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Thermal Conductivity of Methane Hydrate Formed from Sodium Dodecyl Sulfate Solution

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The thermal conductivity of methane hydrate was measured by means of Gustafsson's transient plane source (TPS) technique. The sample was formed from 99.9 vol % methane gas with a 0.9709 $\text{mol}\cdot\text{m}^{-3}$ aqueous sodium dodecyl sulfate (SDS) solution under 6.60 MPa and 273.15 K. The in-situ measurement was performed in the temperature range from (263.06 to 277.87) K, and the thermal conductivity of unimpacted sample was lower than that of the impacted, with values of (0.334 to 0.381) $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and (0.564 to 0.587) $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively. The results showed that the methane hydrate has glasslike thermal properties.

Introduction

Methane hydrate is an inclusion compound or a clathrate hydrate.[1] As a potential promising future energy source,[2] its stability has an important effect on global warming[3] and seafloor slumping. Because of the sensitivity of hydrate stability to temperature fluctuations, it is necessary to know the thermal properties when evaluating the response of the hydrate to environmental change. Some clathrate hydrates appear to have a thermal conductivity that is glasslike.[4] On the molecular level, gas hydrate is similar to the most common form of water ice, ice Ih (ice with a hexagonal close-packed structure), and advances have been made using ice Ih as a gas hydrate analogue.[5] But the thermal conductivity of the hydrate is more similar to liquid water than to ice, and its temperature dependence is positive.[1] Many studies have been made on the glass such as the thermal conductivity of clathrate hydrate.[4,6−9] Most research has concentrated on the tetrahydrofuran (THF) hydrate because THF and water are miscible and THF hydrate is very uniform. Because the gas hydrate is not stable under atmosphere pressure, few studies have been made on the thermal conductivity of methane hydrate. Cook and Leaist[10] measured the thermal conductivity of methane hydrate with a needle probe and their result was 0.49 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 263.15 K, but it required considerable corrections to compensate for 43% of their sample being water ice. Waite et al.[5] measured the thermal conductivity of methane hydrate that was formed from ice powder. They used radial pressure to eliminate the additional pore gas in order to reduce the contact heat resistance between the ice particles. They observed a negative dependence of thermal conductivity on temperature, which meant that their results were affected by a combination of ice and pore gas within the sample.

The surfactant sodium dodecyl sulfate (SDS) has been found to improve the gas hydrate formation ratio and reduce the formation time.[11] When the SDS concentration reaches a critical micelle concentration (CMC) and surfactant molecules associate as micelles, the presence of micelles containing solubilized hydrocarbon gas could account for the observed phenomenon of subsurface hydrate formation previously considered to occur only at the bulk water−gas interface. In this work, the thermal conductivity of methane hydrate formed from a dilute aqueous SDS solution instead of distilled water was measured using the transient plane source (TPS) method. The TPS technique is based on the transient method as well as the needle probe, but it has a smaller probe and a new algorithm.[12,13]

Experimental Section

Apparatus. The experimental arrangement is shown in Figure 1. The gas flux was monitored by a sensor (China Beijing Qi Xing Hua Chuang Company). The gas flux and the temperatures were logged by a data acquisition system (Agilent 34901A). A detailed schematic diagram of the cell used in this work is shown in Figure 2. The sample volume was changeable with the bottom piston. The piston was moved by the hydraulic pressure using a hand pump. The whole cell was immersed in a temperature-controlled alcohol bath, where the temperature could be controlled to within ±0.1 K by using a temperature controller. The temperature of the sample cell was measured with a PT100 (not shown in Figure 2) with an evaluating standard uncertainty of ±0.005 K. The thermal conductivity of the sample was measured by the Hot Disk Thermal Constant Analyzer system. This system was made by the Sweden Hotdisk AB Company, and it was based on the transient plane source (TPS) technique of Gustafsson et al.[12,13] Figure 2 shows its thermal probe, which was made specially for these studies. The probe was sandwiched by two polymethyl methacrylate shells with each shell having a hole in which the probe could contact the sample. This design protected the probe from damage and supported the soft probe.

On the basis of the theory of the TPS technique, the Hot Disk Thermal Constant Analyzer uses a sensor element

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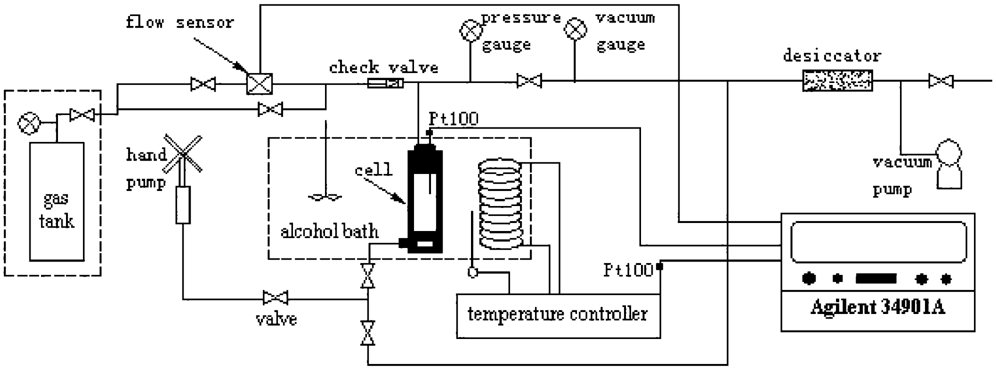

Figure 1. Schematics of methane hydrate formation and the thermal conductivity in-situ measurement system.

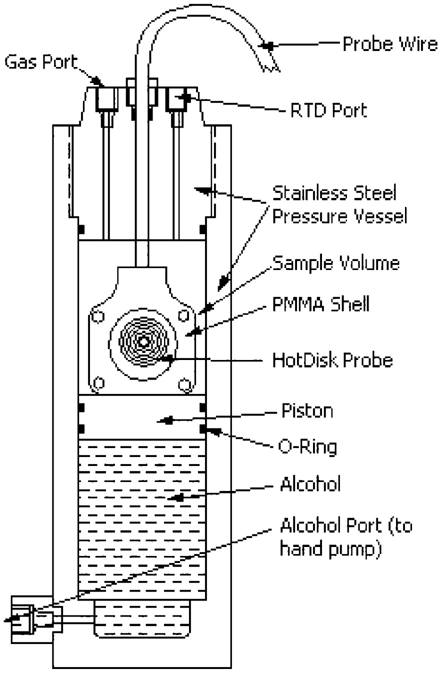

Figure 2. Cell and probe of the in-situ measurement of methane hydrate's thermal conductivity. The cell is made of stainless steel with 250-mm height and 70-mm width (outer diameter). The sample volume can be adjusted by the piston, and the maximum sample volume is 200 mL. The gas pipe, Pt100 RTD, and probe wire are sealed on the top side of the cell lid, and the lid is screwed on tightly with an O-ring.

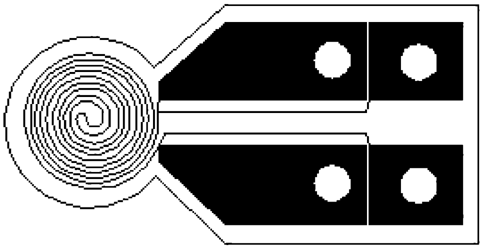

Figure 3. Probe of the Hot Disk Thermal Constants Analyzer composed of a 10-μm-thick nickel metal double spiral. The contact parts and the probe are protected inside the polyimide shell, and the shell is no more than 0.5 mm thick. During measurements, we compensate for heat consumed by the shell.

in the shape of a double spiral. As shown in Figure 3, this hot disk sensor acts both as a heat source to increase the temperature of the sample and a resistance thermometer to record the time-dependent temperature increase. In most cases, the sensor element is made of a 10-μm-thick nickel metal double spiral with precise dimensions (width and number of windings and their radii). This spiral is supported by a polyimide Kapton to maintain its particular shape, give it mechanical strength, and keep it electrically insulated. This allows measurements over the temperature range from 10 to 500 K, and the standard uncertainty of the measured thermal conductivity is $\pm 0.002\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$. The TPS's principle, procedure, and method have been discussed by Log and Gustafsson[14] and Nagai et al.[15]

Procedure. Prior to filling the cell with a 0.9709 $\mathrm{mol \cdot m^{-3}}$ aqueous SDS solution, the cell was rinsed with doubly distilled water and then dried with a blower. The uncertainty of the electronic scale is ±0.005 g. The initial temperature setting of the alcohol bath was 273.15 K. The cell was filled with 73.390 g of the SDS solution so that the surface of the solution just immersed the probe's polymethyl methacrylate shell. Using the hand pump, we raised the water and the probe to a suitable position. In this position, the hydrate formed from the water could just fill the sample volume, and this volume was usually about 1.2 times the solution volume. When the sample filled the volume, it could be impacted without damage to the wire of the probe. After repeatedly flushing the cell with methane, the cell was sealed and evacuated. Then the pressure of the methane gas was set to 6.60 MPa, and the estimated uncertainty of the pressure gauge was 0.05 MPa. The methane purity (99.9 vol %) was obtained from Guangdong Nanhai Gas Co. Ltd. The system was maintained at 273.15 K and 6.60 MPa, where the solid hydrate and gas only coexisted. The sample formed very quickly, and the methane gas flux signal dropped about 5 h after the reaction was started. To form the methane hydrate completely, the sample was kept for 3 days before measuring its thermal conductivity. After the reaction, $(1.5450 \pm 0.0005) \times 10^{-2}\ \mathrm{m^3}$ of methane gas (at 298.15 K and 0.1 MPa) was consumed. If the methane gas occupies all of the clathrate (ideal conditions) and the methane hydrate is given by $CH_4 \cdot 5.75H_2O$, then the conversion ratio was 97.3% (i.e., at least 71.400 g of water reacted with methane gas and formed methane hydrate). After 3 days, the sample's thermal conductivity was measured from (263.06 to 277.87) K (run 1) and then from (277.82 to 263.05) K (run 2). At each temperature, the sample was kept for about 1 h in order to reach thermal equilibrium in the whole sample. The first measurement would be performed after temperature equilibration, and the second would be performed 15 min later. At each temperature in each run, the mean value of the two measurements of the thermal conductivity was recorded. To impact the sample, 2 MPa of pressure was added to the methane hydrate by hand pump. The consolidated sample's thermal conductivity was also measured from (263.13 to 277.97) K and then back from (277.96 to 263.13) K.

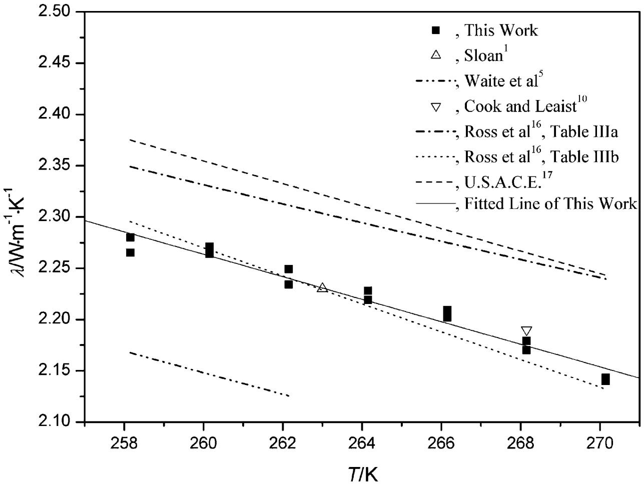

Figure 4. Thermal conductivity of ice Ih in the temperature range from (258.15 to 270.15) K.

Table 1. Ice Ih Thermal Conductivity (λ) Dependence on Temperature

researcher	λ/W·m^{-1}·K^{-1}	T/K
this work	5.124−0.011(T/K)	258.15 to 270.15
Sloan[1]	2.23	263.15
Waite et al.[5]	4.878−0.0105(T/K)	253.15 to 263.15
Cook and Leaist[10]	2.19	268.15
Ross et al.[16] Table 3a	800(T/K)$^{-1.050}$	120 to 270
Ross et al.[16] Table 3b	335/(T/K)+3.27−0.00881(T/K)	120 to 270
U.S.A.C.E.[17]	5.215−0.011(T/K)	

To check the correct operation of the apparatus, the thermal conductivity of ice Ih from (258.15 to 270.15) K was measured in the same cell. Ice Ih was made from doubly distilled water. The cell was filled with distilled water and maintained at 269.15 K for 10 h. When performing in-situ thermal conductivity measurement, the initial temperature of the alcohol bath was set to 258.15 K. Thermal conductivities of ice were measured from (258.15 to 270.15) K in both increasing (run 1) and decreasing (run 2) temperature modes.

Results and Discussion

Ice Ih. Figure 4 compares our measurement of the thermal conductivity of ice Ih with those of other researchers. Our results of ice's thermal conductivity give a maximal relative error of 4.63% with respect to other researchers' measurements.[1,5,10,16,17] The temperature dependence, −0.011, is the same as in previous work (Table 1).[5,17] The ice hexagonal crystal structure has a c_0/a_0 ratio of 1.629, which is very close to the ideal ratio of 1.633.[18] Here c_0 and a_0 are the moduli of the basic vector of ice Ih crystals. Thus, the oxygen−oxygen distances of the four different bonds are all nearly equal in length. This means that the anisotropy in the thermal conductivity should be small. The effect of the anisotropy of ice crystals on the thermal conductivity was ignored.

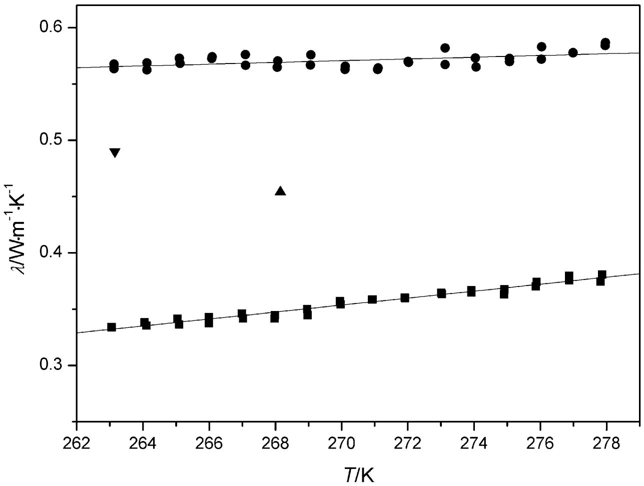

Figure 5. Experimental data of methane hydrate thermal conductivity. The temperature range is from (263.05 to 277.97) K and 6.60 MPa: ■, this work, unimpacted methane hydrate; ●, this work, impacted methane hydrate; ▲, Waite et al.;[5] ▼, Cook and Leaist.[10] The data show a glasslike temperature dependence, and the results are lower than those of Waite et al.[5] and Cook and Leaist[10] when the sample is unimpacted. However, the results are higher when the sample is impacted by the 2 MPa hand pump pressure from the piston. The nearly linear result distribution indicates that the surviving water, if there is some, exhibits a minor effect or no effect in the test zone because the thermal conductivity of ice is 5 times that of liquid water.

Table 2. Thermal Conductivity (λ) of Unimpacted Methane Hydrate from (263.05 to 277.87) K

run 1		run 2	
T/K	λ/W·m^{-1}·K^{-1}	T/K	λ/W·m^{-1}·K^{-1}
277.87	0.381	277.82	0.375
276.87	0.376	276.87	0.380
275.89	0.374	275.87	0.370
274.92	0.368	274.91	0.363
273.92	0.365	273.92	0.367
273.01	0.365	273.03	0.363
271.91	0.360	271.92	0.360
270.94	0.359	270.92	0.359
269.97	0.354	269.95	0.357
268.96	0.350	268.97	0.345
267.98	0.342	267.99	0.345
267.02	0.342	266.99	0.346
265.99	0.343	266.00	0.337
265.05	0.342	265.10	0.336
264.05	0.339	264.10	0.335
263.06	0.334	263.05	0.334

Methane Hydrate. The results of the thermal conductivity of methane hydrate from (263.06 to 277.87) K are plotted in Figure 5 and tabulated in Tables 2 and 3. The λ shows a well-defined positive temperature dependence, which fits well with former researchers' results for the THF hydrate. The impacted methane hydrate sample's thermal conductivity is higher than that of the unimpacted sample because methane hydrate formed from SDS solution has a different formation structure compared with that of pure water and methane hydrate.[11] Zhong and Rogers found that the SDS natural gas hydrates were adsorbed on the cell walls and formed a concentric shell. As the hydrate nuclei formed in the bulk water, the agglomerating particles moved rapidly to be adsorbed on the solid surface at the water−gas interface. Radial growth proceeded, forming concentric layers of hydrate held by the walls until the cell was filled with hydrates. At the end of reaction, the surviving water, if there is some, would exist in a lower place in the cell. As Figure 2 shows, this place is out of the probe's test zone (the hole of probe's polymethyl methacrylate shell) because there is little surviving water and the probe has an upper position. Therefore, the measured thermal conductivities are not contaminated by the surviving water. However, we do not exactly know the role of SDS once hydrate has formed, but the SDS itself does not attend the reaction. We assume that it separates out or dissolves in the surviving water. Under either condition, it drops out

Table 3. Thermal Conductivity (λ) of Impacted Methane Hydrate from (263.13 to 277.97) K

run 1		run 2	
T/K	λ/W·m^{-1}·K^{-1}	T/K	λ/W·m^{-1}·K^{-1}
277.97	0.587	277.96	0.584
276.99	0.578	276.99	0.578
276.03	0.572	276.04	0.589
275.07	0.570	275.07	0.573
274.06	0.565	274.04	0.573
273.13	0.582	273.13	0.567
272.01	0.570	272.02	0.569
271.10	0.564	271.09	0.563
270.10	0.563	270.11	0.566
269.07	0.576	269.06	0.567
268.07	0.570	268.06	0.565
267.10	0.567	267.09	0.576
266.08	0.573	266.09	0.574
265.12	0.568	265.10	0.573
264.12	0.569	264.12	0.563
263.13	0.568	263.13	0.564

of the test zone or exists in the intercrystalline region of methane hydrate as a dopant in trace quantities.

Ice and water have either a higher or similar thermal conductivity compared to that of the methane hydrate,[1] so the lower thermal conductivity values given in Table 2 mean that there are methane gas pores packed in the methane hydrate. To eliminate the surviving gas in the sample, the sample was impacted with 2 MPa of hand pump pressure. The axial pressure was effective at impacting the sample, and the thermal conductivity of methane hydrate increased. Our results of impacted methane hydrate are a little high compared to those of previous studies, but we obtained a well-defined glasslike thermal conductivity of methane hydrate, which was first described by Ross et al.[4] It is found that the high-temperature conductivity of the solid crystal is inversely proportional to T (i.e., the $^1/_T$ law). For crystals chosen at random, this usually means the region above room temperature, and the $^1/_T$ law often seems to be a reasonable approximation to the behavior at such temperatures.[19] However, the thermal conductivity of methane hydrate behaves more like that of amorphous solids than that of crystals. Nowadays, some researchers have found that the clathrate semiconductor's thermal conductivity is also glasslike.[20−22] It is found that cage compounds with a large unit cell containing encapsulated atoms (i.e., clathrate compounds) that can "rattle" inside the voids will have a low thermal conductivity.[21] Slack called such a hypothetical material "a phonon-glass and an electron-crystal". In a crystal, heat is transferred by a phonon or a sound branch of a phonon exactly. If the heat-transfer behavior in a clathrate hydrate is like that of a phonon glass, then we can also consider the fact that the anisotropy of the crystal will have a minor effect on our results. We use the in-situ measurement of bulk methane hydrate instead of the test method of Waite.

Conclusions

The thermal conductivity of methane hydrate was measured by the transient plane source method in the temperature range of (263.06 to 277.87) K at a pressure of 6.60 MPa. The thermal conductivity of methane hydrate forming from 0.9709 mol·m^{-3} sodium dodecyl sulfate solution is lower than other researchers' results for pure methane hydrate, but the impacted sample has a higher value. The difference means that there are many gas pores in our methane hydrate because gas has very low thermal conductivity. The result shows that methane hydrate forming from sodium dodecyl sulfate solution has low thermal conductivity and its temperature dependence is glasslike.

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