Anomalous phase transition behavior of carbon tetrachloride in silica pores

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Abstract

The size-dependent phase transition behavior of carbon tetrachloride confined in silica pores ($r_p = 5$–50 nm) has been investigated by DSC and X-ray measurements. The melting point of CCl_4 in the pores linearly decreased with the reciprocal pore size. The solid-to-solid transition temperature of CCl_4 in the pores also depended on pore size. Below the pore radius of 16.5 nm, the process of phase transition of CCl_4 on cooling was different from that of bulk CCl_4. The decrease in the heats of the transitions in the pores suggested the existence of non-transforming phase in the pores. The geometric restriction of small pore contributes to the anomalous transition behavior of CCl_4 in the pores. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is well-known that liquids confined in small pores show anomalous properties compared to those of bulk state. The behavior and physical properties of liquids confined in small pores are interesting and important for adsorption, catalysis and separation. Many physical properties of liquids confined in small pores have been reported. For example, freezing and melting behavior of liquids confined in small pores are different from those of bulk state [1–5]. It is recognized that the freezing and melting points of liquids confined in pores depend on pore size, however, most of the researches has been studied using water as liquid. It is

practically important to investigate the phase transition behavior of liquids but water. On the other hand, it is expected that solids confined in small pores exhibit different properties relative to those of bulk state just as liquids confined in pores show anomalous behavior. The phase transition behavior is useful to understand physical properties of substances confined in small pores. The anomalous phase transition phenomena in small pores will be applied to stabilization of particular phase which is useful but unstable at bulk state.

In this study, the effects of pore size on the phase transition behavior of CCl_4 confined in small silica pores have been investigated. The reasons for the choice of CCl_4–silica system are as follows: (1) silica materials having various pore sizes are available, (2) confinement in pores is easy because CCl_4 is liquid state at room temperature, (3) phase transitions of CCl_4 at low temperature show not only liquid-to-solid

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transition but solid-to-solid transitions, (4) thermodynamic properties of bulk CCl_4 have been reported, and (5) CCl_4 molecules have no specific interaction (dipole–dipole, hydrogen bond and chemisorption) with silica surfaces in the present experimental conditions, so only size-dependent phase transition behavior can be investigated.

2. Experimental

Porous materials used in this study were silica gels with pore radii in the range from 5 to 50 nm. The physical characteristics of the silica samples are given in Table 1. CCl_4 reagent for trace analysis (99.9%, Kanto Chemical) was used without further purification. The silica samples were outgassed at $200°C$ for 2 h and CCl_4 vapor was condensed in the pores using vacuum glass line in order to avoid contamination of physisorbed water on the samples. A DSC (DSC 7, Perkin-Elmer) was used to measure phase transition temperatures and heats of phase transitions. The DSC measurement was carried out in the temperature range between 0 and $-100°C$. The cooling and heating rate were $10°C \, min^{-1}$. The samples were sealed using aluminum pans and covers. The phase transition temperatures were determined by extrapolation of a peak curve. Powder diffraction data of solid CCl_4 were obtained on a X-ray diffractometer (MXP^{18}, Mac Science) equipped with an attachment for measurement at low temperature.

3. Results and discussion

3.1. DSC curves of bulk CCl_4 and CCl_4 in pores

Many researches on phase transition behavior of CCl_4 and crystal structure of solid CCl_4 under room
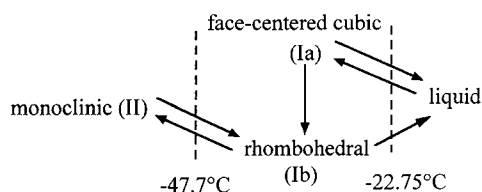

Fig. 1. Phase transition behavior of carbon tetrachloride.

temperature have been reported [6–13]. Fig. 1 shows the schematic diagram of phase transitions of CCl_4 at low temperatures [6]. Carbon tetrachloride solidifies into orientationally disordered crystalline (plastic crystal) phase named Ia phase at $-22.75°C$ and then transforms to rhombohedral crystal phase named Ib phase. Afterward phase transition from the Ib phase to a monoclinic structure named II phase occurs at $-47.7°C$. On heating process, the II phase transforms to the Ib phase and then melts without transforming into the Ia phase.

The DSC cooling and heating curves of bulk CCl_4 and CCl_4 confined in the silica pores are shown in Fig. 2. The amounts of CCl_4 of the samples differ from one another. Three peaks were observed on cooling process of bulk CCl_4. The first peak at higher temperature is attributed to the liquid $\rightarrow$ Ia transition. The second and third peaks indicate solid-to-solid transitions, and correspond to the Ia $\rightarrow$ Ib and Ib $\rightarrow$ II transitions, respectively. The liquid $\rightarrow$ Ia and Ib $\rightarrow$ II transition temperatures slightly shifted to lower temperatures compared to those in the literature [6] because of supercooling. Two peaks were observed on heating process of bulk CCl_4. The peak at lower temperature is attributed to the II $\rightarrow$ Ib transition. The other peak at higher temperature is assigned to the Ib $\rightarrow$ liquid transition. The phase transition temperatures on heating process coincided with those in the literature [6].

On the other hand, the process of phase transition of CCl_4 in the pores was different from that of bulk CCl_4. The phase transition temperatures of CCl_4 in the pores shifted to lower temperature and broadening of the peaks occurred with decrease in pore size. In the range of pore radii from 50 to 25 nm, three peaks were observed on cooling process, however, the peak attributed to the liquid $\rightarrow$ Ia transition shifted to lower temperature. Furthermore, the peak area ratio ($\Delta H_{\text{liquid} \rightarrow \text{Ia transition}}/\Delta H_{\text{Ia} \rightarrow \text{Ib transition}}$) clearly

Table 1
Porous silica properties

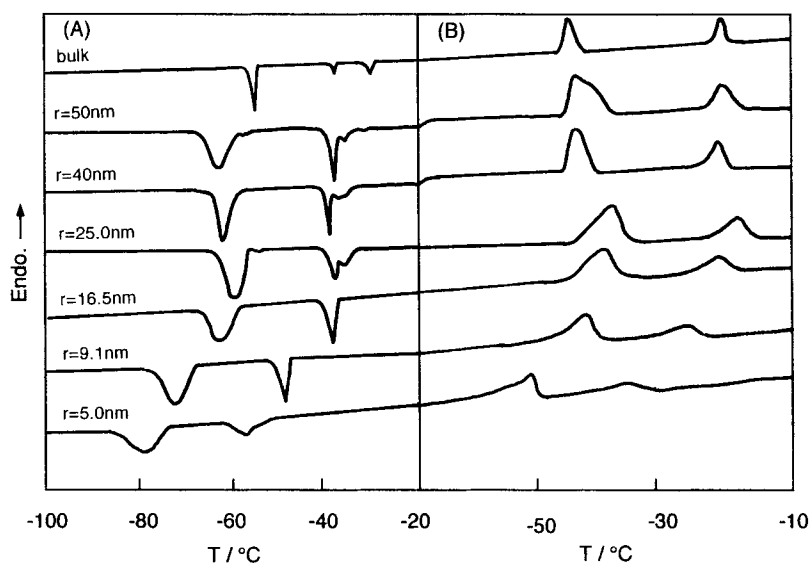| Sample	Surface area ($m^2 \, g^{-1}$)	Pore volume ($cm^3 \, g^{-1}$)	Pore radius (nm)
A	280	1.10	5.0
B	185	1.04	9.1
C	120	1.05	16.5
D	87	1.13	25.0
E	44	1.10	40.0
F	37	1.10	50.0

Fig. 2. DSC cooling (A) and heating (B) curves of bulk CCl$_4$ and CCl$_4$ confined in the silica pores.

changed in the small pores relative to that of bulk CCl$_4$. It is seemed that the change in the peak area ratio shows decrease in amount of phase which transforms from liquid to the Ia phase and increase in amount of phase which directly transforms from liquid to the Ib phase. Below the pore radius of 16.5 nm, the only two peaks were observed on cooling process. The peak first appeared will be assigned to the liquid → Ib transition. The peak second appeared is the Ib → II transition. The peak attributed to the liquid → Ia transition disappeared. On cooling process CCl$_4$ confined in the pores below 16.5 nm pore radius is expected to show direct transformation from liquid into the Ib phase. Whereas the two peaks were observed on heating process about all the samples in analogy with bulk CCl$_4$. So phase transition behavior in the pores on heating is expected to be the same as that of bulk CCl$_4$, i.e., II → Ib → liquid transition.

3.2. Crystal structure of solid CCl$_4$ in pores

The difference in the phase transition process between bulk CCl$_4$ and CCl$_4$ confined in the small pores, especially below the pore radius of 16.5 nm, were observed. The crystal structure of solid phase of CCl$_4$ in the pore (the sample B; $r = 9.1$ nm) were investigated by the X-ray diffraction (XRD) measure-

ment at low temperatures. Fig. 3 shows the XRD patterns of bulk solid CCl$_4$ and solid CCl$_4$ in the pore. The characteristic difference in XRD patterns between rhombohedral and monoclinic structure of solid CCl$_4$ was observed in Fig. 3a. No peak were observed in the temperature range in which the Ia phase (plastic crystal) appears. The peaks in the XRD patterns of solid CCl$_4$ in the pore were very broad. This means that the solid CCl$_4$ in the pore consists of microcrystalline solid or the solid has lattice distortion. The XRD pattern of the solid phase in the pore which first appeared on cooling process resembled the rhombohedral structure, however, the peak positions did not coincide with those of XRD pattern of bulk CCl$_4$. Accurate crystal structure cannot be determined by this XRD pattern. Pseudo rhombohedral phase or new phase will be produced in the pore on cooling process. The XRD pattern of the solid phase in the pore which second appeared on cooling process was almost compatible of that of monoclinic phase. However, the peak positions and relative peak intensities are slightly different from those of bulk solid CCl$_4$, perhaps distortion and orientation of crystal structure of solid CCl$_4$ will occurred in order to restrict crystal growth in the small pore. The XRD patterns of solid CCl$_4$ in the pore on heating process revealed that the monoclinic phase was transformed into
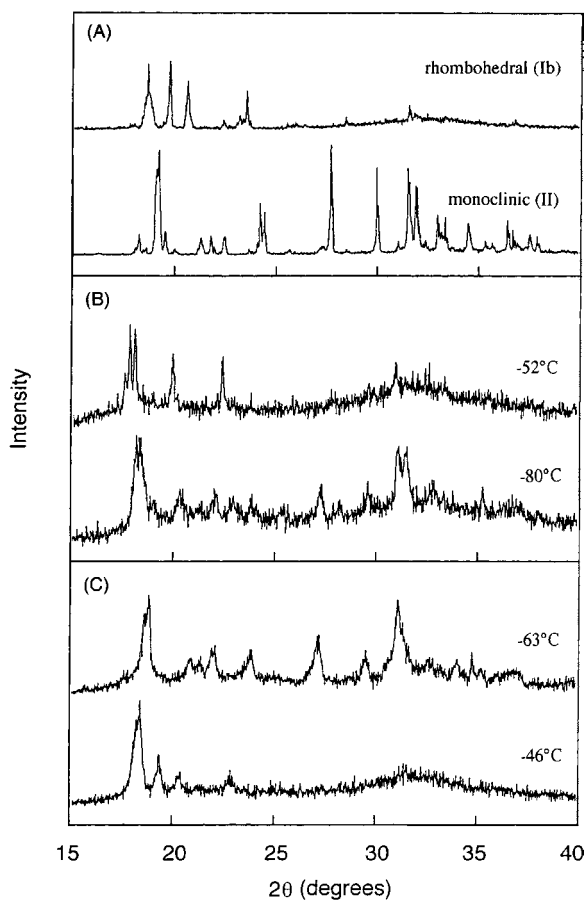
Fig. 3. X-ray diffraction patterns of solid CCl_4: (A) bulk solid CCl_4, (B) solid CCl_4 in the pore ($r = 9.1$ mm) on cooling, and (C) solid CCl_4 in the pore ($r = 9.1$ mm) on heating.

Fig. 4. Phase transition temperatures of CCl_4 confined in the pores as a function of the reciprocal pore radius: (●) Ib → liquid transition, and (○) II → Ib transition.

rhombohedral phase just as bulk CCl_4 transforms on heating process.

From DSC and XRD measurement of solid CCl_4 in the pore below 16.5 nm pore radius, it is concluded that liquid CCl_4 was directly transformed into the pseudo Ib or new phase on cooling process without the transition from liquid into the Ia phase. Further cooling transformed the Ib phase into the II phase. On heating process the phase transition behavior in the pore was the same as that of bulk CCl_4.

The disappearance of transition from liquid into Ia phase in the small pores is related with pore size. It has been reported that Ia phase could not be detected at high pressure region [14]. So the disappearance of the liquid → Ia transition in the small pores suggests that
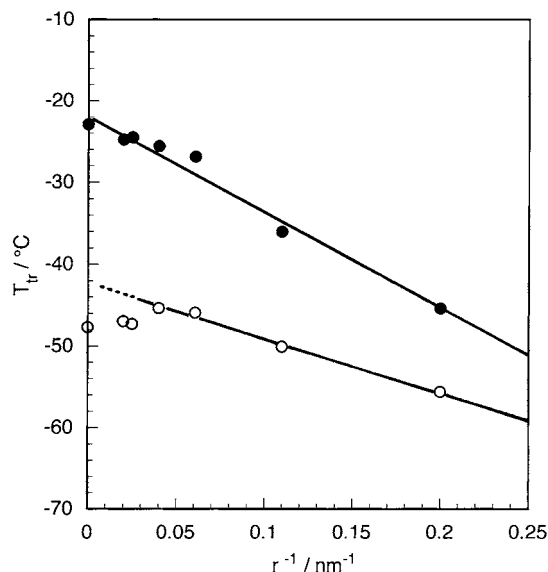
molecules in such a small pore are compressed or difficult to diffuse.

3.3. Phase transition temperatures of CCl_4 in pores

The dependence of phase transition temperature of CCl_4 in the pores on a pore size has been investigated. The phase transition temperatures of the II → Ib transition and Ib → liquid transition on heating process were plotted against the reciprocal pore radius in Fig. 4. The melting point of solid CCl_4 in the pores decreased linearly with the reciprocal pore size. Generally, the depression of melting point of solids in small pores is represented by the following equation [15–17],

$$\Delta T = \frac{2\gamma_{sl} V_m T_0 \cos\theta}{r\Delta H} \tag{1}$$

where γ_{sl} is the surface energy of the solid–liquid interface, V_m the molar volume, T_0 the melting point of bulk phase, θ the contact angle, r the pore radius and ΔH is the heat of fusion.

Eq. (1) is derived from thermodynamic approach using the model of liquid-to-solid phase transition in a cylindrical pore. The depression of melting point is

based on capillary pressure caused by the curvature of liquid–solid interface.

In the case of melting point of solid CCl_4, Eq. (1) have been found to hold in the range of pore radii from 5 to 50 nm. The solid-to-solid (II → Ib) transition temperature also showed the linear relationship with reciprocal pore size. However, the extrapolation of the plot did not agree with the bulk solid-to-solid (II → Ib) transition temperature. It is presumed that this behavior is caused by the difference in crystal structure of solid CCl_4 between bulk and in the pores. The linear relationship between solid-to-solid transition temperature and reciprocal of pore size has been reported in solid oxygen–porous glass [18] and solid cyclohexane–porous silica (Spherosil) [19] systems.

The interfacial energy at the solid–liquid interface of CCl_4 was estimated from Fig. 4 by Eq. (1). We have assumed that the contact angle is zero because the pore wall has been covered with non-freezing phase on melting process. The calculated value of interfacial energy of the solid (rhombohedral)–liquid interface of CCl_4 is 6.04 mJ m^{-2} and reduced by 10% compared to that of bulk state [20].

3.4. Heats of transitions in pores

The heats of the II → Ib and the Ib → liquid transitions on heating process against the reciprocal pore radius were shown in Fig. 5. The heats of transitions of bulk CCl_4 are cited from the literature [10]. The heats of transformation of CCl_4 in the pores drastically decreased with decrease in pore size. In the pore with radii of 5 nm, the heats of the II → Ib and the Ib → liquid transitions reduced to 36 and 53% of those of bulk CCl_4, respectively. Large decrease in heats of transformation in small pores is due to the existence of non-freezing phase. Amounts of non-freezing phase of CCl_4 in the pores with radii of 5 nm were calculated from decrease in the heats of the transitions. In the case of CCl_4 about four adsorbed layers on the surface did not contribute to melting. About three adsorbed layers on the surface did not participate in the solid-to-solid transition. In the case of water in small pores the two or three adsorbed layers on the surface (the pore wall) have been recognized non-freezing water [21]. CCl_4 molecules weakly interact with silica surfaces, however, amount of the non-freezing phase of CCl_4 in a small pore is equiva-

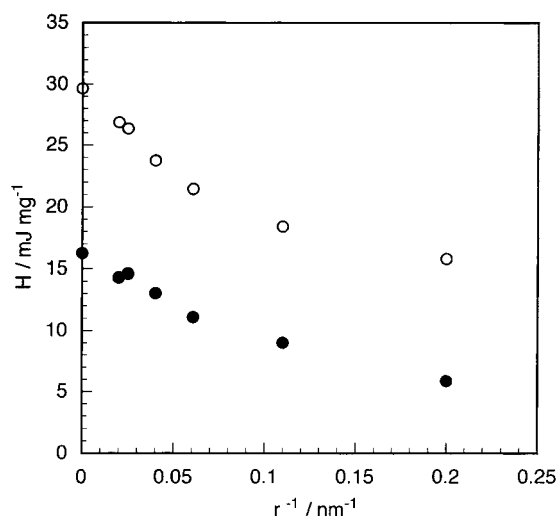Fig. 5. Heats of transitions of CCl_4 confined in the pores as a function of the reciprocal pore radius: (●) Ib → liquid transition, and (○) II → Ib transition.

lent to that of water which strongly interact with silica surfaces. Mu and Malhotra [19] have found that about five layers do not participate in the solid-to-solid transition of cyclohexane in porous silica. Kimmich et al. [22] have found that the diffusion coefficients in polar and non-polar liquids in porous glass estimated by NMR measurement were reduced relative to the bulk values and concluded that the depression of the diffusivity is mainly due to the geometric restrictions rather than to the interaction with surface. In CCl_4–porous silica system, the phase transition behavior is controlled by the geometric restrictions, i.e., pore size rather than the interaction with silica surfaces.

3.5. Effect of surface hydroxyl groups on phase transition temperature

Molecules confined in silica pores expect to interact with polar surface hydroxyl groups. As mentioned above, non-polar CCl_4 molecules weakly interact with surface hydroxyl groups, so it is expected that the effects of surface hydroxyl groups on physical properties of CCl_4 confined in pores are very small. We have reported that the phase transition temperature of n-hexane (non-polar molecules) confined in silica pores is not affected by the amount of surface hydroxyl groups [23]. It is expected that the hydroxyl groups on

Table 2
Phase transition temperature of CCl_4 in pore before and after surface modification

	T (°C)	
	II → lb	lb → liquid
Unmodified	−35.5	−50.1
Modified	−35.8	−50.3

silica surfaces control the wettability of liquids which is important for confinement of liquids in pores experimentally. We have investigated the effects of the surface hydroxyl groups on phase transition temperature. The surface hydroxyl groups of the sample B ($r_p = 9.1$ nm) were reacted with hexamethyldisilazane and substituted by non-polar trimethylsilyl groups. Experimental procedure of the surface modification has been described elsewhere [23]. The phase transition temperatures of CCl_4 confined in the unmodified and modified samples are shown in Table 2. The phase transition temperatures almost did not change by the modification. It is suggested that the hydroxyl groups on the silica surfaces do not affect the physical properties of CCl_4 confined in the silica pores. This observation supports the importance of the size effect for the phase transition behavior of CCl_4 in the small pores rather than the interaction with surfaces.

4. Conclusion

The phase transition behavior of carbon tetrachloride confined in the silica pores ($r_p = 5–50$ nm) has been investigated. The melting point and the solid-to-solid transition temperature of CCl_4 in the pores decreased with decrease in pore size. The linear relationship between these transition temperatures and the reciprocal pore radius was observed. Below the pore radius of 16.5 nm, on cooling process the liquid → Ia transition disappeared and the transition from liquid to the pseudo Ib or new solid phase was presumed. The decrease in the heats of the transitions in the pores suggested the existence of non-freezing

phase in the pores. The anomalous transition behavior of CCl_4 in the silica pores are caused by the geometric restriction of a small pore rather than the interaction with silica surfaces.

Acknowledgements

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