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SHORT COMMUNICATION

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Changes in density and surface tension of water in silica pores

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Abstract The density and surface tension of water in small pores of silicas have been investigated. These physical properties of water in the pores were calculated from a comparison of pore volumes and pore radii which were estimated from adsorption and desorption isotherms of nitrogen and water. Below a pore radius of about 5 nm both the density and the surface tension of water in the pores were smaller than those of the bulk liquid and decreased with a decrease in pore size. The density of water in the pores decreased with an increase in the concentration of surface hydroxyl groups. Similarly the surface tension of water in the pores is influenced by the surface hydroxyl groups. Anomalous changes in the density and surface tension of the water in the pores are attributed to the interaction of water molecules with surface hydroxyl groups and hydrogen-bond formation among water molecules.

Key words Adsorption · Silica · Pore · Water · The Kelvin equation

Introduction

It is well known that the nature of water in the vicinity of a surface or an interface is different from that of bulk water and that it is important for biological systems and material science. Water molecules bound to a protein surface do not freeze at the normal freezing point. This abnormal behavior plays an important role in the protection against the cold for organisms. Water adsorption on solid surfaces causes various phenomena, such as dissolution of solids, changes in surface conductivity and adhesion forces; therefore, information on the nature of water near solid surfaces will contribute to studies of these surface phenomena concerning water adsorption. Silica materials are appropriate samples for studying the nature of water in the vicinity of a surface or an interface because the surface areas and pore sizes of these materials can be controlled by various preparation methods. When water fills in silica pores, the sizes of the water phase are determined by the pore sizes. Many studies of the abnormal behavior of water in silica pores have been reported. Etzler [1] found that the heat capacity in silica pores with radii of 7 nm is about 30% greater than that of the bulk value. The abnormal behavior of the freezing points of adsorbed water has been studied by thermal analysis [2] and NMR spectroscopy [3]. As these abnormal properties are caused by the effects of solid surfaces on the adsorbed layer, changes in the properties of water near solid surfaces are expected to depend on the distance from the solid surfaces and on the nature of the solid surfaces; however, the effects of surface composition and the distance from the solid surfaces are not yet well understood. The effect of distance is investigated by use of porous silica materials having various pore sizes. The surface hydroxyl groups on silicas were altered as nature of silica surfaces, because the surface hydroxyl groups strongly interact with water molecules through forming of hydrogen bonds. The two kinds of porous silica used for this study were commercially available porous silica glass (PSG Corning, no.7930) and highly ordered mesoporous silica (MCM-41). The PSG has monodisperse pore size distributions and the transmission electron microscopy (TEM) images revealed a homogeneous distribution of pores [4]. The characterization of the surface hydroxyl groups on the PSG has been reported [5]. MCM-41 has a cylindrical pore shape and is appropriate for use as a model for pores. In this study the density and the surface tension of the water in these small silica pores have been estimated by the analysis of nitrogen and water adsorption–desorption isotherms. The effects of the distance from the solid surfaces (pore sizes) and of the surface hydroxyl groups on these physical properties have been investigated.

Experimental

The PSG was pulverized to a size of 1–2 mm. Samples having pore sizes in the range of pore radii from 2 to 4 nm were prepared by treating the PSG with 1–2% aqueous HF for 72–288 h. The samples thus obtained were treated with H_2O_2 solution for 4 h at 90–95 °C to eliminate organic impurities and were then washed repeatedly with distilled water. The MCM-41 material was prepared using water glass as a source of silica and hexadecyltrimethylammonium bromide as a template. The organic template was removed by calcination at 823 K in air for 6 h. The calcined MCM-41 sample was exposed to saturated water vapor for 24 h in order to prevent chemisorption of water molecules during the measurement of the water adsorption isotherm. Before use, all the samples were outgassed under a reduced pressure of 10^{-3} Pa for 2 h at 473 K.

The specific surface areas of the samples were calculated from nitrogen adsorption isotherms at 77 K using the Brunauer–Emmett–Teller (BET) method. Pore sizes, ($r(N_2)$), were estimated from nitrogen desorption isotherms at 77 K using the Dollimore–Heal method [6]. The thickness of the adsorbed layer of nitrogen was calculated from the equation which represents a relationship between the thickness of the adsorbed layer and the relative pressure [7]. The reasons for using desorption branches of adsorption and desorption isotherms in order to calculate the pore size distributions are as follows. In the desorption process the pore wall is completely wetted by an adsorbate, so the contact angle in the Kelvin equation can be assumed to be zero. We have reported that the validity of the Kelvin equation is doubtful when estimating pore sizes below about 2 nm using nitrogen adsorption at 77 K [8]; however, a correction for the calculation of the pore size of the MCM-41 sample was not made in this study because our result is applicable to molecular solids such as organic polymers. If our results can be applied to the MCM-41 sample, the pore radius calculated in this study is overestimated by about 0.3 nm. The pore volumes of the PSG samples were determined from the amount of adsorbed nitrogen at $P/P_0 = 1.0$ in the nitrogen adsorption isotherms. In the case of the MCM-41 sample, the increase in the amount adsorbed near the saturated vapor pressure was observed due to capillary condensation of adsorbates into spaces of interparticles of the MCM-41 powder sample. So the pore volume of the sample is obtained by extrapolation of a plateau of the adsorption isotherms and a linear increase in the amount adsorbed after capillary condensation in the intrinsic pores happened. In the calculation of the pore volumes the density of bulk liquid nitrogen at 77 K was employed for that of adsorbed nitrogen.

The density of water in the pores was obtained from the amount of water in a true pore volume, which was determined from the nitrogen adsorption isotherm. The surface tension of water in the pores was estimated as follows.

1. The pore sizes, $r_p(H_2O)$, were calculated from water desorption isotherms using the Kelvin equation. The molar volume of water in the pores determined from the density in this study was employed for the Kelvin equation.
2. If the values of $r_p(H_2O)$ do not agree with those of $r_p(N_2)$, the differences are assumed to be responsible for the deviation of the value of the surface tension of the water in the pores from the value of the bulk liquid.
3. The value of the surface tension of water used in the Kelvin equation was determined as the value of $r_p(H_2O)$ which agrees with that of $r_p(N_2)$.

The thickness of the adsorbed layer of water was evaluated from the adsorption isotherms on the PSG and MCM-41 samples using the monolayer capacity and the average thickness (0.29 nm) [9, 10] of a single layer of adsorbed water molecules.

The adsorption and desorption isotherms of water and nitrogen were measured by a volumetric method at 283 and 77 K, respectively. The pressures of the gases were measured using a capacitance manometer (MKS BARATRON 390HA). In order to avoid experimental errors, the measurements of the nitrogen and water adsorption isotherms were performed using the same samples.

Results and discussion

Characterization of samples and adsorption–desorption isotherms of nitrogen and water

The surface areas, pore radii and pore volumes of the samples measured from the nitrogen adsorption–desorption isotherms are shown in Table 1. A hexagonal arrangement of uniform mesopores of the MCM-41 sample was identified by X-ray diffraction measurement and TEM observation. Treatment of the PSG sample with aqueous HF caused the specific surface areas to decrease and the pore sizes to increase; however, it was confirmed that the pore size distributions of the samples treated with aqueous HF under various conditions remained monodisperse.

The adsorption and desorption isotherms of nitrogen and water on the MCM-41 sample are shown in Fig. 1. That's as maybe. Usually the amount of gas adsorbed is represented by "mlSTP/g" unit. In this paper the "mlSTP/g" unit is converted to "cm^3/g" for understanding of change in density of water. The nitrogen

Table 1 Characterization of the silica samples: porous silica glass (*PSG*) and MCM-41. PSG1–3 were treated with aqueous HF

Sample	S_{BET} (m^2/g)	Pore radius (nm)	Pore volume (cm^3/g)
MCM-41	861	1.55	0.865
PSG0	201	2.03	0.225
PSG1	161	2.36	0.282
PSG2	131	3.21	0.308
PSG3	99	3.90	0.262

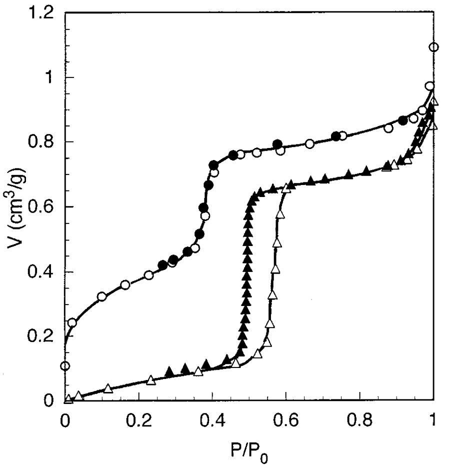

Fig. 1 Adsorption and desorption isotherms of nitrogen and water on MCM-41. Nitrogen adsorption and desorption (○, ●), water adsorption and desorption (△, ▲)

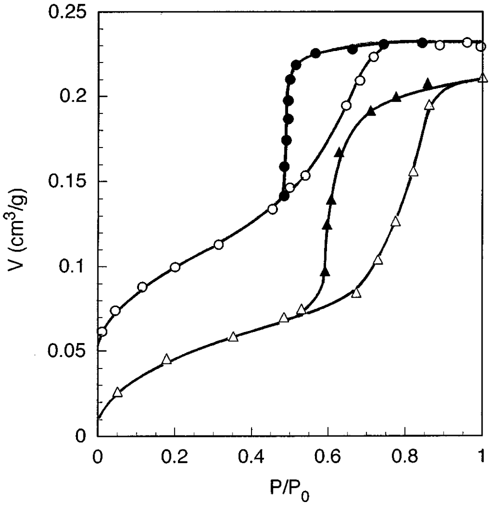

Fig. 2 Adsorption and desorption isotherms of nitrogen and water on porous silica glass (*PSG*) 0. Nitrogen adsorption and desorption (○, ●), water adsorption and desorption (△, ▲)

adsorption and desorption isotherms did not show a hysteresis loop. This observation is characteristic of nitrogen adsorption–desorption isotherms of MCM-41 [11]. The steep increase and the steep decrease in the amount adsorbed around $P/P_0 = 0.4$ are due to pore filling or capillary condensation in the intrinsic pores and capillary evaporation from the pores, respectively. The increase in the amount adsorbed around $P/P_0 = 1.0$ is attributed to condensation into spaces of interparticles because the MCM-41 sample was obtained as powder particles. On the other hand, the water adsorption and desorption isotherms of the MCM-41 sample exhibited a definite hysteresis loop. The shape of the water adsorption isotherm in the region of low relative pressure (about 0.5) represented hydrophobic character. Sharp increases and decreases in the amount adsorbed were observed at $P/P_0 = 0.5$–0.6. Such behavior is caused by the capillary condensation in the pores and evaporation of water from the pores just as was observed in nitrogen adsorption and desorption. The relative pressures at which the capillary condensation and evaporation of water occurred shifted toward higher relative pressure compared to the nitrogen adsorption and desorption isotherms.

The adsorption and desorption isotherms of nitrogen and water on the PSG0 sample are shown in Fig. 2. Both isotherms exhibited hysteresis loops. The water adsorption isotherms on the PSG samples exhibited hydrophilicity in contrast to the MCM-41 sample. The adsorption and desorption branches of the hysteresis loop of the water adsorption and desorption isotherm shifted toward higher relative pressures compared to those of the nitrogen adsorption and desorption isotherms. The other PSG samples with different pore sizes also showed hysteresis loops in the adsorption and desorption isotherms of nitrogen and water. Naturally, each adsorption and desorption branch of the hysteresis loop was located at different relative pressures because of differences in pore sizes. The adsorption and desorption branches of the hysteresis loops of the water adsorption isotherms shifted toward higher relative pressures compared to those of the corresponding nitrogen adsorption and desorption isotherms. In the case of PSG it is easy to determine the amount adsorbed at $P/P_0 = 1.0$ because the steep increase and decrease in the amount adsorbed near $P/P_0 = 1.0$ did not occur owing to negligible, small external surface areas.

Density of the water in the pores

The ratios of the densities of the water in the pores to the density of bulk water at 283 K are shown in Fig. 3 as a function of pore radius. The density of the water in the pores for radii in the range 1.5–4 nm is lower than that of the bulk liquid. The density of the water in the pore of 2-nm radius is 12–16% lower than that of bulk water. In the series of the PSG samples which show hydrophilicity, the density of the water in the pores depends on the pore size. With an increase in the pore size, the density of the water in the pores approaches the value of the bulk liquid and becomes identical to its value at a pore radius of about 5 nm. The decrease in the density of the water in the pores means that the structure of the water in the pores is different from that of bulk water. The structure of the water near the solid surfaces (pore walls) is affected by the interaction with the solid surfaces. The effects of the solid surfaces on the structure of the water in the pores decrease with an increase in the distance from the surfaces, i.e. an increase in the pore sizes.

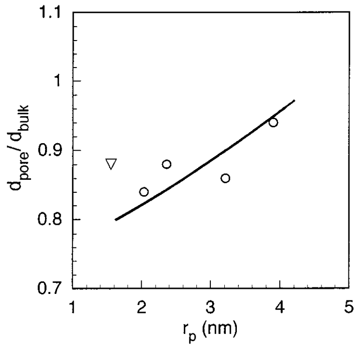

Fig. 3 The ratio of the densities of the water in the pores to the density of bulk water as a function of pore radius. PSG (○), MCM-41 (▽)

One of the reasons for a decrease in the density of the water is a decrease in the coordination numbers of the water molecules. It is well known that the density of ice is lower than that of liquid water. The difference in density between ice and liquid water is attributed to a difference in the coordination number of the water molecules. The coordination numbers of the water molecules of the structures of ice (I_h) and liquid water are 4.0 and 4.4, respectively. It is suggested that the coordination numbers of the water molecules in the small pores are lower than that of bulk liquid water. Iiyama et al. [12] have found that the number of nearest-neighbor molecules of adsorbed water in microporous carbon is less than that of the bulk liquid. The structure of the water in the pores cannot be determined definitely from our results; however, the structure of the water in the pores will be disordered like an amorphous solid water rather than the regular structure of crystalline ice. Because the PSG and MCM-41 samples are amorphous solids and adsorption sites (hydroxyl groups) of water molecules on these materials will be randomly located, it is difficult to construct a crystalline ice lattice by physisorbed water molecules on the surfaces. It has been reported that the density of a low-density form of amorphous solid water at 77 K is 0.94 g/cm^3 [13], which is nearly equal to that of crystalline ice at 77 K.

In spite of hydrophilicity of the PSG samples, the surface coverage of the water molecules at monolayer completion calculated from application of the BET equation is 0.7–0.8 on the basis of the surface areas estimated from nitrogen adsorption at 77 K using a cross-sectional area of 0.105 nm^2 for a water molecule. This fact suggests that physisorbed water molecules are localized on the silica surfaces because of strong interactions with the surface hydroxyl groups. The second adsorbed layer is formed on the first adsorbed layer through the formation of hydrogen bonds, so the structure of the second adsorbed layer is affected by the configuration and orientation of the water molecules in the first adsorbed layer. The effects of solid surfaces are gradually reduced with an increase in the thickness of the adsorbed layer. The results obtained show that the structure of water is affected up to at least 4 nm from the solid surface. If the thickness of a single adsorbed layer of water is 0.29 nm [10] or 0.35 nm, which corresponds to the apparent diameter of a molecule and is calculated from the liquid density, the effects of solid surfaces extend to 11–14 molecular layers in small pores. Etzler and Fagundus [14] reported that the density of the water in silica pores is lower than that of the bulk liquid and that then water is structurally modified up to 3–5 nm from the solid surface. Their results agree with our data except for the absolute values of the density of the water in the pores.

Effect of surface hydroxyl groups on the density of the water in the pores

It is expected that the density of the water in small pores does not only depend on pore sizes but also on the nature of the silica surfaces. In general, the surface affinity of silicas for water molecules, i.e. hydrophilicity and hydrophobicity of silicas, is controlled by the number and the type of surface hydroxyl groups because the surface hydroxyl groups on silicas are effective adsorption sites for water molecules through the formation of hydrogen bonds. From this point of view, the effect of the surface hydroxyl groups on the density of the water in the pores was investigated. The number of hydroxyl groups on the PSG sample ($r_p = 3.21$ nm) was controlled by heat treatment in vacuo. The surface hydroxyl concentration was measured from the reaction of surface hydroxyl groups with the Grignard reagent [15]. In the case of water adsorption, the number of surface hydroxyl groups after measurement of the water adsorption was employed because of chemisorption during the water adsorption. The relationship between the surface hydroxyl concentration and the ratio of the densities of the water in the pores to the density of bulk water is shown in Fig. 4. The density of the water in the pores decreased remarkably for high concentrations of surface hydroxyl groups. At low surface hydroxyl concentrations the free (no hydrogen-bonded) hydroxyl groups dominate on the surface because the hydrogen-bonded hydroxyl groups are preferentially removed by heat treatment. On the other hand, at high surface hydroxyl concentrations the surface hydroxyl groups form hydrogen bonds with each other because these groups exist close together. These hydrogen-bonded hydroxyl groups interact strongly with water molecules rather than with free (non-hydrogen-bonded) hydroxyl groups [16, 17]. So the effect of the hydroxyl groups on the density of the water in the pores could be clearly seen at high surface hydroxyl concentrations.

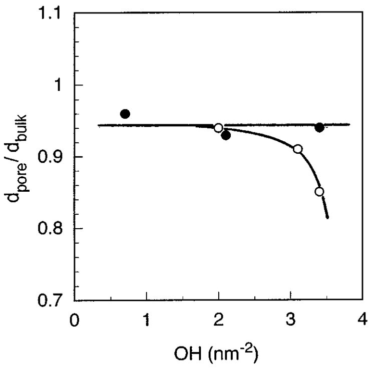

Fig. 4 The ratio of the densities of liquids in the pores of the PSG samples to those of bulk liquids as a function of surface hydroxyl concentration. Water (○), CCl_4 (●)

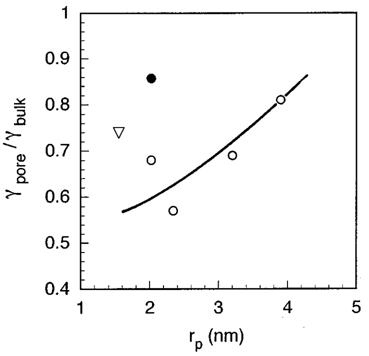

Fig. 5 The ratio of the surface tensions of liquids in the pores to those of bulk liquids as a function of pore radius. Water (PSG) (○), water (MCM-41) (▽), CCl_4 (PSG) (●)

The hydrogen bonds as a short-range force and dipole–dipole interactions as long-range forces should be noticed in the water–silica system. Our results indicated that these two kinds of interactions are important for the change in the liquid structure in small pores. We investigated the effects of hydrogen-bond formation and dipole–dipole interaction of adsorbate using CCl_4 as an adsorbate. CCl_4 molecules have no dipole moment and do not form hydrogen bonds and interact weakly with the surface hydroxyl groups only by the dispersion force. The density of CCl_4 in the pores was measured in a similar manner to that of water. The result is shown in Fig. 4. The density of CCl_4 in the pores was independent of the concentration of the surface hydroxyl groups. From these results the decrease in the density of the water is caused by the ability of water molecules to form hydrogen bonds and to develop dipole–dipole interactions; however, the density of CCl_4 in the pores was slightly lower than that of the bulk liquid. Narrow spaces in the cylindrical pores of the MCM-41 sample restrict the packing structure of CCl_4 molecules in the pores because the pore diameter of the MCM-41 sample is only about 5 times larger than the diameter of a CCl_4 molecule. It is difficult to construct an arrangement of a bulk liquid structure in such small pores. The decrease in the density of CCl_4 in the pores compared to that of the bulk liquid might be caused by a restriction of the packing structure in the narrow pore rather than by the interaction with the surface hydroxyl groups.

Surface tension of the water in the pores

Figure 5 shows the change in the ratio of the surface tensions of the water in the pores to the surface tension of bulk water against the pore radius. In the series of PSG samples, the surface tension of water in the pores decreased with a decrease in the pore radius. As the pore size increased, the surface tension of the water in the pores approached the value of the bulk liquid and became identical to it at a pore radius of about 5 nm. This behavior is analogous to that of the change in the density of the water in the pores. The change in the density of the water in the pores is closely related to that of the change in the surface tension of the water in the pores. A decrease in the surface tension means a decrease in the intermolecular forces of the water molecules. Several reasons for a decrease in the surface tension can be considered.

1. A decrease in the coordination numbers of the water molecules.
2. An increase in the distance between nearest-neighbor water molecules.
3. The change in O—H···O angles.

The first and second configurations in the structure of the water cause a direct decrease in the density of the water. The O—H···O angles affect the strength of the hydrogen bonds and control the intermolecular force.

The surface tension of the water in the pores of the PSG0 (r_p = 2.03 nm) and MCM-41 (r_p = 1.55 nm) samples deviated from the behavior of the change in the surface tension of the water in the pores. This behavior is caused by the difference in affinity of the solid surfaces for water molecules. It is expected that the surface tension of water in small pores is affected by the surface hydroxyl groups in analogy with the density of water in small pores. In the case of the PSG samples, the surface coverage of water molecules at monolayer completion changes from 0.7 to 0.8 on treatment with aqueous HF. So the affinity of the PSG0 sample (no treatment with aqueous HF) for water molecules is slightly less than that of the other PSG samples treated with aqueous HF. The shape of the adsorption isotherm of water on the MCM-41 sample was classified into a type III isotherm in the IUPAC recommendation [18], i.e. the MCM-41 sample surface showed hydrophobicity.

Water molecules interact weakly with the surface of the MCM-41 sample compared to the PSG samples. The decrease in affinity of the PSG0 and MCM-41 samples for water molecules will weaken the effect of the pore sizes on the surface tension. Our results suggest that the affinity of the solid surfaces for water is controlled by the concentration and that the types of the surface hydroxyl groups greatly influence the surface tension of the water in small pores compared to the influence of the density of the water. The surface tension of CCl_4 in PSG0 ($r_p = 2.03$ nm) is shown in Fig. 5. The decrease in the surface tension of CCl_4 in the pores of PSG0 is smaller than that of water. It is confirmed that the effect of hydrogen bonds between surface hydroxyl groups and water molecules is important for the decrease in the surface tension of the water in small pores as well as for the decrease in the density of the water in small pores.

The effect of the meniscus curvature of a liquid surface on the surface tension has been theoretically predicted by the statistical-mechanical or thermodynamic approach. Melrose [19] is based on Melrose paper [20], has reported that the surface tension of a liquid deviates remarkably from the value of the bulk liquid below a mean radius of curvature of the meniscus, r_m of about 10 nm and increases by 30% at $r_m = 2$ nm. Ahn et al. [21] have calculated the surface tension of various liquids such as Ar, N_2, C_6H_6, C_6H_{12} and H_2O. They found that the surface tensions of liquids show appreciable change below $r_m \sim 10$ nm and increase with the concavity and decrease with the convexity of the liquid surfaces. In such theoretical approaches it is necessary to notice the concept of a meniscus in a system containing a small number of molecules and the effect of a solid surface on the surface tension of the liquid in a small pore. There have been many calculations of the effect of meniscus curvature on the surface tension of a liquid; however, few studies on the basis of experimental data have been reported because of the difficulty of measuring very small dimensions. Recently Machin and Golding [22] studied the adsorption of Xe on a microporous silica gel and found that the surface tension of capillary-liquid Xe is less than that of the bulk liquid.

Conclusions

The density and the surface tension of the water in pores with a pore radius between 1.55 and 3.90 nm were lower than those of bulk liquid water. These physical properties of water in the pores are closely associated with each other and depend on the pore size and the number of surface hydroxyl groups. The anomalous behavior of the water in a small silica pore is mainly governed by the ability of the hydrogen-bond formation of water molecules and by the surface hydroxyl groups. It is suggested that the effects of the surface on the layer of water adsorbed extend up to about 4 nm from the solid surfaces.

References

1. Etzler FM (1988) Langmuir 4:878–883
2. Rennie GK, Clifford J (1977) J Chem Soc Faraday Trans 173:680–689
3. Overloop K, Gerven LV (1993) J Magn Reson Ser A 101:179–187
4. Levitz P, Ehret G, Sinha SK, Drake JM (1991) J Chem Phys 95:6151–6161
5. Kanazawa T, Chikazawa M, Takei T, Mukasa K (1984) Yogyo Kyokai Shi 92:654–659
6. Dollimore D, Heal GR (1964) J Appl Chem 14:109–114
7. Makishima A, Sakaino T (1969) J Mater Sci Jpn 6:49–55
8. Takei T, Chikazawa M, Kanazawa T (1997) Colloid Polym Sci 275:1156–1161
9. Gregg SJ, Sing KSW (1967) Adsorption, surface area and porosity. Academic, New York, pp 157–158
10. Hagymassy J, Brunauer S, Mikhail RSH (1969) J colloid Interface Sci 29:485–491
11. Branton PJ, Hall PG, Sing KSW, Reichert H, Schüth F, Unger KK (1994) Langmuir 10:2965–2967
12. Iiyama T, Nishikawa K, Otowa T, Kaneko K (1995) J Phys Chem 99:10075–10076
13. Sceats MG, Rice SA (1982) In: Frank F (eds) Water – a comprehensive treatise, vol. 7. Plenum, New York, pp 83
14. Etzler FM, Fagundus DM (1987) J Colloid Interface Sci 115:513–519
15. Fripiat JJ, Uytterhoeven (1962) J Phys Chem 66:800–805
16. Hair ML, Hertl W (1969) J Phys Chem 73:4269–4276
17. Takei T, Chikazawa M (1998) J Colloid Interface Sci 208:570–574
18. Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouqérol J, Siemieniewska T (1985) Pure Appl Chem 57:603–619
19. Gregg SJ, Sing KSW (1982) Adsorption, surface area and porosity, 2nd edn. Academic, New York, pp 153–154
20. Melrose JC (1966) Am Inst Chem Eng J 12:986–995
21. Ahm WS, Jhon MS, Pak H, Chang S (1972) J Colloid Interface Sci 138:605–608
22. Machin WD, Golding PD (1990) J Chem Soc Faraday Trans 86:171–174