

Equilibrium conditions for clathrate hydrates formed from carbon dioxide or ethane in the presence of aqueous solutions of 1,4-dioxane and 1,3-dioxolane



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ARTICLE INFO

Article history:

Received 12 May 2014

Received in revised form 17 October 2014

Accepted 20 October 2014

Available online 24 October 2014

Keywords:

Clathrate hydrate

Gas hydrate

Carbon dioxide

Ethane

Hydrate promoters

ABSTRACT

Equilibrium conditions for clathrate hydrates formed from carbon dioxide or ethane in aqueous solutions of 1,4-dioxane and 1,3-dioxolane were determined experimentally using an isochoric method. Addition of the 1,4-dioxane and 1,3-dioxolane to water shifted the equilibrium conditions of carbon dioxide hydrates to a higher temperature, indicating that they promote carbon dioxide hydrate formation. In contrast, 1,4-dioxane and 1,3-dioxolane inhibited ethane hydrate formation at pressures greater than 0.7 MPa.

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1. Introduction

Clathrate hydrates are crystalline compounds formed by hydrogen-bonded water molecules that can encapsulate relatively small guest molecules, such as methane, ethane, and carbon dioxide [1]. In general, these hydrates can form three different structures depending on the size and shape of the guest gas. Structure I and II hydrates have two different cavity sizes, whereas a structure H hydrate has three different cavity sizes. Clathrate hydrates are of interest in the oil and gas industries because the formation of hydrates in pipe lines and processing facilities can plug them, leading to serious accidents. Many studies have been reported on hydrate inhibitors, such as methanol and ethylene glycol, which prevent hydrate formation [2]. In addition, some technological applications using clathrate hydrate formation have been proposed, such as the storage and transportation of natural gases in a hydrate form, using hydrate promoters [3].

Ng and Robinson [4] reported that acetone can promote methane hydrate formation. Their experiments involving the formation of clathrate hydrates from methane and aqueous acetone solutions showed addition of a small amount of acetone into water shifted the hydrate equilibria to a higher temperature, indicating that acetone acts as a methane hydrate promoter.

However, excess acetone (>0.06 mole fractions of acetone) inhibited the hydrate formation. Similar experiments using hydrates formed from methane and aqueous acetone solutions have been conducted [5–7].

However, Javanmardi et al. [8] investigated the effect of acetone on R22 (CHClF₂) hydrate equilibria, and showed that acetone has only an inhibiting effect on R22 hydrate formation, in contrast to methane hydrate formation.

Thus, the inhibiting or promoting effect of acetone on clathrate hydrate formation depends on its concentration in solution and the type of guest gas molecule. Acetone in solution can decrease water activity, causing hydrate equilibrium shifts toward lower temperatures. In addition, acetone can form a structure II hydrate, in which the molecules are held in large cavities of the structure [9]. The promoting effect of acetone on methane hydrate formation occurs because structure II hydrates are stabilized by the presence of methane and acetone in the small and large cavities, respectively. In addition to methane, the hydrate promotion effect of acetone was also observed for nitrogen [6] and krypton [10], which can enter the small cavities. For the R22 hydrate, however, the structure II hydrate cannot be stabilized because R22 molecules cannot enter small cavities of the hydrate. Therefore, only inhibition by acetone on structure I hydrates was observed upon a decrease in water activity.

Some cyclic ethers, such as tetrahydrofuran, 1,4-dioxane, and 1,3-dioxolane, promote methane hydrate formation [11] in a manner similar to that of acetone. Jager et al. [12] determined

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Table 1
Suppliers and purities of gases and chemicals used in the present study.

Chemical	Supplier	Purity
Carbon dioxide	Showa Tansan Co. Ltd.	0.99999 ^a
Ethane	Takachiho Chemical Industrial Co., Ltd.	0.9999 ^a
1,4-dioxane	Wako Pure Chemical Industries, Ltd.	>0.995 ^b
1,3-dioxolane	Wako Pure Chemical Industries, Ltd.	>0.990 ^b

^a Volume fraction.

^b Mass fraction.

methane hydrate equilibria in the presence of different concentrations of aqueous 1,4-dioxane solutions and found that 1,4-dioxane reduced the equilibrium pressure of hydrate formation in solution at concentrations of up to 0.06 mol fraction. de Deugd et al. [13] obtained similar results for methane hydrate formation in the presence of aqueous 1,3-dioxolane solutions. The results of these experiments and of thermodynamic modeling indicated that structure II hydrates could form from methane and aqueous solutions of 1,4-dioxane or 1,3-dioxolane.

The present study is part of a continuing investigation into clathrate hydrate equilibria in solutions containing water-soluble organic compounds. The effects of acetone on hydrate equilibria for propane [14], carbon dioxide [15], and xenon [16] have been

Table 2
Equilibrium conditions of carbon dioxide hydrates in the presence of aqueous 1,4-dioxane solutions (w = mass fraction of 1,4-dioxane).^a

T/K	p/MPa	T/K	p/MPa
Pure water			
272.4	1.12	278.0	2.18
273.5	1.27	280.2	2.92
274.5	1.44	281.7	3.58
276.5	1.80	282.9	4.34
1,4-dioxane ($w = 0.04$)			
271.2	1.05	277.9	2.34
271.9	1.14	279.3	2.81
273.5	1.38	280.6	3.33
274.9	1.61	281.8	4.00
276.4	1.93		
1,4-dioxane ($w = 0.06$)			
271.3	0.89	276.3	1.99
272.1	1.03	277.7	2.39
273.3	1.27	278.9	2.80
274.1	1.47	280.1	3.27
275.1	1.73	281.2	3.87
275.7	1.85		
1,4-dioxane ($w = 0.08$)			
272.5	0.92	278.3	2.67
274.2	1.26	278.6	2.82
275.3	1.53	279.0	2.97
276.6	1.92	279.5	3.17
277.5	2.29	279.9	3.37
277.9	2.47	280.7	3.77
1,4-dioxane ($w = 0.10$)			
272.5	0.80	279.2	2.83
274.8	1.22	280.0	3.32
276.9	1.79	280.3	3.56
278.1	2.26		
1,4-dioxane ($w = 0.16$)			
273.8	0.82	279.1	2.24
275.8	1.19	280.5	2.93
277.7	1.69	281.2	3.41
1,4-dioxane ($w = 0.224$)			
274.5	0.89	279.6	2.33
276.9	1.38	280.6	2.88
278.4	1.84		

^a $u(T) = 0.2$ K, $u(p) = 0.04$ MPa, $u(w) = 0.0004$.

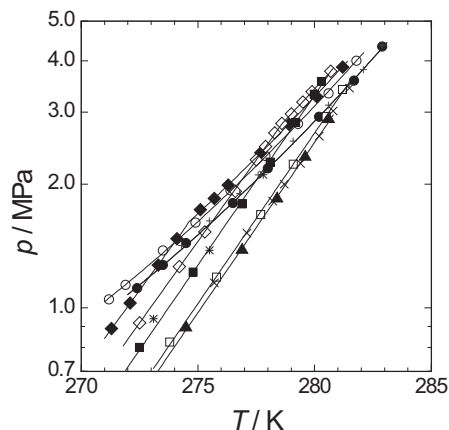


Fig. 1. Equilibrium conditions for clathrate hydrates formed from carbon dioxide and aq. 1,4-dioxane solutions. ● Pure water; ○ $w = 0.04$; ◆ $w = 0.06$; ◇ $w = 0.08$; ■ $w = 0.10$; □ $w = 0.16$; ▲ $w = 0.224$ + Pure water ([22]); * $w = 0.10$ ([7]); × $w = 0.224$ ([19]). Solid lines were obtained from regression of the experimental data of each hydrate of structure I or II into a line parallel to that of pure water or an exponential form.

reported previously. Acetone inhibits propane hydrate formation, whereas it can act as a promoter for hydrate formation of carbon dioxide and xenon. In addition, the promoting effects of 1,4-dioxane and 1,3-dioxolane on xenon hydrate formation were observed to be similar to the behavior of acetone [16].

In the present study, the effects of 1,4-dioxane and 1,3-dioxolane on hydrate formation for carbon dioxide and ethane were investigated experimentally. Carbon dioxide and ethane are often

Table 3
Equilibrium conditions of carbon dioxide hydrates in the presence of aqueous 1,3-dioxolane solutions (w = mass fraction of 1,3-dioxolane).^a

T/K	p/MPa	T/K	p/MPa
1,3-dioxolane ($w = 0.02$)			
271.6	0.97	276.8	1.98
272.1	1.07	278.1	2.34
272.8	1.21	279.8	2.92
273.3	1.30	281.0	3.43
274.0	1.41	282.0	4.03
274.9	1.57		
1,3-dioxolane ($w = 0.04$)			
273.6	0.82	279.8	2.94
275.1	1.13	280.2	3.21
276.2	1.41	280.9	3.60
277.2	1.72	281.5	3.96
278.5	2.26		
1,3-dioxolane ($w = 0.06$)			
275.4	0.88	279.8	2.21
277.1	1.25	280.9	2.81
278.5	1.68	281.9	3.46
1,3-dioxolane ($w = 0.08$)			
276.1	0.82	281.0	2.36
277.2	1.05	282.1	3.03
278.1	1.27	282.8	3.56
279.8	1.82		
1,3-dioxolane ($w = 0.10$)			
277.1	0.87	280.7	1.94
278.0	1.08	282.2	2.67
279.2	1.41	283.0	3.27
1,3-dioxolane ($w = 0.20$)			
277.5	0.78	281.1	1.74
278.8	1.03	282.4	2.30
279.7	1.27		

^a $u(T) = 0.2$ K, $u(p) = 0.04$ MPa, $u(w) = 0.0004$.

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