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Layering in water adsorption and desorption on porous Vycor observed by dielectric measurements

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Water adsorption and desorption on porous Vycor were systematically examined by using dielectric spectroscopy at room temperature. Two relaxation peaks were observed, one for surface water (peak 1) and the other water beneath the surface water (peak 2). Quantitative analysis of the data demonstrated that the dielectric relaxation strength of peak 2 varies in an obviously stepwise way, indicating that water molecules were adsorbed and desorbed layer by layer. These experimental results supported the delayed meniscus theory for the long-debated issue of the mechanism of adsorption.

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I. INTRODUCTION

The mechanism of gas adsorption on porous materials is of fundamental interests in scientific researches and in various industrial operations.[1] Although it has been studied for a long time, since the beginning of 1900s,[2] the critical issue to understand the hysteresis in adsorption isotherms remains open.[3] On the basis of the macroscopic Kelvin equation, Zsigmondy[4] explained the process of adsorption by capillary condensation and attributed adsorption hysteresis to the presence of impurities on adsorbent.[2–4] Foster[5] and Cohan[6] believed that the adsorption hysteresis was caused by the differences in meniscus shapes of adsorbate during adsorption and desorption processes (the delayed meniscus theory).[2,3] On the other hand, Kraemer[7] and McBain[8] proposed a so-called ink bottle theory in which the hysteresis occurred when pores with different diameters were connected.[2,3] Subsequent experimental results were against the impurity model and the ink bottle model, indicating that the hysteresis phenomenon is an intrinsic property in adsorption.[3,9–11]

Various simulation and analytical approaches[12–15] favored the delayed meniscus theory that states that "the mechanism for adsorption involves the formation of a monolayer of dense gas on the walls followed by other layers and the formation of density fluctuations along the pore axis ultimately leading to capillary condensation. Desorption starts with the formation of menisci at the pore ends. The menisci recede, as the chemical potential is lowered, to the point where they interact with each other causing the system to jump to the more stable gaslike configuration."[14] However, although this scenario had been frequently quoted in the past several decades, experimental evidences that could support this theory remain scarce.

In this paper, water adsorption and desorption processes on porous Vycor were systematically studied by using dielectric spectroscopy. Obvious layering transitions were observed. Quantitative analysis of these results supported the delayed meniscus theory for the long-debated issue of the mechanism of adsorption.

II. EXPERIMENT

The adsorbent was slabs of porous Vycor (Corning Glass, code 7930), a silica glass with a random interconnected network of cylindrical pores,[16] which has been well characterized[17] and widely used.[17,18] Routine characterization of the sample by N_2 adsorption at 77 K based on the Brunauer-Emmett-Teller analysis showed that the sample has a porosity of about 0.30 and the average pore diameter is 6 nm. Before experiment, the glass was cleaned in 30% H_2O_2 solution at about 90 °C for 6 h and then was washed in distilled water for over 48 h.[16] After this, the glass was stored in distilled water for further usage.

The adsorption isotherm was measured at ambient temperature using the dynamic method[19] in which the relative vapor pressure [for water, the relative humidity (RH)] was controlled by adjusting the ratio of two flows of pure N_2 (99.999%), one dry and the other was blown through distilled water for three times and hence was saturated with water vapor. The product gas flowed at about 50 ml/min through a sealed sample cell, about 3.0 g in weight, where there was about 1.0 g of sample glasses. At each set RH, over 6 h were needed for the adsorption and desorption processes to become in equilibrium. Then, the sample cell together with the sample was weighted on an electronic balance of with a readability of 0.001 g, from which the adsorption isotherm was derived.

After this, a slab of glass with a thickness of 0.8 mm and 7.0 mm in diameter was taken out from the sample cell for immediate dielectric measurement. The measurement cell for dielectric spectroscopy consisted of two copper electrodes, both 7.0 mm in diameter and 0.2 mm in thickness, tightly surrounded by a Teflon cylinder, 7.5 and 40 mm in inner and outer diameters. Both sides of the glass were separated from the electrodes by a Teflon film of less than 0.1 mm in thickness to avoid any direct contact between the sample and the electrodes. Possible inaccuracies in measurement were considered according to Ref. 20 Dielectric measurements were performed on a Hewlett-Packard impedance analyzer HP4192A from 0.5 kHz to 13 MHz. It is noted that the present dielectric measurements were performed under ambient atmosphere. To make certain the influences of possible errors caused by this, a subsequent round was performed after dielectric measurement at each RH and no obvious differences were observed, indicating that in the course of present dielectric measurement, the influence of atmosphere changing was negligible.

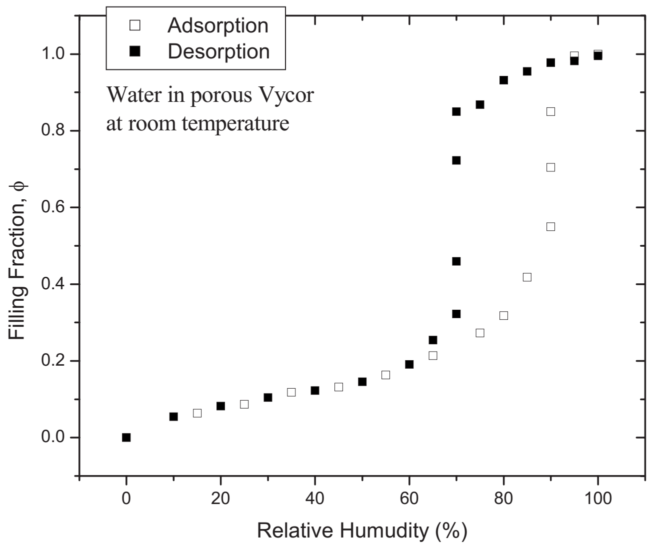

FIG. 1. Measured adsorption isotherm of water on porous Vycor at room temperature.

III. RESULTS AND DISCUSSION

In Fig. 1, we plotted the measured adsorption isotherm of water on porous Vycor. An H2-type hysteresis loop was observed, which is typical for porous glasses.[21] In Fig. 1, it is concluded that the present control in RH and weight measurement was reliable.

Dielectric loss ε'' against frequency f for a Vycor glass sample with different filling fractions ϕ of water was shown in Fig. 2. For convenience, of all the measured data, only selected ϕ were shown in the figure). In general, the present results are in good accordance with previous studies of water in porous Vycor by Pissis *et al.*[22] and in SBA-15 molecular sieves by Frunza *et al.*,[23] indicating that the present measurements were reliable. However, our results contained systematic studies on various water filling fractions, which will be further discussed in the following.

In the adsorption process, Fig. 2(a), one basically found no relaxation peaks when water content was very low, $\phi = 0.05$, and the signals of ε'' at low frequency regions were mainly contributed by conductivity.[24] With ϕ increasing, e.g., $\phi=0.13$, a relaxing peak (peak 1) occurred at the low frequency region, which was recognized as the slow dynamics of water molecules on Vycor surfaces according to relating literatures[22,23,25] [see Fig. 3(i)]. Further increasing ϕ, a second peak (peak 2) above 1 MHz was observed, the dielectric strength of which increased with ϕ. Finally, when the glass was nearly fully filled, only peak 2 was observed.

In subsequent desorption measurements, peak 1 and peak 2 were again observed, but, however, more clearly [see Fig. 2(b)]. Specifically, peak 2 showed a strong tendency to fall into several groups. Since at lower filling fractions the position of peak 2 basically did not change much from the fully filled state, we concluded that peak 2 corresponded not only to relaxations of capillary condensed water but also to water molecules adsorbed on solid walls but beneath the surface water [see Fig. 3(ii)].

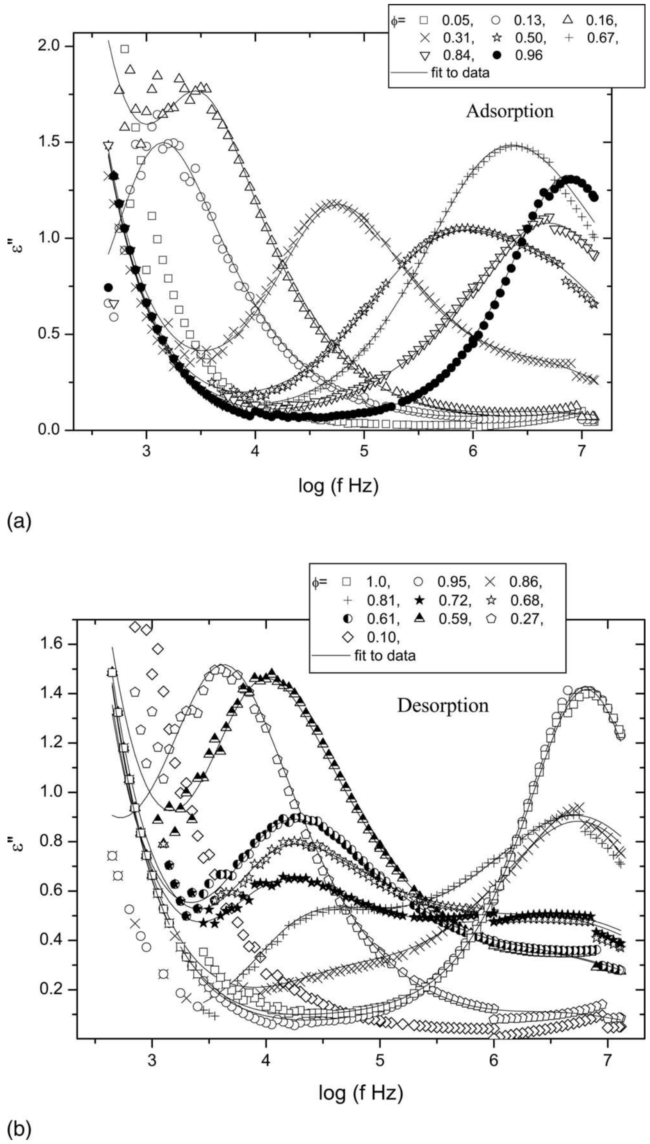

FIG. 2. Dielectric loss ε'' against frequency f for a Vycor glass sample with different filling fractions ϕ of water measured during (a) adsorption and (b) desorption at room temperature. The solid lines indicate fits to the data.

To be quantitative, the measured dielectric spectroscopy data were fitted and analyzed according to Ref. 24 The imaginary part ε'' of the dielectric response $\varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega)$, where $\varepsilon'(\omega)$ is the real part, $\omega = 2\pi f$, and $i = \sqrt{-1}$, was best fitted by a sum of three terms: one for the conductivity,

$$\varepsilon''(\omega) = -ia\frac{\sigma_0}{\varepsilon_0 \omega^s}, \tag{1}$$

where σ_0 is the dc conductivity of the sample, ε_0 is the dielectric permittivity of vacuum, and a and s are parameters used to account for the so-called Maxwell-Wagner polarization effects;[24] one Havriliak-Negami (HN) function for relaxation peaks below 1 MHz,

$$\varepsilon^*_{HN} = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau_{HN})^\beta]^\gamma}, \tag{2}$$

where $\Delta\varepsilon = \varepsilon_S - \varepsilon_\infty$ is the dielectric relaxation strength with ε_S and ε_∞ the low and the high frequency limit of $\varepsilon'(\omega)$,

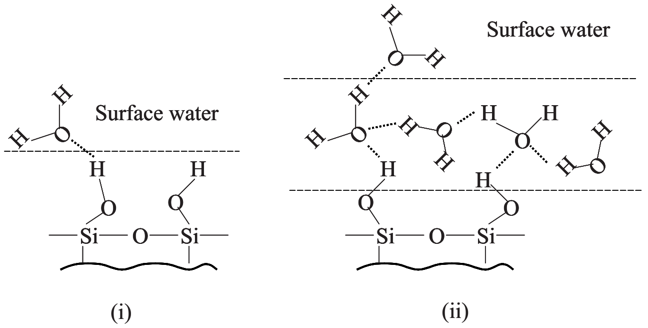

FIG. 3. Sketchy diagrams of possible conformations for (i) pure surface water and (ii) one layer of water (in between the dashed lines) beneath the surface water. The solid lines represent covalent bonds and the dotted lines H bonds. The solid curves are the surfaces of Vycor and the dashed lines guide for the eyes.

$0<\beta$, $\beta\gamma\leqslant 1$, and $2\pi f_p \tau_{HN}=\sin^{1/\beta}[\beta\pi/(2+2\gamma)]\times\sin^{-1/\beta}[\beta\gamma\pi/(2+2\gamma)]$ (f_p is the maximum loss frequency); and one Cole-Cole (CC) function for relaxation peaks above 1 MHz,

$$\varepsilon^*_{CC}=\varepsilon_\infty+\frac{\Delta\varepsilon}{1+(i\omega\tau_{CC})^\beta}, \tag{3}$$

where $0<\beta\leqslant 1$ and $\tau_{CC}2\pi f_p=1$.

Evolutions of the dielectric relaxation strength $\Delta\varepsilon$ for peak 2 in adsorption and desorption processes were illustrated in Fig. 4. Clear steps were observed in $\Delta\varepsilon$ against water content, indicating that the relaxation behavior of water beneath the surface changed step by step, not continuously. With water content increasing from zero, the first stepwise increment in $\Delta\varepsilon$ occurs at $\phi=0.25$. (It is noted that the nonzero value of $\Delta\varepsilon$ for at $\phi<0.25$ should come from measurement inaccuracies of the present impedance analyzer at high frequencies.) On the basis that the pores in porous Vycor are cylindrical and 6 nm in diameter, we found that this filling fraction corresponded to one layer of water adsorbed on the Vycor surface, approximately 4 Å in thickness. Similarly, the second and the third steps at $\phi=0.40$ and 0.55, respectively, corresponded to two and three layers of water molecules. Consequently, it was concluded that the steps in $\Delta\varepsilon$ were indications that, at low filling fractions, water molecules were adsorbed and desorbed on porous Vycor surface layer by layer, i.e., adsorption and desorption of a second layer did not begin until a first layer of molecules' adsorption and desorption processes finished. In the region of $\phi=0.55-0.80$, capillary condensation occurred (see Fig. 1) and $\Delta\varepsilon$ for the adsorption process basically kept unchanged. However, in desorption process, the way $\Delta\varepsilon$ decreased was sort of complicated: one may take it as either discontinuous or continuous, which was out of the present consideration. From $\phi=0.80$ to 1.0 was the capillary condensation states and $\Delta\varepsilon$ did not change much.

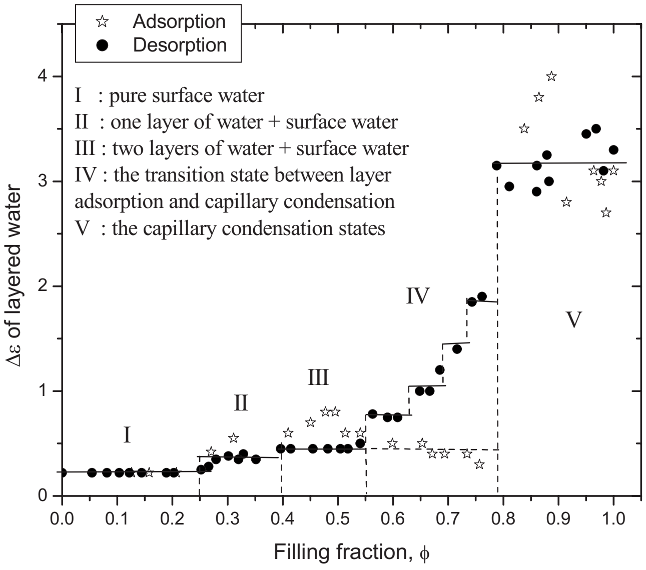

FIG. 4. Variations of the dielectric strength $\Delta\varepsilon$ of layered water with water contents ϕ in adsorption and desorption processes. The whole range of filling fractions was divided into five regions (I–V) as were annotated in the figure. The solid and dashed lines are guide for the eyes.

Accordingly, Fig. 4 was divided into five regions, as demonstrated and annotated in the figure. These five regions are in good accordance with the delayed meniscus theory for the mechanism of adsorption and desorption which were sketchily shown in Fig. 5. The adsorption process consisted of the formation of one or two layers of water on porous Vycor and then an abrupt condensation. The large deviations in $\Delta\varepsilon$ for adsorption process should result from the large fluctuations of the convex lens of surface water. The following abrupt condensation corresponded to the block of the pore. The desorption process consisted of the condensation state (V), the vaporization state (IV), and subsequent three well shaped stepwise desorption processes (I–III). The differences between adsorption and desorption in region IV resulted from the differences in the shapes of liquid meniscus in this region, convex in adsorption and biconcave in desorption (see Fig. 5).

In addition to leading to a better understanding of the fundamentals of adsorption, the present results may shed light on the structure and dynamics of water molecules in confined geometries.[26] This issue has been the interest of researchers in various fields in the past several decades (and this interest is increasing)[26–38] for the reason that in many important situations, water is confined in different environments such as in rocks, in sandstones, in molecular sieves, in biological cells, or at the surface of proteins and membranes. As such, knowledge on the behavior of water confined in different geometries, with length scales comparable to its diameter, is crucial for understanding many biological and geological processes as well as for advancing technological developments at the nanoscale. Various methods have been applied such as neutron scattering,[26–30] nuclear magnetic resonance (NMR),[30,34–38] dielectric spectroscopy,[22,23,29] molecular dynamics simulation,[31,33] so on and so forth.

The dielectric results demonstrated here, together with those by Pissis *et al.*[22] and by Frunza *et al.*,[23] were qualitatively in accordance with the results from neutron scattering experiments[27,28] that the dynamics of water molecules will significantly slow down in confined geometries or when ad-

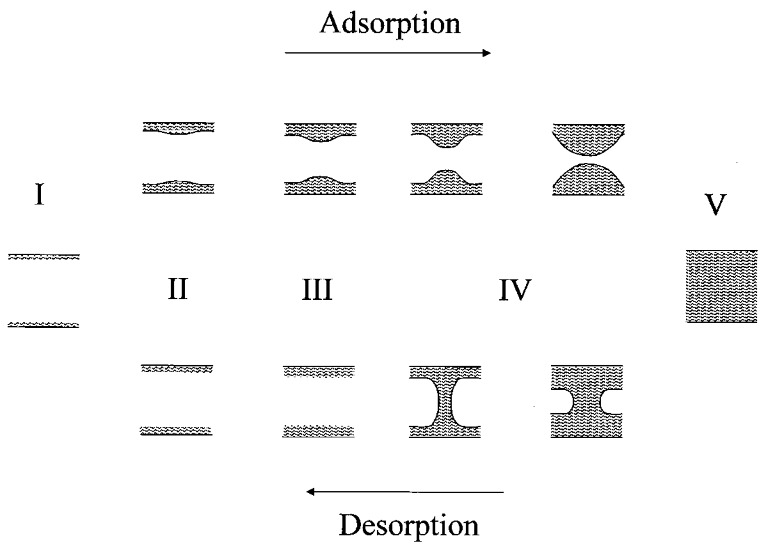

FIG. 5. Sketchy Diagram of water adsorption and desorption processes on porous Vycor. The numbers indicate the various stages demonstrated in Fig. 4.

sorbed on solid surfaces. However, our results contained systematical studies that cover the whole range of filling fractions from 0 to 1.0 of water in porous Vycor, which will of course enrich our understanding of the dynamics of confined water. In this sense, the recent works of Valiullin *et al.*[37] and Karger *et al.*[38] were of great value in which molecular diffusion dynamics was systematically inspected and was clearly demonstrated within the whole range of filling fractions.

Finally, the recent NMR work by Grunberg *et al.*[36] on water dynamics in mesoporous silica MCM-41 and SBA-15 deserves special attention. By using ^{1}H magic angle spinning and static solid-state NMR spectroscopy, they extensively studied hydrogen bonding of water molecules confined in mesoporous silica MCM-41 (pore diameter of 3.3 nm) and SBA-15 (pore diameter of 8 nm) with various water filling fractions. After careful analysis of their data, Grunberg *et al.* concluded that the process of water adsorption on SBA-15 consisted of an initial wetting layer to the pore surface and further smooth filling from the pore wall toward the center of the pore (i.e., radial growth). This actually qualitatively coincided with the adsorption process that we have shown in Fig. 5. This coincidence between the NMR data and the present dielectric results makes our conclusions in this paper more credible. (The so-called axial filling mechanism for MCM-41 in Ref. 36 was actually a special case of radial growth when the pore size is small and hence capillary condensation happens before radial growth.)

IV. CONCLUSIONS

By using dielectric spectroscopy, we have systematically examined the adsorption and desorption processes of water on porous Vycor at room temperature. Two relaxation peaks were observed with one for surface water (peak 1) and the other water beneath the surface water (peak 2). Subsequent quantitative analysis of the data showed that the relaxation strength of peak 2 varies in an obviously stepwise way, which corresponded to the fact that water molecules were adsorbed and desorbed layer by layer. These experimental results supported the delayed meniscus theory for the long-debated issue of the mechanism of adsorption, which has been extensively studied by various simulation and analytical approaches.

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