Original

Anomaly of Desorbed Water from Molecular Sieve 3A

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ABSTRACT

Anomalous physical properties of desorbed water from molecular sieve 3 A were studied. The viscosity ratio of desorbed water to the original distilled water was 0.95 and the surface tension ratio thereof were 0.86. No noticeable anomalies for the density and the refractive index were found.

KEYWORDS

molecular sieve 3 A, anomalous water, viscosity, surface tension.

1. INTRODUCTION

We have studied the hydrogen isotope effect on the desorption of water from several molecular sieves.[1] Deuterated or tritiated water was at first adsorbed in a kind of molecular sieve in vacuum. Then, as the molecular sieve was heated, the adsorbed water was gradually desorbed and was collected by freezing in a test tube cooled with liquid nitrogen. We have noticed that it took much longer time to collect the desorbed water from molecular sieve 3 A, while in the case of other molecular sieves, the collection of water was finished in about an hour, when the temperature of the molecular sieve was around 250 ℃. As the desorbed water from molecular sieve 3 A was condensed as dew on the inner wall of the glass tube between the molecular sieve and the collecting test tube before freezing onto the test tube at the molecular sieve temperature 250 ℃, we were obliged to reduce the temperature to near 100 ℃. This procedure made the collecting time much longer. It seemed that the desorbed water from molecular sieve 3 A might have somewhat different characteristics from that in the case of other molecular sieves. We then studied several physical characteristics of desorbed water from molecular sieve 3 A using distilled water made from natural water.

2. EXPERIMENTAL

2.1 Production of water

As shown in Fig. 1, about six milliliters of distilled water were frozen in test tube 1 with liquid nitrogen N in a glass vacuum system, where M: molecular sieve 3A (~40 g), H: heater, G: vacuum gauge, DP: diffusion pump, RP: rotary pump, T: trap. When N was removed, the water evaporated was gradually adsorbed in the molecular sieve. After

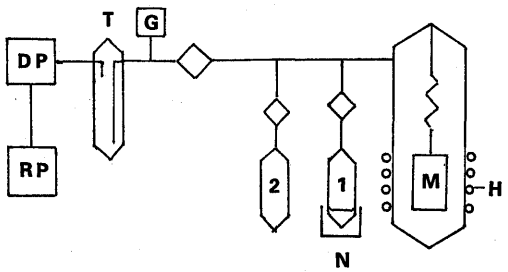

Fig. 1 Glass vacuum system

complete adsorption, test tube 2 was cooled with liquid nitrogen. When the molecular sieve was heated to about 100 ℃, the adsorbed water was gradually desorbed, almost condensing into a cooled test tube in 6~8 hours.

2.2 Measurement of viscosity

A capillary glass tube C whose inner diameter and length were 1 mm and 1.5 m, respectively, was placed horizontally beside vertical tube B whose inner diameter and length were about 5 mm and 25 cm, respectively. Both tubes were connected with gum tubes through stopcock S as shown in Fig. 2. The capillary tube was kept at a constant tem-

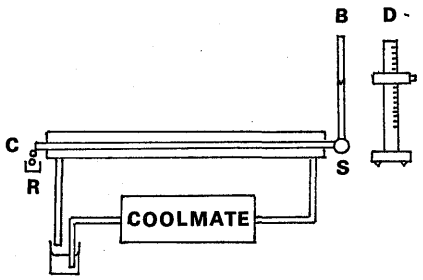

Fig. 2 Viscosity measurement

perature by circulating water supplied from "Coolmate". A smaple of water was poured into tube B. When stop-cock S was opened for t seconds, water flowed through capillary tube C pouring into vial R. The initial and final water leveles of tube B were h_1 and h_2 from the level of tube C, respectively. These levels were measured with cathetometer D Viscosity η of the water sample was derived with the following relation based on the Poiseille formula.

$$\ln\frac{h_1}{h_2}=\frac{\pi\rho g r^4 t}{8l\eta S} \tag{1}$$

where ρ: density of water, g: gravitational acceleration, r: inner diameter of capillary tube, l: length of capillary tube, S: inner cross sectional area of tube B. If h_1, h_2, ρ, η and t measured with distilled water berore adsorption are written as h_1', h_2', ρ', η' and

t′, respectively, the relation

$$\frac{\eta}{\eta'}=\frac{t\rho \ln h_1'/h_2'}{t'\rho' \ln h_1/h_3} \tag{2}$$

holds. As denoted later, since the density of the desorbed water was about the same as that before adsorption

$$\rho=\rho' \tag{3}$$

holds. In addition, since we fixed the flowing time t and t′ as 70 seconds for all samples, $t=t'$ holds. (4)

Then equation (2) was simplified as

$$\frac{\eta}{\eta'}=\frac{\ln h_1'/h_2'}{\ln h_1/h_2} \tag{5}$$

In all cases h_1 was kept almost constant (15.5 cm).

2.3 Measurement of surface tension

When a glass capillary tube d is immersed in the sample water, and then placed vertically with one end in the water, the water rises in the tube to a height h above the surface. h is denoted as

$$h=\frac{2\sigma\cos\theta}{\rho g r} \tag{6}$$

where σ: surface tension, θ: angle of contact, ρ: density, g: gravitational acceleration, r: inner radius of the capillary tube. If h, σ, θ, ρ measured with distilled water before adsorption are written as h′, σ', θ' and ρ', respectively and considering $\rho\simeq\rho'$, $\theta\simeq\theta'$, the following relation holds

$$\frac{\sigma}{\sigma}=\frac{h}{h'} \tag{7}$$

During the experiment the depth of the end of glass capillary tube d was kept constant (0.72 cm).

2.4 Measurement of density

Densities of water were measured with a density meter made by Shibayama Kagaku-kikai Company.

2.5 Measurement of refractive index

The refractive indices of water were measured with an Abbe refractometer made by Atago Company.

3. RESULTS

3.1 Viscosity

The ratios of η to η' for the samples collected from April 1988 to March 1989 and measured from April to May 1989 were

$$\eta/\eta'=0.947\pm0.067 \tag{8}$$

Days from collection of the sample to measurement were 25～218 days. Measurements of

η and η' were done on the same day.

3.2 Surface tension

The ratio of σ to σ' for the samples were

$$\sigma/\sigma' = 0.86 \pm 0.14 \quad (9)$$

3.3 Refractive index

The refractive indices of the samples were 1.330~1.337. The differences between the refractive indices of samples were below 1 %.

3.4 Density

For densities of the three samples above, diffrerences between samples and control distilled water were below 0.03 %.

4. DISCUSSION

The relation between σ/σ' and η/η' for every sample is shown in Fig. 3. Since the correlation coefficient between σ/σ' and η/η' was 0.57, there may be some positive correlation between them, considering that the significant correlation threshold is 0.5.

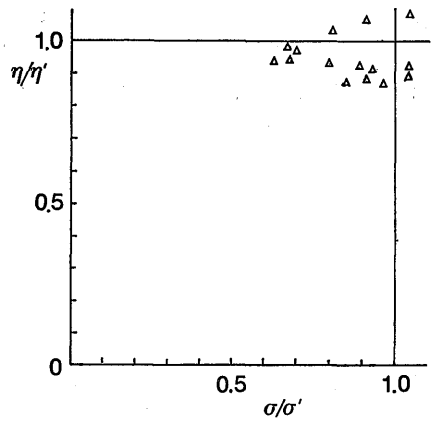

Fig. 3 σ/σ' vs. η/η' relation

During surface tension measurement, the rise of water level h in a capillary tube is given in the well-known formula (6). However, h seemed to depend upond d, the depth of the end of the capillary tube and conditions of the inner surface of the tube. In our experiement, the tube was cleaned with acetone and dried completely every time; nevertheless, some errors were unavoidable. Therefore, in the case of surface tension measurement a more advanced method should be applied. Even considering the somewhat incompleteness of this measurement, σ/σ' seems to be below 1.

During viscosity measurements the average η/η' is significantly below 1.

From these results the characteristics of desorbed water from molecular sieve 3 A may have some different physico-chemical properties and, moreover, these properties seem to be fairly stable.

Several awaiting problems may be: measurements for other kinds of molecular sieves and for deuterated water, for other physicochemical properties in addition to η, σ, density and refractive index.

REFERENCE

1) H. Kawai, H. Morishima, T. Koga and T. Niwa: Separation Factors at Desorption of Deuterated and Tritiated Water from Molecular Sieves; J. the Chem. Soc. Japan 1989 (3) p.637～639 (In Japanese).