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Phase equilibria of hydrogen sulphide clathrate hydrates in the presence of single or mixed salt aqueous solution

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ABSTRACT

This work reports the dissociation pressures of hydrogen sulphide clathrate hydrates in the presence of single and mixed aqueous solutions of NaCl, KCl and $CaCl_2$ at different temperatures and various concentrations of salt(s) in aqueous solution. The equilibrium data were generated using an isochoric pressure-search method. These data are compared with some selected experimental data from the literature on the dissociation conditions of hydrogen sulphide clathrate hydrates in the presence of pure water to show the inhibition effects of the aforementioned aqueous solutions. Comparisons between our experimental data and the corresponding literature data show some disagreements in the literature data.

1. Introduction

Gas hydrates, or clathrate hydrates, are ice-like crystalline compounds in which small molecules, like methane, hydrogen sulphide, carbon dioxide, *etc.* are trapped in special cages of hydrogen-bonded water molecules under low-temperatures and elevated pressures [1]. Pipeline blockage and other operational problems in the petroleum industry can be caused by formation of gas hydrates [1]. Glycols and alcohols are normally used to inhibit formation of gas hydrates [1]. The presence of salt in the saline water produced 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 boundary of gas hydrate formation [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 salt and/or organic inhibitor aqueous solutions [1]. To the best of our knowledge, few sets of experimental data are available in the open literature on the dissociation conditions of hydrogen sulphide clathrate hydrates in the presence of single and mixed salt aqueous solutions [2–4]. The latter experimental data could be of interest for developing predicting tools with the aim of studying the hydrate stability zones of sour reservoir fluids.

In this communication, we report the dissociation conditions of hydrogen sulphide clathrate hydrates in the presence of single and mixed aqueous solutions of NaCl, KCl and $CaCl_2$ at different temperatures and various concentrations of salt in aqueous solutions. The equilibrium data were generated using an isochoric pressure-search method [5–8]. The experimental data reported in this work are compared with some selected experimental data from the literature on the dissociation conditions of hydrogen sulphide clathrate hydrates in the presence of pure water [4,6,9] to show the hydrate inhibition effects of the aforementioned aqueous solutions. The reliability of the literature data is finally discussed.

2. Experimental

2.1. Chemicals

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

2.2. Apparatus [10]

Briefly, the main part of the apparatus is a cylindrical vessel made of Hastelloy, which can withstand pressures up to 20 MPa. The vessel has a volume of 30 cm^3. A stirrer ensures sufficient agitation to facilitate reaching equilibrium. Two platinum resistance thermometers (Pt100) inserted into the vessel are used to measure

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TABLE 1
Purities and suppliers of chemicals.[a]

Chemical	Supplier	Mole fraction purity
Hydrogen sulphide	Air Liquide	0.999
NaCl	Sigma Aldrich	0.995 (GC)
KCl	Sigma Aldrich	0.995 (GC)
$CaCl_2$	Merck	0.98 (GC)

[a] Deionized water was used in all experiments.

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 is 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.

2.3. Experimental method

The hydrate dissociation points were measured with isochoric pressure-search procedure [5–8]. The vessel containing the aqueous solution (approximately 17% 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 achieving 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 [5–7]. 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 [5–7]. Therefore, a pressure–temperature diagram was sketched for each experimental run, from which we determined the hydrate dissociation point [5–7]. 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 [5–7]. Consequently, the real hydrate dissociation point can be determined when the slope of the pressure-temperature diagram changes suddenly [5–7]. The maximum uncertainties for the hydrate dissociation temperatures and pressures are expected to be 0.3 K and 0.05 MPa, respectively, based on our previous studies.

3. Results and discussion

The experimental data are reported in tables 2 and 3 and are plotted in figures 1–6. A semi-logarithmic scale has been used in these figures to show the data consistency, as the logarithm of hydrate dissociation pressure versus temperature has approximately linear behaviour [1]. Some selected experimental data from the literature on the dissociation conditions of hydrogen sulphide clathrate hydrates in the presence of pure water [4,6,9] have also been shown in these figures to show thermodynamic inhibition effects of the aqueous solutions studied. Note that the inhibition effect results in shifting hydrate dissociation conditions to high pressures/low temperatures due to the presence of salt(s) in aqueous solution. Figures 1–3 indicate that the experimental dissociation data for hydrogen sulphide clathrate hydrates in high concentration salt aqueous solution are limited. So far, we found out that there are some disagreements in some experimental dissociation data reported in the literature for clathrate hydrates of hydrogen sulphide in high concentration methanol/ethylene glycol aqueous solutions [5,11]. However, as mentioned in reference [11], the experimental data for the ethylene glycol containing systems were found generally in acceptable agreement. Such disagreements can be partly attributed to the experimental procedure used to perform the

TABLE 2
Dissociation conditions of hydrogen sulphide clathrate hydrates in the presence of single NaCl, KCl and $CaCl_2$ aqueous solutions.[a]

Temperature / K		Pressure / MPa
	0.15 Mass fraction NaCl	
271.7		0.155
275.2		0.222
279.6		0.365
	0.22 Mass fraction NaCl	
268.8		0.185
271.4		0.245
274.8		0.361
	0.05 Mass fraction KCl	
272.9		0.131
279.2		0.231
283.5		0.363
	0.12 Mass fraction KCl	
273.6		0.172
277.9		0.256
280.5		0.328
	0.10 Mass fraction $CaCl_2$	
273.0		0.157
276.5		0.232
280.3		0.353
	0.20 Mass fraction $CaCl_2$	
271.8		0.332
272.9		0.382
273.8		0.432

[a] The maximum uncertainties for the hydrate dissociation temperatures and pressures are expected to be 0.3 K and 0.05 MPa, respectively.

TABLE 3
Dissociation conditions of hydrogen sulphide clathrate hydrates in the presence of mixed NaCl, KCl and $CaCl_2$ aqueous solution.[a]

Temperature/K		Pressure/MPa
	0.05 Mass fraction NaCl +0.05 Mass fraction KCl	
273.1		0.136
277.9		0.228
283.1		0.385
	0.10 Mass fraction NaCl +0.05 Mass fraction KCl	
272.2		0.155
278.8		0.322
281.4		0.422
	0.05 Mass fraction NaCl +0.05 Mass fraction $CaCl_2$	
274.2		0.162
279.5		0.281
282.9		0.398
	0.10 Mass fraction NaCl +0.05 Mass fraction $CaCl_2$	
269.5		0.131
275.1		0.233
279.6		0.372
	0.05 Mass fraction NaCl +0.05 Mass fraction KCl +0.05 Mass fraction $CaCl_2$	
268.6		0.110
275.4		0.222
280.5		0.368

[a] The maximum uncertainties for the hydrate dissociation temperatures and pressures are expected to be 0.3 K and 0.05 MPa, respectively.