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Hydrogen gas hydrate—Measurements and predictions

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ABSTRACT

Hydrate formation conditions were measured for gas mixtures with concentrations of hydrogen from 5 mol% to 66 mol%. The thermodynamic models were proposed to calculate hydrate formation conditions for such systems. By treating hydrogen as a hydrate former, the Kihara parameters and the interaction coefficients between hydrogen and other less volatile hydrate formers in the Ng–Robinson hydrate model were determined from the experimental data. The proposed models were applied to the predictions of hydrate formation for multicomponent systems containing hydrogen. A good agreement was reached between the predictions and the measured data.

1. Introduction

Clathrate hydrates are crystalline solid compounds, in which water molecules are linked through hydrogen bonding and create cavities enclosing a large variety of guest molecules. The initial experimental work on hydrate as pipeline plug was carried out by Hammerschmidt [1], who discovered thermodynamic inhibitors and proposed the Hammerschmidt equation for estimating the temperature depression in the hydrate formation due to the presence of an inhibitor. Deaton and Frost [2] investigated the hydrate formation for pure light gases and their mixtures with heavier components in real and simulated natural gases. Later on, many scientific developments and applications have been made on the hydrate formation to the natural gas industry.

The study of the phase behavior of hydrate formation for hydrogen-containing natural gas mixtures has become important since the 1980s with the development of alternative energy sources by coal gasification. Holder et al. [3] was the one to measure hydrate formation of a hydrogen-rich gas to examine the potential of raw recycle gas to form gas hydrates in many coal conversion processes. Zhang et al. [4] presented the hydrate formation conditions of a series of hydrocarbon gas mixtures containing hydrogen to investigate the feasibility of hydrogen recovery process. Ma et al. [5] proposed a novel technique for hydrogen recovery from the high-pressure recycled hydrogen gas mixtures. They measured the gas hydrate phase equilibrium data for two gas mixtures containing hydrogen in pure water and the oxacyclopentane aqueous solutions, respectively. Although the experimental hydrate formation data for the systems containing hydrogen are available in the literatures, much information is still required for hydrate formation of gas mixtures containing hydrogen to investigate the influence of hydrogen on hydrate formation in natural gases.

The hydrate thermodynamic properties can be predicted by a statistical thermodynamic approach. The foundation of this approach was first proposed by van der Waals and Platteeuw [6]. The modification has been made on the model by introducing an adjustable interaction parameter into the prediction scheme in the work of Ng and Robinson [7]. Many researchers assume that hydrogen can hardly form hydrate at relative low pressures since its molecule size is too small to contribute to the stability of clathrate hydrates. However, a number of researchers have explored hydrate as a storage material for hydrogen since 1999. Dyadin et al. [8] discovered that hydrogen can form a clathrate hydrate at high pressure (1.5 GPa). The recent study by Mao et al. [9] indicates that the formation of a hydrogen hydrate was observed to take place at relatively high pressure and low temperature (200 MPa and 0 °C).

In this work, the experimental hydrate formation data on binary and multicomponent systems containing hydrogen are presented. The data collection was carried out in early 1980s and has not been published. These data are used to extend the application of Ng–Robinson hydrate model by treating hydrogen as a hydrate former.

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Nomenclature

a_w	activity of water
C_{mj}	Langmuir constant for component j in cavity m
f_j	fugacity of component j
k	Boltzmann constant, 1.38×10^{-23} J/K
P	total pressure
R	gas constant, 8.3144 J/(mol K)
R	cell radius of cavity
T	temperature
$w(r)$	spherically symmetric cell potential
y_j	mole fraction of the component j in the gas mixture

Greek symbols

α_j	interaction coefficient in Eq. (3)
μ	chemical potential
ν_m	number of cavities of type m per water molecule in hydrate

2. Experimental

2.1. Materials and experimental procedure

The experiment apparatus used in this work was essentially the same as that was described by Wu et al. [10]. The equipment consisted of a simple windowed equilibrium cell mounted in a temperature bath, and with a working volume of approximately 80 cm^3 and the design working pressure up to 28 MPa. The temperature of the cell could be controlled by externally cooled liquid which was circulated through the space between the cell and the temperature bath. The temperature of the bath and the cell contents were measured by copper-constantan thermocouples read out on a digital voltmeter. The pressure was adjusted by the addition or removal of mercury using a constant volume displacement pump, and was measured with calibrated Heise bourdon tube gauges.

Gas mixtures were prepared gravimetrically from pure gases with minimum purity of 99.5% for hydrogen, nitrogen, methane, ethane, propane, carbon dioxide and ethylene, and minimum purity of 99.0% for other gases and liquids. For each hydrate formation study, the system was thoroughly evacuated. A suitable amount of water was then introduced into the equilibrium cell. This was followed by the gas or gas mixtures to be used for the experiment. Since the solubility of carbon dioxide in water is appreciably higher than that of hydrocarbons, the total water in the cell was kept to a minimum for the systems containing carbon dioxide. As a result of this, the overall composition of the gas mixture remained constant.

Hydrate formation was initiated by cooling the bath temperature about 3–4 °C below the estimated hydrate formation conditions. Hydrate nucleation was then started with the agitation of the cell. The temperature was increased slightly until the hydrate began to decompose. The temperature was kept slightly higher than the melting point to make all of the hydrate dissociate. The temperature was then lowered to re-crystallize the hydrate. The temperature was raised very slowly again until the hydrate just began to melt. The condition at this data point was considered as the hydrate equilibrium point. Then the pressure and temperature were readjusted for the next data point until it reached the hydrate equilibrium condition.

2.2. Experimental results

The experimental measurements on hydrate forming conditions were made for methane–hydrogen, carbon dioxide–hydrogen, ethylene–hydrogen, and natural gas mixtures containing hydrogen and carbon dioxide. The pressure covered a range from about 1.5 MPa to 20 MPa, and the temperature from 0 °C to 22 °C. The experimental data of the hydrate forming temperatures and pressures for 4.55, 28.03, 33.85, 41.9 and 65.9 mol% of hydrogen in methane are presented in Table 1. The experimental data for 49.63 mol% of hydrogen in carbon dioxide and for 51.38 mol% of hydrogen in ethylene are given in Table 2. The experimental results for a 6-component natural gas mixture and for the same mixture diluted with hydrogen to a concentration of 27.02 mol% are presented in Table 3. Table 4 shows the results for the hydrate forming condition in a 7-component natural gas mixture containing carbon dioxide diluted with hydrogen to 17.61 mol%.

Table 1
Hydrate forming conditions for methane in the presence of hydrogen.

P/MPa	T/°C	P/MPa	T/°C
4.55% H_2 + 95.45% CH_4		33.85% H_2 + 66.15% CH_4	
3.11	1.3	4.51	1.2
3.50	2.7	4.96	1.9
5.57	7.1	6.70	4.8
7.03	9.1	10.60	8.9
10.62	13.1	14.18	11.5
14.40	15.7	17.31	13.1
17.42	17.1	20.73	14.4
20.51	18.3		
28.03% H_2 + 71.97% CH_4		41.90% H_2 + 58.10% CH_4	
4.68	2.6	5.33	0.7
6.39	5.5	5.53	0.8
9.16	8.7	7.85	3.9
11.28	10.6	10.54	6.7
14.19	12.4	10.56	6.8
17.28	14.0	13.73	8.8
20.52	15.3	17.42	10.9
		20.64	12.2
		65.90% H_2 + 34.10% CH_4	
		11.19	1.2
		14.50	3.7
		17.22	5.2
		20.41	6.8

Table 2
Hydrate forming conditions for hydrogen in carbon dioxide and ethylene.

P/MPa	T/°C	P/MPa	T/°C
49.63% H_2 + 50.37% CO_2		51.38% H_2 + 48.62% C_2H_4	
3.50	1.0	1.57	1.9
4.17	2.2	3.11	6.9
5.98	4.6	5.02	11.0
8.52	7.6	8.44	14.5
13.50	9.3	13.22	16.5
14.18	9.2	19.50	17.9
18.54	10.0		
18.68	10.0		
20.38	10.1		

2.3. Thermodynamic model

The statistical thermodynamic relation between the properties of gas hydrates and their molecular parameters was developed by van der Waals and Platteeuw [6] and can be expressed as follows:

$$\Delta\mu_W^H = RT\sum_m \nu_m \ln\left(1+\sum_j C_{mj} f_j\right) \qquad (1)$$

where R is the universal gas constant; T is the absolute temperature; ν_m is the number of cavities of type m per water molecule in the lattice; f_j is the fugacity of gas component j, which can be calculated