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PHASE STABILITY CONDITIONS OF CARBON DIOXIDE CLATHRATE HYDRATE IN THE PRESENCE OF ETHANOL AND ETHANOL + SALT AQUEOUS SOLUTIONS

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Abstract

This work reports the hydrate dissociation conditions of carbon dioxide in the presence of ethanol and ethanol + NaCl, KCl, $CaCl_2$, $MgCl_2$ aqueous solutions in the temperature and pressure ranges of (268.0 - 281.9)K and (1.39 - 4.10) MPa, respectively. The concentration of ethanol in aqueous solution was 0.1 mass fraction and the concentration of salt was 0.1 mass fraction. The equilibrium data were generated using an isochoric pressure-search method. These data are compared with the experimental data on hydrate dissociation conditions of carbon dioxide in the presence of pure water to prove the inhibition effects of the aforementioned aqueous solutions. It is shown that the studied aqueous solutions have thermodynamic inhibition effects on carbon dioxide clathrate hydrate.

Keywords: *Gas hydrate; Ethanol; NaCl; KCl; $CaCl_2$; $MgCl_2$.*

1. Introduction

Gas hydrates, or clathrate hydrates, are icelike crystalline compounds in which a small molecule(s), like carbon dioxide, methane, *etc*. is trapped in special cages of hydrogen-bonded water molecules under low-temperature and high pressure conditions. Pipeline blockages and other operational problems in petroleum industry can be blocked by formation of gas hydrates. Aqueous solutions of glycols and alcohols are typically used to inhibit formation of gas hydrates. The presence of salt in produced brine can also inhibit formation of gas hydrate. Knowledge of gas hydrate phase equilibria in the presence of aqueous solutions of glycol, alcohol and/or salt is important to estimate gas hydrate formation conditions. A study indicates that most of the latter data have been reported for methane hydrate dissociation conditions in the presence of salt and/or organic inhibitor aqueous solutions [1]. To the best of our knowledge, limited information is available in literature on carbon dioxide hydrate dissociation conditions in the presence of ethanol aqueous solutions [2] and there is no information on carbon dioxide hydrates dissociation conditions in the presence of ethanol + salt aqueous solutions. The latter experimental data could be important in developing predicting tools with the aim of studying the hydrate stability zones of sour reservoir fluids [1].

In this communication, we report carbon dioxide hydrate dissociation conditions in the presence of ethanol and ethanol + salt (NaCl, KCl, $CaCl_2$, $MgCl_2$) aqueous solutions at 0.1 mass fractions of ethanol and ethanol in the temperature and pressure ranges of (268.0 - 281.9) K and (1.39 - 4.10) MPa, respectively. The equilibrium data were generated using an isochoric pressure-search method [1-11]. The data reported in this study are compared with the experimental data on carbon dioxide hydrate dissociation conditions in the presence of pure water to study the inhibition effects of the aforementioned aqueous solutions.

2. Experimental section

2.1. Chemicals

The purities and suppliers of the chemicals used in this work are reported in Table 1. Aqueous solutions were prepared following the gravimetric method, using an accurate analytical balance (mass uncertainty ± 0.0001 g).

Table 1. Purities and suppliers of the chemicals*

Chemical	Supplier	Purity (%)
Carbon dioxide	Air Products	99.9
NaCl	Sigma Aldrich	99.5
KCl	Sigma Aldrich	99.5
$CaCl_2$	Merck	98
$MgCl_2$	Merck	98

** Deionized water was used in all experiments*

2.2. Experimental apparatus

Briefly, the main part of the apparatus is a cylindrical vessel made of stainless steel, which can withstand pressures up to 10 MPa. The vessel has a volume of 57.5 cm^3. A stirrer ensures sufficient agitation to facilitate reaching equilibrium. One platinum resistance thermometer (Pt100) inserted into the vessel is used to measure temperature within temperature measurement uncertainty, which is estimated to be less than 0.1 K. The pressure in the vessel is measured with a pressure transducer. Its accuracy is estimated to be better than 5 kPa.

2.3. Experimental method

Using an isochoric pressure-search procedure, the hydrate dissociation points were measured [1-11]. The vessel containing the aqueous solution (approximately 20 % by volume of the vessel was filled with the aqueous solution) was immersed into the temperature controlled bath, and the gas was supplied from a cylinder through a pressure regulating valve into the vessel. The vessel was evacuated before introducing any aqueous solution and gas. After getting temperature and pressure stability (far enough from the hydrate formation region), the valve between the vessel and the cylinder was closed. Subsequently, the temperature was slowly decreased to form the hydrate. Hydrate formation in the vessel was observed when a pressure drop at constant temperature was detected in a computer connected to a data acquisition unit. The temperature was then increased with steps of 0.1 K. At every temperature step, the temperature was kept constant with enough time to obtain an equilibrium state in the equilibrium cell [2-9]. Therefore, a pressure-temperature diagram was sketched for each experimental run, from which we determined the hydrate dissociation point [2-9]. During the dissociation of the hydrate crystals inside hydrate formation region, the pressure is gradually increased by increasing the temperature. However, outside this region, slighter pressure increase is observed during increase of temperature. Consequently, the hydrate dissociation point can be determined when the slope of the pressure-temperature diagram changes suddenly [2-9]. The maximum uncertainties for the hydrate dissociation temperatures and pressures are expected to be ± 0.1 K and ± 0.05 MPa based on our previous studies [2-9].

3. Results and discussion

Table 2 and Figure 1 report the experimental data. A semi-logarithmic scale has been used in this figure to show the data consistency, as the logarithm of hydrate dissociation pressure versus temperature has approximately linear behaviour [1].

In this figure, some selected experimental data from the literature on carbon dioxide hydrate dissociation conditions in the presence of pure water [10] have also been reported to prove thermodynamic inhibition effects of the studied aqueous solutions. The inhibition effect results in shifting hydrate dissociation conditions to high pressures/low temperatures due to the presence of inhibitor in aqueous solution. On the other hand, satisfactory agreement between our data and the data reported in reference [10] for the carbon dioxide + water system proves the reliability of the experimental method employed in this work.

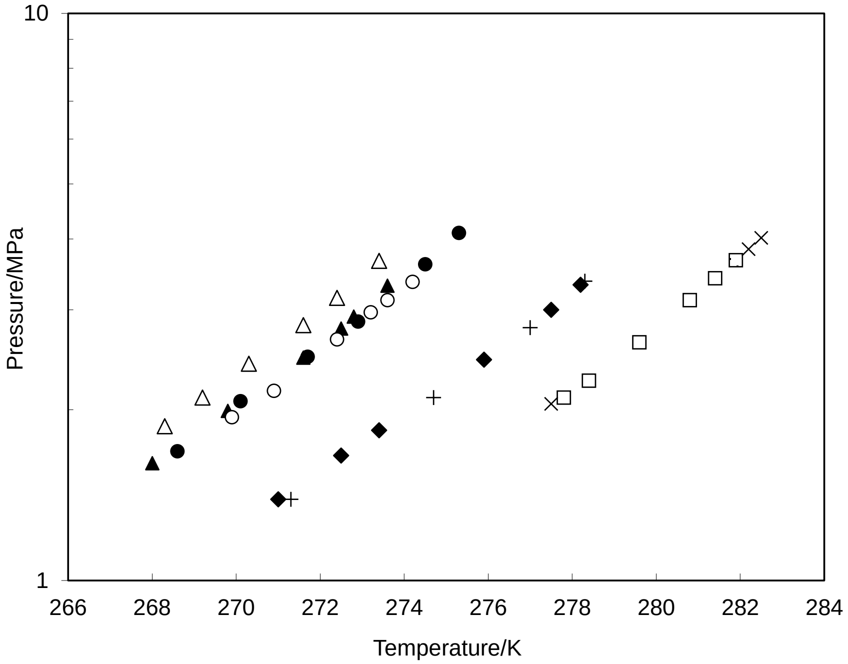

Figure 1. Carbon dioxide hydrate dissociation conditions in the presence of pure water, ethanol and ethanol + NaCl/ KCl/$CaCl_2$/$MgCl_2$ aqueous solutions. Symbols represent hydrate dissociation conditions. Carbon dioxide + water system: □, this work, ×, [10]. Carbon dioxide + 0.10 mass fraction ethanol + water system: ♦, this work, +, [2]. Carbon dioxide + 0.10 mass fraction ethanol + 0.10 mass fraction NaCl + water system: ●, this work. Carbon dioxide + 0.10 mass fraction ethanol + 0.10 mass fraction KCl + water system: ▲, this work. Carbon dioxide + 0.10 mass fraction ethanol + 0.10 mass fraction $CaCl_2$ + water system: ○, this work. Carbon dioxide + 0.10 mass fraction ethanol + 0.10 mass fraction $MgCl_2$ + water system: Δ, this work

Table 2. Carbon dioxide hydrate dissociation conditions in the presence of pure water, ethanol and ethanol + NaCl/ KCl/$CaCl_2$/$MgCl_2$ aqueous solutions.*

Temperature/K	Pressure/MPa	Temperature/K	Pressure/MPa	Temperature/K	Pressure/MPa
Pure water		0.10 Mass Fraction Ethanol + 0.10 Mass Fraction NaCl		0.10 Mass Fraction Ethanol + 0.10 Mass Fraction $CaCl_2$	
277.8	2.10	268.6	1.69	269.9	1.94
278.4	2.25	270.1	2.07	270.9	2.16
279.6	2.63	271.7	2.48	272.4	2.66
280.8	3.12	272.9	2.86	273.2	2.97
281.4	3.41	274.5	3.61	273.6	3.12
281.9	3.67	275.3	4.10	274.2	3.36
0.10 Mass Fraction Ethanol		0.10 Mass Fraction Ethanol + 0.10 Mass Fraction KCl		0.10 Mass Fraction Ethanol + 0.10 Mass Fraction $MgCl_2$	
271.0	1.39	268.0	1.61	268.3	1.87
272.5	1.66	269.8	1.99	269.2	2.10
273.4	1.84	271.6	2.47	270.3	2.41
275.9	2.45	272.5	2.78	271.6	2.82
277.5	3.00	272.8	2.92	272.4	3.15
278.2	3.32	273.6	3.31	273.4	3.66

Figure 1 indicates that data on carbon dioxide hydrate dissociation conditions in the presence of ethanol aqueous solution (0.10 mass fraction) are limited. The latter experimental data is found in acceptable agreement with the previously reported data [2]. It should be menioned that it has been previously reported that ethanol behaves as thermodynamic promoter rather than thermodynamic inhibitor at its high concentrations in aqueous solution (typically higher than 0.15 mass fraction) [11]. Therefore no attempt was done in the present work to study high concentrations of ethanol in aqueous solutions.

As can be observed in Figure 1. the presence of the studied salts (0.10 mass fraction) in ethanol aqueous solution (0.10 mass fraction) leads to more thermodynamic inhibition effects on carbon dioxide hydrate. In particular. $MgCl_2$ leads to more thermodynamic inhibition effect in comparison with other salts. NaCl. KCl and $CaCl_2$ have similar thermodynamic inhibition effects on hydrate formation in the carbon dioxide + 10 mass fraction ethanol + water system.

4. Conclusion

Carbon dioxide hydrate dissociation conditions in the presence of ethanol and ethanol + NaCl. KCl. $CaCl_2$. $MgCl_2$ aqueous solutions are reported in the temperature and pressure ranges of (268.0 - 281.9) K and (1.39 - 4.10) MPa. respectively. The aqueous solutions studied in this work show thermodynamic inhibition effects on carbon dioxide hydrate formation. Presence of the studied salts in ethanol aqueous solution increases thermodynamic inhibition effect and $MgCl_2$ leads to more inhibition effect. Similar thermodynamic inhibition effects on hydrate formation in the carbon dioxide + 10 mass fraction ethanol + water system are observed when using NaCl. KCl and $CaCl_2$ in ethanol aqueous solution.

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