Vapor−Hydrate Equilibria for the Methane + Hydrogen + Tetrahydrofuran + Water System[†]

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Vapor−hydrate equilibria data for the methane + hydrogen + tetrahydrofuran + water system were obtained using the sapphire cell device. The influence of temperature, pressure, initial gas−liquid volume ratio, and the mole fraction of tetrahydrofuran was investigated to evaluate the separation efficiency by forming hydrate at different operating conditions. The experimental results show that decreasing operating temperature or the initial gas−liquid volume ratio and increasing operating pressure or initial tetrahydrofuran mole fraction will be effective to increase the content of hydrogen in the vapor phase. But their influence on the recovery degree of hydrogen in the vapor phase and the operating cost should also be taken into account synthetically when designing a separation process.

Introduction

Environmental restrictions, fuel reformulation, and increased processing of heavier sour crude are leading to the substantial increase of hydrogen consumption in refinery for hydrodesulfurization, aromatics and olefins saturation, and product quality improvement. These trends will accelerate the demand for supplementary hydrogen production during the half of the 1990s and beyond.[1] Hydrogen is generally separated from hydrogen-containing gas mixtures in petroleum refining and petrochemical processes. Since the formation pressure of hydrogen hydrate is much higher than that of light hydrocarbon components,[2,3] it is a promising method for separating hydrogen from hydrocarbon gas mixtures through forming and dissociating hydrates.[4] The basic mechanism of the separation process by forming hydrate is the selective partition of target components between the hydrate phase and the gas phase.[4–8] For the hydrogen-containing system, the formation pressure of hydrate will be high,[9] and hydrate-based separation methods will be industrially impractical. Tetrahydrofuran (THF) was used as a hydrate thermodynamics promoter to reduce the hydrate formation pressure and increase the formation rate.[6,10–14] It was also a promising hydrogen storage method by the formation of THF + hydrogen binary hydrate at low pressure and near-ambient temperature.[15,16]

Besides hydrogen, methane is usually a main component in petroleum refining and petrochemical processes. Since methane forms hydrates at much higher pressure than other light hydrocarbons,[3] it is a key component for the separation of these gas mixtures through hydrate formation. In this work, an experimental study on the separation of hydrogen from (CH_4 + H_2) feed mixture with two hydrogen contents was then performed. Vapor−hydrate equilibrium data was obtained to check the single stage separation efficiency of the hydrogen and methane mixture with the presence of THF as a promoter.

Experimental Section

Materials and Preparation of Samples. Analytical grade hydrogen (99.99 %) and methane (99.99 %) supplied by Beifeng Gas Industry Corporation were used in preparing the synthetic binary gas mixtures. A Hewlett-Packard gas chromatograph (HP 6890) was used to analyze the composition of gas mixtures. The THF used for preparing the aqueous solution was supplied by Beijing Reagents Corporation. An electronic balance with a precision of ± 0.1 mg was used in preparing the aqueous solution with the required concentration of THF. Distilled water was used in preparing the aqueous solution.

Experimental Apparatus. The experimental apparatus used in this work is shown in Figure 1 and has been described in detail in the previous papers by this laboratory.[11–13] The apparatus consists mainly of a cylindrical variable-volume high-pressure [(0 ∼ 25) MPa] transparent sapphire cell (2.54 cm in diameter, effective volume approximately 60 cm^3) installed in an air-bath and equipped with a magnetic floating piston inside for accelerating the phase equilibrium process. The formation of the hydrate crystals in the solution can be observed directly through the transparent cell wall. The accuracies of temperature and pressure measurements are within ± 0.2 K and ± 0.02 MPa, respectively.

Experimental Procedure. First, the sapphire cell was washed using distilled water, and then it was rinsed three times with the prepared aqueous solution. After the cell was thoroughly cleaned, a suitable quantity of liquid sample was added into the cell. The gas space of the cell was purged with the prepared gas sample four to five times to ensure the absence of air. Subsequently, the air-bath temperature was adjusted to the desired value. Once the cell temperature was constant, the gas sample was charged into the cell until the given pressure was achieved, and hydrate nucleation was then induced by agitation of the magnetic stirrer. During the hydrate formation process, the system pressure was maintained at a constant value by pushing the piston upward continuously. When, if without pushing the piston upward, the drop in system pressure was less than 0.02 MPa over 3 h, the hydrate formation process was assumed to be complete. Afterward, the residual gas (vapor) was kept in touch with the hydrate phase and residual liquid phase for over 8 h to ensure vapor−hydrate equilibrium. When the vapor−hydrate equilibrium was established, the connecting pipe was vacuumized and purged with the equi-

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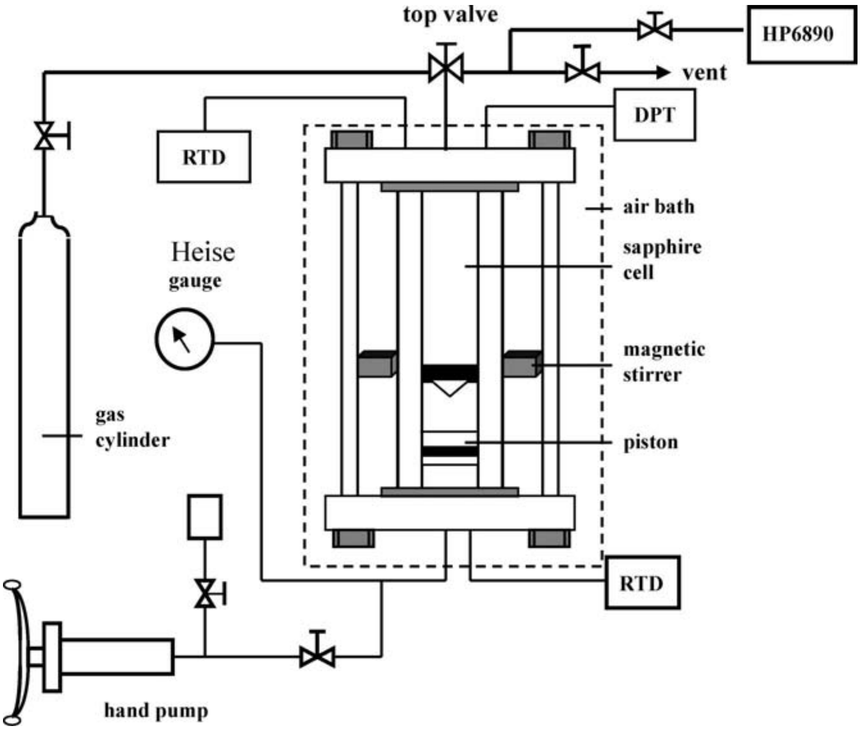

Figure 1. Schematic of experimental apparatus: DPT, differential pressure transducer; RTD, resistance thermocouple detector.

Table 1. Vapor−Hydrate Equilibria Data for the CH_4 (1) + H_2 (2) + H_2O (3) + THF (4) System with Respect to Different Temperatures while Pressure, Initial Gas−Liquid Volume Ratio ϕ, and THF Mole Fraction in the Initial Aqueous Solution Are Specified to $P = 12.0$ MPa, $\phi = 100$, and $x_4 = 0.01$

T/K	z_2	y_2	x_2	100α
278.15	0.8744	0.9528	0.2888	96.18
279.15		0.9482	0.2335	97.24
280.15		0.9453	0.1601	98.24
281.15		0.9430	0.1024	99.05
278.15	0.7874	0.9159	0.1170	97.61
279.15		0.9120	0.0941	98.17
280.15		0.9087	0.0733	98.64
281.15		0.9023	0.0549	99.15

Table 2. Vapor−Hydrate Equilibria Data for the CH_4 (1) + H_2 (2) + H_2O (3) + THF (4) System with Respect to Different Pressures while Temperature, Initial Gas−Liquid Volume Ratio, and THF Mole Fraction in the Initial Aqueous Solution Are Specified to $T = 278.15$ K, $\phi = 100$, and $x_4 = 0.01$

P/MPa	z_2	y_2	x_2	100α
12.00	0.8744	0.9528	0.2888	96.18
11.50		0.9520	0.2638	96.60
11.00		0.9516	0.2271	97.23
10.50		0.9497	0.1883	97.87
10.00		0.9482	0.1441	98.48
12.00	0.7874	0.9159	0.1170	97.61
11.50		0.9125	0.1096	97.89
11.00		0.9104	0.0778	98.54
10.50		0.9078	0.0581	98.95
10.00		0.9054	0.0441	99.23

librium vapor gas and then analyzed with HP 6890 online while the system pressure was maintained at a constant value by pushing the piston. The vapor phase was sampled and analyzed at least three times, and the average values were then taken as the compositions of the vapor phase. For the hydrate phase, it is in the form of slurry at the experimental conditions. After the vapor phase was analyzed, it was discharged slowly from the cell at a constant pressure value by pushing the piston until the hydrate slurry flows out of the connecting pipe. Then, we closed the cell and specified a high temperature value to dissociate the hydrate slurry. After the hydrate was dissociated completely, the dissociated gas was analyzed by HP 6890 online as the composition of the hydrate phase.

It should be noted that the compositions of the vapor phase and hydrate phase concerned in this work are both in the water + THF-free basis; i.e., they are only the relative compositions of methane (1) and hydrogen (2) in two phases. The content of water (3) and THF (4) has been deducted from the normalization of compositions, where z_2, x_2, and y_2 represent the mole fraction of hydrogen in the feed gas mixture, the hydrate phase, and the vapor phase in such basis, respectively. That is, $z_2 = n_{2,\mathrm{feed}}/(n_{1,\mathrm{feed}} + n_{2,\mathrm{feed}})$, $x_2 = n_{2,\mathrm{H}}/(n_{1,\mathrm{H}} + n_{2,\mathrm{H}})$, $y_2 = n_{2,\mathrm{g}}/(n_{1,\mathrm{g}} + n_{2,\mathrm{g}})$, where n_{feed}, n_{H}, and n_{g} are the moles of methane (1) or hydrogen (2) in the feed gas mixture, hydrate phase, and vapor phase, respectively. The recovery degree, α, of hydrogen in the vapor phase was defined as

$$\alpha = \frac{ey_2}{z_2} \tag{1}$$

where the ratio of the mole of vapor phase at equilibrium, e, is determined with the following mass balance equation

$$e = \frac{z_2 - x_2}{y_2 - x_2} \tag{2}$$

Results and Discussion

To evaluate the factors affecting the separation efficiency, a series of experiments on the vapor−hydrate equilibria for the CH_4 (1) + H_2 (2) + H_2O (3) + THF (4) system were performed. The experimental data were tabulated in Tables 1 to 4.

Table 1 shows the influence of temperature upon the partition of hydrogen between the vapor and hydrate phases, where pressure, the mole fraction of THF in the initial aqueous solution, and the initial gas−liquid volume ratio were fixed at 12.0 MPa, x_4 =0.01, and 100 standard volumes of gas per unit volume of liquid (i.e., $\phi = 100$), and the feed

Table 3. Vapor−Hydrate Equilibria Data for the CH_4 (1) + H_2 (2) + H_2O (3) + THF (4) System with Respect to Different Initial Gas−Liquid Volume Ratio while Temperature, Initial Pressure, and THF Mole Fraction in Initial Aqueous Solution Are Specified to T = 278.15 K, P = 12.0 MPa, and x_4 = 0.01

ϕ	z_2	y_2	x_2	100α
80	0.8744	0.9622	0.3398	94.52
100		0.9528	0.2888	96.18
120		0.9504	0.1248	98.69
140		0.9487	0.1083	98.91
80	0.7874	0.9197	0.1724	96.12
100		0.9159	0.1170	97.61
120		0.9110	0.0924	98.73
140		0.9053	0.0723	98.95

Table 4. Vapor−Hydrate Equilibria Data for the CH_4 (1) + H_2 (2) + H_2O (3) + THF (4) System with Respect to Different Initial Mole Fraction of THF in Aqueous Solution while Temperature, Pressure, and Initial Different Gas−Liquid Volume Ratio Are Specified to T = 278.15 K, P = 12.0 MPa, and ϕ = 100

x_4	z_2	y_2	x_2	100α
0.005	0.8744	0.9281	0.2289	97.99
0.010		0.9528	0.2888	96.18
0.015		0.9571	0.3193	95.27
0.020		0.9614	0.3986	92.00
0.005	0.7874	0.8747	0.0752	98.96
0.010		0.9159	0.1170	97.61
0.015		0.9191	0.1724	96.14
0.020		0.9214	0.2725	92.85

gas compositions, z_2, were specified to 0.8744 and 0.7874, respectively. Table 1 shows that the hydrogen is enriched in the vapor phase remarkably due to the formation of gas hydrate, and the recovery degree of hydrogen in the vapor phase is very high. The amount of hydrogen lost in the hydrate phase is less than 5 %. Both y_2 and x_2 decrease, while the recovery degree α increases with increasing temperature. However, y_2 is less sensitive to temperature than x_2, which implies that more hydrogen is enclathrated in the hydrate lattice at lower temperature. Therefore, one should balance between the increase in the hydrogen composition in the gas phase and the hydrate formation rate by decreasing temperature. The composition of hydrogen in the vapor phase also depends on the feed gas composition. For the feed gas of z_2 = 0.8744, the highest y_2 reached was 0.9528 at 278.15 K, but for the feed gas of z_2 = 0.7874, it was only 0.9159 at 278.15 K. The recovery degree of hydrogen can reach 99 % for the feed gas with z_2 = 0.7874. That is, a higher recovery degree could be obtained when z_2 was smaller, implying that higher composition of hydrogen could be obtained by a two-stage or multistage separation, while a satisfying recovery degree was remained.

Table 2 shows the influence of pressure upon the partition of hydrogen between the vapor and hydrate phases, where temperature, the mole fraction of THF in the initial aqueous solution, and the initial gas−liquid volume ratio ϕ were fixed at 278.15 K, 0.01, and ϕ = 100, and the feed gas mole fractions, z_2, were specified to 0.8744 and 0.7874, respectively. As shown in Table 2, y_2 increases slightly while x_2 increases remarkably with an increase in pressure, which leads to the decrease of the recovery degree α. Just increasing the hydrogen composition and hydrate formation rate by decreasing operating temperature, one should also be careful in the design to increase the hydrogen composition and hydrate formation rate by increasing pressure.

Table 3 shows the influence of initial gas−liquid volume ratio, ϕ, upon the vapor−hydrate equilibrium of the present system, where temperature, pressure, and the mole fraction of THF in initial aqueous solution were fixed at 278.15 K, 12.0 MPa, and 0.01 and the feed gas mole fractions, z_2, were specified to 0.8744 and 0.7874, respectively. Both y_2 and x_2 increase with the decrease of initial gas−liquid volume ratio; however, x_2 was more sensitive to ϕ than y_2, leading to the decrease of the recovery degree α with the decrease of ϕ. The reason that ϕ affects the vapor−hydrate equilibria should be that the quantity of the formed hydrate increases with a decrease of ϕ because the mole fraction of THF in the residual aqueous solution decreases less when ϕ is lower.

Table 4 shows the influence of the mole fraction of THF in the initial aqueous solution upon the vapor−hydrate equilibrium, where temperature, pressure, and the initial gas−liquid volume ratio were fixed at 278.15 K, 12.0 MPa, and ϕ = 100, and the feed gas mole fractions, z_2, were specified to 0.8744 and 0.7874, respectively. At lower mole fraction (x_4 < 0.01), y_2 could be increased remarkably by increasing the initial THF mole fraction. However, when initial THF mole fraction is higher than 0.01, this effect was not obvious. On the other hand, the recovery degree of hydrogen decreases remarkably with increasing THF mole fraction. Therefore, x_4 = 0.01 is recommended for the initial THF mole fraction.

From the above experimental study, it can be concluded that some measures can be taken to increase the content of hydrogen in the vapor phase, e.g., decreasing operating temperature, increasing operating pressure, decreasing the initial gas−liquid volume ratio, and increasing the initial THF mole fraction. These measures can also increase the hydrate formation rate. However, these measures always decrease the recovery degree of hydrogen in the vapor phase and increase the operating cost. Therefore, an optimization should be made when designing a separation process.

From the data listed in Tables 1 to 4, one can see that x_2 increases rapidly with an increase in y_2, implying that the quantity of hydrogen enclathrated into the hydrate lattice increases. This work supports the idea of storing hydrogen as hydrate in aqueous THF solution as by Florusse et al.[15]

Conclusions

The vapor−hydrate equilibrium data were measured for the (CH_4 + H_2 + THF + H_2O) system with two hydrogen mole fractions (0.8744 and 0.7874) in the feed gas. The influence of temperature, pressure, initial gas−liquid volume ratio, and the mole fraction of THF in the initial aqueous solution was examined to evaluate the separation efficiency at different conditions. The experimental results show that decreasing operating temperature or the initial gas−liquid volume ratio and increasing operating pressure or initial THF mole fraction will be effective to increase the content of hydrogen in the vapor phase. However, these measures always decrease the recovery degree of hydrogen in the vapor phase and increase the operating cost. An optimization should be made when designing a separation process.

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