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Phase behaviour of water confined in Vycor glass at high temperatures and pressures

Yusuke Hiejima[1] **and Makoto Yao**

Department of Physics, Graduate School of Science, Kyoto University, 606-8502 Kyoto, Japan

E-mail: y-hiejima@aist.go.jp and yao@scphys.kyoto-u.ac.jp

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Abstract
The phase behaviour of water confined in porous Vycor glass is investigated by means of dielectric measurements. The effective static permittivity $\varepsilon^{\mathrm{eff}}(0)$ of the sample, which consists of Vycor glass and water confined in the pores, is obtained over a wide range of temperature and pressure. The boiling point of the confined water is higher than that of bulk water by $\simeq$15 K. The enthalpy of vaporization for confined water is practically the same as that for bulk water. The critical point of the confined water is determined as lying at $T_c^{\mathrm{H_2O/Vycor}} = 623(\pm 3)$ K and $P_c^{\mathrm{H_2O/Vycor}} = 14(\pm 1.5)$ MPa; both of these values are lower than those for bulk water.

1. Introduction

Confined systems, which have been widely utilized in industrial processes, attract scientific interest in a variety of research fields such as physics, chemistry, biology and geology [1]. However, the fundamental understanding of the confined systems is still insufficient, presumably because the matrix materials have complex structures. For this reason, Vycor glass [2] has been commonly used as a model hydrophilic matrix; it is thought to have interconnected roughly cylindrical pores whose average pore diameter is 7 nm [3].

Phase behaviours of confined systems are among the most interesting topics [1]. The introduction of wall forces may induce novel phenomena such as layering and wetting, which result in the emergence of new phases. Some simple fluids confined in Vycor glass have been studied experimentally [4, 5]. Shifts of the boiling point to high temperature have been observed for Ar and Kr [4], and the critical temperature has been found to become lower for carbon dioxide [5].

[1] Present address: Supercritical Fluid Research Centre, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan.

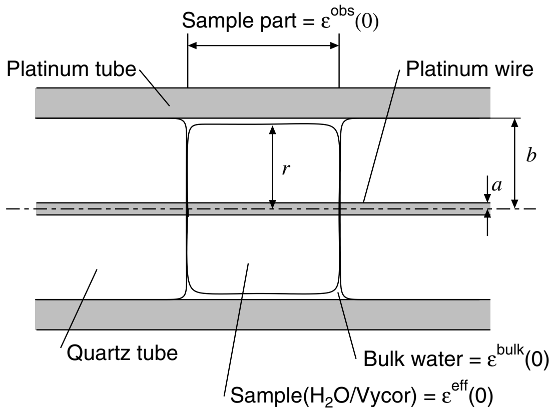

Figure 1. A schematic picture of the central parts of the sample cell. The cell has the shape of a coaxial cable. The radius and the static permittivity of each part are shown.

However, the phase behaviour of water, which is the most important system in Nature, has not been studied at high temperatures and pressures, although many efforts have been devoted to investigating confined water under ambient conditions and in the supercooled region [6–8].

In a simulation study [9], water confined in cylindrical pores with various surface potentials was reported on. The liquid–gas coexistence curves are found to show complex patterns, especially under strongly hydrophilic conditions.

In the present work, the effective static permittivity $\varepsilon^{\mathrm{eff}}(0)$ of water confined in porous Vycor glass has been obtained over a wide range of the fluid phase including supercritical conditions. By utilizing $\varepsilon^{\mathrm{eff}}(0)$, the phase behaviour of the confined water is discussed.

2. Experimental details

The experimental set-up and the method of analysis for dielectric measurements under high temperature and pressure were reported by our group [10].

The sample cell, which had the shape of a coaxial cable, was settled in an internally heated high pressure vessel, and the transmission rates and the reflection rates were measured by using a vector network analyser (Wiltron37269A) over the frequency range from 40 MHz to 40 GHz. The transmission and reflection signals in the time domain were obtained from the Fourier transform of the experimental spectra. The static permittivity $\varepsilon^{\mathrm{obs}}(0)$ of the sample part was obtained from the transmission time estimated from the time domain signals [11]. The typical experimental errors in temperature and pressure were less than ± 3 K and ± 0.2 MPa, respectively.

A rod made of Vycor glass (Vycor 7930) was shaped into a thick walled tube, and it was washed several times in 30% hydrogen peroxide at 373 K. As shown in figure 1, the Vycor glass tube with 18.5 mm length was soaked in water in the sample part. Before introducing the water, the sample part was heated at 453 K for one hour in a vacuum. After cooling it in a vacuum, water purified by Millipore MILLI-Q Labo was introduced immediately. Porous alumina, whose average pore size is 7.4 μm, was also used as the matrix for comparison.

3. Results

In figure 2, representative results on the observed static permittivity $\varepsilon^{\mathrm{obs}}(0)$ for a Vycor glass containing water are displayed as a function of temperature along nearly isobaric paths. Each

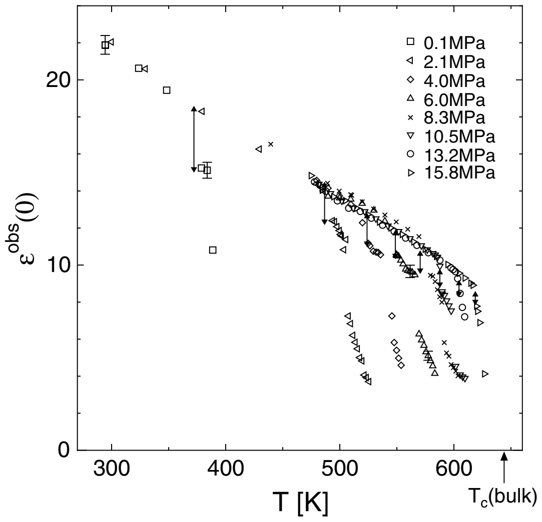

Figure 2. The temperature dependence of the observed static permittivity $\varepsilon^{\mathrm{obs}}(0)$, along nearly isobaric experimental paths. The numbers in MPa are the pressures when each path crosses the bulk liquid–gas transition line. The vertical bars with triangles at both ends indicate the jump in $\varepsilon^{\mathrm{obs}}(0)$ due to the liquid–gas transition of bulk water.

experimental path was intersected by the saturated vapour pressure curve of bulk water at a pressure indicated in MPa in the figure. $\varepsilon^{\mathrm{obs}}(0)$ is considerably smaller than the static permittivity of bulk water under ambient conditions, because some of the water is replaced by the matrix (Vycor glass), whose permittivity is $\sim$4. Below the bulk boiling point, $\varepsilon^{\mathrm{obs}}(0)$ depends mainly on temperature, and it decreases with increasing temperature. These features are qualitatively the same as those for bulk water [10]. Near the bulk boiling point, $\varepsilon^{\mathrm{obs}}(0)$ exhibits two consecutive transitions: first, a small drop occurs at the bulk boiling point; and a secondary transition occurs at a temperature higher than the bulk boiling point by $\simeq$15 K. These transitions were reversible over heating and cooling runs. The thermodynamic stability of the intermediate state between the two transitions was confirmed by an additional experiment in which the temperature was kept constant for more than half an hour. After the secondary transition, $\varepsilon^{\mathrm{obs}}(0)$ decreases continuously with increasing temperature, and approaches the static permittivity of dry Vycor (=3.1 [2]). It may be interesting to note that, at high temperatures where the bulk water is transformed to vapour, the temperature dependence of $\varepsilon^{\mathrm{obs}}(0)$ is still relatively large.

There may be a problem of corrosion of Vycor glass by supercritical water. However, it has been proved that the reproducibility of $\varepsilon^{\mathrm{obs}}(0)$ is very good as long as the experiments are performed under 660 K, which is slightly higher than the bulk critical temperature.

4. Discussion

On the basis of the present experiments, one might think that the multi-step transitions should actually be realized, as predicted by some theoretical and computer simulation works [1, 9, 12]. However, we should consider the possibility that the first transition is due to the liquid–gas transition of bulk water for the following reasons.

Although the Vycor glass tube was fabricated so that it could fit the interior of the outer platinum tube as tightly as possible, there was some clearance between them, into which the

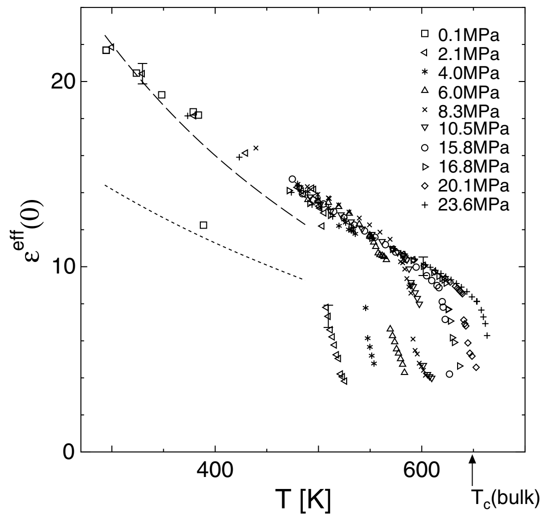

Figure 3. The effective static permittivity $\varepsilon^{\mathrm{eff}}(0)$ of the sample (confined water + Vycor) at various pressures is shown as a function of temperature. The broken curve and dotted curve are calculated using equation (2) with $\phi_2 = 0.45$ and 0.35, respectively.

bulk water intruded (see figure 1). Hence, the observed static permittivity $\varepsilon^{\mathrm{obs}}(0)$ may be described by

$$\frac{\log(b/a)}{\varepsilon^{\mathrm{obs}}(0)} = \frac{\log(r/a)}{\varepsilon^{\mathrm{eff}}(0)} + \frac{\log(b/r)}{\varepsilon^{\mathrm{bulk}}(0)}, \tag{1}$$

where $r = 1.73$ mm, $a = 0.25$ mm and $b = 1.75$ mm are the radii of the Vycor tube, the platinum wire (= inner conductor) and the platinum tube (= outer conductor), respectively, as indicated in figure 1. Here $\varepsilon^{\mathrm{eff}}(0)$ is the effective static permittivity of the sample (i.e. Vycor glass containing water), and $\varepsilon^{\mathrm{bulk}}(0)$ is the static permittivity of bulk water. Thus, $\varepsilon^{\mathrm{eff}}(0)$ can be evaluated from $\varepsilon^{\mathrm{obs}}(0)$ by using equation (1). The resultant $\varepsilon^{\mathrm{eff}}(0)$ is displayed in figure 3, in which experimental data taken in different runs are also included.

In this way, the discontinuous change at the bulk boiling point seen in $\varepsilon^{\mathrm{obs}}(0)$ is properly subtracted in $\varepsilon^{\mathrm{eff}}(0)$. Except for in the bulk liquid–gas transition region, $\varepsilon^{\mathrm{eff}}(0)$ has nearly the same value as $\varepsilon^{\mathrm{obs}}(0)$, because the volume fraction of the clearance is small ($\simeq$0.03). In figure 2, the jump in $\varepsilon^{\mathrm{obs}}(0)$ at the bulk boiling point is depicted by the bars terminated by triangles. The size of jump gradually decreases with increasing temperature and it becomes very small near T_c. Then, one may conclude that the first small jump of $\varepsilon^{\mathrm{obs}}(0)$ is explained as the vaporization of bulk water in the clearance between the Vycor tube and the platinum tube.

According to the Bruggeman's effective medium theory (EMT) [13], the effective permittivity $\varepsilon^{\mathrm{eff}}(0)$ of a two-component system satisfies the following equation:

$$\phi_1 \frac{\varepsilon_1(0) - \varepsilon^{\mathrm{eff}}(0)}{\varepsilon_1(0) + 2\varepsilon^{\mathrm{eff}}(0)} + \phi_2 \frac{\varepsilon_2(0) - \varepsilon^{\mathrm{eff}}(0)}{\varepsilon_2(0) + 2\varepsilon^{\mathrm{eff}}(0)} = 0, \tag{2}$$

where $\varepsilon_i(0)$ and ϕ_i ($i = 1, 2$) are the static permittivity and the volume fraction of each component.

Before applying Bruggeman's EMT to the water confined in the Vycor glass, we have checked that it can correctly predict the effective permittivity of water confined in a porous alumina tube with the average pore size of $\simeq$7 μm over a wide temperature and pressure

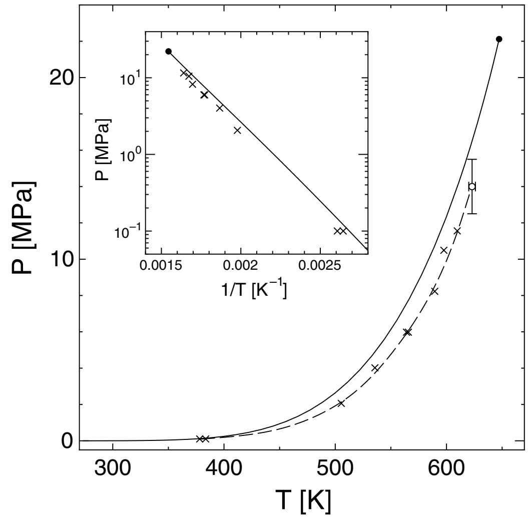

Figure 4. The phase behaviour of water confined in Vycor glass. The boiling point of confined water at various pressure is denoted by the crosses. The liquid–gas coexistence curve and the critical point of the confined water are indicated by the broken curve and the open circle. The solid curve and the closed circle denote the liquid–gas coexistence curve and the critical point of bulk water, respectively.

range. This is reasonable, because the properties of water are not expected to change when it is confined to a space whose dimension is on a macroscopic scale.

Since Vycor glass contains 96% SiO_2 glass [2], the static permittivity of the Vycor skeleton may be given by the value for fused quartz ($\varepsilon_1(0) = 3.8$ [14]). As the volume fraction ϕ_2 of water, we first took a reported porosity value (around 0.35 [15]) of Vycor glass, and calculated the effective permittivity on the assumption that the properties of water do not depend on whether it is confined or not. The calculated values are denoted by the dotted line in figure 3; they are substantially smaller than the experimental $\varepsilon^{\mathrm{eff}}(0)$. Then we assumed $\phi_2 = 0.45$ so that the experimental $\varepsilon^{\mathrm{eff}}(0)$ at room temperature could be reproduced. The results denoted by the dashed line also deviate downward from the experimental values as the temperature increases. Thus it is suggested that the static permittivity should be increased when water is confined in the Vycor matrix. The surface field from the inner wall may enhance the orientational correlations between water molecules.

Since the static permittivity strongly depends on the density, the large jump in $\varepsilon^{\mathrm{eff}}(0)$ above the bulk boiling point should be assigned to a liquid–gas transition of water confined in Vycor glass. In figure 4, the state points where this secondary transition occurs are plotted as the crosses on the temperature and pressure plane. The solid curve is the vapour pressure curve of bulk water, and the broken curve is a guide to the liquid–gas transition points for the confined water. It should be noticed that the increment of the boiling point for water ($\simeq$15 K) is remarkably large compared with that for Ar or Kr ($\simeq$2 K) confined in Vycor glass [4]. This may be due to the strong interaction between water molecules and the hydrophilic wall of the Vycor glass.

The liquid–gas critical temperature and pressure for water confined in Vycor may be estimated as 623($\pm$3) K and 14($\pm$1.5) MPa, respectively, from the disappearance of the jump in $\varepsilon^{\mathrm{eff}}(0)$. Both of these critical values are smaller than those for bulk water ($T_c = 647.3$ K, $P_c = 22.1$ MPa [14]). The decrease of T_c caused by confinement has been experimentally observed for various systems such as CO_2 in Vycor [5], as many theoretical works and computer simulations have predicted [1]. Especially interesting are simulation works by Brovchenko *et al* [9], who have suggested that T_c for water should be substantially reduced by confinement. Our result for the phase behaviour is consistent with their simulations for a weakly hydrophilic cylindrical wall, but it differs from simulations for a strongly attractive wall. In the former case, the interaction energy ($U_0 \sim 10$ kJ mol^{-1} [9]) amounts to the enthalpy of hydrogen bonding in bulk water [16].

Finally, we estimate the enthalpy of vaporization for confined water by making use of a plot of log P against $1/T$ [17]. As shown in the inset of figure 4, the enthalpy of vaporization does not significantly depend on whether the water is confined or not.

5. Conclusion

Dielectric measurements were carried out for water confined in porous Vycor glass at high temperatures and pressures. The effective static permittivity $\varepsilon^{\text{eff}}(0)$ of water confined in the pores of Vycor glass was obtained over a wide range of the fluid phase. The boiling point of the confined water is found to be higher than that of bulk water by $\simeq$15 K, while the enthalpy of vaporization is practically the same. The critical temperature and pressure of the confined water are determined as $T_c^{\text{H}_2\text{O/Vycor}} = 623(\pm 3)$ K and $P_c^{\text{H}_2\text{O/Vycor}} = 14(\pm 1.5)$ MPa, respectively. These changes in the phase behaviour have not been observed for water confined in porous alumina with $\simeq 7\ \mu$m pores.

Acknowledgments

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