



Phase equilibria of hydrogen sulfide and carbon dioxide simple hydrates in the presence of methanol, (methanol + NaCl) and (ethylene glycol + NaCl) aqueous solutions [☆]

Amir H. Mohammadi ^{*}, Dominique Richon

MINES ParisTech, CEP-TEP, Centre Énergétique et Procédés, 35 Rue Saint Honoré, 77305 Fontainebleau, France

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ABSTRACT

This work aims at reporting the dissociation pressures of hydrogen sulfide and carbon dioxide simple hydrates in the presence of methanol, (methanol + NaCl) and (ethylene glycol + NaCl) aqueous solutions at different temperatures and various concentrations of inhibitor in aqueous solution. The equilibrium results were generated using an isochoric pressure-search method. These values are compared with some selected experimental data from the literature on the dissociation conditions of hydrogen sulfide and carbon dioxide simple hydrates in the presence of pure water to show the inhibition effects of the above mentioned aqueous solutions. Comparisons are finally made between our experimental values and the corresponding literature data. Some disagreements among the literature data and our data are found.

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1. Introduction

Gas hydrates, or clathrate hydrates, are a group of non-stoichiometric, ice-like crystalline compounds formed through a combination of water and small molecule(s), like methane, hydrogen sulfide, carbon dioxide, *etc.* under low-temperatures and elevated pressures [1]. In gas hydrates, the small molecule(s) is trapped inside the cavities formed by water molecules [1]. Formation of gas hydrates can cause pipeline blockages and other operational problems in the petroleum industry [1]. To inhibit formation of gas hydrates, glycols, and alcohols are normally used [1]. The presence of salt in produced saline water can also inhibit gas hydrate formation [1]. Knowledge of gas hydrate phase equilibrium in the presence of glycol, alcohol and/or salt aqueous solutions is therefore of interest to estimate the boundary of gas hydrate formation [1]. Most of experimental measurements have been reported for single glycol, alcohol or salt aqueous solutions containing systems, while the experimental measurements for the systems containing mixed glycol, alcohol, and salt aqueous solutions are limited [1–14]. The latter systems are especially of interest in natural gas production

and transportation in deepwater operations, where the gas hydrate inhibition effects of produced saline water is not enough and glycols or alcohols are therefore used [1]. A preliminary study shows that most of the latter data have been reported for the dissociation conditions of methane hydrates in the presence of the mixed salt and organic inhibitor aqueous solutions [7–10]. To the best of our knowledge, few data are available in the open literature on the dissociation conditions of hydrogen sulfide and carbon dioxide simple hydrates in the presence of the mixed salt and organic inhibitor aqueous solutions [11,12]. Moreover, the dissociation data for hydrogen sulfide and carbon dioxide simple hydrates in the presence of high concentration methanol aqueous solutions are also limited [15–20].

In this work, we report the dissociation conditions of hydrogen sulfide and carbon dioxide simple hydrates in the presence of (methanol + NaCl) and (ethylene glycol + NaCl) aqueous solutions at different temperatures and various concentrations of inhibitors in aqueous solutions. The equilibrium results were obtained using an isochoric pressure-search method [21]. The experimental values reported in this work are compared with some selected experimental data from the literature on dissociation conditions of hydrogen sulfide and carbon dioxide simple hydrates in the presence of pure water [22–27] to show the inhibition effects of the above mentioned aqueous solutions. The reliability of the literature data is finally discussed.

[☆] Paper for gas hydrate initiative

^{*} Corresponding author. Tel.: +33 1 64 69 49 70; fax: +33 1 64 69 49 68.

E-mail address: amir-hosseini.mohammadi@mines-paristech.fr (A.H. Mohammadi).

TABLE 1
Purities and suppliers of chemicals.^a

Chemical	Supplier	Mole fraction purity
Hydrogen sulfide	Air Liquide	0.999
Carbon dioxide	Air Liquide	0.99995
NaCl	Sigma Aldrich	0.995 (GC)
Ethylene glycol	Aldrich	0.990 (GC)
Methanol	Aldrich	0.999 (GC)

^a Deionised water was used in all experiments.

2. Experimental

2.1. Chemicals

Table 1 contains the purities and suppliers of materials used in this work. Aqueous solutions were prepared following the gravimetric method, using an accurate analytical balance (mass uncertainty ± 0.0001 g). Consequently, uncertainties on the basis of mole fraction are estimated to be <0.01 .

2.2. Experimental apparatus

2.2.1. Apparatus-1 [28,29]

Briefly, the main part of the apparatus is a vertical cylindrical vessel made of Hastelloy, which can withstand pressures up to 20 MPa. The vessel has a volume of 30 cm³. A stirrer ensures sufficient agitation to facilitate reaching equilibrium. Two platinum resistance thermometers (Pt100) inserted into the vessel were used to measure temperatures and check for their equality within temperature measurement uncertainty, which is estimated to be less than 0.1 K. This temperature uncertainty estimation comes from calibration against a 25 Ω reference platinum resistance thermometer. The pressure in the vessel was measured with a DRUCK pressure transducer (Druck, type PTX611 for pressures up to 1.6 MPa). The pressure measurement accuracy is estimated to be better than 5 kPa. This apparatus was used to perform the measurements for hydrogen sulfide clathrate hydrates.

2.2.2. Apparatus-2 [30–32]

Briefly, the main part of this apparatus is a horizontal cylindrical equilibrium cell made of austenitic stainless steel, which can withstand pressures up to 60 MPa. The equilibrium cell has an inner volume of 201.5 cm³ and two sapphire windows. A motor-driven turbine agitation system (Top Industrie) ensures sufficient agitation to facilitate reaching equilibrium even during the hydrate formation. The temperature of the equilibrium cell is controlled using a thermostatic bath (Tamson Instruments, TV400LT), which allows the visual observation of the cell content throughout the experiments. One platinum resistance sensor (Pt100) inserted in the cell interior is used *in situ* to measure the temperature within ± 0.02 K uncertainty estimated after calibration against a 25- Ω reference platinum resistance thermometer. This 25- Ω reference probe was calibrated, following the ITS 90 protocol, by Laboratoire National d'essais (Paris). Pressure is measured using a pressure transducer (Druck, type PTX611): High pressure sensor (HPT) for pressures up to 40 MPa. The result of calibration against a dead weight balance (Desgranges & Huot 5202S CP, Aubervilliers, France), pressure uncertainty is estimated to be within ± 0.002 MPa. This apparatus was used to perform the measurements for carbon dioxide clathrate hydrates.

2.3. Experimental method

The hydrate dissociation points were measured with an isochoric pressure-search procedure [21]. The vessel containing the

aqueous solution (10% 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. Note that 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 by the data acquisition unit [33]. 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 [33]. Therefore, a pressure–temperature diagram was sketched for each experimental run, from which we determined the hydrate dissociation point [33]. 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 [33]. Consequently, the real hydrate dissociation point can be determined when the slope of the pressure–temperature diagram changes suddenly [33]. The uncertainties for the hydrate dissociation temperatures and pressures are expected to be ± 0.1 K and ± 0.02 MPa based on our previous studies.

3. Results and discussion

The experimental data are reported in tables 2 to 5 and are plotted in figures 1 to 6. A semi-logarithmic scale has been used in these figures to show the data consistency, as the logarithm of hydrate dissociation pressure versus temperature shows approximately linear behavior [1]. Some selected experimental data from the literature on the dissociation conditions of hydrogen sulfide and carbon dioxide simple hydrates in the presence of pure water [22–27] have also

TABLE 2
Dissociation conditions of hydrogen sulfide clathrate hydrates in the presence of (ethylene glycol + NaCl) and (methanol + NaCl) aqueous solutions.

Temperature/K	Pressure/MPa
<i>0.15 mass fraction ethylene glycol + 0.05 mass fraction NaCl aqueous solution</i>	
272.7	0.180
278.3	0.315
284.4	0.584
290.1	1.082
<i>0.10 mass fraction methanol + 0.05 mass fraction NaCl aqueous solution</i>	
273.4	0.189
277.2	0.288
281.6	0.456
286.8	0.777

TABLE 3
Dissociation conditions of carbon dioxide clathrate hydrates in the presence of (ethylene glycol + NaCl) and (methanol + NaCl) aqueous solutions.

Temperature/K	Pressure/MPa
<i>0.15 mass fraction ethylene glycol + 0.05 mass fraction NaCl aqueous solution</i>	
264.4	0.995
266.1	1.221
268.8	1.602
<i>0.10 mass fraction methanol + 0.05 mass fraction NaCl aqueous solution</i>	
266.3	1.223
269.7	1.805
272.5	2.512

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