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Phase Equilibrium Measurements of Structure sH Hydrogen Clathrate Hydrates with Various Promoters[†]

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The potential of clathrate hydrates for hydrogen storage has already been demonstrated in various publications. Today, a major scientific and technological challenge would be the finding of a storage material that allows for storage of larger quantities of hydrogen, as required for new energy applications such as, for instance, in the transport sector and fulfilling the goals set by some energy agencies which require the achievement of storage capacities up to a mass fraction of 6 % of hydrogen and with an environmentally clean and safe method by the end of 2010. If it would be possible to store hydrogen in structure sH clathrate hydrate (sH), this goal possibly could be achieved. Our previous work demonstrated for the first time the possibility to crystallize hydrogen clathrate hydrate in structure sH with 1,1-dimethylcyclohexane, methyl *tert*-butyl ether (MTBE), and methylcyclohexane as promoters. In this work, phase equilibrium data (p, T data) are reported for hydrogen clathrate hydrate systems with liquid hydrocarbon promoters, all of them forming the structure sH. Experiments were carried out at pressures up to 100.0 MPa.

Introduction

Clathrate hydrates are crystalline structures, composed of icelike lattices, with well-defined cages, formed by hydrogen-bonded water molecules in which guest molecules can be entrapped and stabilizing the crystalline structure.[1] The potential of these compounds to store hydrogen was first described by Mao et al.[2] They showed that the hydrogen clathrate hydrate could be stabilized at extreme conditions only, i.e., at pressures above 200 MPa. The storage of hydrogen in its molecular form in the clathrate cages offers some advantages that make them highly attractive for practical applications.[3] It is of great interest to stabilize the hydrogen hydrates at relatively low pressures and high temperatures to explore the possibility of using these solids as a safe hydrogen storage material, particularly for application in the transportation sector. Gas clathrate hydrates are systems composed of gas + water + promoter. Synthesis of the hydrogen hydrates is extremely simple, and it is a reversible process. Just by tuning temperature, it is possible to obtain a solid-phase system in which hydrogen is entrapped or a melted phase in which hydrogen is released from the solid phase. This can be of major interest for the industry. Furthermore, mild conditions are used for its production leading to low energy consumption processes.

Florusse et al.[4] proved that inclusion of a second guest molecule, tetrahydrofuran, made it possible to stabilize the hydrogen clathrate hydrate at pressures as low as 5.0 MPa and at near ambient temperatures.

Besides the stability of these materials at appreciable conditions, another issue is their storing capacity. For that purpose, this parameter must be as high as possible to achieve the goals set by some energy agencies which require it to be as high as a mass fraction of 6 % of hydrogen and, in addition, with an environmentally clean and safe storage and handling method, by the end of 2010.

If it would be possible to store hydrogen in sH hydrate, this goal possibly could be achieved. Our group was the first to report on the possibility to crystallize hydrogen clathrate hydrate in structure sH hydrate, using 1,1-dimethylcyclohexane, methyl *tert*-butyl ether (MTBE), and methylcyclohexane as promoters.[5] Spectroscopic evidence that hydrogen was trapped within structure sH hydrate was confirmed by Strobel et al.[6] If it is assumed that both the small 5^{12} cavity and the medium sized $4^35^66^3$ cavity only can store one hydrogen molecule each, it can be concluded that the H_2/H_2O molar ratio can be as high as 1/6.8. Earlier findings with tetrahydrofuran as the stabilizing agent to store hydrogen as a clathrate hydrate in structure sII showed an H_2/H_2O molar ratio of 1/8.5, which means an increase in potential storage capacity of almost 25 % by mass.

In this study, other guest molecules (promoters), known to be sH hydrate formers, were tested, and the hydrate formation conditions (p, T data) are presented. Pressures up to 100.0 MPa were applied.

Materials and Methods

Materials. Table 1 lists the different hydrocarbons studied and shows the molecular structure of the promoter. Doubled distilled water was used. Hydrogen (99.998 mol %) was supplied by Hoek Loss. All chemicals were used without any further purification.

Experimental Procedure. The phase behavior measurements were carried out in a stainless steel optical high-pressure cell applicable at pressures up to 100.0 MPa and temperatures up to 360 K. See De Loos et al.[7] for details.

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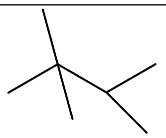
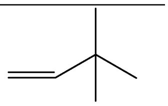
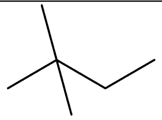
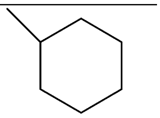
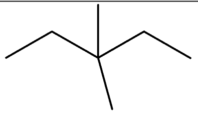
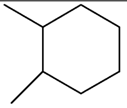
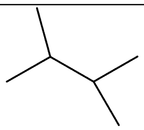
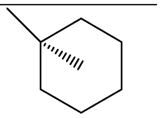
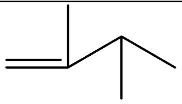
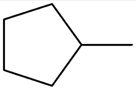
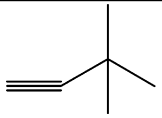
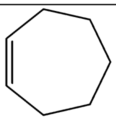
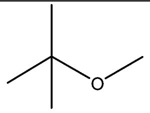
Table 1. List of the Promoters and Some of Their Properties Studied in This Work

Promoter	Molecular structure	Promoter	Molecular structure
2,2,3 trimethylbutane C_7H_{16} MW = 100.2 CAS[464-06-2] Fluka		3,3 dimethyl-1- butene C_6H_{12} MW = 84.2 CAS [558-37-2] Fluka	
2,2dimethylbutane C_6H_{14} MW = 86.2 CAS [75-83-2] Fluka		Methylcyclohexane C_7H_{14} MW = 99.2 CAS [108-87-2] Fluka	
3,3 dimethylpentane C_7H_{16} MW = 100.2 CAS [562-49-2] Aldrich		1,2 dimethylcyclohexane C_8H_{16} MW = 121.2 CAS [2207-01-4] Aldrich	
2,3dimethylbutane C_6H_{14} MW = 86.2 CAS [79-29-8] Aldrich		1,1 dimethylcyclohexane C_8H_{16} MW = 112.2 CAS [590-66-9] Aldrich	
2,3 dimethyl-1-butene C_6H_{12} MW = 84.2 CAS [563-78-0] Fluka		Methylcyclopentane C_6H_{12} MW = 84.2 CAS [96-37-7] Fluka	
3,3 dimethyl-1-butyne C_6H_{10} MW = 82.4 CAS [917-92-0]		Cycloheptene C_7H_{12} MW = 97.2 CAS [628-92-2] Aldrich	
Methyl tert-buthyl ether $C_5H_{12}O$ MW = 88.2 CAS [1634-04-4] Fluka			

A weighed quantity of water + promoter is frozen by liquid nitrogen in the top of a glass measuring vessel, which also contains a magnetic stainless-steel stirrer. The maximum error in the mole fraction x in $\{(1 - x)$ promoter $+ xH_2O\}$ is estimated to be 0.002. After degassing the water by repeatedly melting and freezing the water in a vacuum, a volumetrically determined amount of hydrogen is pressed into the measuring vessel by mercury and cooled in the sapphire top. The glass vessel is then placed in a mercury-filled container and held in place by a perforated cover. The top of the measuring vessel with the stirrer and the (promoter + hydrogen + water) mixture protruded from the container.

The vessel is inserted into a special construction of the closing plug of the high-pressure cell. The closing plug and the pressure cell, which is partly filled with a mixture of water + ethylene glycol, are assembled, and perfect sealing is achieved using a copper-coated mild-steel ring. Before the frozen mercury in the top of the measuring vessel can melt, the pressure in the cell is quickly raised up to 20 MPa by pumping water into the vessel.

To achieve equilibrium in the measuring vessel, intensive stirring is accomplished by magnetic movement of the stirrer inside the vessel top.

The pressure cell is cooled externally with two electric mantles, controlled by electronic regulators. The temperature is measured with a platinum resistance thermometer which is placed in a shaft inserted in the closing plug. The autoclave temperature uncertainty was 70 mK and controlled by a Shimaden DSM temperature control unit. A high-pressure bench is connected to the cell by means of a silicone oil-to-mercury-to-hydraulic oil separator. A pressure balance is used to measure the pressure and to keep it constant. The pressure was accurate to ± 0.02 MPa at pressures up to 40 MPa and to ± 0.05 MPa at higher pressures. The achieved accuracy of the temperature measurements was ± 0.01 K. The temperature difference between appearance and disappearance of the solid phase was ± 0.2 K. The accuracy of the pressure measurements using a dead weight gauge is better than ± 0.04 % of the reading from (3.0 to 200.0) MPa.

Table 2. $H-L_w-L_H-V$ Four-Phase Equilibrium Data of the Systems Hydrogen + Promoter (Alkane)

promoter	T/K	P/MPa
2,2,3-trimethylbutane	277.71	85.1
	278.18	90.1
	278.52	95.1
	279.01	100.1
2,2-dimethylbutane	274.13	80.1
	275.29	85.1
	275.76	90.1
	276.21	95.1
	276.68	100.1
3,3-dimethylpentane	272.32	85.1
	273.19	90.1
	273.54	95.1
	274.04	100.1
2,3-dimethylbutane	273.69	85.1
	274.11	90.1
	274.74	95.1
	275.09	100.1

Table 3. $H-L_w-L_H-V$ Four-Phase Equilibrium Data of the Systems Hydrogen + Promoter (Alkene/Alkyne)

promoter	T/K	P/MPa
2,3-dimethyl-1-butene	269.87	90.1
	270.21	95.1
	270.61	100.1
3,3-dimethyl-1-butyne	268.38	90.1
	268.66	95.1
	269.59	100.1
3,3-dimethyl-1-butene	273.93	100.1

Table 4. $H-L_w-L_H-V$ Four-Phase Equilibrium Data of the Systems Hydrogen + Promoter (Cycloalkane/Alkene)

promoter	T/K	P/MPa
methylcyclohexane	274.05	83.1
	274.45	85.1
	274.87	90.1
	275.43	95.1
	275.9	100.1
1,2-dimethylcyclohexane	274.93	95.1
	275.42	100.1
1,1-dimethylcyclohexane	274.74	60.1
	276.14	70.1
	277.77	80.1
	278.92	90.0
	279.49	95.1
methylcyclopentane	271.47	85.1
	271.89	90.1
	272.59	95.1
	272.93	100.1
cycloheptene	272.08	90.1
	272.57	95.1
	273.2	100.1

For an experiment with a known composition, the mixture was brought at conditions in terms of temperature and pressure that the solid hydrate phase was formed. Then the temperature was increased slowly until melting of the solid phase occurred. The disappearance of this phase was determined for different pressures, giving the hydrogen clathrate hydrate equilibrium conditions as a p,T-curve.

Results and Discussion

This work presents experimental data on the thermodynamic equilibrium conditions of hydrogen hydrates for several promoters known to be structure sH formers (Table 1).

In Tables 2, 3, 4, and 5 the experimental phase equilibrium results for the various systems studied are presented, while the experimental data are depicted in $p-T$ diagrams as presented in Figures 1, 2, 3, and 4, respectively.

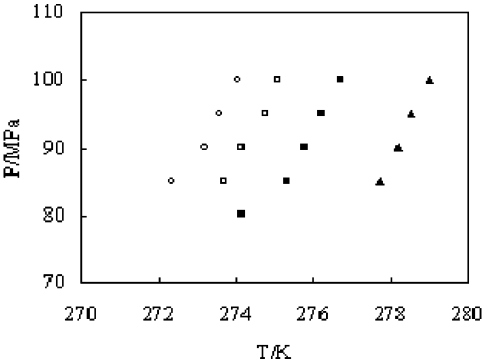


Figure 1. $p-T$ diagram of $H-L_w-L_H-V$ four-phase equilibrium data of the systems hydrogen + promoter (alkanes). ○, 3,3-Dimethylpentane; □, 2,3-dimethylbutane; ■, 2,2-dimethylbutane; ▲, 2,2,3-trimethylbutane.

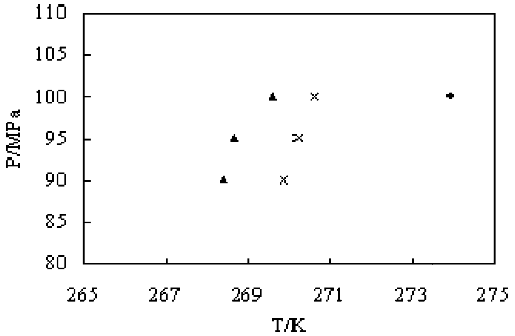


Figure 2. $p-T$ diagram of $H-L_w-L_H-V$ four-phase equilibrium data of the systems hydrogen + promoter (alkenes/alkynes). ▲, 3,3-Dimethyl-1-butene; ×, 2,3-dimethyl-1-butene; ●, 3,3-dimethyl-1-butyne.

Table 5. $H-L_w-L_H-V$ Four-Phase Equilibrium Data of the Systems Hydrogen + Promoter (Ether)

promoter	T/K	P/MPa
methyl *tert*-butyl ether	269.16	70.1
	269.90	75.1
	270.26	80.1
	270.86	85.1
	271.39	90.1
	271.99	95.1
	272.47	100.1

Since in all cases the organic promoter was not miscible with the aqueous phase, we were dealing with four-phase equilibria of the nature: hydrate phase (H) + aqueous phase (L_w) + hydrocarbon phase (L_H) + gas phase (V).

The data presented in this contribution correspond to the melting curves of the hydrates, i.e., the maximum temperature at which the hydrate is stable for a given pressure. The experimental data points limit the region where a solid phase (hydrogen hydrate) exists.

It is interesting to notice that phase equilibrium changes significantly for promoters with the same molecular weight but with different molecular structure. This is most apparent for, for instance, the two alkanes: 2,2-dimethylbutane and 2,3-dimethylbutane.

A similar observation applies for the alkane, 2,3-dimethylbutane, and the alkene, 2,3-dimethyl-1-butene. The introduction of a double bond in the alkyl chain, leads to a shift toward temperatures below 273.15 K for the location of the phase equilibria. Furthermore, the hydrate was found to be stable for pressures higher than 90.1 MPa.

One of the most striking differences can be observed for the systems with 1,1-dimethylcyclohexane and 1,2-dimethylcyclohexane. When 1,1-dimethylcyclohexane is used as promoter,

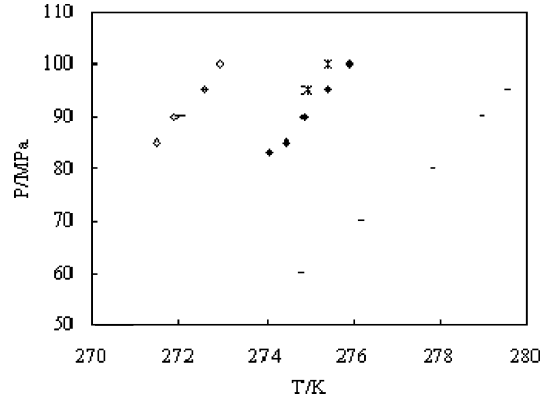


Figure 3. $p-T$ diagram of $H-L_w-L_H-V$ four-phase equilibrium data of the systems hydrogen + promoter (cycloalkanes/alkenes). ◇, Methylcyclopentane; +, cycloheptene; *, 1,2-dimethylcyclohexane; ♦, methylcyclohexane; ▲, 1,1-dimethylcyclohexane.

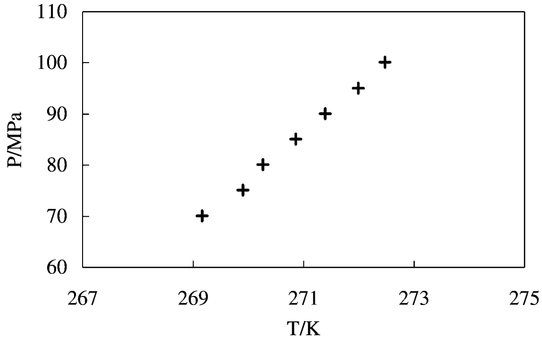


Figure 4. $p-T$ diagram of $H-L_w-L_H-V$ four-phase equilibrium data of the systems hydrogen + promoter (ether). +, Methyl *tert*-butyl ether.

the hydrate can be stabilized at pressures as low as 60.1 MPa, while with 1,2-dimethylcyclohexane, no stable hydrate could be found for pressures lower than 95.1 MPa.

The Clapeyron equation is used to determine the heat of formation from phase equilibrium data obtained in this study. van der Waals and Platteeuw[8] pointed out that for hydrates this equation also holds as we are dealing with univariant systems. If the enthalpy of formation, the compressibility factor, and the stoichiometric ratios of water to guest molecules are assumed to be constant, the enthalpy of hydration can be calculated from the experimental data applying the Clausius−Clapeyron equation[9]

$$\frac{\partial(\ln p)}{\partial(1/T)} = -\frac{\Delta H}{Z\cdot R}$$

ΔH is the enthalpy of hydration; Z is the compressibility factor; and R is the universal gas constant.

A semilogarithmic plot of the formation pressure versus reciprocal absolute temperature is a straight line over limited temperature range. In Figure 5, an example is given for MTBE, and Table 6 summarizes the results obtained for each system studied.

The enthalpies calculated are in the range of the values described in the literature for formation of the sH hydrates.[1]

Conclusions

The possibility to store hydrogen in its molecular form in structure H clathrate hydrates has been proven to be possible. This was already reported in a previous study. In this study, we report equilibrium data of an additional number of hydrocarbons, not miscible with the aqueous phase, which are able to stabilize the hydrogen clathrate hydrate that was formed in these systems. It is interesting to notice that the phase equilibria change significantly for promoters with the same molecular weight but with different molecular structure. Although not completely understood yet, this study clearly demonstrates how the geometry of the promoter may have a major impact on the stabilization conditions of the hydrate. The understanding of this observation should be most challenging for extended computational studies, to develop predictive thermodynamic models, offering a correlation between the experimentally observed phase equilibria and the molecular properties of the promoters.

From the experimental data collected in this study, we conclude that the minimum pressure at which structure sH hydrogen clathrate hydrate can be stabilized is as high as 60.1 MPa, which is still much too high for practical applications. However, on one hand this study offers helpful information on how to stabilize structure H at a much more appreciable conditions, while, on the other hand, the data obtained are the most important for developing predictive thermodynamic models and consequently reducing the extent of time-consuming experiments.

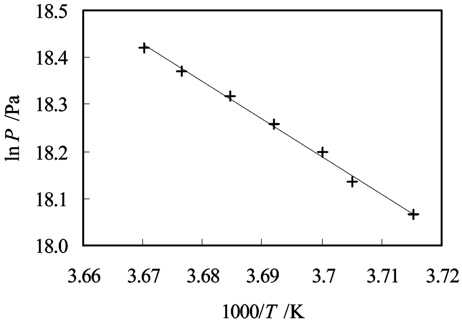


Figure 5. Semilogarithmic plot of formation pressure versus reciprocal absolute temperature, for the system MTBE + H_2O + H_2; $y = -7962.8x + 47.651$, $R^2 = 0.9955$.

Table 6. Formation Enthalpies for the Systems Studied

promoter	ΔH/kJ·mol^{-1}
methylcyclohexane	65
2,2,3-trimethylbutane	81.8
2,2-dimethylbutane	55.7
2,3-dimethyl-1-butene	86.1
1,2-dimethylcyclohexane	65.8
3,3-dimethylpentane	58.9
methyl *tert*-butyl ether	66.2
1,1-dimethylcyclohexane	60.7
3,3-dimethyl-1-butene	−
methylcyclopentane	64.6
2,3-dimethylbutane	69.4
cycloheptene	57.7
3,3-dimethyl-1-butyne	47.5

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