.1	0.296
268.6	0.974	243.9	0.276
268.2	0.941	242.3	0.247
262.3	0.707	241.1	0.222
260.1	0.650	239.8	0.204
257.7	0.588	238.6	0.175
255.3	0.531	237.8	0.158

The Hahn spin−echo pulse sequence containing a "square" magnetic field gradient pulse in each τ period was used for the translational diffusion measurements. For a single diffusing species, the echo signal attenuation, E, is related to the experimental parameters and the diffusion coefficient, D, by[14,18]

$$E = \exp(-\gamma^2 g^2 D \delta^2 (\Delta - \delta/3)) \qquad (3)$$

where γ is the gyromagnetic ratio, g is the magnitude, and δ (not to be confused with the chemical shift) is the duration of the gradient pulses, Δ (not the Δ in eqs 1 and 2) is the separation between the leading edges of the gradient pulses. The diffusion coefficients were determined by fitting eq 3 to the spin−echo attenuation data based on the integral of the resonance in question. The experimental parameters used were $\Delta = 30$ ms and $\delta = 4$ ms, and g was incremented in the range from 0 to 0.5 T m^{-1}. Typically at least 10 points (i.e., different values of g) were used at each temperature and four scans were averaged for each value of g. The accuracy of each diffusion measurement should be within 1%.[19]

Results and Discussion

A major problem in conducting experiments in a superconducting magnet is to reliably calibrate the temperature. Generally, only a thermocouple is used which is positioned in the air/cooling gas flow before the sample. However, it is well-known that a thermocouple can be a very inaccurate guide to temperature and does not faithfully reflect the temperature *in* the sample, especially at temperatures away from ambient.[15] Consequently, we decided that the most prudent approach was to place a methanol capillary next to the water-containing capillaries so that the temperature in the NMR tube could be accurately gauged. A ^{1}H spectrum of the absolute methanol-containing capillary showed only the methyl and −OH resonances with no residual water being detected. The feedback system on the spectrometer temperature control unit was carefully set, and the temperature uncertainty is estimated to be ±0.2 K at most. The use of such small capillaries meant that any temperature gradients present should be very small—on either its effects on the measured water self-diffusion coefficients or on the temperature measurement using the methanol chemical shifts.

Our results for the diffusion coefficient determination are shown in Table 1. It should be noted that in our data we defined the diffusion coefficient at 298.15 K to be 2.30×10^{-9} m^2 s^{-1}. This value is the most well-defined value of the self-diffusion coefficient of water.[9] This was the basis for the calibration of g. An Arrhenius plot of the data is given in Figure 1. In the present work we measured the diffusion along the long axis of the capillaries (i.e., the direction of the gradient), thereby avoiding any possibility of restricted diffusion effects which otherwise would have greatly complicated the determination of accurate diffusion coefficients from the PGSE data.[13,14,20] It is also probably worthwhile to briefly discuss the possibility of surface effects influencing the translational diffusion coefficient of the water. In the present experiments, the diameter of the very fine capillaries used (i.e., 0.13 mm = 13 000 Å) is still relatively enormous compared to the dimensions of a water molecule. Further, by noting the time scale of the PGSE diffusion measurement (i.e., $\Delta = 30$ ms) and using the room-temperature diffusion coefficient of water cited above, we can calculate an upper limit for the mean-square displacement of about 2000 Å. Thus, it can be realized that any surface effects on the diffusion coefficient must be small. Indeed, previously published supercooled water diffusion data[11] which was obtained using different diameter capillaries gives rather good agreement with our data over the temperature range common to both data sets (see below).

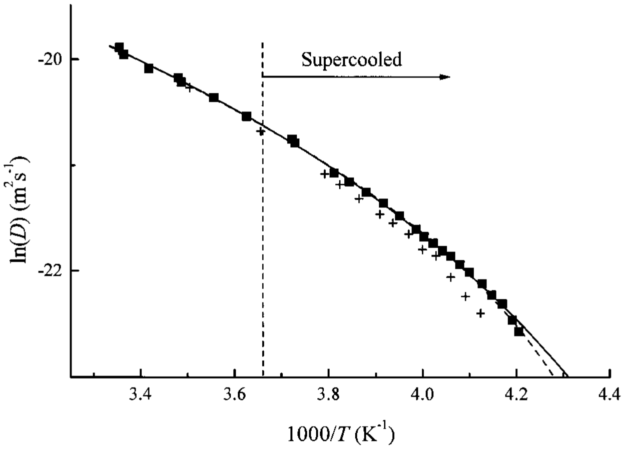

Figure 1. Arrhenius plot of the diffusion coefficient of H_2O versus temperature. The values obtained in the current work are marked by squares, and those from Gillen et al.[11] are denoted by crosses. The errors in the current measurement are smaller than the symbols denoting the data points. Although the two data sets have different offsets (i.e., at 298.15 K we have $D = 2.30 \times 10^{-9}$ m^2 s^{-1} and Gillen et al. obtain $D = 2.23 \times 10^{-9}$m^2 s^{-1}), the overall trend is similar but diverges more at low temperatures. The dashed vertical line denotes 273 K. The results of regressing the VTF equation (i.e., eq 4) onto the data is shown by the solid line, and similarly the results of regressing the FPL equation (i.e., eq 5) onto the data are denoted by the dashed line.

We found that above 242 K, our data was well described by an empirical Vogel−Tamman−Fulcher (VTF)-type relationship

$$D = D_0 \exp\{-B/(T - T_0)\} \qquad (4)$$

where T is temperature, T_0 is often related to the glass transition temperature, and D_0 and B are fitting constants. By regressing eq 4 onto the data, the following values were obtained, $D_0 = 4.00 \pm 0.87 \times 10^{-8}$ m^2 s^{-1}, $B = 371 \pm 45$ K^{-1}, and $T_0 = 169.7 \pm 6.1$ K. The result is plotted in Figure 1. A dynamic scaling behavior (i.e., fractional power law; FPL) of the form

$$D = D_0 T^{1/2}\left(\frac{T}{T_S} - 1\right)^{\gamma} \qquad (5)$$

where γ (not the gyromagnetic ratio) is a fitting parameter and T_S represents a low-temperature limit where D extrapolates to zero was also regressed onto the data (see Figure 1) and found to provide a better fit to the data at lower temperatures than the VTF equation. This power-law behavior constitutes the grounds for the stability limit conjecture, which, assuming a true

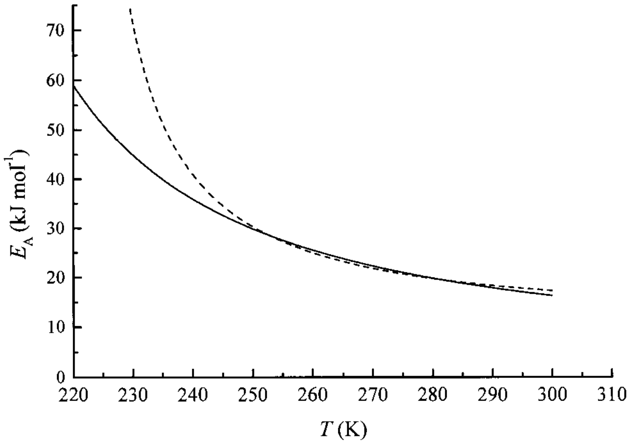

Figure 2. Plot of E_A for diffusion according to the differential of the VTF equation (—) and the FPL equation (- - -). The curve derived from the VTF equation underestimates E_A for temperatures below 240 K, however, the curve derived from the FPL equation rapidly increases below about 250 K.

singularity at T_S, predicts that there is no continuity of states between the liquid and solid states.[21,22] The parameters of best fit are given by $D_0 = 7.66 \pm 0.24 \times 10^{-8}$ m^2 s^{-1}, $T_S = 219.2 \pm 2.6$ K, and $\gamma = 1.74 \pm 0.10$. Our results for the two series of regressions are in reasonable agreement with those obtained for the FPL and VTF equations by Prielmeier et al.,[5,8] who performed regressions on diffusion data only down to 242 K and for the FPL equation by Lamanna et al.[6] We note that the values of T_S obtained by Prielmeier et al. ($T_S = 220$ K in ref 5 and $T_S = 223$ K in ref 8, note the $T^{1/2}$ term in eq 5 was omitted in determining the latter value) and Lamanna et al.[6] ($T_S = 225$ K) are in close agreement with the value that we obtained. Interestingly, the value that we obtained for T_S is more than 7 K below that obtained by Speedy[23,24] by extrapolation from conductivity measurements down to 241 K.

Also shown in Figure 1, for comparison, are the results of Gillen et al.,[11] however, they determined the diffusion coefficient at 298.15 K to be 2.23×10^{-9} m^2 s^{-1}. The two data sets are quite similar, however, at low temperatures the two data sets diverge with the slope of Gillen et al.'s data increasing more rapidly than ours. Nevertheless, we succeeded in obtaining the lowest recorded self-diffusion coefficient of water (237.8 K) 1.58×10^{-10} m^2 s^{-1} at ambient pressure, which was considerably below the previous record set by Gillen et al.[11] of 1.87×10^{-10} m^2 s^{-1}. Thus, we have extended the lower limit of the measurement of the diffusion coefficient of water much closer to the apparent limit (i.e., homogeneous nucleation temperature, T_H) of around 231 K for supercooled water.[2] Since T_H is well above the apparent value for T_S, any direct experimental observation of T_S is precluded.

By taking the derivative of eqs 4 and 5, we are able to obtain the apparent activation energy for the diffusive process with temperature; see Figure 2. It can be seen from the plot that the activation energy increases with decreasing temperature and exceeds 36 kJ mol^{-1} (8.6 kcal mol^{-1}) if E_A is determined from the VTF equation or 41 kJ mol^{-1} (9.8 kcal mol^{-1}) if determined from the FPL equation for temperatures below 240 K. In fact, by using the lowest two temperatures we can calculate that at around 238 K, E_A is of the order of 44.4 kJ mol^{-1} (10.6 kcal mol^{-1}). At lower temperatures, the values extrapolated for E_A from the two different equations diverge dramatically since at T_S (i.e., 219.2 K) the FPL equation implies a singularity.

Our results show that the diffusion of supercooled water follows a smooth trend down to at least 238 K with the data, particularly at the lowest temperatures, being better described by a fractional power law than the VTF equation. This further supports the view that water is not approaching a glass transition[5] and, thus, that there is no continuity of states between the supercooled liquid and solid phases. We note, however, that Lamanna et al.[6] have recently presented a model which suggests the possible existence of a continuity of states between the supercooled water and ice phases. Work in this laboratory is currently aimed at investigating ways to measure diffusion at even lower temperatures and to increase the accuracy of the temperature measurements.

References and Notes

(1) Angell, C. A. In *Water and Aqueous Solutions at Subzero Temperatures*; Franks, F., Ed.; Plenum: New York, 1982; pp 1−81.
(2) Angell, C. A. *Annu. Rev. Phys. Chem.* **1983**, *34*, 593−630.
(3) Stillinger, F. H. *Science* **1980**, *209*, 451−457.
(4) Poole, P. H.; Sciortino, F.; Essmann, U.; Stanley, H. E. *Nature* **1992**, *360*, 324−328.
(5) Prielmeier, F. X.; Lang, E. W.; Speedy, R. J.; Lüdemann, H.-D. *Phys. Rev. Lett.* **1987**, *59*, 1128−1131.
(6) Lamanna, R.; Delmelle, M.; Cannistraro, S. *Phys. Rev.* **1994**, *E49*, 2841−2850.
(7) Tanaka, H. *Nature* **1996**, *380*, 328−330.
(8) Prielmeier, F. X.; Lang, E. W.; Speedy, R. J.; Lüdemann, H.-D. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1111−1117.
(9) Weingärtner, H. *Z. Phys. Chem.* **1982**, *132*, 129−149.
(10) Pruppacher, H. R. *J. Chem. Phys.* **1972**, *56*, 101−107.
(11) Gillen, K. T.; Douglass, D. C.; Hoch, M. J. R. *J. Chem. Phys.* **1972**, *57*, 5117−5119.
(12) Angell, C. A.; Finch, E. D.; Woolf, L. A.; Bach, P. *J. Chem. Phys.* **1976**, *65*, 3063−3066.
(13) Price, W. S. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1996; pp 51−142.
(14) Price, W. S. *Concepts Magn. Reson.* **1997**, *9*, 299−336.
(15) Price, W. S. *Concepts Magn. Reson.* **1998**, *10*, 197−237.
(16) Mills, R. *J. Phys. Chem.* **1973**, *77*, 685−688.
(17) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679−680.
(18) Stejskal, E. O. *J. Chem. Phys.* **1965**, *43*, 3597−3603.
(19) Furó, I.; Jóhannesson, H. *J. Magn. Reson.* **1996**, *A119*, 15−21.
(20) Price, W. S.; Barzykin, A. V.; Hayamizu, K.; Tachiya, M. *Biophys. J.* **1998**, *74*, 2259−2271.
(21) Speedy, R. J. *J. Phys. Chem.* **1982**, *86*, 982−991.
(22) Speedy, R. J. *J. Phys. Chem.* **1982**, *86*, 3002−3005.
(23) Cornish, B. D.; Speedy, R. J. *J. Phys. Chem.* **1984**, *88*, 1888−1892.
(24) Speedy, R. J. *J. Phys. Chem.* **1987**, *91*, 3354−3358.