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ORIGINAL CONTRIBUTION

T. Takei
M. Chikazawa
T. Kanazawa

Validity of the Kelvin equation in estimation of small pore size by nitrogen adsorption

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Mr. T. Takei (✉) · M. Chikazawa
T. Kanazawa
Department of Industrial Chemistry
Faculty of Engineering
Tokyo Metropolitan University
1-1, Minami-ohsawa
Hachioji, Tokyo 192-03
Japan

Abstract We have investigated a practical lower limit of a pore-size estimation by the nitrogen desorption isotherms at 77 K using the Kelvin equation. Changes in pore size of porous silica glasses before and after the monolayer preadsorption of *n*-propylalcohol were estimated by measuring the nitrogen adsorption and desorption isotherms. These changes should correspond to the thickness of monolayer of adsorbed *n*-propylalcohol. The thickness of monolayers obtained for the samples whose pore sizes are below ca. 2 nm were underestimated, when the Kelvin equation was applied to the nitrogen desorption isotherms using the values of surface tension and molar volume of bulk liquid nitrogen at 77 K. Below ca. 2 nm pore radius a careful application of the Kelvin equation is required to estimate a pore size. These results suggest that a change in the physical properties of liquid nitrogen in such a small pore occurs. It is supposed that the interaction between the solid surface and adsorbate molecules causes the changes in the surface tension and density of liquid nitrogen in such a narrow pore.

Key words Adsorption – silica – pore analysis – the Kelvin equation – porous glass

Introduction

The pore-size distributions in mesoporous materials are usually measured by a gas adsorption method. The relative vapor pressure (P/P_0) at which capillary condensation occurs is related to the Kelvin radius (r_k) by the following Kelvin Eq. (1):

$$r_k = -2\gamma V_m \cos\theta / RT \ln(P/P_0) , \quad (1)$$

where γ and V_m are the surface tension and molar volume of an adsorbate condensed in pores at measuring temperature, respectively. The symbol θ represents the contact angle between capillary condensate and the pore walls. This value is usually assumed to be zero. R and T are gas constant and measuring temperature, respectively.

The pore radius (r_p) is expressed by the summation of the Kelvin radius (r_k) and the thickness (t_{ad}) of the adsorbed layer formed on the pore walls when the capillary condensation occurs.

$$r_p = r_k + t_{ad} . \quad (2)$$

Generally, in applying the Kelvin equation to pore analysis, the values of the surface tension γ and molar volume V_m of bulk liquid are used as those values of the capillary condensed liquids in pores. However, in the case of extraordinarily narrow pores, physical properties of the capillary condensed liquids such as surface tensions and molar volumes (densities), are assumed to be different from those of bulk liquids on account of the strong effects of a solid surface on the liquid structures in these pores [1]. Therefore, in such a case, correct value of pore radius will not be obtained from the Kelvin equation using γ and V_m values of bulk liquids. Many researchers have investigated the validity of the Kelvin equation in narrow pores. Harris [2] has compared pore radii obtained from the Kelvin equation with those values calculated by the Gurvitch procedure, and reported that the application of the Kelvin equation to the pores below the radius of 2 nm is not accurate when the γ and V_m values of bulk liquid are used as the values of the condensed liquid. Fisher and Israelachvili [3] have experimentally found that the Kelvin equation is valid for menisci with mean radius of curvature as low as 4 nm. Gubbins et al. [4, 5] have investigated the fluid behavior in pores by computer simulation, and pointed out that in the case of pores below mesopore size, especially micropore size, the analysis by the Kelvin equation underestimates the pore sizes.

The nitrogen adsorption and the desorption isotherms at 77 K have been widely used for the estimation of the pore-size distribution in the mesopore size range. Therefore, in this paper, we investigate the accuracy in the estimation of a small pore radius, when the Kelvin equation is applied to the adsorption and desorption isotherms using the γ and V_m value of bulk liquid nitrogen at 77 K.

Experiment

Materials

The adsorbent used here was the porous silica glass (Corning #7930). Samples having various pore sizes were prepared by treating the porous glass with 1% HF aqueous solution (HF_{aq}) for 6 ~216 h. The samples thus obtained were dealt with H_2O_2 solution for 4 h at 90–95 °C to eliminate organic impurities, and then washed repeatedly with distilled water. Before the experimental use, the samples were outgassed under reduced pressure of 10^{-3} Pa for 4 h at 180 °C.

Nitrogen gas, of purity 99.99%, was further purified by passing through a liquid nitrogen trap before experimental use. N-propylalcohol used as pre-adsorptive molecule was guaranteed reagent grade and degassed by several repeating of freeze–thaw cycles under reduced pressure before the adsorption experiment. N-propylalcohol is suitable for preadsorbate molecules considering the following points: vapor pressure of the adsorbate can be ignored at 77 K and the size of the molecule is large enough to measure exactly a change in pore radius by preadsorption of n-propylalcohol monolayer. In the case of a sample having pore radius of 3 nm, it is expected that the decrease in pore size by the preadsorption of n-propylalcohol monolayer (ca. 0.4 nm thickness) deduces a decrease in the equilibrium pressure of nitrogen gas by ca. 4.8×10^3 Pa. The accuracy (1.333×10^{-1} Pa) of pressure gage used is sufficient to estimate such pressure change.

Adsorption measurement and calculation of pore size

The adsorption and desorption isotherms of nitrogen on the samples were measured volumetrically at 77 K using a capacitance manometer. The specific surface areas of the samples were determined by applying the BET equation to the nitrogen adsorption data, assuming the cross-sectional area of 0.162 nm^2 for a nitrogen molecule. Similarly, the adsorption isotherms of n-propylalcohol were measured volumetrically at 20 °C. Monolayer capacity was calculated using the Langmuir equation (refer to the following section).

Pore-size distributions were obtained from nitrogen desorption isotherms using the Dollimore–Heal equation [6], because sharp pore-size distribution is obtained by analysis of desorption isotherm rather than the adsorption one and change in pore size by preadsorption is estimated precisely. In the case of porous glass samples the origin of adsorption and desorption hysteresis will be responsible for the network effect (pore-blocking effect), so the pore size estimated from desorption branch will be controlled by the neck size of pore. The neck-size distribution of agglomerate of particles calculated from desorption branch assuming packed particle model is very similar to the pore-size distribution calculated from the desorption branch assuming cylindrical pore model [7]. In applying the Kelvin equation, the surface tension 8.80 dyn/cm and molar volume 34.67 cm^3/mol of bulk liquid nitrogen at 77 K were used as those values of the condensed liquid in the pores. Afterwards, we tried to estimate the correctness of these values in a small pore on the basis of a change in pore size by preadsorption. Since the pore-size distribution is calculated from a desorption isotherm, contact angle θ will be assumed to be zero. The thickness (t_{ad}) of the adsorbed nitrogen layer formed on pore walls at a relative pressure P/P_0 was estimated by the t-curve which is obtained from the nitrogen adsorption isotherm on nonporous silica glass powder. When n-propylalcohol molecules are preadsorbed, the thickness of the adsorbed nitrogen layer compared to that on silica glass surface will vary because of a change in surface properties. However, the change in the thickness of the adsored nitrogen layer is ignored at relative pressures above $P/P_0 = 0.4$ in spite of a change in adsorbent–adsorbate interactions whose values reflect in C-value in the BET equation [8]. Therefore, the correction of the thickness of the adsorbed nitrogen layer is not required above a relative pressure of 0.4 at which evaporation of the condensed liquid has been complete. The value of 0.354 nm is employed as the thickness of a molecular layer of nitrogen [9].

The samples whose surfaces are covered with a complete monolayer of *n*-propylalcohol were slowly cooled to liquid nitrogen temperature without disturbing the equilibrium and then the nitrogen adsorption and desorption isotherms were measured.

Pore volumes of the samples were estimated from the amount of nitrogen adsorbed at the saturated vapor pressure by assuming that the density of condensed liquid nitrogen is equal to that of bulk liquid.

Results and discussion

Adsorption and desorption of nitrogen and *n*-propylalcohol on samples

The adsorption–desorption isotherms of nitrogen on the untreated sample and one typical sample treated with HF_{aq} are shown in Fig. 1. These isotherms showed Type IV isotherms [10] which are often found for mesoporous solids. The type of hysteresis loops of these isotherms is classified to Type H2 loop [10]. Assuming that the pore shape is cylindrical, the pore-size distributions are given in Fig. 2. As expected from the steep desorption branches at medium relative pressure, the pore-size distribution curves of these two samples have very sharp peaks. It was found that the shapes of their distribution curves are similar to one another, but the pore radii at peaks in the curves became larger by treatment with HF_{aq}. The pore radius can be controlled by immersion in HF_{aq}. This result suggests that the surface layers of the original sample are eliminated uniformly by HF_{aq} and that the monodispersed pore radius is maintained even after the treatment with HF_{aq}. Therefore, the pore radii (values at the sharp peaks in the distribution curves) of the samples will be estimated exactly, before and after the preadsorption of *n*-propylalcohol. The pore volumes of the samples treated with HF_{aq} increased with treatment time.

Adsorption isotherms of *n*-propylalcohol on the samples are given in Fig. 3. There is no difference adsorptive nature of *n*-propylalcohol between the untreated and treated samples with HF_{aq} for various periods. All these isotherms show the Langmuir-type isotherms with the sharp knees. This fact suggests that *n*-propylalcohol molecules strongly interact with surface polar hydroxyl groups, and the molecules are adsorbed on the surface orienting their hydroxyl groups toward the surface. At further adsorption, that is, the second layer adsorption is hardly constructed because the solid surface is covered with alkyl groups in alcohol molecules at the completion of monolayer. Such a phenomenon is called "autophobic adsorption". The alkyl groups of *n*-propylalcohol adsorbed on the surface will freely rotate. It is expected that the cross-sectional area of *n*-propylalcohol resembles that of propane. Generally, the cross-sectional area of an

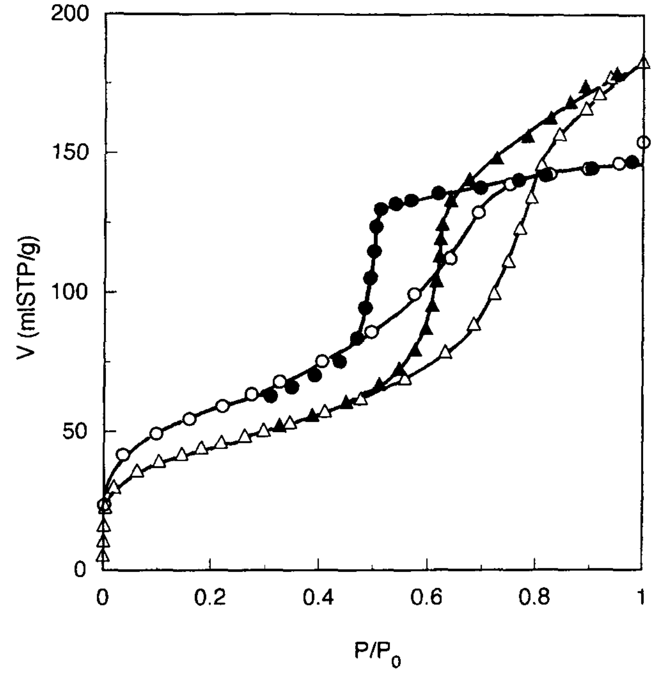

Fig. 1 Adsorption and desorption isotherms of nitrogen on porous silica glasses: (○●) original; (△▲) treated with HF_{aq} for 72 h

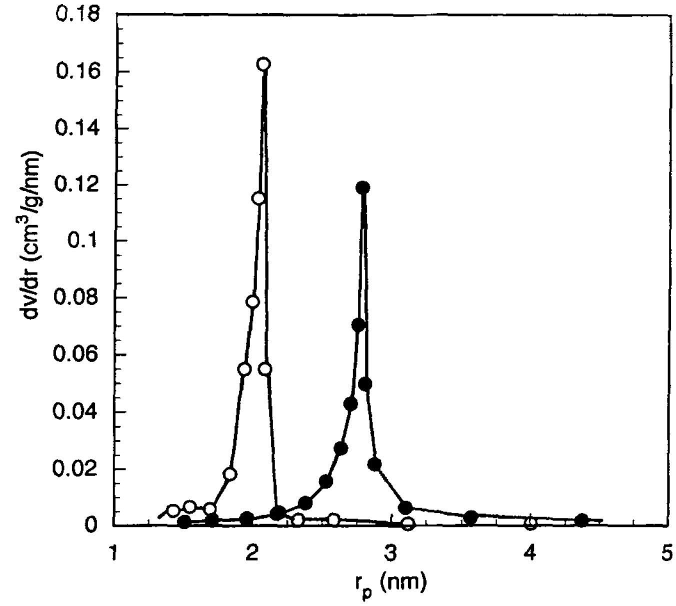

Fig. 2 Pore-size distributions of porous silica glasses: (○) original; (●) treated with HF_{aq} for 72 h

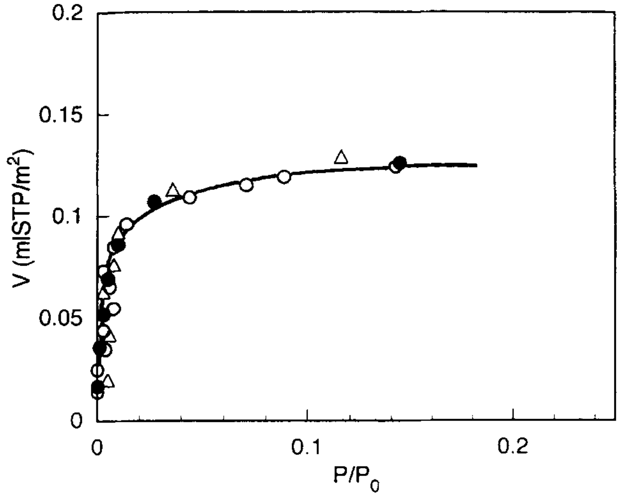

Fig. 3 Adsorption of *n*-propylalcohol on porous silica glasses: (○) original; (△) treated with HF$_{aq}$ for 72 h; (●) treated with HF$_{aq}$ for 216 h

adsorbed molecule is calculated from the density of adsorbate at liquid state, assuming an adsorbed molecule is spherical shaped. If the structure of adsorbed layer is hexagonal close packing, the cross-sectional area of an adsorbed molecule is represented by the following eqution:

$$\sigma = 1.091[M/(N \cdot d)]^{2/3} , \qquad (3)$$

where the symbols are represented as follows, 1.091: packing factor, M: molecular weight, N: Avogadro number, d: density at experimental temperature. The cross-sectional area of propane calculated from Eq. (3) is 0.273 nm^2. This value agrees with the cross-sectional area of *n*-propylalcohol (0.272 nm^2) calculated from Eq. (3). Using the monolayer capacity of *n*-propylalcohol obtained by the Langmuir equation and the value of 0.272 nm^2 as the cross-sectional area of *n*-propylalcohol, the surface coverage with *n*-propylalcohol was estimated to be 0.9.

Adsorption and desorption of nitrogen on samples preadsorbing *n*-propylalcohol

Figure 4 shows a typical example of the nitrogen adsorption–desorption isotherms on a sample before and after the preadsorption of *n*-propylalcohol. The preadsorption of *n*-propylalcohol caused a decrease in the amount of nitrogen adsorbed and rounded the knee in the isotherm at the monolayer completion. These results correspond to a depression of C value in the BET equation. Moreover, the nearly vertical desorption branch at medium relative pressure slightly shifts to a lower relative pressure after preadsorption. Changes in the surface areas, pore volumes and peak values in the pore-size distribution curves of the samples before and after the preadsorption are summarized in Table 1.

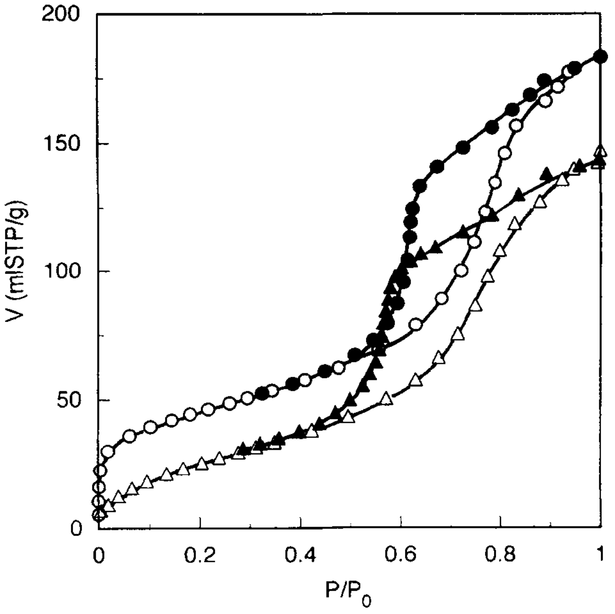

Fig. 4 Adsorption and desorption isotherms of nitrogen on porous silica glass before and after preadsorption of *n*-PrOH: (○●) bare (treated with HF$_{aq}$ for 72 h); (△▲) preadsorbing *n*-PrOH

The surface areas of the samples decreased after the preadsorption. The decrease in surface area is due to the reduction of pore size. Moreover, the surface of the sample preadsorbing *n*-propylalcohol is considered to be covered with alkyl groups. Therefore, these surfaces are similar to the low-energy surface such as molecular solid surfaces [11]. Jelinek and Kováts [12] pointed out that the adsorbed nitrogen in first layer on organic surface is loosely packed and the apparent cross-sectional area of a nitrogen molecule is slightly larger than the usual value (0.162 nm^2).

The peak values in the pore-size distributions decreased by the preadsorption of *n*-propylalcohol. The expected reduction of the peak values in the pore-size distributions by the preadsorption must be equal to the value of the thickness of monolayer of *n*-propylalcohol. The thickness of monolayer is calculated from the following equation [13]:

$$t = [M/(N \cdot d)]^{1/3}/1.091 , \qquad (4)$$

where the symbols are the same as those in Eq. (3). In the case of *n*-propylalcohol, the thickness of the monolayer is calculated to be 0.43 nm from Eq. (4) at 77 K. However, the value of the thickness depends on the orientation of *n*-propylalcohol molecules to the surface. The orientation of adsorbed *n*-propylalcohol is already predicted by the

Table 1 Changes in surface properties of porous silica glasses by preadsorption of *n*-PrOH

No.	Treatment[1] time [hr]	Before preadsorption				After preadsorption			
		S_{BET} [m²/g]	C_{BET}	V_p [cm³/g]	r_p [nm]	S_{BET} [m²/g]	C_{BET}	$V_{p(PrOH)}$ [cm³/g]	$r_{p(PrOH)}$ [nm]
1	0	211	190	0.218	1.92	127	20	0.140	1.83
2	6	218	268	0.241	2.11	173	27	0.205	1.90
3	10	206	330	0.261	2.32	126	26	0.185	2.00
4	72	161	170	0.282	2.69	104	22	0.211	2.32
5	216	141	202	0.304	2.88	98	23	0.250	2.51

[1] With 1% HF_{aq}.

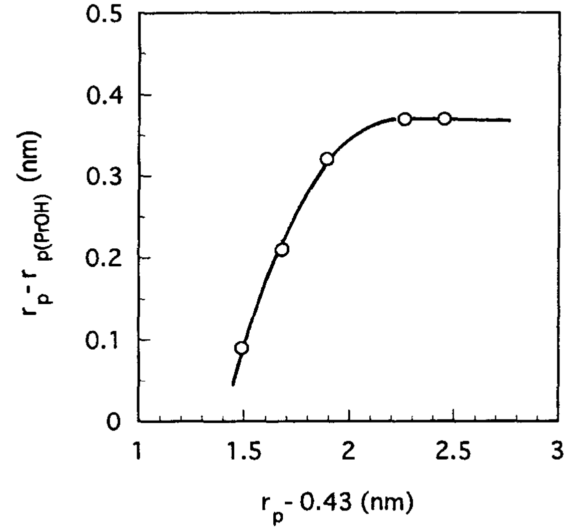

Fig. 5 Changes in the pore-size reduction $r_p - r_{p(PrOH)}$ against the pore size

estimation of the cross-sectional area of molecule. On the basis of the predicted orientation, the monolayer thickness of *n*-propylalcohol is estimated to be 0.4–0.5 nm. Therefore, it is suitable to estimate the approximate thickness of an adsorbed monolayer by Eq. (4). The pore-size reductions ($r_p - r_{p(PrOH)}$) were plotted to the corrected pore radius ($r_p - 0.43$ nm) of the corresponding samples preadsorbing *n*-propylalcohol in Fig. 5. If the pore sizes of the samples preadsorbing *n*-propylalcohol are estimated precisely, the pore-size reductions ($r_p - r_{p(PrOH)}$) should be equal to the monolayer thickness of *n*-propylalcohol. That is, the reduction values will show a constant value of 0.43 nm. The experimental value of $r_p - r_{p(PrOH)}$ represented a constant value of 0.37 nm for the pores above ca. 2 nm pore radius. However, these values ($r_p - r_{p(PrOH)}$) steeply decreased in the range of pore radii smaller than ca. 2 nm. For the pores with radii above ca. 2 nm, the experimental value of the thickness (0.37 nm) of a preadsorbed layer is slightly smaller than the calculated value of 0.43 nm. As the monolayer capacity of *n*-propylalcohol is slightly smaller than the amount required to cover the surface completely, the statistical thickness is considered to become smaller than the value calculated from Eq. (4). So in the range of pores with radii above 2 nm, the experimental value of 0.37 nm will be appropriate for the thickness of the preadsorbed monolayer. On the other hand, for the pores with radii below about 2 nm the changes in pore sizes by the preadsorption could not be estimated exactly. It is supposed that such case the physical properties of the capillary-condensed nitrogen in the pores are different from those of bulk liquid nitrogen.

Physical properties of capillary-condensed nitrogen in small pore

Ahn et al. [14] and Melrose [15] have theoretically derived the effect of curvature of liquid surface on surface tension by adopting a statistical-mechanical and thermodynamic approach, respectively. Their results predict that the surface tension of liquid increases with concavity and decreases with convexity of the liquid surface remarkably below 10 nm radius of curvature, i.e., the change in surface tension is reversed by the shape of meniscus. However, the concept of meniscus is obscure in a system containing a small number of molecules, and the effect of a solid surface on physical properties of the liquids condensed in pores is not considered in these calculations. There are few experimental studies about the estimation of surface tension and molar volume of capillary-condensed liquids in small pores. Machin et al. [16] have suggested that capillary-condensed water has a molar volume greater than that of ordinary water. They considered that the negative pressure is capable of rupturing the liquid adsorbate; the expansion of the adsorbate occurs. We estimated the changes in the surface tension and molar volume of liquid nitrogen at 77 K in a small pore from experimental results as follows. The product value of $\gamma \cdot V_m$ is revised so that the pore-size reduction (0.37 nm) by the preadsorption will be estimated precisely. The $\gamma \cdot V_m$ values thus obtained are shown in Fig. 6 as a ratio of $\gamma \cdot V_m$ in the pore to $\gamma \cdot V_m$ of

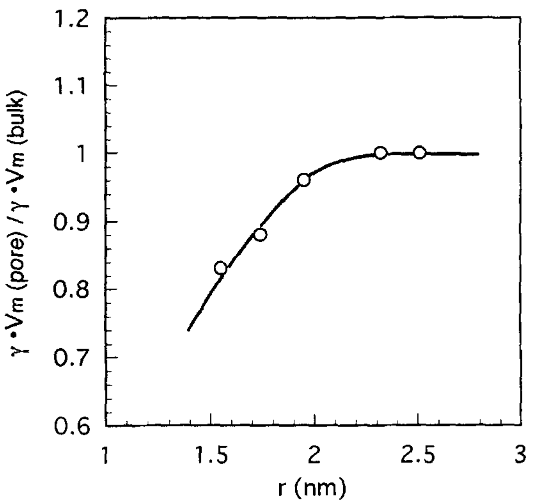

Fig. 6 The relationship of the pore size and a ratio of $\gamma \cdot V_m$ in the pore to $\gamma \cdot V_m$ of bulk liquid at 77 K

bulk liquid. The value of $\gamma \cdot V_m$ in the pore decreases remarkably below 2.0 nm pore radius. Generally, the molar volume and surface tension of liquids are related to the kind of elements, structure and polarity of their liquid molecules, and depend on intermolecular force of liquid molecules. In the case of the condensed liquid in a pore, solid surface (pore wall) will have some effect on the molecular arrangement of the adsorbate, and cause the change in the structure of condensed liquids. This structural change induces the change in molar volume (or density) and intermolecular force. The change in intermolecular force produces the change in surface tension. According to the estimation of surface tension of liquid from heat of evaporation [17], the decrease in liquid density causes the decrease in surface tension. Assuming the thickness of a molecular layer of nitrogen to be 0.354 nm [9], the effect of the solid surface on liquid structure is considered to extend to about fifth layer of nitrogen molecules.

Recently highly uniform mesoporous silicas (MCM-41, FSM-16) have been synthesized [18, 19]. These new materials have unconnected pore channels and their pore shapes are cylindrical. Rathousky et al. [20] reported that the occurrence of hysteresis in nitrogen adsorption and desorption isotherms on MCM-41 at 77 K depends on pore size. The adsorption and desorption isotherms on MCM-41 having pores ranging in radius from 1.5 to 1.8 nm exhibited no hysteresis. On the other hand, for pores with radii above 1.8 nm the hysteresis appeared. This phenomenon suggests that the nature of adsorption will change in small pore below 1.8 nm pore radius and such an observation will relate to our results.

Conclusions

In the measurement of pore size below ca. 2 nm pore radius by the nitrogen-adsorption method at 77 K, the Kelvin equation using the γ and V_m value of bulk liquid nitrogen does not estimate the corrected Kelvin radius r_k ($r_p = r_k + t$). It is supposed that the value $\gamma \cdot V_m$ of condensed liquid nitrogen at 77 K in such a small pore decreased on account of the effect of solid surfaces.

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