

# Equilibrium PT curve of methane hydrates in the presence of $\text{AlCl}_3$

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**Abstract** Using an experimental transparent sapphire high-pressure cell, three-phase (methane hydrate +  $\text{AlCl}_3$  solution + methane) equilibrium conditions of methane hydrates in the aqueous solution containing  $\text{AlCl}_3$  have been investigated under conditions of temperature from 272.15 to 278.15 K and pressure from 4.040 to 8.382 MPa. It could be clearly verified that  $\text{AlCl}_3$  is of stronger inhibitive effect than that observed for other electrolytes, such as  $\text{KCl}$ ,  $\text{CaCl}_2$ , at the same mole fraction. The induction time of the methane hydrate formation becomes longer when the water activity decreases with the increase of ion charge numbers. Methane hydrates tend to crystallize more easily with higher concentration ( $\text{AlCl}_3$  concentration of 18%) than lower one ( $\text{AlCl}_3$  concentration of 10%) in the same electrolyte solution. An empirical exponential equation is presented to calculate the equilibrium temperature and pressure of methane hydrate stable occurrence, and to correlate the measured data for aqueous  $\text{AlCl}_3$  solution. The results show that there was infinitely small discrepancy between the theoretical computed values and the data observed in actual experiments.

**Keywords:** methane hydrate, phase equilibrium, PT curve,  $\text{AlCl}_3$  solution, inhibitive effect.

As is well known, natural gas hydrate might be a large potential energy source in the future. However, in the shallow Earth crust, its instability can make some serious problems, such as hazards at sea floor, effect on the global carbon cycle, and long-term climate changes in the atmosphere<sup>[1,2]</sup>. It can also reach rather low temperature to form hydrate crystals that plug production facilities. For these reasons, people have developed many methods, such as physical, chemical or physico-chemical methods, to gain understandings of conditions of hydrate formation and decomposition. The determination of hydrate equilibrium data could lay the basis for controlling hydrate in the exploration and development of oil and gas fields. In or-

der to evaluate and utilize the potential large source, many countries want to obtain new exploration methods, such as pressure decreasing, temperature increasing, and have already succeeded in the Messoyaha gas field in Russia. And there were even some experimental procedures trying to develop electronic magnet and supersonic wave to produce natural gas from gas hydrates in sediments at sea floor. But all of the above are limited by high expense. Lately, a lot of experiments for studying the equilibrium conditions of gas hydrates in aqueous electrolyte solutions or other inhibitors have been reported. Ng, H. -J.<sup>[1]</sup>, Ng, H. -J. and Robinson, D. B.<sup>[3]</sup>, and Song, K. Y. et al.<sup>[4]</sup> studied the equilibria of some carbonate gas hydrates, like methane, ethane and propane hydrate, in different media (such as salt and alcohol), and the formation and decomposition of them. Researches investigated hydrate equilibrium conditions with different gas hydrate systems solutions in the presence of electrolytes with different concentrations and compositions, and showed that salt and alcohol could inhibit the gas hydrate formation very well<sup>[5-13]2,3)</sup>. Recently, other people researched the mechanism of the gas hydrate formation and obtained some dynamic inhibitors of high molecular polymers. Electrolytes, as a currently hot topic in studies on inhibitors, have the ability to suppress the hydrate formation and to change the equilibrium conditions of gas hydrates. In  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solution systems, several phase equilibrium models of gas hydrates have been presented. However,  $\text{AlCl}_3$ , having the effect on the gas hydrate stability and substantial occurrence in strata, has rarely been considered, and how it can affect the equilibrium temperature and pressure conditions is not very clear.

## 1 Experimental

A set of apparatus, which consists of the high-pressure cell, constant temperature air bath, thermometer and manometer, mixer, and computer data-acquisition system, is used to perform the experimental procedure. A high-pressure cell, the JEFRI transparent sapphire cell with a volume of  $\sim 78 \text{ cm}^3$ , can stand up to the pressure of 20 MPa and the temperature ranging from  $-90$  to  $150^\circ\text{C}$ , in which methane hydrates are formed. A WGD4025A thermal equilibrium test case with the precision of  $\pm 0.1^\circ\text{C}$  and the uniformity of  $\pm 0.3^\circ\text{C}$  can keep temperature in the air bath constant and provide temperature control. Two platinum resistance (Pt 100) thermometers (PRT) are located at the upper and bottom parts of the cell, which are calibrated against an NBS-certified thermocouple and connected to the data acquisition system through a universal temperature transmitter. The manometer is a variable-span differential pressure transducer connected to

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2) Berecz, E., Balla-Achs, M., Research Report No. 37 (185-XI-1-1974 OGIL), NME, Technical University of Heavy Industry, Miskolc Hungary, Gas Hydrates, Studies in Inorganic Chemistry, Vol. 4, New York: Elsevier, 1983, 343.

3) Maekawa, T., Imai, N., Equilibrium conditions of methane and ethane hydrates in aqueous electrolyte solutions, Geological Survey of Japan, 1995.

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the data acquisition system and to a MPa (from 0 to 25 MPa) HEISE pressure gauge at the same time, with the uncertainty of  $\pm 0.025$  MPa. The pressure and temperature in the cell can be monitored by the thermometer and manometer. The mixer, which is made of permanent magnetic material, mixes the aqueous system and speeds up the reaction of the methane hydrate formation. The computer data-acquisition system carries out automatically the acquisition and analysis of experimental equilibrium temperature and pressure data of the hydrate formation and decomposition.

Methane gas samples with a purity of 99.95% by volume used in this study are from Beifen Gas Industry Company of Beijing.  $\text{AlCl}_3$  used for preparing the aqueous solution is the research-grade chemical supplied by Beijing Reagents Corporation. The deionized water is distilled prior to use and used without further purification. Appropriate quantities of  $\text{AlCl}_3$  and distilled water are weighed on a top-loading electronic balance with a readability of  $\pm 0.1$  mg.

After preparing systems and reaching the temperature and pressure equilibrium, the experiment began. The system was cooled and the temperature and pressure inside the high-pressure cell were recorded as a function of time at every 10 s. After enough hydrates formed, the pressure was reduced to a value slightly less than the expected equilibrium pressure by withdrawing the floating piston. The system was left to equilibrate. If the temperature and pressure of the system could be maintained to be constant for 4–6 h with very tiny hydrate crystals present in the solution, the system was taken at the equilibrium condition and the experiment was terminated.

## 2 Results and discussions

(i) PT curve of methane hydrates in pure water.

For the calibration of the experimental apparatus and procedure, methane hydrate phase equilibria in the pure water system must be investigated first. The stability conditions of the methane gas in pure water were measured within the temperature range of 273.7–286.4 K and the pressure range of 2.75–9.99 MPa, and the results<sup>1)</sup> were compared with the previous data<sup>[14,2,3)</sup> (Fig. 1) to check the experimental apparatus and the experimental procedure. The experimental data of methane hydrates in pure water are in good agreement with the previous data<sup>[14,2,3)</sup>. This indicates that the following experimental data are correct.

(ii) PT curve of methane hydrates in  $\text{AlCl}_3$  solution.

A series of experiments with the aqueous electrolyte solution were performed. The electrolytes used are  $\text{AlCl}_3$ . The eight numerical values of the measured data are

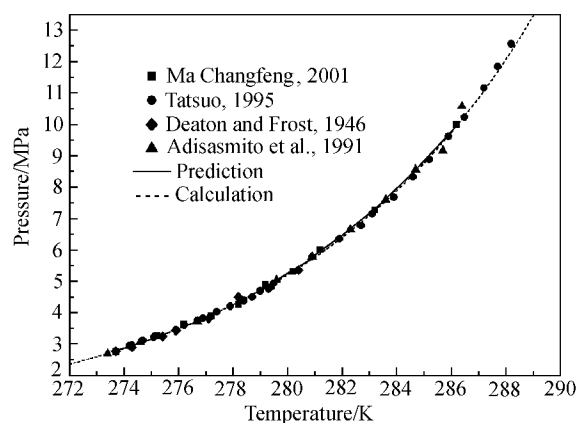


Fig. 1. Comparison of PT lines of methane hydrates in pure water.

Table 1 Experimental data on hydrate equilibrium conditions ( $T$ ,  $P_{\text{exp}}$ ), calculation result ( $P_{\text{calc}}$ ) using the empirical equation and  $\Delta P$  of methane in aqueous electrolyte containing  $\text{AlCl}_3$

Solution	$T/\text{K}$	$P_{\text{exp}}/\text{MPa}$	$P_{\text{calc}}/\text{MPa}$	$\Delta P/\text{MPa}$
10% $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	272.15	4.040	4.044	-0.004
	273.15	4.540	4.488	-0.052
	276.15	6.070	6.160	-0.090
	278.15	7.680	7.638	0.042
18% $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	272.15	4.523	4.468	0.052
	273.15	4.921	4.948	-0.027
	276.15	6.675	6.750	-0.075
10% $\text{KCl}^{[6]}$	278.15	8.382	8.340	0.042
	269.16	1.83	1.856	-0.026
	272.16	2.59	2.577	0.013
	275.9	3.94	3.919	0.021
	278.96	5.56	5.571	-0.011

shown in Table 1. Our results show that the equilibrium pressure of methane hydrates is higher and temperature lower, which indicates that  $\text{AlCl}_3$  solutions in the layer could lead methane hydrate to occur in the conditions of lower temperature and higher pressure. The equilibrium pressure increases and the equilibrium temperature decreases with the concentration of the  $\text{AlCl}_3$  solution increasing (Fig. 2). Moreover, the experimental three-phase equilibrium line of the solution (methane + methane hydrate +  $\text{AlCl}_3$ ) moves toward the left and enlarges the area of hydrate instability, but the zone of hydrate stability reduced. The comparison between the experimental data of 18% $\text{AlCl}_3$  and that of 10% $\text{KCl}$  from the literature, with the same mole fraction shows that the inhibiting effect of  $\text{AlCl}_3$  is stronger than that of  $\text{KCl}$  (Fig. 3). We interpret that this is relevant to the water activity in solutions. When the water activity coefficient is lower, the formation of methane hydrates is more difficult. Fig. 4 shows that

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2) See footnote 1) on page 53.

3) Deaton, W. M., Frost, E. M., Gas hydrate and their relation to the operation of natural gas pipe line, Bur. Mines Morogr., 1946, 8.

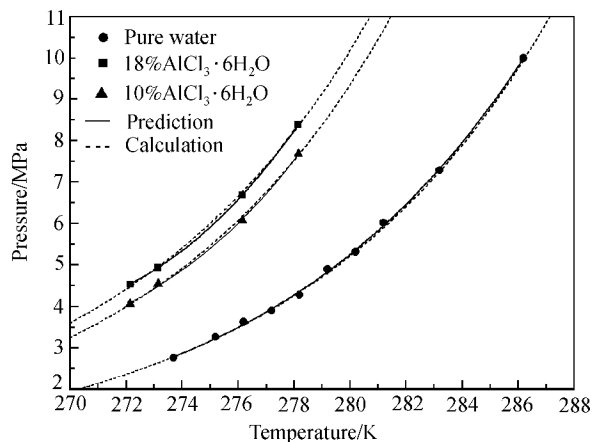


Fig. 2. Experimental data and calculated curves for methane hydrate equilibrium conditions in  $\text{AlCl}_3$  solutions with different concentrations.

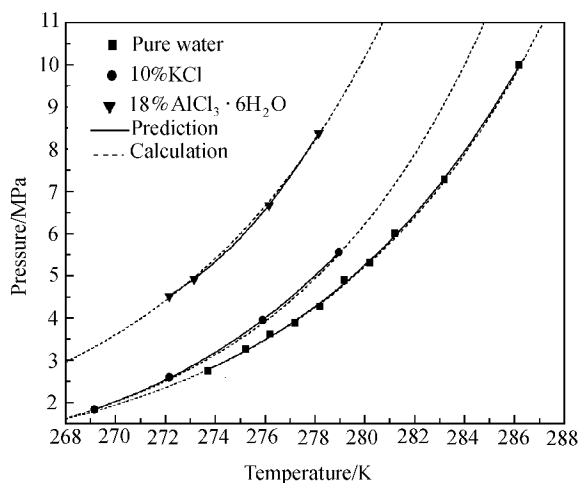


Fig. 3. Experimental data and calculated curves for methane hydrate equilibrium conditions in  $\text{AlCl}_3$  and  $\text{KCl}$  solutions.

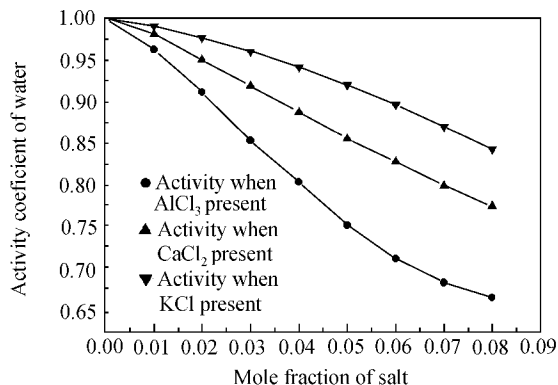


Fig. 4. Activity coefficient of water in brines of  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{AlCl}_3$  plotted at different concentrations.

1) See footnote 1) on page 53.

the water activity decreases with the increase of ion charges, that is  $\text{AlCl}_3 < \text{CaCl}_2 < \text{KCl}$ .

The water activity is dependent on the water confu-sion produced by salt ions and the ions charge. The effect of charges is expressed through the surface charge, which is the charge divided by the surface area of ion. The ions are considered hard spheres. The water activity coefficient decreases with salt concentration increasing. This is accounted for by the mole fraction of the ions. We have obtained the new empirical equation on the equilibrium conditions of methane hydrate in the aqueous solutions together with the literature using statistical analyses. The following empirical experimental equation was used to correlate the experimental data:

$$P = \exp(A + BT^3),$$

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 from the system. The fitted values of  $A$  and  $B$  for various systems are listed in Table 2. The numerical values of the measured data and those calculated by the empirical equation are shown in Table 1. Figs. 1, 2 and 3 show the calculated data using the empirical equation together with the experimental data obtained in this work. There is a very good agreement among all the experimental data and the data calculated by the empirical equation of methane hydrate in the  $\text{AlCl}_3$  aqueous solution. The standard error between the experimental data obtained and the calculation by the empirical equation is 2.6%—7.9%. In addition, the predicted hydrate formation pressures and temperatures using the method of Englezos et al.<sup>[10]</sup> are also shown in the figures. The model has been applied in hydrate formation pressures and temperatures in the presence of either single electrolyte solutions or mixed electrolyte solutions. The maximum absolute deviation between the experimental data and the prediction is 5.9%.

Table 2 Fitted values of constants  $A$  and  $B$

Solution	$A$	$B$
Pure water <sup>1)</sup>	-7.8806	$4.3441 \times 10^{-7}$
10% $\text{KCl}$ <sup>[10]</sup>	-9.0846	$4.9709 \times 10^{-7}$
10% $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	-8.0089	$4.6664 \times 10^{-7}$
18% $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	-7.7360	$4.5805 \times 10^{-7}$

During the experimental period, we found that, when the  $\text{AlCl}_3$  solution with the same concentration is used to perform the experiment at different time, the induction time for methane hydrates is different. That is to say, the longer the  $\text{AlCl}_3$  solution is prepared, the longer the in-

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duction time and the more difficult the formation of methane hydrates are. There were lots of phenomena that hydrate cannot form in  $\text{AlCl}_3$  solutions within about 24 h. The explanation, we think, is that  $\text{AlCl}_3$  in the aqueous solution usually forms halogenated anions, that is,  $\text{AlCl}_3 + \text{Cl}^- = \text{AlCl}_4^-$ . Thus,  $\text{AlCl}_4^-$  in the aqueous solution has a kind of hydration with water. This can result in the formation for methane hydrates at the higher pressure at the given temperature. The reason needs further discussions. According to this result and the higher phase equilibrium pressure and the lower temperature for the formation of methane hydrates in the presence of  $\text{AlCl}_3$ , we think that  $\text{AlCl}_3$  is a better inhibiting agent relative to  $\text{KCl}$ . It could be applied in the oil-gas industry to inhibit the formation of gas hydrates so as to prevent pipelines from plugging.

### 3 Conclusions

Experimental three-phase (methane + methane hydrate +  $\text{AlCl}_3$ ) solution equilibrium conditions of aqueous solutions within the temperature range of 272.15—278.15 K, and the pressure range of 4.040—8.382 MPa were obtained. It is significance for the prediction of the hydrate formation and decomposition in actual strata. The pressure of hydrate stable occurrence is higher and the temperature tended to be lower. The hydrate stability range is smaller than the unstability range. The results suggest that  $\text{AlCl}_3$  has a significant inhibitive effect, which is stronger than other electricytes, such as  $\text{KCl}$  and  $\text{CaCl}_2$ , on the same mole fraction basis. It is also shown that the reduction time of the methane hydrate formation becomes longer when the water activity decreases with the increase of the ion charge. Methane hydrates tend to crystallize more easily with higher concentration than the lower one in the same electricyte solution. Here, we correlate the experimental pressure and temperature data for the formation of methane hydrates in  $\text{AlCl}_3$  or  $\text{KCl}$  solutions using an empirical equation and find that there is only discrepancy between calculations and experiments. Hence,  $\text{AlCl}_3$  is a better inhibitor and will be applied to industry in the future. In addition, the experimental data for the systems are compared with the predictions according to the method of Englezos and Bishnoi<sup>[10]</sup> and they are in good agreement with each other.

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