A quasielastic neutron scattering study of the dynamics of calcium chloride aqueous solution confined in Vycor glass

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ABSTRACT

Quasielastic neutron scattering was used to probe the diffusion of water molecules in 2.3 molal $CaCl_2$ solution confined in 100 % hydrated Vycor glass in the temperature range of 220 K to 260 K. We observed a gradual transition from the restricted diffusion regime at lower temperatures to unrestricted diffusion regime at higher temperatures. The diffusion parameters were compared with the data on pure water confined in Vycor available in the literature. We found that the effect of dissolved ions onto the diffusion dynamics of the water molecules in the solution was amplified by confinement by at least an order of magnitude compared to bulk form, even though the dissolved ions were found to have little effect on the spatial characteristics of the restricted diffusion process of water molecules. At 260 K, the local diffusion coefficient of water molecules in the H2O-CaCl2 confined in Vycor was only 6 % of the value reported for pure water confined in Vycor.

INTRODUCTION

Aqueous solutions play a prominent role in various geochemical and industrial processes. To date, the solutions in bulk form have attracted the most attention, even though in nature such solutions are typically confined in small pores of either mineral or biological matrices. While pure water in confinement has been investigated in numerous studies, the behavior of confined solutions remains unexplored territory.

Quasielastic neutron scattering (QENS) is a technique of choice for investigating the mobility of confined water. This is because of the large incoherent scattering cross section of hydrogen compared to other elements, which allows obtaining scattering spectra dominated by the scattering from hydrogen-containing species in confinement rather than from the confining matrix. However, to date QENS studies of confined liquids have concentrated mostly on pure H_2O. A few QENS studies of aqueous solutions that have been carried out mainly involved the solutions in bulk form.

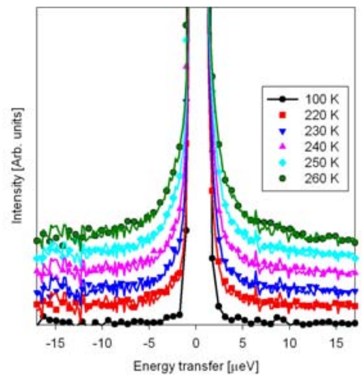
In this work, we present the results of our study of the translational dynamics of water in 2.3 molal $CaCl_2$ solution confined in nano-sized voids of porous Vycor glass. We chose calcium chloride because (1) it is one of the most common salts found in nature (2) is a key biological constituent, and (3) earlier QENS data on H_2O-$CaCl_2$ bulk solution indicate that the Ca^{2+}-H_2O subsystem is in the fast exchange limit. The latter means that the binding time of the first shell water molecules to the cation is short compared to the characteristic observation time, and during this observation time a water molecule experiences the entire range of environments present in the solution. In turn, this allows simple interpretation of the QENS data.

We used a high energy resolution neutron backscattering spectrometer to probe the translational dynamics on the timescale of hundreds of picoseconds in the temperature range of 220 to 260 K. We compare our results with the previously available QENS data on the dynamics of pure water confined in Vycor glass and bulk H_2O-$CaCl_2$.

- **TEM picture of the structure of nano-voids (white) in Vycor (black). The average pore size is about 5 nm. In our experiment, the pores were completely filled with 2.3 molal $CaCl_2$-H_2O solution (the molar ratio of H_2O to $CaCl_2$ was about 24.2).**

- **High Flux Backscattering Spectrometer (HFBS) at the NIST Center for Neutron Research. The spectrometer was operated with the resolution of 0.9 μeV (FWHM), and the dynamic range of ±17 μeV.**

DATA AND FITS

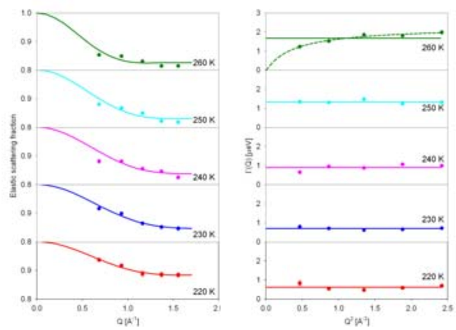


The temperature dependence of the data collected at Q = 1.16 Å^{-1} is shown as an example. The baselines of the spectra are vertically shifted for clarity. The elastic peaks are truncated to emphasize the QENS signal. The data were fit using the expression:

$$I(Q,E) = R(Q,E) \otimes \left(x(Q)\delta(E) + [1 - x(Q)] \frac{1}{\pi} \frac{\Gamma(Q)}{E^2 + \Gamma(Q)^2} + (B_1 E + B_2) \right)$$

where $x(Q)$ and $\Gamma(Q)$ are the elastic fraction and QENS broadening (half width at half maximum, HWHM), respectively, $\delta(E)$ is a delta function in the energy space at zero energy transfer, (B_1E+B_2) is a linear background term, and $R(Q,E)$ is the resolution function. The wiggles in the fits are due to convolution of the model scattering function with the experimentally measured resolution function (the data at 100 K) that has wiggles.

FIT PARAMETERS



The elastic fraction was fit using the expression:

$$x(Q) = (1 - C)\left[\frac{3 j_1(Qa)}{Qa}\right]^2 + C$$

that represents the EISF for the restricted diffusion within a sphere of radius a and a Q-independent background C. In this model, the HWHM is essentially constant and equals to $4.33 D_{local}/a^2$ for momentum transfers up to $Q = 3.3/a$. The model yields a good agreement with the experimental $x(Q)$ at low temperatures, but not at higher temperatures. Concurrently, the HWHM of the QENS broadening appears to exhibit an increase with Q in the high temperature data. In particular, at 260 K, instead of a Q-independent $\Gamma(Q)$, which yields reasonable fits for the low temperature data, the Q dependence is better described by an unrestricted diffusion law with an exponential distribution of the diffusion jump lengths:

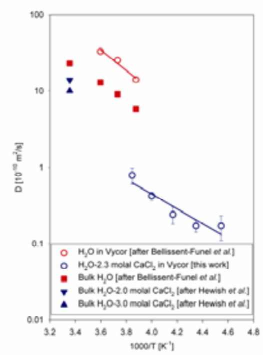
$$\Gamma(Q) = \frac{\hbar}{\tau}\left[1 - \frac{1}{1 + DQ^2\tau}\right]$$

where τ is the residence time between jumps, and D is the diffusion coefficient.

TEMPERATURE DEPENDENCE

T, K	a, Å	D_{local}, ×10^{-10} m^2/s	C
278*	5.0*	33.0*	
268*	4.5*	25.3*	
258*	3.5*	14.1*	
260	3.7 (0.1)	0.79 (0.19)	0.83 (0.01)
250	3.0 (0.1)	0.42 (0.05)	0.83 (0.01)
240	2.8 (0.1)	0.24 (0.06)	0.84 (0.01)
230	2.6 (0.1)	0.17 (0.03)	0.85 (0.01)
220	2.8 (0.2)	0.17 (0.06)	0.88 (0.01)

The fit parameters: confinement radius, a, local diffusion coefficient, D_{local}, and fraction of elastic scattering, C. Standard deviation values are shown in parentheses. The numbers with the asterisk were obtained by Bellissent-Funel *et al.* [PRE, *51*, 4558 (1995)] for pure water in 100 % hydrated Vycor glass and are shown for comparison.



The diffusion coefficient of water is affected by either adding the $CaCl_2$ salt or confinement in Vycor, but the cumulative effect of confinement and adding $CaCl_2$ on the diffusion coefficient of water is unexpectedly large.

SUMMARY

We observed a dramatic decrease in the water diffusion coefficient in the Vycor-confined aqueous solution of $CaCl_2$. This decrease was an order of magnitude larger compared to that expected from the comparison of the dynamics in pure water and solution in bulk form. Interestingly, the parameters describing the confinement radius in the restricted diffusion model were similar between Vycor-confined H_2O and Vycor-confined H_2O-$CaCl_2$. We observed a gradual transition from the restricted to unrestricted diffusion regimes at higher temperatures, similar to the one found in Vycor-confined pure H_2O. To summarize, we found that the effect of dissolved ions onto the diffusion dynamics of the water molecules in the solution is amplified by confinement by at least an order of magnitude compared to bulk form, even though the dissolved ions were found to have little effect on the spatial characteristics of the diffusion process of water molecules.

One way to explain the dramatically affected dynamics and unchanged spatial characteristics of the H_2O diffusion in a confined solution is to assume that confinement promotes stabilization of the Ca^{2+}-H_2O hydration complexes on the time scale of the neutron backscattering measurement of hundreds of picoseconds. Then the water molecules belonging to the hydration shells appear immobile on the time scale of the neutron experiment, contributing to the elastic signal. The implication is that the mobile water molecules outside the hydration shells see the confining volume much smaller than the Vycor pore size. Thus, confinement in the Vycor pores may slow down the dynamic of the hydrated water molecules, making the hydration complexes more stable, which, in turn, slows down the dynamics of the free water molecules that yields the QENS signal measured in the current experiment.

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