Phase Equilibria of Ethane Hydrate in $MgCl_2$ Aqueous Solutions

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In this work, phase equilibrium data for ethane hydrate in the presence of $MgCl_2$ aqueous solutions were reported at concentrations of (0.05, 0.3, 0.5, 0.8, and 1.2) $mol\cdot dm^{-3}$ $MgCl_2$ in the temperature and pressure ranges of (276.2 to 286.0) K and (1.12 to 2.70) MPa, respectively. Measurements were made using the isochoric pressure-search method. The results showed that the addition of $MgCl_2$ caused the phase equilibrium temperatures to be lowered. The difference of phase equilibrium temperatures between pure water and a solution at a given pressure increased with the increasing concentration of $MgCl_2$.

Introduction

Gas hydrates are ice-like crystalline compounds that are formed by water and natural gas components under certain temperature and pressure conditions. The hydrate-forming gases like methane, ethane, and carbon dioxide form structure I, whereas propane, argon, and oxygen form structure II. Besides, gas hydrates are found to exist in other distinct forms including structure H[1] and many more complex hydrate structures, named as structure III to VII and structure T (sT).[2–4]

Since the discovery of gas hydrates in deep-sea sediments and in permafrost regions, gas hydrates have been regarded as a possible means of solving current energy problems. In addition, hydrate-related technologies, including gas transportation and storage, gas separation, green gas sequestration, seawater desalination, and so on, can be applied. On the other hand, hydrate formation always occurs during drilling, oil and gas production, transportation, and processing, sometimes resulting in pipeline blockage and other problems. So phase equilibrium data for gas hydrates in the presence or absence of electrolytes are essential for cost-effective design and operation and are necessary to be determined.

The effect of various electrolytes on hydrate formation has been studied extensively. Knox et al.[5] and Kubota et al.[6] studied propane hydrate formation in the presence of NaCl to develop a seawater desalination process via gas hydrate formation. Englezos and Ngan[7] presented incipient equilibrium experimental data for propane hydrate formation in pure water and aqueous single, binary, and ternary solutions of NaCl, KCl, and $CaCl_2$. Dholabhai et al.[8] were the first to report methane hydrate formation in the presence of mixed electrolyte solutions. Haghighi et al.[9] reported experimental dissociation data for methane simple hydrates in the presence of aqueous solutions containing different concentrations of NaCl, KCl, and $MgCl_2$. Kang et al.[10] determined methane and carbon dioxide hydrate formation at the $MgCl_2$ mass fraction w from 0.03 to 0.15 and 0.03 to 0.10, respectively. The experimental hydrate equilibrium data for carbon dioxide hydrates in aqueous solutions of KNO_3, $MgSO_4$, and $CuSO_4$ were made first by Clarke et al.[11]

Table 1. Experimental Materials Used in This Work

chemical	purity	supplier
ethane	99.99 %	South China Special Gas Co., Ltd.
$MgCl_2$	98 %	Tianjin Qilun Chemical Technology Co., Ltd.
deionized water		laboratory-made

For ethane hydrate phase equilibrium data in systems containing single and mixed electrolytes, most of the available literature mainly deal with NaCl, KCl, $CaCl_2$, and their mixtures. Englezos and Bishnoi[12] reported experimental equilibrium data for ethane hydrate formation in single and mixed electrolyte solutions of NaCl, KCl, $CaCl_2$, and KBr. Tohidi et al.[13,14] determined ethane hydrate dissociation conditions in the presence of $w = 0.20$ mass fraction NaCl and then completed those data at $w = 0.10$ and 0.15 NaCl. Mohammadi et al.[15] studied experimental dissociation data for ethane simple hydrates in the presence of $w = 0.05$ NaCl and $w = 0.05$ and 0.10 KCl and $CaCl_2$. However, such data in the $MgCl_2$ solution/C_2H_6 system have not been appeared in the literature. In the present work, the experimental data of hydrate phase equilibria for the $MgCl_2$ solution + C_2H_6 system are obtained at molar concentration $c = (0.05, 0.3, 0.5, 0.8, \text{and } 1.2)$ $mol\cdot dm^{-3}$ $MgCl_2$ in the temperature range of (276.2 to 286.0) K and in the pressure range of (1.12 to 2.70) MPa.

Experimental Apparatus and Procedures

The source and purity of materials used in this work are described in Table 1. Figure 1 shows a schematic diagram of the experimental apparatus. It consists of a cylindrically shaped stainless steel reaction cell with an internal volume of 159 cm^3, the temperature control alcohol bath with a motor stirrer, an ethane gas intake pipeline, vacuum pumping system, and computer-based data-acquisition system. The cell mixtures are fully agitated by a magnetic stirrer matched with an external magnet. The cell is immersed into a temperature-controlled bath to keep a constant temperature. The temperature in the cell is measured by a platinum resistance (Pt100) thermometer with a given uncertainty of ± 0.1 K. The cell pressure is measured by a pressure transmitter (CYB-20) ranging from (0 to 5) MPa with an uncertainty of ± 5 kPa, which is manufactured by Beijing Westzh Machiner & Electron Co., Ltd. Water and magnesium chloride were weighed on an electronic balance with a read-

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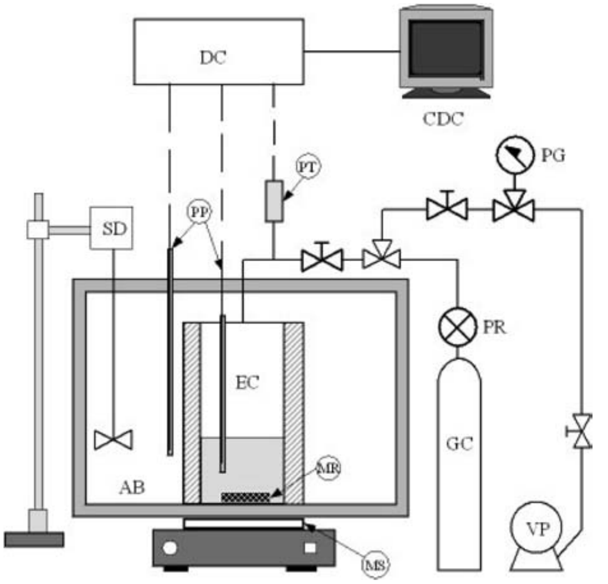

Figure 1. Schematic of the experimental apparatus. AB, alcohol bath; CDC, central desktop computer; DC, data collector; EC, equilibrium cell; GC, gas cylinder; MR, magnetic rotor; MS, magnetic stirrer; PP, platinum resistance thermometer (platinum probe) for temperature; PT, pressure transducer; PR, pressure regulator; PG, pressure gauge; VP, vacuum pump; SD, stirring device with variable speed motor.

ability of ± 0.1 mg. The uncertainty of the solution concentration was less than 0.2 %. The computer-based data-acquisition system can automatically record real-time changes of pressure and temperature in the cell every 10 s.

The reaction cell was first rinsed three times with the prepared solutions. The cell was pumped to evacuate and then purged with ethane gas before the experiments. An amount of 45 mL of the prepared solution was charged into the cell. The equilibrium point was measured with the isochoric pressure-search method.[16] After the cell was pressurized to an expected starting value, the system temperature was slowly lowered to form hydrates, which was detected by a pressure drop. The system temperature was then increased at a rate of (0.1 to 0.5) K. At every temperature step, the temperature was kept constant for about (4 to 6) h to achieve a steady equilibrium state in the cell. In this way, a pressure−temperature diagram is obtained for each experimental run, from which the hydrate dissociation point is determined. Therefore, the point at which the slope of $p-T$ curve changes sharply is considered as the hydrate dissociation point at which all hydrate crystals have dissociated and which is also the last point of each dissociation process. The system pressure is changed, and the procedure is repeatedly performed to obtain other hydrate phase equilibrium points.

Experimental Results and Discussion

To check the reliability of the experimental apparatus and the procedure, five experiments of ethane hydrate formation in pure water were carried out. The $p-T$ data obtained in this work are given in Table 2 and are plotted in Figure 2 together with previous data reported by Avlonitis,[17] Holder and Hand,[18] and Deaton and Frost[19] using the visual observation method. Figure 3 indicated the deviations of the experimental data in the present study and those reported in the literature from the empirical correlation determined by fitting the experimental data sourced from the present study with a third-order polynomial. The definition of the deviation was $100(p_{\mathrm{exp}} - p_{\mathrm{calc}})/p_{\mathrm{calc}}$, where p_{exp} was the experimental equilibrium pressure and p_{calc} was the pressure calculated by the empirical third-order polynomial correlation mentioned above. The uncertainty of the measurements in the present study was also shown in Figure 3. In Figure 3, the uncertainty of the present measurement was 100 multiplied by the ratio of the uncertainty of the pressure measurement to p_{calc}. The maximal value was 0.53 at 279 K. As seen from Figure 3, the deviation of the data obtained in the present study was within the uncertainty of the measurements. The absolute average deviation was within 4 % between the data obtained in the present study and the data in the literature. The difference may be caused by different measuring methods applied in the experiment.

Table 2. Equilibrium Data for Ethane Hydrate in Pure Water

T/K	p/MPa
280.1	1.11
280.7	1.18
282.1	1.42
284.2	1.91
285.6	2.32

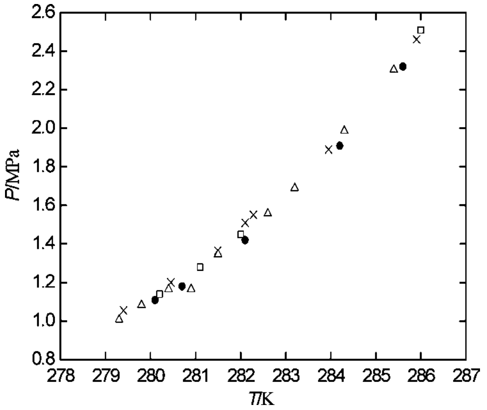

Figure 2. Equilibrium data for ethane hydrate in pure water. ●, this work; ×, ref 17; □, ref 18; △, ref 19.

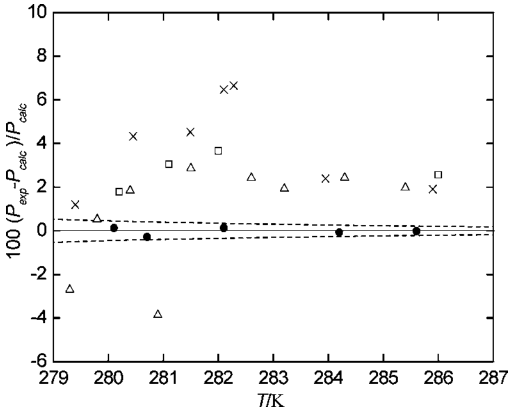

Figure 3. Deviations of the experimental equilibrium pressures for ethane hydrate in pure water from those calculated by the empirical correlation determined on the basis of the experimental data obtained in the present study. ●, this work; ×, ref 17; □, ref 18; △, ref 19; dashed line, uncertainty of the present measurement.

Following the experiments in the ethane + pure water system, the phase equilibrium data of ethane hydrate at c = (0.05, 0.3, 0.5, 0.8, and 1.2) mol·dm^{-3} $MgCl_2$ solutions were determined. The results were listed in Table 3 and plotted in Figure 4. The $p-T$ data in pure water obtained in this work were also presented to illustrate the inhibition effect of $MgCl_2$. As the concentration of $MgCl_2$ increased, the phase equilibrium condition for ethane

Table 3. Equilibrium Data for Ethane Hydrate in $MgCl_2$ Aqueous Solutions with Five Different Concentrations c

c / $mol \cdot dm^{-3}$	T / K	p / MPa
0.05	280.1	1.12
	280.9	1.24
	283.6	1.81
	285.3	2.26
	286.0	2.47
0.3	279.6	1.17
	280.9	1.39
	282.3	1.63
	283.6	1.98
	284.9	2.37
0.5	279.8	1.38
	281.5	1.73
	282.5	2.03
	283.5	2.31
	284.3	2.55
0.8	279.3	1.52
	280.9	1.88
	281.7	2.15
	282.4	2.37
	283.3	2.70
1.2	276.2	1.40
	277.2	1.60
	278.2	1.82
	278.8	2.00
	279.6	2.29

hydrate shifted to a lower temperature and higher pressure region. The stability shift of ethane hydrate relative to that in pure water was also plotted via Cl^- molar concentration. As seen in Figure 5, there was an excellent linear correlation between the shift in equilibrium condition of ethane hydrate with $MgCl_2$ molar concentration.

To compare the role of different cations in affecting ethane hydrate stability in chloride electrolyte solutions, the stability shift against Cl^- molar concentration in NaCl, KCl, and $CaCl_2$ solutions is also plotted in Figure 5. Like the line for $MgCl_2$, lines for NaCl, KCl, and $CaCl_2$ were also statistically regressed from the stability data points in their electrolyte solutions by Englezos and Bishnoi,[12] Tohidi et al.,[14] and Mohammadi et al.[15] Similar to the stability shift in $MgCl_2$ solution discussed in the paragraph above, shifts in the equilibrium condition of ethane hydrate in NaCl, KCl, and $CaCl_2$ solutions all showed an excellent linear correlation with Cl^- concentrations, no matter the cation type and concentration in solutions. Moreover, the slopes of the regression lines corresponding to electrolyte solutions composed of different cations but of the same anion were very near, even though there was a small difference among them. Thus, it implied that the anion of Cl^- played a more important role than the Na^+, K^+, Ca^{2+}, and Mg^{2+} cations in affecting the stability condition of ethane hydrate in the chloride electrolyte solution. Lu et al.[20] recognized the phenomenon mentioned above based on the experimental results on stability conditions of CO_2, CH_4, and C_3H_8 hydrates in various electrolyte solutions and suggested that it could be attributed to the different hydration characteristics of the cation and anion in electrolyte solution.

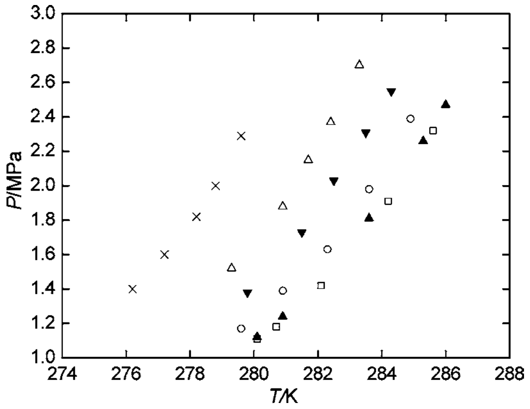

Figure 4. Equilibrium data for ethane hydrate in $MgCl_2$ aqueous solutions. ×, $c = 1.2\ mol \cdot dm^{-3}$; △, $c = 0.8\ mol \cdot dm^{-3}$; ▼, $c = 0.5\ mol \cdot dm^{-3}$; ○, $c = 0.3\ mol \cdot dm^{-3}$; ▲, $c = 0.05\ mol \cdot dm^{-3}$; □, pure water.

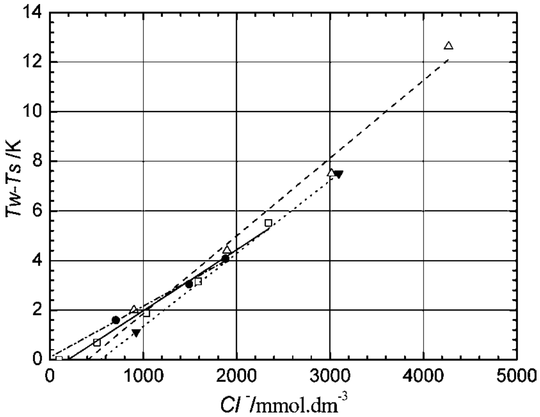

Figure 5. Relationship between Cl^- concentration and the shift in equilibrium conditions of ethane hydrate in various electrolyte solutions. □, $MgCl_2$, this work; △, NaCl, refs 12, 14, and 15; ●, KCl, refs 12 and 15; ▼, $CaCl_2$, ref 15; solid line, the regression line of data in $MgCl_2$; dashed line, the regression line of data in NaCl; dash−dotted line, the regression line of data in KCl; dotted line, the regression line of data in $CaCl_2$.

Conclusions

Experimental equilibrium data for ethane hydrate in $MgCl_2$ aqueous solutions in the temperature range of (276.2 to 286.0) K and the pressure range of (1.12 to 2.70) MPa are obtained. The salt molality ranged from (0.05 to 1.2) $mol \cdot dm^{-3}$. The $MgCl_2$ solution is seen to have an inhibiting effect on the formation of ethane hydrates. The inhibition effect of $MgCl_2$ solution becomes stronger with the increasing concentration of $MgCl_2$. Through making a comparison of the stability shift of ethane hydrate in single solutions of $MgCl_2$, NaCl, KCl, and $CaCl_2$ relative to that in pure water, it was recognized that the stability condition of ethane hydrate in the chloride electrolyte solution was mainly determined by the anion of Cl^- but comparatively less by the Na^+, K^+, Ca^{2+}, and Mg^{2+} cations. The difference of the inhibition effect among cations on the hydrate stability condition was relatively slight.

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