Stability Boundary of the Structure-H Hydrate of *cis*-1,4-Dimethylcyclohexane Helped by Methane

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The structure-H hydrate of *cis*-1,4-dimethylcyclohexane in the presence of methane was investigated in the temperature range 274.1 to 287.9 K and the pressure range 1.62 to 9.13 MPa. *cis*-1,4-Dimethylcyclohexane in the presence of methane was enclathrated into the largest cage of the structure-H hydrate, while *trans*-1,4-dimethylcyclohexane was not enclathrated. The present study reveals that *cis*-1,4-dimethylcyclohexane as well as 1,1- and *cis*-1,2-dimethylcyclohexanes can generate the structure-H hydrate with the help of methane.

Introduction

Gas hydrates of the structure-H (s-H) type found by Ripmeester et al.[1] are composed of three types of cages, S-cages (pentagonal dodecahedron, 5^{12}), S′-cages ($4^3 5^6 6^3$), and U-cages ($5^{12}6^8$). The structure of the s-H hydrate becomes stable with the cooperative interaction between methane or xenon (so-called help gas) and a heavy species which is unable to generate the s-H hydrate by itself. The heavy species, such as adamantane[2] or methylcyclohexane,[3−7] can be entrapped in the U-cage while the help gas occupies selectively both S- and S′-cages. Other heavy species of s-H hydrates in the case of the xenon help system have been investigated by means of ^{129}Xe NMR.[8]

In our previous study,[7] the *cis*-1,2-dimethylcyclohexane (*cis*-1,2-DMCH) generates the s-H hydrate assisted by methane as help gas, while *trans*-1,2-DMCH, *cis*-1,3-DMCH, and *trans*-1,3-DMCH do not form any hydrates. It has also been reported that 1,1-DMCH generates the s-H hydrate with the help of methane.[6] The occupancy limit for the largest hydrate cage is one of the most interesting subjects for studying the thermodynamic stability of gas hydrates. We speculate from the above findings that the border of the largest guest species would be in the vicinity of DMCH stereoisomers. In the present study, the stereoisomers of 1,4-DMCH, which are slightly larger than *cis*-1,2-DMCH in molecular effective volume, are investigated as to whether they are able to generate the s-H hydrate in the presence of methane in the temperature range 274.1 to 287.9 K and the pressure range 1.62 to 9.13 MPa.

Experimental Section

The experimental apparatus and procedures in the present study are the same as the previous one.[7] The inner volume and maximum working pressure of the high-pressure cell are 150 cm^3 and 10 MPa, respectively. The cell has a set of windows for visually observing the phase behavior in the high-pressure cell. The contents are agitated using an up-and-down mixing bar driven by an exterior permanent magnetic ring. In the temperature and pressure ranges of the present study, the densities of gas, liquid hydrocarbon, hydrate, and water phases become larger in that order. This up-and-down mixing method is most efficient in the preparation of the s-H hydrate because gas, liquid hydrocarbon, and aqueous phases effectually keep in touch with each other. All of them are immersed in a temperature-controlled water bath. The equilibrium temperature was measured within an accuracy of ±0.02 K using a thermistor probe (Takara D-632), which was inserted into a hole in the cell wall. The probe was calibrated with a Pt resistance thermometer. The system pressure was measured with a pressure gauge (Valcom VPRT) calibrated with a RUSKA quartz Bourdon tube gauge within an accuracy of ±0.01 MPa.

A sufficient amount of *cis*-1,4-DMCH or *trans*-1,4-DMCH was charged with H_2O into the vacuumed high-pressure cell in order that both 1,4-DMCH (either *cis*- or *trans*-configuration) and water phases may not disappear by the s-H hydrate formation. Under the liquid−liquid equilibrium (the upper is the hydrocarbon phase and the lower is the aqueous phase), the methane was introduced into the cell until a desired pressure (not to go over the equilibrium pressure of pure methane hydrate, which was measured in advance by an ordinary method). It is important to keep away from an overloading of pressure; otherwise, the s-I hydrate of pure methane would be generated first, and then it would take a long time to reach the equilibrium pressure of s-H hydrates. To determine the four-phase equilibrium pressure precisely, the s-H hydrate was formed or dissociated by the pressure control method.[7] When the pressure change became within 0.01 MPa, the system was regarded as the equilibrium state. Usually, it takes about 2 or 3 days to establish the equilibrium in the present study. In the high-temperature region, it takes >4 days for completing the equilibrium. This time is as long as that of the *cis*-1,2-DMCH + methane hydrate system.

Research grade methane (purity 99.95%) was purchased from Takachiho Trading Co., Ltd. The distilled water was obtained from Yashima Pure Chemicals Co., Ltd. Tokyo Kasei's Guaranteed Reagent (TCI-GR) samples of *cis*-1,4-DMCH (purity > 98 mol %) and *trans*-1,4-DMCH (purity > 96 mol %) were obtained from Tokyo Chemical Industry Co., Ltd. All of them were used without further purification.

Results and Discussion

The four-phase coexisting curve of the *cis*-1,4-DMCH + methane hydrate (s-H) system is summarized in Table 1

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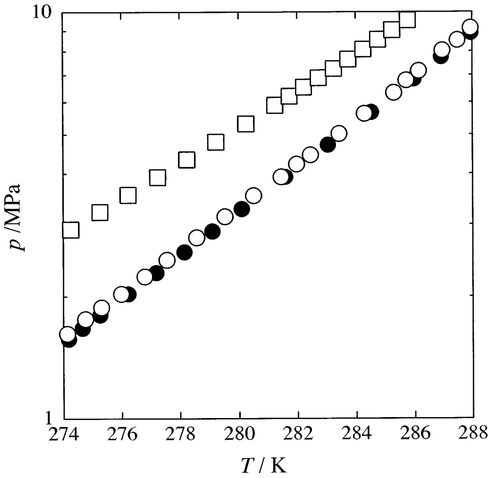

Figure 1. Pressure−temperature relations of hydrate stability boundaries: □, three-phase coexisting curve of the pure methane hydrate (s-I);[7] ●, four-phase coexisting curve of the *cis*-1,2-DMCH + methane hydrate (s-H);[7] ○, four-phase coexisting curve of the *cis*-1,4-DMCH + methane hydrate (s-H).

Table 1. Four-Phase Coexistence Data for the s-H Hydrate of *cis*-1,4-DMCH and Methane

T/K	p/MPa	$\Delta_{hyd}H$/ kJ·mol^{-1}	T/K	p/MPa	$\Delta_{hyd}H$/ kJ·mol^{-1}
274.13	1.62	368	281.97	4.22	370
274.75	1.76	366	282.45	4.45	372
275.30	1.88	367	283.43	5.01	370
275.98	2.03	371	284.30	5.62	365
276.79	2.24	372	285.30	6.32	364
277.55	2.46	372	285.72	6.78	355
278.57	2.79	372	286.15	7.16	352
279.53	3.14	371	286.97	8.04	342
280.50	3.53	371	287.49	8.53	342
281.44	3.93	373	287.95	9.13	336

and shown in Figure 1 accompanied by that of the *cis*-1,2-DMCH + methane hydrate (s-H) system[7] and the three-phase coexisting curve of the methane hydrate (s-I) system. The four-phase coexisting curve of the *cis*-1,4-DMCH + methane hydrate (s-H) system is located to the slightly higher pressure (lower temperature) side than that of the *cis*-1,2-DMCH + methane hydrate (s-H) system. Generally, the equilibrium pressure of the s-H hydrate is lower than that of the pure help gas hydrate. In the case of the s-H hydrate of *cis*-1,4-DMCH assisted by methane, the equilibrium pressure (3.5 MPa) is much depressed from that of the pure methane hydrate (5.3 MPa) at 280 K. The depression of equilibrium pressure is strongly dominated by the molecular size and symmetry of the heavy guest species. From the slope of the four-phase coexisting curve, the overall enthalpy of hydrate formation (per 1 mol of s-H hydrate), $\Delta_{hyd}H$, is evaluated by use of the Clapeyron equation under the assumption of ideal hydration ($5CH_4$ + *cis*-1,4-DMCH + $34H_2O$), where the volumetric properties of fluid methane and *cis*-1,4-DMCH are calculated from the IUPAC recommendation equation[9] and the Rackett equation,[10] respectively. The molar volume of the s-H hydrate is calculated from the hexagonal lattice constant of the s-H hydrate (a =1.226 nm and c =1.017 nm).[11] The $\Delta_{hyd}H$ of the *cis*-1,4-DMCH + methane (s-H) hydrate has weak temperature dependent; the value is almost constant around 370 kJ/mol in the low-temperature range and slightly decreases in the high-temperature and high-pressure regions. The $\Delta_{hyd}H$ of the *cis*-1,4-DMCH system is smaller by about 13 kJ/mol than that of the *cis*-1,2-DMCH system[7] in the low-temperature range.

Table 2. Gas Hydrate Formation of DMCH Stereoisomers in the Presence of Methane

chemical	*cis*- configuration	*trans*- configuration
1,1-DMCH	s-H formation	
1,2-DMCH	s-H formation	none
1,3-DMCH	none	none
1,4-DMCH	s-H formation	none

The *trans*-1,4-DMCH system was also investigated; however, no s-H hydrate was generated. It is summarized in Table 2 whether the DMCH stereoisomers in the presence of methane can generate the s-H hydrate or not. In seven types of DMCH stereoisomers, it has already been reported that the 1,1-DMCH generates the s-H hydrate with the help of methane.[6] According to the previous paper, neither *cis*-1,3-DMCH nor *trans*-1,3-DMCH has generated the s-H hydrates in the presence of methane with the same procedures as those for the *cis*-1,2- and *cis*-1,4-DMCHs. These results reveal that the U-cage of s-H hydrates can discern the slight configuration differences of the DMCH stereoisomers. Only 1,1-, *cis*-1,2- and *cis*-1,4-DMCHs helped by methane can generate s-H hydrates in seven types of the DMCH stereoisomers.

Conclusion

The four-phase coexisting curve for the *cis*-1,4-DMCH + methane hydrate system was measured in the temperature range 274.1 to 287.9 K, and it is clear for the first time that *cis*-1,4-DMCH generates the s-H hydrate in the presence of methane. In the case of selecting methane as the help gas, only 1,1-, *cis*-1,2-, and *cis*-1,4-DMCHs can generate the s-H hydrates while the other DMCH stereoisomers have never generated the s-H hydrates. The result of the present investigation implies that *cis*-1,4-DMCH is the largest molecule of the guest species in the U-cage.

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