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Hydrate Formation of a Synthetic Natural Gas Mixture in Aqueous Solutions Containing Electrolyte, Methanol, and (Electrolyte + Methanol)

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Hydrate formation has been studied for a synthetic natural gas mixture in pure water and in aqueous solutions containing electrolyte(s), methanol, and a combination of (electrolyte + methanol). Special attention has been given to (electrolyte + methanol) systems, as such data are extremely scarce in the open literature yet are of industrial significance. Sixteen experiments (a total of 107 data points) have been performed in the temperature range of (260.8−281.9) K and pressure range of (0.54−11.18) MPa using the isothermal pressure search method. The generalized hydrate model proposed by Zuo et al. (1996) has been applied successfully to predict the measured data for aqueous systems containing pure water, electrolyte(s), or methanol. A simple exponential expression is proposed to correlate the measured data for aqueous systems containing both electrolyte and methanol. It was found that the addition of methanol would affect the sequence of inhibiting strength of electrolytes.

Introduction

The discovery of huge deposits of natural gas hydrate in situ and the problem of hydrate blockage in gas/oil production and transportation processes have motivated an interest in hydrate research during the past decade. Although numerous measurements on gas hydrate formation conditions are available in the literature, most data have been measured for systems containing pure water. In the real production environment, salts (electrolytes) are present in the formation water, and industrial hydrate formation inhibitors (e.g., methanol, ethylene glycol, etc.) are often injected. For developing or testing a thermodynamic model for application to real natural gas hydrate systems, a sufficient amount of basic data is required. In recent years, a number of experimental measurements on systems containing electrolytes or other inhibitors have been reported (Song and Kobayashi, 1989; Ross and Toczylkin, 1992; Dholabhai et al., 1991, 1993; Englezos and Ngan, 1993; Dholabhai and Bishnoi, 1994); however, results for systems containing both electrolytes and methanol are very scarce. The only values now available are those reported by Dholabhai et al. (1996) on (carbon dioxide + electrolytes + methanol) systems.

The objectives of this work are to measure systematically the hydrate formation conditions of a synthetic natural gas mixture in pure water and aqueous solutions containing electrolyte(s), methanol, and a combination of (electrolyte + methanol). In addition, the performance of the generalized hydrate model proposed by Zuo et al. (1996) is tested on the systems studied, and a simpler correlation is proposed. Special attention has been given to those systems containing both electrolyte(s) and methanol.

Experimental Section

Apparatus. A schematic diagram of the experimental apparatus used in this work is shown in Figure 1. The apparatus was described in detail by Mei et al. (1996). For easy reference, a brief description is given below.

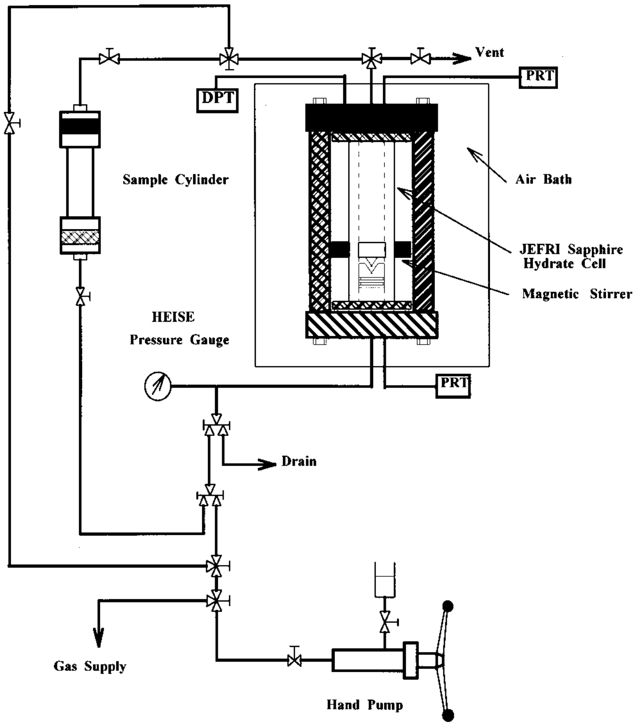

Figure 1. Schematic diagram of the experimental apparatus. DPT, differential pressure transducer; PRT, platinum resistance thermometer.

The apparatus consisted mainly of a variable-volume high-pressure sapphire cell (manufactured by DB Robinson Design & Manufacturing Ltd.), the effective volume (excluding the floating piston) being approximately 60 cm^3, and the maximum working pressure being 20 MPa. The working volume of the cell could be adjusted by the floating piston, which was driven by a positive displacement pump. An aqueous ethanol solution (50/50 mass %) was used as the displacement fluid. Isolation between the experimental

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Table 1. Composition of the Synthetic Natural Gas Studied

component	composition/ mol %	component	composition/ mol %
methane	97.25	propane	1.08
ethane	1.42	2-methylpropane	0.25

system and the pressure transmitting agent in the cell was achieved by using two fluorosilicone O-rings. The top and bottom caps of the cell were connected by socket-head screws and sealed by Enflon cushions and gland rings. The sapphire cell was installed in an air bath, the working temperature range was (233 K to 403 K) and could be controlled to within ±0.2 K by using a digital programmable temperature controller. The stirring system consisted of a magnetic stirrer coupled with a magnet mounted outside the cell. A variable-speed dc motor provided up and down reciprocating motion of the magnet through a driving rod. The experimental temperature was measured by two platinum resistance thermometers (PRT) located at the upper and bottom parts of the cell. The two PRTs were calibrated against an NBS-certified thermocouple and connected to the data acquisition system through a universal temperature transmitter. The accuracy of the temperature measurement in this study was estimated at ±0.1 K. The pressure in the cell was measured by a variable-span differential pressure transducer (connected to the data acquisition system) and a (0 to 25) MPa HEISE pressure gauge simultaneously. The pressure measure-

Table 2. Hydrate Formation Data of the Synthetic Natural Gas in Pure Water and Aqueous Electrolyte/Aqueous (Electrolyte(s) + Methanol) Solutions

aqueous phase	T/K	P/MPa	aqueous phase	T/K	P/MPa
pure water	273.5	0.92	pure water	278.8	1.63
	275.0	1.15		279.7	1.87
	276.6	1.36		280.9	2.24
	277.7	1.50		281.9	2.67
10 mass % NaCl	267.1	0.81	10 mass % NaCl	275.5	2.12
	269.2	1.01		277.6	2.66
	271.0	1.30		277.7	2.68
	273.4	1.66		279.8	3.43
10 mass % KCl	269.1	0.78	10 mass % KCl	275.6	1.81
	271.3	0.97		277.7	2.26
	273.3	1.25		279.8	2.81
10 mass % $CaCl_2$	266.7	0.63	10 mass % $CaCl_2$	275.4	1.88
	269.2	0.88		277.4	2.48
	271.1	1.14		279.7	3.34
	273.5	1.44			
2.0 mass % NaCl + 0.5 mass % $CaCl_2$ + 0.5 mass % KCl	270.9	0.60	2.0 mass % NaCl + 0.5 mass % $CaCl_2$ + 0.5 mass % KCl	277.4	1.60
	273.2	0.93		279.2	2.06
	275.2	1.20		281.2	2.75
10 mass % methanol	266.8	0.61	10 mass % methanol	275.4	1.68
	269.0	0.79		277.5	2.14
	271.2	1.00		279.5	2.71
	273.2	1.03			
20 mass % methanol	264.5	0.74	20 mass % methanol	272.8	2.48
	266.6	1.20		275.4	3.40
	268.6	1.51		277.6	4.50
	270.6	1.91			
10 mass % KCl + 10 mass % methanol	266.5	1.16	10 mass % KCl + 10 mass % methanol	275.5	3.47
	269.3	1.42		277.5	4.61
	270.9	1.84		279.5	6.03
	273.4	2.67			
10 mass % NaCl + 10 mass % methanol	264.7	1.05	10 mass % NaCl + 10 mass % methanol	273.4	3.18
	267.0	1.40		275.4	3.98
	269.0	1.78		277.5	4.90
	271.0	2.47			
30 mass % methanol	262.6	1.60	30 mass % methanol	267.9	2.56
	264.7	1.97		268.9	2.85
	266.9	2.24		270.2	3.20
10 mass % NaCl + 20 mass % methanol	260.8	1.70	10 mass % NaCl + 20 mass % methanol	265.5	3.06
	262.4	2.06		267.5	3.98
	264.0	2.56		269.0	4.96
10 mass % $CaCl_2$ + 10 mass % methanol	267.0	1.10	10 mass % $CaCl_2$ + 10 mass % methanol	275.5	3.42
	269.0	1.58		277.5	4.43
	270.8	1.84		279.4	5.95
	273.5	2.57			
10 mass % KCl + 20 mass % methanol	264.6	1.80	10 mass % KCl + 20 mass % methanol	271.3	5.53
	266.6	2.50		273.4	7.76
	268.6	3.46		275.5	11.18
10 mass % $CaCl_2$ + 20 mass % methanol	264.5	1.47	10 mass % $CaCl_2$ + 20 mass % methanol	269.1	3.44
	266.1	2.05		270.7	4.34
	267.6	2.66		272.4	5.89
2.0 mass % NaCl + 0.5 mass % $CaCl_2$ + 0.5 mass % KCl + 20 mass % methanol	266.5	1.47	2.0 mass % NaCl + 0.5 mass % $CaCl_2$ + 0.5 mass % KCl + 20 mass % methanol	274.8	4.52
	268.7	1.96		276.9	5.92
	270.7	2.57		279.0	7.88
	272.9	3.40			
2.0 mass % NaCl + 0.5 mass % $CaCl_2$ + 0.5 mass % KCl + 10 mass % methanol	268.6	0.78	2.0 mass % NaCl + 0.5 mass % $CaCl_2$ + 0.5 mass % KCl + 10 mass % methanol	276.4	2.48
	271.3	1.18		278.9	3.46
	273.8	1.66		281.5	4.69

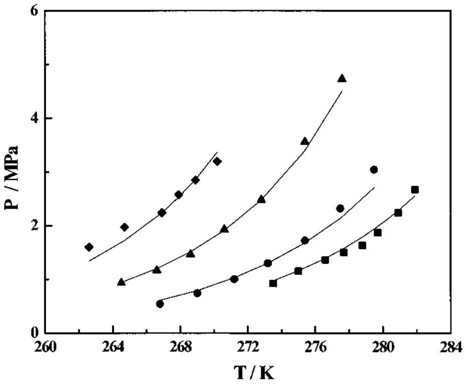

Figure 2. Comparison of experimental and predicted hydrate formation data for a synthetic natural gas mixture in pure water and aqueous methanol solutions: (■) pure water; (●) 10 mass % methanol; (▲) 20 mass % methanol; (◆) 30 mass % methanol; (—) prediction.

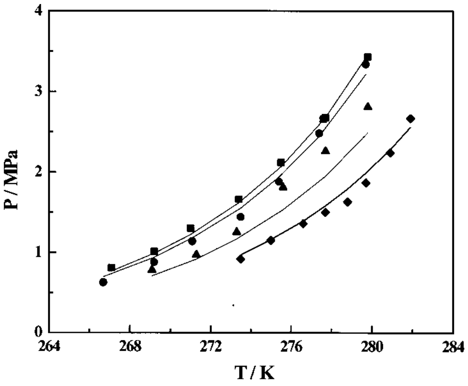

Figure 3. Comparison of the inhibiting effects of NaCl, KCl, $CaCl_2$ at 10 mass % salt concentration: (◆) pure water; (■) NaCl; (●) $CaCl_2$; (▲) KCl; (—) prediction.

ment instruments were calibrated against a RUSKA deadweight gauge (Model 2480-700, RUSKA Corp.), and the uncertainty of the pressure measurement was estimated as ±0.025 MPa.

Materials and Preparation of Fluid Samples. The synthetic natural gas mixture was prepared for simulating a typical field natural gas that occurred at the South China Sea area. Research-grade pure gases (≥99.95%) were purchased from AP Beifen Gas Industry Corporation. The composition of the prepared gas mixture reported in Table 1 was analyzed by HP-5890A gas chromatography. The two parallel analyses matched within ±0.1% mole fraction.

The salts (electrolytes) and methanol used for preparing the aqueous solutions were research-grade chemicals supplied by the Beijing Reagents Corporation, and the deionized water was distilled prior to use. Appropriate quantities of salt, methanol, and deionized water were weighed on a top-loading electronic balance with a readability of ±0.1 mg. For ensuring no salt precipitation had occurred, all the prepared aqueous samples were inserted into the air bath maintained at the lowest experimental temperature over 24 h. The compositions of the aqueous solutions prepared for this study are given in Table 2.

Experimental Method. The experiments were performed using the isothermal pressure search method. Prior to charging the liquid sample, the cell was rinsed three times with deionized water. Approximately 10 cm^3 of the aqueous solution was introduced for each experiment. The vapor phase of the cell was then purged with the prepared natural gas mixture three times to remove the residual air. The system was then allowed to equilibrate at the preset experimental temperature for 2 h.

To diminish the hysteresis phenomenon during the hydrate formation process, the system was raised to a pressure exceeding the estimated equilibrium pressure (using in-house software) by about 1.0 MPa prior to taking measurements. In this way, a large amount of hydrate crystals were observed in the cell. The system pressure was then decreased slowly by withdrawing the floating piston (or venting the excess gas) until the hydrate crystals were decomposed thoroughly. This pretreatment was repeated two times for each experimental run.

In measuring the hydrate formation pressure at a selected temperature, the system was initially kept at the estimated formation pressure for 3−4 h. If no hydrate crystals were appeared, the system pressure was raised in steps of about 0.5 MPa and the observation was repeated. If hydrate crystals did appear at the initial pressure, the system pressure was then accordingly reduced. This pressure search procedure was terminated when the pressure adjustment step was reduced to 0.05 MPa. The onset of hydrate formation was determined by the appearance of a small number of very tiny hydrate crystals in the cell once the pressure and temperature were stable during a 4−6 h time period. A different temperature was subsequently selected, and the procedure was repeated to obtain the next hydrate equilibrium condition. Finally, it should be emphasized that the hydrate formation pressures and temperatures reported in this work could be reproduced to within ±0.05 MPa and ±0.1 K.

Experimental Results and Discussion

Sixteen sets of hydrate formation data (a total of 107 values) have been measured for the synthetic natural gas mixture in the presence of pure water and aqueous solutions containing electrolyte(s), methanol, and (electrolyte(s) + methanol). The experimental results are tabulated in Table 2.

The generalized hydrate model proposed by Zuo et al. (1996) has been applied successfully to predict the hydrate formation data of various systems containing methanol or electrolyte(s). The comparisons of experimental hydrate formation data and prediction based on Zuo's model for systems containing pure water and 10, 20, and 30 mass % aqueous methanol solutions are presented in Figure 2. The *average absolute deviations* (AAD) and the *maximum absolute deviations* (MAD) of the calculated values were 3.6% and 6.1% for pure water, 6.3% and 11.1% for 10 mass % methanol solution, 2.4% and 4.7% for 20 mass % methanol solution, and 6.1% and 12.6% for 30 mass % methanol solution, respectively.

The pure salt species studied involved NaCl, KCl, and $CaCl_2$. The measured hydrate formation pressures for those systems containing a single salt were also well-predicted by using the Zuo et al. model. The comparison between experimental and predicted results at 10 mass % salt concentration is shown in Figure 3. The AADs and MADs for the three single salts were 2.1% and 5.9% for NaCl, 5.4% and 7.9% for $CaCl_2$, and 10.2% and 13.8% for KCl, respectively. The observed inhibiting effect was in the following sequence:

$$NaCl > CaCl_2 > KCl$$

However, the inhibiting effects of NaCl and $CaCl_2$ were quite similar, in accordance with the observation reported by Dholabhai et al. (1991, 1993) and Dholabhai and Bishnoi (1994).

Table 3. Fitted Values of Constants *A* and *B*

aqueous phase	A	B
10 mass % NaCl + 10 mass % methanol	8 991.38	34.02
10 mass % KCl + 10 mass % methanol	9 811.96	36.87
10 mass % $CaCl_2$ + 10 mass % methanol	9 796.24	36.80
10 mass % NaCl + 20 mass % methanol	9 890.87	35.33
10 mass % KCl + 20 mass % methanol	12 219.8	46.75
10 mass % $CaCl_2$ + 20 mass % methanol	12 442.3	47.45
2.0 mass % NaCl + 0.5 mass % $CaCl_2$ + 0.5 mass % KCl + 10 mass % methanol	10 607.4	39.26
2.0 mass % NaCl + 0.5 mass % $CaCl_2$ + 0.5 mass % KCl + 20 mass % methanol	10 047.1	38.06

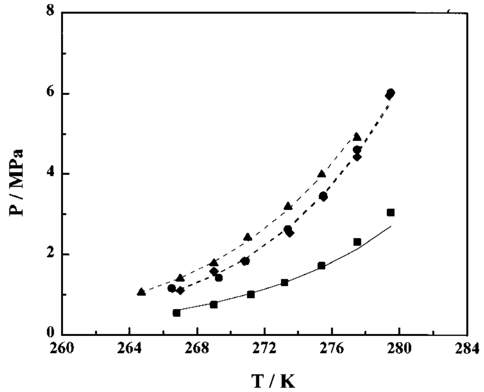

Figure 4. Comparison of the inhibiting effects of the aqueous solutions containing 10 mass % salt (NaCl/KCl/$CaCl_2$) and 10 mass % methanol: (■) salt-free methanol; (▲) (NaCl + methanol); (●) (KCl + methanol); (◆) ($CaCl_2$ + methanol); (—) prediction based on Zuo et al. model; (- - -) calculated by eq 1.

Due to the lack of required binary interaction parameters, it is difficult to apply the Zuo et al. model to systems containing both methanol and electrolytes. For such systems, the following empirical exponential equation was used to correlate the experimental data

$$P = \exp(-A/T + B) \tag{1}$$

where P is the pressure in MPa, T is the temperature in K, and A and B are the two constants determined by regression on the hydrate formation data obtained for a specific system. The fitted values of A and B for various (electrolyte + methanol) systems are listed in Table 3.

The inhibiting effects of a single salt (NaCl, $CaCl_2$, or KCl at 10 mass %) in 10 mass % and 20 mass % methanol solutions are shown in Figures 4 and 5, respectively. The experimental data are excellently represented (MAD $\leq$ 3%) by eq 1 (for salt-containing methanol solutions) and by the Zuo et al. model (for salt-free methanol solutions). It is interesting to notice that the inhibiting effect of methanol is significantly affected in the presence of salt, and KCl shows a slightly stronger inhibiting effect than $CaCl_2$ in the methanol solutions. The reason for the change of the inhibiting effect sequence could be because the hydration effect of di-valent ions is weaker than that of monovalent ions in aqueous methanol solutions.

Finally, the hydrate formation data of the synthetic natural gas in aqueous solutions containing mixed electrolytes (NaCl + $CaCl_2$ + KCl) and (mixed electrolytes + methanol) are presented in Figure 6. The AAD and MAD of the calculated formation pressures based on the Zuo et al. model were 9.3% and 14.5%, respectively.

Conclusions

Sixteen sets of hydrate formation data were measured for a synthetic natural gas mixture in the presence of pure water and aqueous solutions containing single electrolytes (NaCl/KCl/$CaCl_2$), mixed electrolytes, methanol, and (eletrolyte(s) + methanol). It was found that the inhibiting strength of the salt species studied is in the order of NaCl > $CaCl_2$ > KCl in pure water and NaCl > KCl > $CaCl_2$ in methanol solutions. This difference can be explained in that the presence of methanol in salt solutions would affect the ion hydration to different degrees for ions with different valences. The generalized hydrate model developed by Zuo et al. (1996) is capable of predicting the hydrate formation data satisfactorily for systems containing salt(s) or methanol. However, for systems containing both electrolyte(s) and methanol, an empirical equation, eq 1, is suggested for correlating the experimental data.

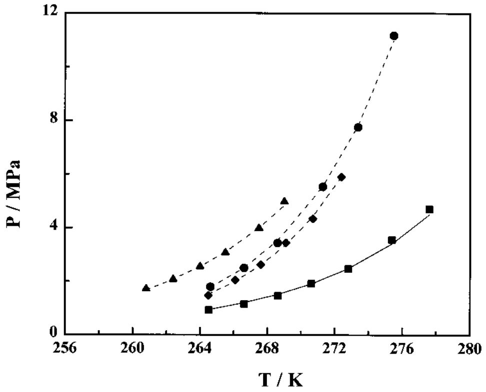

Figure 5. Comparison of the inhibiting effects of the aqueous solutions containing 10 mass % salt (NaCl/KCl/$CaCl_2$) and 20 mass % methanol: (■) salt-free methanol; (▲) (NaCl + methanol); (●) (KCl + methanol); (◆) ($CaCl_2$ + methanol); (—) prediction based on Zuo et al. model; (- - -) calculated by eq 1.

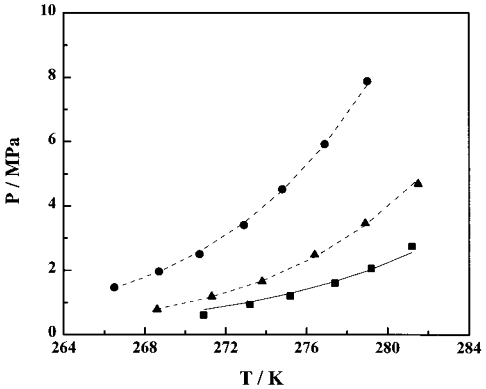

Figure 6. Experimental hydrate formation conditions for a synthetic natural gas in aqueous solutions containing mixed electrolytes and (mixed electrolytes + methanol): (■) (2 mass % NaCl + mass % $CaCl_2$ + 0.5 mass % KCl); (▲) (2 mass % NaCl + 0.6 mass % $CaCl_2$ + 0.5 mass % KCl + 10 mass % methanol); (●) (2 mass % NaCl + 0.5 mass % $CaCl_2$ + 0.5 mass % KCl + 20 mass % methanol); (—) prediction based on Zuo et al. model; (- - -) calculated by eq 1.

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