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LETTERS

Water Dynamics near a Dissolved Noble Gas. First Direct Experimental Evidence for a Retardation Effect

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Deuteron magnetic relaxation rates and self-diffusion coefficients measured by the ^1H spin-echo technique are reported for aqueous solutions of xenon in the temperature range from 273 to 333 K at pressures up to 6 MPa. The data enable the determination of the reorientational correlation time and self-diffusion coefficient of water in the first coordination sphere of xenon and provide the first direct experimental proof of a perceptible slowing down of these motions. At 298 K we find a retardation by a factor of 1.3 of rotational and translational motions in the first hydration shell of xenon above those in the bulk. The data are compared with the results of computer simulations and with estimates extracted from experimental data for alkyl groups in larger molecules. A comparison of results for rotational and translational motions shows that at high temperatures both are affected to the same degree. Below 298 K this strong coupling is lost. This phenomenon appears to be related to known anomalies of water in the supercooled regime, possibly associated with a thermodynamic singularity near $T_s = 228$ K. Xenon may shift T_s to higher temperatures.

1. Introduction

This work is part of a project using noble gases as test particles for probing the local structure and dynamics of liquids by NMR techniques. It follows studies on the self-diffusion of neon¹ and xenon² in water. There is widespread interest in the properties of noble gases in water, related to their use for modeling the hydrophobic hydration and mutual interaction of nonpolar groups in more complex molecules of biological interest. It is believed that these properties result from an ordering of water molecules near apolar solutes above that in pure water.³

One aspect of this picture is that translational and rotational motions of water molecules are retarded by apolar solutes. Experimentally, this was first observed by Hertz and Zeidler in magnetic relaxation studies on aqueous solutions of alcohols,

fatty acids, and other hydrophobic solutes.⁴ Such solutes possess apolar and polar groups, the effects of which can be qualitatively disentangled by studying homologous series. For a long time, more direct measurements with dissolved noble gases appeared to have little prospects, as low gas solubilities generate very small changes in the dynamics of water. General instrumental developments in NMR have, however, led to an increased experimental accuracy, and an attempt to detect such effects now seems more promising than expected previously. We present here first results for aqueous solutions of xenon between about 273 and 330 K.

2. Experimental Section

Samples. Samples of xenon in H_2O and D_2O at elevated pressure were prepared as described elsewhere.² At equilibrium, the accessible pressure range is limited by the precipitation of solid clathrates. For illustration, at 2 MPa the melting point of the clathrate is about 290 K. However, metastable samples can

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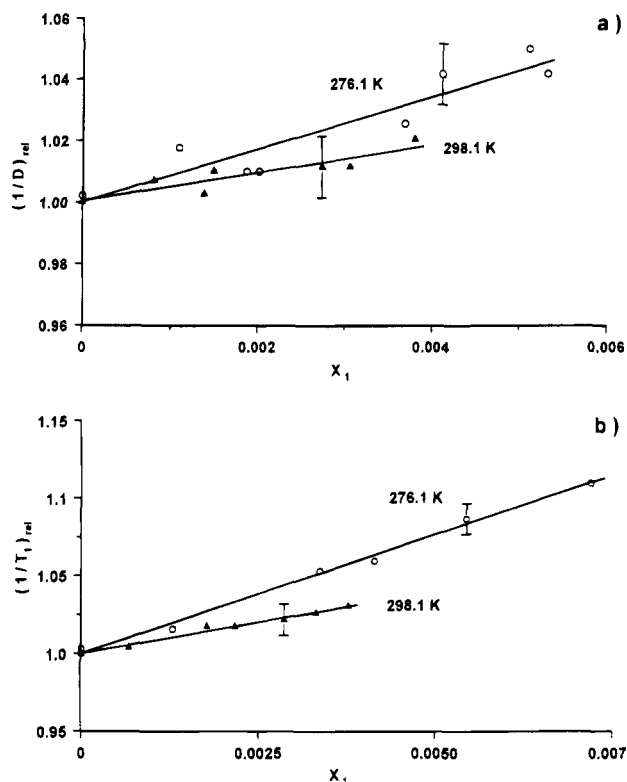


Figure 1. Concentration dependence of (a) the inverse self-diffusion coefficient $1/D$ of water (H_2O) and (b) the ^2D magnetic relaxation rate of water (D_2O) in aqueous solutions of xenon at two temperatures. x_1 is the mole fraction of xenon.

be easily prepared, and in our experiments metastable samples could be prepared at pressures up to 9 MPa. Xenon concentrations at the temperature of interest were calculated from the known solubilities⁵ and were also determined experimentally by recording the integrals of ^{131}Xe resonance signals.

Measurements. ^2D spin-lattice relaxation rates $(1/T_1)$ of D_2O were measured at 46.1 MHz with a Bruker pulsed FT-NMR spectrometer. Self-diffusion coefficients (D) of H_2O were measured by ^1H NMR with a home-built instrument using the pulsed field gradient technique.⁶ Sample temperatures were controlled to within 0.2 K by liquid thermostating of the probe. Each data point is an average over at least 10 measurements with a reproducibility of 1% or better.

3. Results and Data Evaluation

^2D magnetic relaxation rates of D_2O and self-diffusion coefficients of H_2O were determined as a function of the xenon concentration from about 273 to 330 K. The concentration dependence of $1/T_1$ and $1/D$ at 276 and 298 K is shown in Figure 1. The data are given as relative quantities $(1/T_1)_{\text{rel}} = (1/T_1)/(1/T_1)_0$ and $(1/D)_{\text{rel}} = D_0/D$, where subscript "0" refers to the properties of pure water. x_1 is the mole fraction of xenon. For illustration, a pressure of 5 MPa corresponds to a mole fraction of about $x_1 = 4 \times 10^{-3}$. It is seen that the addition of xenon leads to a variation up to the order of 3–10%, depending on the temperature, so that an experimental accuracy of at least 1% is needed to obtain meaningful results.

Theory relates ^2D relaxation rates to the correlation time τ_2 of the time correlation function of the second-order spherical harmonics for the reorientation of the O–D axis in D_2O through

$$\frac{1}{T_1} = \frac{3}{2} \pi^2 \chi_D^2 \tau_2 \quad (1)$$

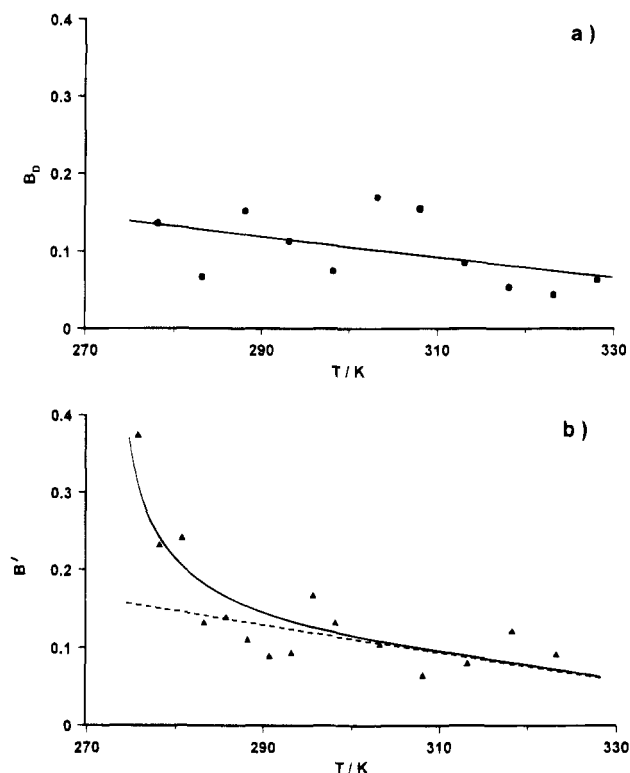


Figure 2. Temperature dependence of the coefficients B_D and B' as defined by eqs 2 and 3 in aqueous solutions of xenon. For comparison, the solid line in part a is shown as a dashed line in part b.

χ_D is the ^2D quadrupole coupling constant which for D_2O near 300 K possesses a temperature-independent value of 256 kHz.⁷ As in other studies of this type, its concentration dependence is assumed to be negligible.

For further data evaluation, it is useful to express the effect of xenon upon τ_2 and $1/D$ by molal increments, B' and B_D defined through the relative initial slopes of their concentration dependence. To this end, the concentration is expressed in the aqua molality scale \bar{m} (moles of solute per 55.5 mol of solvent) with $\bar{m} = 55.5x_1$, yielding⁸

$$B' = \frac{1}{\tau_{2,0}} \lim_{\bar{m} \rightarrow 0} \frac{d\tau_2}{d\bar{m}} \quad (2)$$

and

$$B_D = D_0 \lim_{\bar{m} \rightarrow 0} \frac{d(1/D)}{d\bar{m}} \quad (3)$$

B' or $B_D > 0$ means that molecular motions are retarded by a "structure-forming" solute. B' or $B_D < 0$ means an enhancement of molecular mobilities by so-called "structure breakers".

Figure 2 shows that xenon may be classified as a structure former. At 298 K we find $B' \approx B_D = 0.13$. Note that uncertainties in the primary data are magnified by an order of magnitude in B' and B_D . In the entire temperature range B' and B_D remain positive; also, we find $dB'/dT < 0$ and $dB_D/dT < 0$. We point out that B' refers to solutions in D_2O , while B_D values refer to solutions in H_2O . As H_2O and D_2O possess slightly different solvent properties, the comparison of rotational and translational dynamics requires a correction for the dynamic isotope effect. From our experience with other solutes, numerical agreement of B' in H_2O and D_2O is attained, if data for H_2O at 298 K are compared with data for D_2O at 305 K, corresponding to the widely accepted view that D_2O is "by about 7 K colder" than H_2O .

If in a two-state model water molecules are classified into bulk water with the properties of pure water and cosphere water, it is possible to estimate the retardation of molecular motions in the shell around xenon through⁸

$$\xi' = \frac{\tau_2^{\text{shell}}}{\tau_2^{\text{bulk}}} = 1 + \frac{55.5}{n_h} B' \quad (4)$$

and

$$\xi_D = \frac{D^{\text{bulk}}}{D^{\text{shell}}} = 1 + \frac{55.5}{n_h} B_D \quad (5)$$

We lack experimental knowledge about the first hydration number n_h of xenon entering into these expressions. As for argon the figure $n_h = 16$ deduced from neutron scattering data⁹ agrees with results from molecular dynamics (MD) simulations; we adopt the value $n_h = 21.5$ obtained in a MD simulation of xenon in water.¹⁰ A perfect clathrate-I structure yields $n_h = 23$.

Results for ξ' and ξ_D are shown in Figure 3. At 298 K we find a retardation by a factor of 1.3 in both translational and rotational motions. Any account for a retardation in the second hydration sphere would lead to a decrease in the figures for ξ' and ξ_D for the first shell. It is also possible to calculate from eqs 4 and 5 absolute values for τ_2 and $1/D$ in the shell, based on the data for pure water.⁷ These results are also shown in Figure 3.

4. Discussion

Our results provide the first experimental proof of a slowing down of the translational and rotational mobilities of water near a noble gas. We first compare our data with the MD results of Geiger et al.¹¹ and Zichi and Rossky.¹² Other MD studies^{10,13,14} generally support these MD results but do not contain data which can be directly compared with our results. Geiger et al.¹¹ have considered the dynamics of water molecules near a Lennard-Jones solute of a size of 3.1 Å, intermediate between neon and argon. Zichi and Rossky¹² have studied water dynamics near a solvent-separated krypton pair, thereby distinguishing between "exterior" water near one krypton atom of the pair and "interior" water between the krypton atoms. There is evidence for the existence of such solvent-separated hydrophobic pairs in real systems. Both studies suggest a retardation of translational and rotational motions of water molecules near the apolar solute, which is particularly strong in the case of "interior" water.¹² In total, the effects are of the same order of magnitude as observed experimentally, so that it would appear that the major experimental features are correctly captured by the MD studies.

There remain, however, some open problems on a more detailed level of interpretation. One concerns the coupling of rotational and translational motions. Geiger et al.¹¹ find $\xi' > \xi_D$ for the reorientation of the various molecular axis, while Zichi and Rossky¹² find for the dipolar axis $\xi_D > \xi'_z$. Neither result is confirmed by us at the temperatures of the simulations. Another problem concerns the dependence of water dynamics upon the solute size. MD results would indicate that for solute diameters between 3 and 4 Å the major features of shell water dynamics are the same. As the solubilities of noble gases decrease strongly in going from xenon to neon, it seems very difficult to study size effects. In the case of *solute* diffusion a surprisingly large size dependence has been found by us:¹² Near room temperature neon diffuses about 2.2 times faster than xenon and about 1.8 times faster than water itself.¹ This is certainly at contrast with MD results for a particle with 3.1 Å

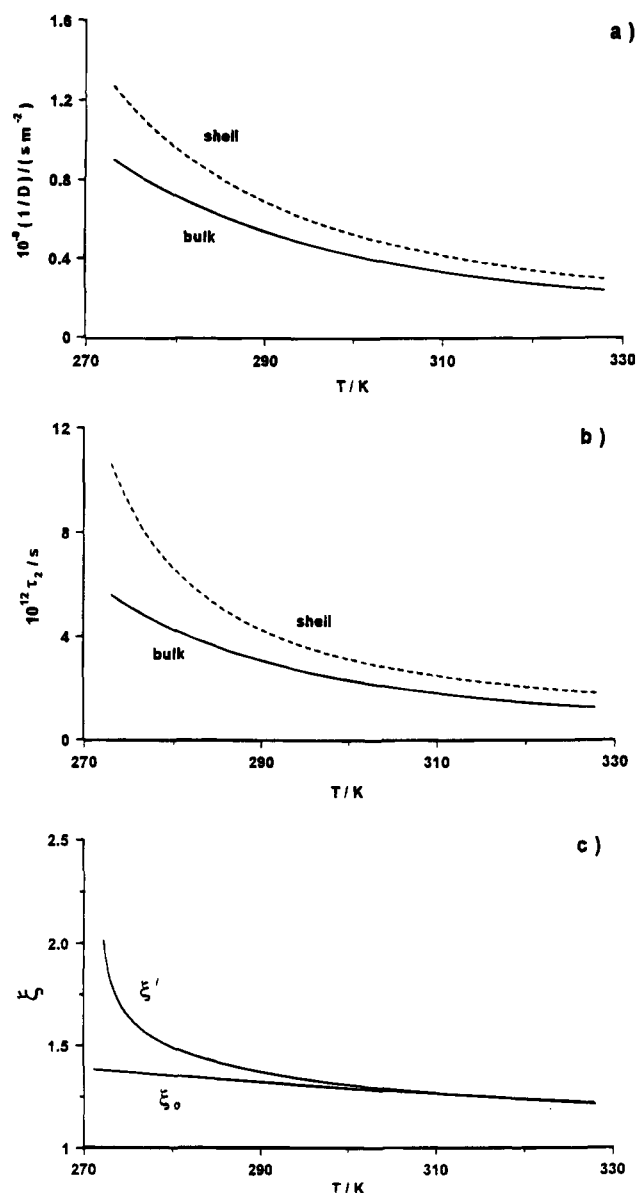


Figure 3. Temperature dependence of molecular motions of water in the first hydration shell of xenon as compared with those in the bulk: (a) inverse self diffusion coefficients; (b) reorientational correlation times τ_2 of the O-H axis; (c) ratios ξ_D and ξ' as defined in the text. The data for the water reorientation refer to D_2O , as calculated with $\tau_2 = 2.4$ ps at 298.1 K.⁷ The data for $1/D$ refer for pure H_2O with $D = 2.30 \times 10^{-9} m^2 s^{-1}$ at 298.1 K.⁶

which predict an equal mobility of the solute and water (albeit with low statistical significance for solute diffusion).¹³

We also note that the diameter of methane is about as large as that of xenon, so that xenon is often considered to represent the behavior of an apolar residue. It is therefore intriguing to compare our data with data extracted for water molecules near the apolar residues of amphiphilic molecules. This retardation was first noted in an NMR study of Hertz and Zeidler⁴ and in a dielectric relaxation study of Pottel and Kaatz.¹⁶ Since then, numerous similar experiments have resulted in more or less the same conclusion,¹⁷ and it is now believed that the motions of water molecules near alkyl groups are slowed down by a factor of 2 or 3,¹⁷ as qualitatively confirmed by a MD study of Rossky and Karplus¹⁸ on water dynamics near the methyl groups of a dipeptide. As compared with our results, these figures seem to be distinctly high. We may however note that, from an experimental point of view, any data analysis for amphiphilic molecules relies on an assumption for disentangling hydrophobic

and hydrophilic effects in the solute–water interaction and on an estimate of the fraction of water molecules in the cosphere of the residue. Neither aspect is understood in detail.

It remains to discuss briefly the effect of temperature upon the various quantities. One aspect is that $dB'/dT < 0$ and $dB_D/dT < 0$. It is easy to verify that in this case the effective activation energies are larger in the shell than in the bulk. This conforms to the picture that in the first shell molecular motions are more hindered than in the bulk, as already previously reported by Hertz and Zeidler for amphiphilic molecules.⁴ Another aspect is related to the rapid increase of B' , but not B_D , at low temperatures. The effect is significant, as shown by the slopes in the $1/T_1$ and $1/D$ plots of the primary data in Figure 1. It can be traced back to a pronounced increase of τ_2^{shell} , while for $1/D^{\text{shell}}$ this effect is obviously not present, as may be seen from Figure 3c. This means a decoupling of rotational and translational motions of water molecules near the apolar solute at low temperatures. We are not aware of any similar results for water in the literature. The results appear to be closely related to the peculiar properties of supercooled water. As noted by Speedy and Angell,¹⁹ some thermodynamic and dynamical properties of pure water appear to exhibit a singular behavior at the temperature $T_s = 228$ K. Stillinger has proposed that clathrate-forming solutes may displace T_s toward higher temperatures.²⁰ Hence, upon addition of xenon, peculiarities associated with this singular behavior might be observable already near 273 K. The decoupling of rotational and translational motions observed by us may represent an important new feature of the dynamics near T_s . Further experiments concerning this subject are currently conducted and will be discussed in a forthcoming paper.

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- (15) Strictly speaking, the data obtained by us refer to the reorientation of the OH axis in the water molecule, while MD simulations have mainly considered the motion of the dipolar axis. The work of Geiger et al.¹¹ shows that the retardation of water reorientation may be slightly different for various axes in the molecule, but the general picture is retained for all axes.
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