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Vapor-hydrate phases equilibrium of $(CH_4+C_2H_6)$ and $(CH_4+C_2H_4)$ systems

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Abstract: Separation of the $(C_1 + C_2)$ hydrocarbon system is of importance in natural gas processing and ethylene production. However it is the bottleneck because of its high refrigeration energy consumption, and needs to be urgently addressed. The technology of separating gas mixtures by forming hydrate could be used to separate $(C_1 + C_2)$ gas mixtures at around 0 °C and has attracted increasing attention worldwide. In this paper, investigation of vapor-hydrate two-phase equilibrium was carried out for $(C_1 + C_2)$ systems with and without tetrahydrofuran (THF). The compositions of vapor and hydrate phases under phase equilibrium were studied with model algorithm when structure I and structure II hydrates coexisted for the (methane + ethane) system. The average deviation between the modeled and actual mole fractions of ethane in hydrate and vapor phases was 0.55%, and that of ethylene was 5.7% when THF was not added. The average deviation of the mole fraction of ethane in vapor phase was 11.46% and ethylene was 7.38% when THF was added. The test results showed that the proposed algorithm is practicable.

Key words: Chen-Guo model, vapor-hydrate equilibrium, gas separation

1 Introduction

Separation of (methane + ethane) or (methane + ethylene) gas mixtures is usually involved in oil and gas processing and ethylene production. Ethylene is an essential chemical feedstock which plays an important role in the national economy of China. Methane, ethane and ethylene are all low-boiling gases. Separation of such gas mixtures is a bottleneck in practical production because it is usually done by the conventional distillation method and requires cooling to very low temperatures. Developing a new separation technology is an important aim.

It is known that when a gas mixture partially forms hydrate, the composition of the components in the hydrate phase and in the residual vapor phase is different. Many separation technologies based on the hydrate principle have been reported (Glew, 1966; Spencer, 2000; Kang and Lee, 2000; Kang et al, 2001; Ma et al, 2001; Yamamoto et al, 2002; Ballard and Sloan, 2002; Klauda and Sandler, 2003; Zhang et al, 2004; Zhang et al, 2005). The advantage of separating gas mixtures by using the hydrate technology is that the low-boiling gas mixture could be separated at a temperature around 0 ºC and consequently the refrigeration energy consumption would be reduced enormously. Moreover it could simplify the process flow and reduce facility investment. In order to apply the hydrate technology to practical production, tetrahydrofuran(THF) is usually used as a thermodynamic promoter to lower the operation pressure and accelerate hydrate formation.

In this work, single stage vapor-hydrate equilibrium separation was carried out and P-T-x-y experimental data were obtained with a (methane + ethylene) gas mixture. An algorithm for vapor-hydrate equilibrium of a $(C_1 + C_2)$ system was developed. The Petal-Teja equation of state (PT EOS) (Patel and Teja, 1982) coupled with the Chen-Guo hydrate model (Chen and Guo, 1998) were used to calculate the equilibrium between vapor and hydrate phases.

Gas hydrates have three potential hydrate structures: structure I, structure II and structure H. Structure I is a body-centered lattice structure, formed by natural gas components smaller than propane with water molecules. Structure II is a diamond lattice structure within a cubic framework, formed by natural gas or oil components larger than ethane but smaller than pentane with water molecules. Structure H is a hexagonal framework with cavities large enough to contain molecules the size of common components of naphtha and gasoline. Normally, pure methane or ethane will form structure I hydrate. However, when $(CH_4 + C_2H_6)$ mixture forms hydrate, structure I (sI) and structure II (sII) hydrates will coexist over a range of composition (Subramanian et al, 2000; Ballard and Sloan, 2000). A model was developed to calculate the composition of the hydrocarbons in the hydrate phase. The comparison of the calculated results with the experimental data showed that the prediction was satisfactory when two hydrate structures coexisted.

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2 Experimental

The vapor-hydrate equilibrium for the (CH_4 + C_2H_6) hydrocarbon (HC) system has been studied in our laboratory (Zhang et al, 2004). This work was mainly aimed at the (CH_4 + C_2H_4) system.

2.1 Setup for experiment

As shown in Fig. 1, the setup used consists mainly of a cylindrical high-pressure (0-16 MPa) stainless steel cell with an effective volume of 256 cm^3. The high-pressure cell is installed in an air-bath and equipped with a magnetic stirrer inside for accelerating the formation of hydrate. Water or THF aqueous solution can be added or drained out through a valve at the bottom of the cell, and (CH_4 + C_2H_4) gas mixture can be charged or vented through valves on the top of the cell. The feed gas sample is prepared in a gas cylinder. The precision of temperature and pressure measurements are within ±0.1 K and ±0.025 MPa, respectively.

2.2 Materials and preparation of samples

Methane (analytical grade, 99.9%) and ethylene (analytical grade, 99.5%) supplied by Beijing AP Beifen Gases Industry were used for preparing the feed gas mixtures of (CH_4 + C_2H_4). The composition of the (CH_4 + C_2H_4) gas mixtures was analyzed by a Hewlett-Packard gas chromatograph (HP 6890). THF used for preparing aqueous solution was supplied by Beijing Chemical Reagents Company. An electronic balance with a precision of ±0.1 mg was used in preparing required THF aqueous solution.

2.3 Experimental procedures

The stainless steel cell was first washed with distilled water, and then it was washed three times with either just water or the prepared THF aqueous solution. Then a measured amount of liquid sample was added into the cell, which was then installed in an air bath, and the cell was purged with prepared (CH_4 + C_2H_4) gas mixture four or five times to ensure the absence of air. The air-bath temperature was then tuned to the required temperature, and then the cell was charged with the (CH_4 + C_2H_4) gas mixture until the required pressure was reached. The liquid phase was stirred with a magnetic stirrer and hydrate nucleation began. After the system pressure was stabilized for 4 hours, the vapor–hydrate equilibrium was achieved. The vapor phase was sampled and analyzed at least three times by gas chromatography. The average value of measurement was regarded as the composition of vapor phase, when the measurement precision of mole fraction of gas mixture was less than 0.01%. Then the air-bath temperature was lowered below 0 °C to avoid decomposition of the hydrate phase because of the decreased pressure caused by venting vapor, which would result in measurement error of the composition of hydrate phase. After the vapor was vented completely, the hydrate was decomposed by heating and the gas was released. The relative concentrations of methane and ethylene in the hydrate phase were obtained by analyzing by gas chromatography the gas released from the hydrate phase.

2.4 Experimental results

In this work, the compositions of (C_1 and C_2) mixtures

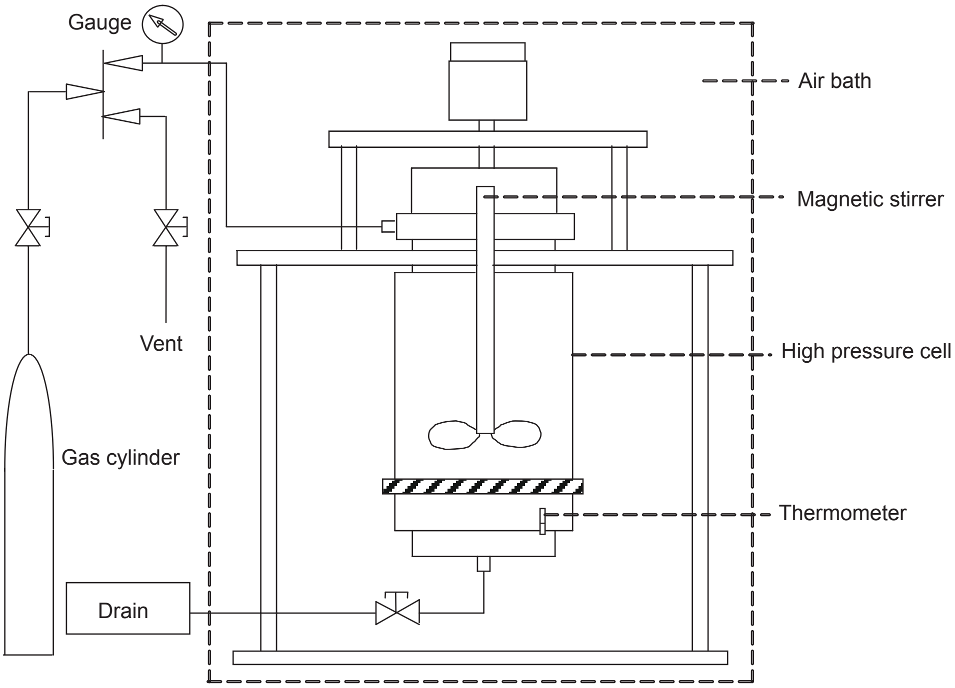

Fig. 1 Setup for experiment

in the vapor and hydrate phases are on water- and THF-free basis, i.e. they are the relative compositions of methane and ethylene in two phases. z_2, x_2 and y_2 represent the content of ethylene in the feed gas (i.e. the prepared (CH_4 + C_2H_4) gas mixture), hydrate and vapor phase, respectively, on a water- and THF-free basis. *W* represents the mole fraction of the water or THF aqueous solution in the feed (gas + water) mixture.

The vapor–hydrate equilibrium for the binary system (CH_4 + C_2H_4) with just water was measured, and the results are listed in Table 1, which shows that the separation efficiency of (CH_4 + C_2H_4) system with just water is not satisfactory.

Table 1 Vapor-hydrate equilibrium data for system of (CH_4(1)* + C_2H_4(2)) with just water (T = 274.15 K, z_2 = 19.86 mol%)

P, MPa	W, mol%	y_2, mol%	x_2, mol%	e**, %	R_2***, %
2.75	62	14.77	35.12	74.99	44.23
2.98	63.5	13.14	35.39	69.80	53.82
3.27	66	11.20	37.38	66.92	62.26
3.74	67	10.16	40.78	68.32	65.05

Notes: *-The numbers in parentheses means component 1 or 2 in (CH_4 + C_2H_4) system;
**-The mole fraction of the vapor phase in phase equilibrium;
***-The recovery ratio of ethylene in enrichment phase.
R_2=(1-e)x_2/z_2

It has been recognized that THF can be used as hydrate promoter because it can easily form hydrate. In this work, THF not only acted as a thermodynamic promoter but also to enhance separation efficiency, because it can occupy large cavities in the hydrate more easily than ethylene and consequently inhibits the occupancy of ethylene molecules in hydrate. The vapor–hydrate equilibrium for system of (CH_4 + C_2H_4) with THF aqueous solution was measured. The experimental data are listed in Table 2. Table 3 shows the results at different temperatures and pressures.

Table 2 Vapor-hydrate equilibrium data for system of (CH_4(1) + C_2H_4(2)) with 6 mol% THF aqueous solution (T = 274.15 K, z_2 = 68.06 mol%)

P, MPa	W, mol%	y_2, mol%	x_2, mol%	e, %	R_2*, %
1.38	87.6	86.57	52.27	67.34	85.66
1.56	87	88.91	55.34	59.74	78.04
1.72	86.3	90.64	57.85	53.58	71.36
1.88	85.5	87.23	50.73	48.45	62.10
1.93	85	85.97	48.57	41.50	52.42

Notes: *R_2=ey_2/z_2

Table 3 Vapor-hydrate equilibrium data for system of (CH_4(1) + C_2H_4(2)) with 6 mol% THF aqueous solution at different temperatures and pressures (z_2 = 68.06 mol%)

T, K	P, MPa	W, mol%	y_2, mol%	x_2, mol%	e,%	R_2*,%
273.15	1.57	86.5	89.11	55.74	48.07	62.94
274.15	1.72	86.5	90.64	57.85	53.58	71.36
276.15	1.83	86.5	90.36	57.13	57.70	76.60
278.15	1.92	87	88.71	55.27	59.29	77.28
280.15	2.04	87	86.46	52.96	63.61	80.81
282.15	2.12	87	85.58	51.57	66.52	83.64

Notes: *R_2=ey_2/z_2

Compared with the data in Table 1, Table 2 shows that the distribution of ethylene in vapor phase and in hydrate phase was reversed when THF existed in water, i. e. ethylene was obviously enriched in vapor phase. The reason is that the occupancy of large cavities of hydrate was dominated by THF molecules and the occupancy of small cavities was dominated by methane molecules, and ethylene molecules could hardly occupy small cavities. Therefore the overall occupancy of ethylene molecules in hydrate cavities is obviously lower than that of methane.

3 Development of the mathematic model

3.1 Algorithm for calculation of vapor-hydrate phase equilibrium

Because the solubility of (C_1 + C_2) gas mixture in water is very low, and the amount of water in vapor phase could be ignored, the vapor-hydrate two-phase equilibrium calculations could be done on water-free basis, which is similar to vapor –liquid two-phase equilibrium calculations for isothermal flash. Therefore, the overall and component material-balance equations are expressed as follows:

$$F = V + H \tag{1}$$

$$Fz_i = Vy_i + Hx_i \tag{2}$$

where F, V and H denote the mole fractions of feed, vapor phase and hydrate phase, respectively; z_i , y_i and x_i denote the compositions (mole fraction) of feed, vapor phase and hydrate phase, respectively. Define e as the mole fraction of the vapor phase in phase equilibrium, V/F, Eq. (2) can be expressed as follows:

$$z_i = ey_i + (1-e)x_i \tag{3}$$

or

$$y_i = \frac{z_i - (1-e)x_i}{e} \tag{4}$$

According to the Chen-Guo hydrate model, the mole fraction of guest component i in hydrate phase can be expressed as

$$x_i = \frac{x_i^* + \alpha\theta_i}{\sum_{i=1}^{c}\left(x_i^* + \alpha\theta_i\right)} \tag{5}$$

$$\theta_i = \frac{f_i^{\mathrm{V}} C_i}{1 + \sum_j f_j^{\mathrm{V}} C_j} \tag{6}$$

$$x_i^* = \frac{f_i^{\mathrm{V}}}{f_i^0\left[1 - \sum_j \theta_j\right]^{\alpha}} \tag{7}$$

$$f_i^0 = f_{Ti}^0 \cdot \exp\left[\frac{\beta P}{T}\right] \cdot a_w^{-1/\lambda_2} \tag{8}$$

$$f_{Ti}^0 = \exp\left[\frac{-\sum_j A_{ij}\theta_j}{T}\right] \cdot \left[A_i' \exp\left(\frac{B_i'}{T - C_i'}\right)\right] \tag{9}$$

where $\alpha = \lambda_1/\lambda_2$. λ_1 and λ_2 stand for the numbers of small and large cavities per water molecule, respectively. λ_1= 2/46 and λ_2= 6/46 for structure I hydrate; λ_1= 16/136 and λ_2= 8/136 for structure II hydrate. Therefore α = 1/3 for structure I hydrate; α = 2 for structure II hydrate. θ_i denotes the fractional filling of small cavities by guest molecules i. x_i^* denotes mole fraction of hydrocarbon component i in large cavities. a_w is the activity of water, in the case of just water, a_w=1. The vapor-phase fugacity (f_i^{V}) of component i can be calculated by PT EOS. β = 0.4242 K· bar^{-1} for structure I hydrates and β = 1.0224 K·bar^{-1} for structure II hydrates. f_i^0 denotes the hydrate-phase fugacity of component i when the small cavities are not occupied by hydrocarbon molecules. f_{Ti}^0 denotes the effect of temperature on f_i^0. The Langmuir constant C_i in Eq. (6) is formulated as

$$C_i = X_i \exp\left[\frac{Y_i}{T - Z_i}\right] \tag{10}$$

The constants A_i', B_i', C_i' and binary interaction coefficients A_{ij} in Eq. (9) and the constants X_i, Y_i and Z_i in Eq. (10) are from Chen and Guo (1998).

Generally independent variables are as Table 4.

Table 4 Independent variables

Independent variable	Number of variable
F	1
z_i	$c-1$
P	1
T	1
W	1
Total	c+3

In Table 4, c is the number of components of gas mixture; F denotes the flux of feed the feed gas mixture on water-free basis; W stands for mole fraction of water or aqueous solution in feed (gas + water) mixture. The amount of water in feed mixture will determine the fraction of hydrate phase and its composition. The fraction (e) of vapor phase is related to W as follows in the case of just water

$$e = 1 - \frac{W}{1-W}\sum_{i=1}^{c}\left(\lambda_1\theta_i + \lambda_2 x_i^*\right) \tag{11}$$

In the case of THF in aqueous phase, e is related to W as follows

$$e = 1 - \frac{W(1 - x_{\mathrm{inh}})}{1-W}\sum_{i=1}^{c}\left(\lambda_1\theta_i + \lambda_2 x_i^*\right) \tag{12}$$

where x_{inh} denotes the mole fraction of THF in water.

The calculation procedures are summarized as follows:

1) Input specified temperature (T), pressure (P) and composition (z_i) of feed on water-free basis. Input water mole fraction (W) of HC feed (gas + water) mixture.

2) Based on T and z_i, calculate hydrate formation pressure (P_{H}). Judge whether $P > P_{\mathrm{H}}$ is satisfied. If not, the hydrate phase will not be formed, so stop the two-phase flash calculation. If $P>P_{\mathrm{H}}$ is satisfied, then the hydrate phase is present and continue the following steps.

3) Based on T, P_{H} and z_{i}, calculate the initial value of composition (x_i) of the HC mixture in the hydrate phase. Calculate the mole fraction (e) of vapor phase using Eq. (11).

4) Calculate the mole fraction (y_i) of each component in vapor phase using Eq. (4).

5) Based on T, P and y_i, calculate the vapor-phase fugacity (f_i) using PT EOS.

6) Calculate the fraction (θ_i) of small cavities occupied by each component i using Eq. (6). Calculate the mole fraction (x_i^*) of gas component i in large cavities using Eq. (7).

7) Calculate the mole fraction (x_i) of each component in hydrate phase from vapor-phase fugacity (f_i) using Eq. (5).

8) Calculate the new value of the mole fraction (e) of vapor phase using Eq. (11).

9) Judge whether the difference between e' and e meets the precision requirement ($\left|\frac{e'-e}{e}\right| < 10^{-3}$). If not, adjust e to e' and repeat steps (4) to (9) until the precision is satisfied.

For the THF aqueous solution, the calculation procedures are the same as mentioned above except that, in this case, the activity (a_w) of water in Eq. (8) is not equal to 1. The Wilson activity model (Wilson, 1964) was used to calculate the activity of water and the fugacity of THF in the aqueous phase. THF can only form sII hydrate and only occupy the large cavities. Therefore the fraction (θ_{THF}) of small cavities occupied by THF is equal to zero, that is, $C_{\mathrm{THF}} = 0$. The hydrate model parameters of THF in Eq. (9) were determined, under hydrate formation conditions of systems containing THF, as follows:

$$(A'_{THF})^{\mathrm{II}} = 20.5\times10^{24}\ \mathrm{MPa},\ (B'_{THF})^{\mathrm{II}} = -24787.5\ \mathrm{K},$$

$$(C'_{THF})^{\mathrm{II}} = -130.0\ \mathrm{K}$$

We need to pay more attention to the (CH_4 + C_2H_6) system. Normally pure methane or ethane forms sI hydrate. However their mixture would form both sI and sII hydrates simultaneously when methane content of (CH_4 + C_2H_6) mixture is in a specific range. When sI and sII hydrates coexist, the ratio of the two hydrate structures needs to be determined.

When the pressure of (CH_4 + C_2H_6) mixture system was higher than that of forming both sI and sII hydrates, these two hydrates would be formed simultaneously. The amounts of these two hydrates depended on their rates of formation. According to hydrate formation kinetics, the hydrate formation rate can be expressed as follows

$$\frac{dn}{dt} = K\left[\exp\left(-a\frac{\Delta G}{RT}\right) - 1\right] \tag{13}$$

where a is a dimensionless parameter, $a = 8.16$. K is reaction rate constant. G denotes Gibbs free energy, which is expressed as

$$\Delta G = RT\left[\lambda_2 \sum_i x_i^* \ln\frac{f_i^0}{f_i} + \lambda_1 \ln\left(1 - \sum_i \theta_i\right)\right] \tag{14}$$

Hence, the ratio (η) of two hydrate structures can be given as follows

$$\eta = \frac{n^{\mathrm{II}}}{n^{\mathrm{I}}} = \left[\exp\left(-a\frac{\Delta G^{\mathrm{II}}}{RT}\right) - 1\right] \Big/ \left[\exp\left(-a\frac{\Delta G^{\mathrm{I}}}{RT}\right) - 1\right] \tag{15}$$

where n^{I} and n^{II} stand for the amount of sI and sII hydrates in hydrate phase, respectively.

The mole fractions of HC component i in sI and sII hydrates, x_i^{I} and x_i^{II}, can be calculated using Eq. (5). The total mole fraction of component i in the hydrate phase therefore can be obtained as follows

$$x_i = \frac{n^{\mathrm{I}} x_i^{\mathrm{I}} + n^{\mathrm{II}} x_i^{\mathrm{II}}}{n^{\mathrm{I}} + n^{\mathrm{II}}} = \frac{x_i^{\mathrm{I}} + \eta x_i^{\mathrm{II}}}{1+\eta} \tag{16}$$

For the (CH_4 + C_2H_6) gas mixture, if the content of methane is in the range of 40-75 mol% (Subramanian et al, 2000; Deaton and Frost, 1946) and the system pressure is higher than the formation pressure of sI and sII hydrates, the composition of HC mixture in hydrate phase could be calculated using Eq. (15) and Eq. (16).

3.2 Results and discussion

A comparison of prediction results with experimental data for (CH_4 + C_2H_6) and (CH_4 + C_2H_4) gas mixtures was made.

Assuming that (CH_4 + C_2H_4) HC mixture only formed structure I or structure II hydrate and without THF in water, the vapor-hydrate phase equilibrium was calculated. Table 5 shows the calculated result and the experimental data which are listed in Table 1 for (CH_4 + C_2H_4) gas mixture. The average deviation (AADX) of the mole fraction of ethylene in hydrate phase was 13.97% for sI and 7.15% for sII, indicating that structure II hydrate was more likely to be formed under our experimental conditions. The calculated result and the experimental data for (CH_4 + C_2H_6) system are listed in Table 6. It can be seen that the predicted mole fraction of ethane in structure I hydrate was greater than experimental data whereas the mole fraction of ethane in structure II hydrate was less than experimental data. The average deviation (AADX) of the mole fraction of ethane in hydrate phase was 14.96% for sI and 28.82% for sII. The agreement between calculated and experimental data was low.

Assuming that structure I and structure II hydrates coexisted, the vapor-hydrate equilibrium was calculated

Table 5 Calculated and experimental mole fractions of C_2H_4 in vapor and hydrate phases for (CH_4(1) + C_2H_4(2)) gas mixture with just water ($T = 274.15$ K, $z_2 = 0.1986$)

P, MPa	W, %	y_2^{exp}	y_2^{cal}(sI)	y_2^{cal}(sII)	x_2^{exp}	x_2^{cal}(sI)	x_2^{cal}(sII)
2.75	66.2	0.1477	0.1368	0.1413	0.3512	0.3973	0.3832
2.98	67	0.1314	0.1367	0.1319	0.3539	0.3934	0.3768
3.27	67.8	0.1120	0.1087	0.1183	0.3738	0.3377	0.3689
3.74	68	0.1016	0.1021	0.1084	0.4078	0.3183	0.3600
AAD*, %			3.71	4.26		13.973	7.15

Notes: *–$AADY\% = (1/N_{\mathrm{p}}) \sum_{i=1}^{N\mathrm{p}} \left|(y^{\mathrm{cal}} - y^{\mathrm{exp}})/y^{\mathrm{exp}}\right|_j \times 100$;

$AADX\% = (1/N_{\mathrm{P}}) \sum_{i=1}^{N\mathrm{p}} \left|(x^{\mathrm{cal}} - x^{\mathrm{exp}})/x^{\mathrm{exp}}\right|_j \times 100$

Table 6 Calculated and experimental mole fractions of C_2H_6 in vapor and hydrate phases for (CH_4(1) + C_2H_6(2)) gas mixture with just water (T = 274.15 K, z_2 = 0.6011)

P, MPa	W mol%	y_2^{exp}	y_2^{cal}(sI)	y_2^{cal}(sII)	x_2^{exp}	x_2^{cal}(sI)	x_2^{cal}(sII)
2.5	62	0.5825	0.5445	0.6323	0.6592	0.7658	0.4750
3.0	67	0.5773	0.5297	0.6500	0.6567	0.7502	0.4603
4.0	76	0.5748	0.4790	0.7107	0.6253	0.7158	0.4464
AAD, %			10.48	14.93		14.96	28.82

again for system of (CH_4 + C_2H_6) and the results are shown in Fig. 2 and Fig. 3. It is seen that the calculated results was improved greatly. The average deviation (AADX) of the mole fraction of ethane in hydrate phase was 0.87%, indicating that the two hydrate structures coexisted under the experimental conditions and the proposed algorithm for calculating the composition of the (CH_4 + C_2H_6) mixture in hydrate phase is feasible when two hydrate structures coexist.

The test results of (CH_4 + C_2H_6) and (CH_4 + C_2H_4) systems with THF in water are shown in Figs. 4-7. Fig. 4 and Fig. 5 show the calculated results and the experimental data of ethane mole fraction in vapor and hydrate phases at different pressures for (75.61 mol% CH_4 + 24.39 mol% C_2H_6) feed gas mixture with 6mol% THF in aqueous solution. Compared with the results with no THF in water (Fig. 2 and Fig. 3), the separation efficiency of ethane was improved when THF was added in water (Fig. 4 and Fig. 5). In the absence of THF in water, the concentration of ethane was enriched slightly from 60.11 mol% to 67.16 mol% in hydrate phase (Fig. 3), whereas in the case of THF in water, the content of ethane was enriched from 24.39 mol% to approximately 56 mol% in vapor phase (Fig. 4 and Fig. 5). This is because THF prevented ethane from forming hydrate. The same results can

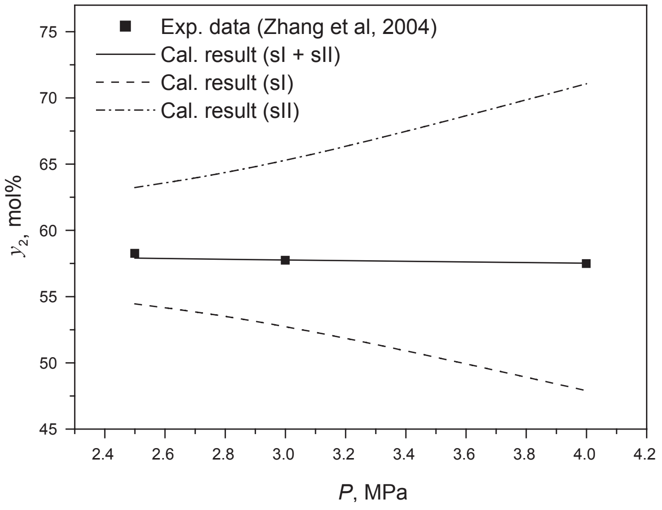

Fig. 2 Comparison of calculated and experimental mole fraction of C_2H_6 in vapor phase for (39.89 mol% CH_4 + 60.11 mol% C_2H_6) gas mixture with just water

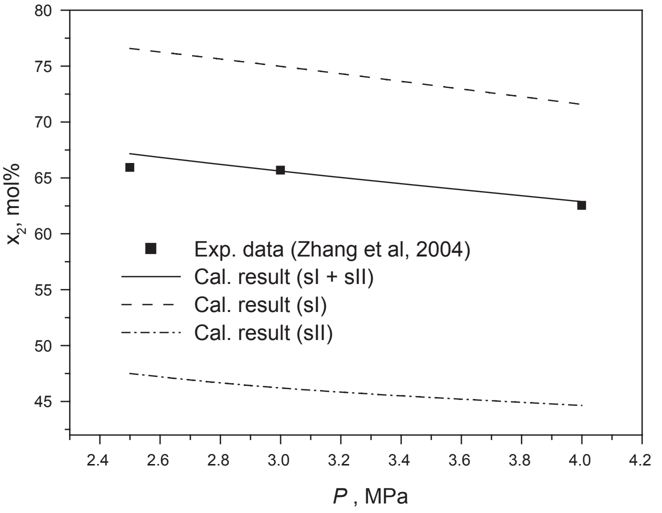

Fig. 3 Comparison of calculated and experimental mole fraction of C_2H_6 in hydrate phase for (39.89 mol% CH_4 + 60.11 mol% C_2H_6) gas mixture with just water

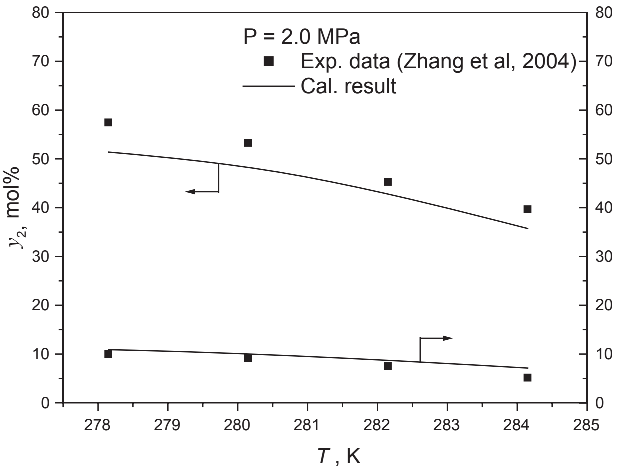

Fig. 4 Comparison of the calculated and experimental mole fractions of C_2H_6 in vapor and hydrate phases for (75.61 mol% CH_4 + 24.39 mol% C_2H_6) gas mixture with 6 mol% THF in aqueous solution (P = 2 MPa)

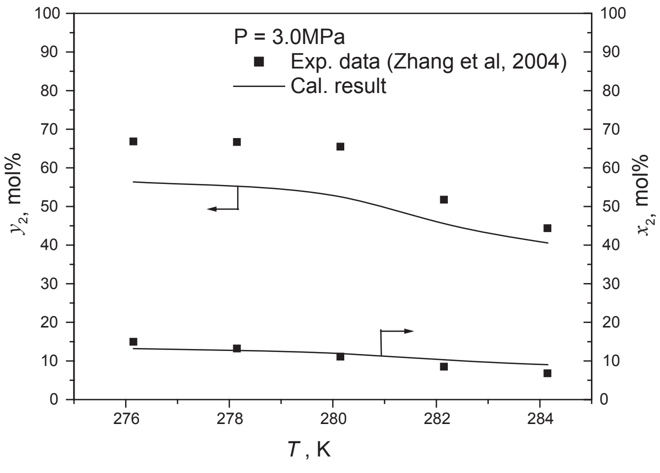

Fig. 5 Comparison of the calculated and experimental mole fractions of C_2H_6 in vapor and hydrate phases for (75.61 mol% CH_4 +24.39 mol% C_2H_6) gas mixture with 6mol% THF in aqueous solution (P = 3 MPa)

be obtained for (CH_4 + C_2H_4) gas mixture as shown in Fig. 6 and Fig. 7 where experimental data are listed in Table 2 and Table 3. The average deviation (AADY) of the mole fraction of ethane in vapor phase was 11.46% (Fig. 4 and Fig. 5) and that of ethylene was 7.38% (Fig. 6 and Fig. 7).

From the calculated results of systems containing THF, the average deviation (AADY) is greater than that of systems with just water (0.24% for methcme and 4.26% for ethylene). The reason is that water and THF are both polar substances. Calculation precision of thermodynamic properties for such substances needs to be enhanced. Moreover it is recognized that it is difficult to determine experimentally the composition of HC mixture in the hydrate phase, because hydrate is very unstable, therefore the measurement error will be great, which will bring some difficulty for testing the calculation model.

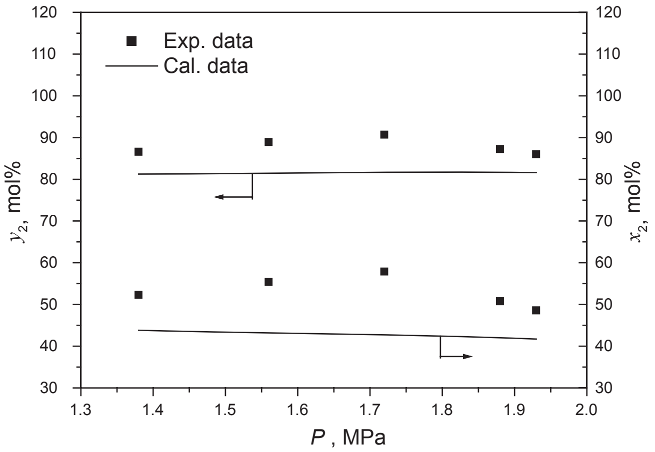

Fig. 6 Comparison of the calculated and experimental mole fractions of C_2H_4 in vapor and hydrate phases for (31.94 mol% CH_4 + 68.06 mol% C_2H_4) gas mixture with 6mol% THF in aqueous solution (T = 274.15 K)

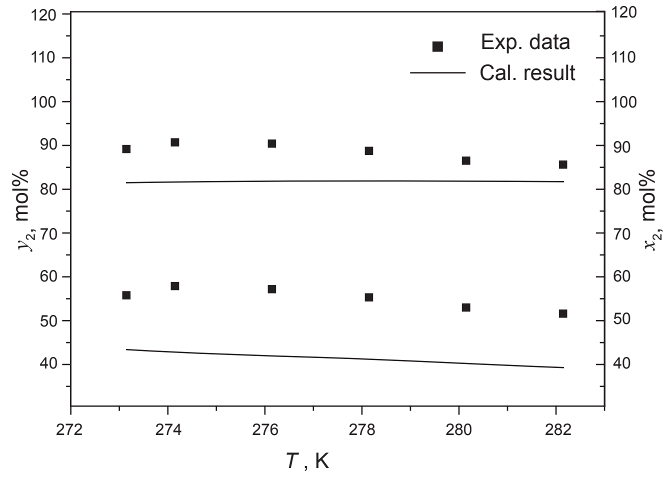

Fig. 7 Comparison of the calculated and experimental mole fractions of C_2H_4 in vapor and hydrate phases for (31.94 mol% CH_4 + 68.06 mol% C_2H_4) gas mixture with 6 mol% THF in aqueous solution (T = 273.15-282.15 K, P = 1.57-2.12 MPa)

4 Conclusion

The vapor-hydrate equilibrium data of (methane + ethylene) feed gas mixture with and without THF in water were measured, which is of significance for recovering ethylene from catalytic cracking gas through hydrate technology. With THF in water, the separation efficiency of C_2 from C_1 could be improved.

The Chen-Guo hydrate model was used for the system containing THF. An algorithm for estimating vapor-hydrate equilibria was developed. The composition of the hydrate phase for (methane + ethane) mixture was investigated. Under the conditions of 274.15 K, 2.5-4.0 MPa, it was likely that two hydrate structures coexist for the (CH_4 + C_2H_6) mixture. We applied the hydrate formation kinetics to controlling the ratio of two hydrate structures in the hydrate phase. Using the proposed calculation method, the average deviation of the mole fraction of ethane in hydrate and vapor phases was 0.55%, and that of ethylene was 5.7% when THF was not added. With THF in water, the average deviation of the mole fraction of ethane in vapor phase was 11.46% and that of ethylene was 7.38%, showing that the predicted results was approximately consistent with our experimental data.

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