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Chemical Engineering Journal 71 (1998) 145–151

Chemical Engineering Journal

A new approach to gas hydrate modelling

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Received 24 March 1998; received in revised form 8 August 1998; accepted 13 August 1998

Abstract

A two-step hydrate formation mechanism is proposed for gas hydrate formation: (1) a quasi-chemical reaction process to form basic hydrate and (2) an adsorption process of smaller gas molecules in the linked cavities of basic hydrate. Based on the new concepts introduced in a previous article and the two kinds of equilibrium: the quasi-chemical reaction equilibrium of step 1 and the physical adsorption equilibrium of step 2, a simpler hydrate model has been developed. Extensive test results indicate that the new model is adequate for predicting the hydrate formation conditions for pure gases and gas mixtures. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Gas hydrate; Formation mechanism; Modelling; Natural gas mixtures

1. Introduction

Most of the existing thermodynamic models for predicting hydrate formation are various modifications of the vdW-P model proposed by van der Waals and Platteeuw [1]. The authors have recently proposed an alternate statistical mechanics based hydrate model [2], and thereby introduced some new concepts. The objective of this work is to develop a simpler hydrate model based on those concepts and a new hydrate formation mechanism.

The vdW-P model was developed based on the assumption of the similarity between hydrate formation and Langmuir adsorption. Although the adsorption mechanism is capable of interpreting the nonstoichiometric property of hydrates, however, there are a number of differences between the two processes. A somewhat more realistic hydrate formation mechanism is proposed in this work, and a corresponding hydrate model is derived.

2. The proposed hydrate formation mechanism

A two-step hydrate formation mechanism is proposed.

> First step: The formation of a stoichiometric *basic hydrate* through a quasi-chemical reaction. The concept of basic hydrate has been discussed in detail in a previous article [2].
>
> Second step: The adsorption of gas molecules into the empty *linked cavities* of basic hydrate, resulting in the nonstoichiometric property of hydrates.

In the first step, following Long and Sloan [3], we assume the gas molecules dissolved in water will form labile clusters with a number of water molecules surrounding each guest molecule. The clusters will in turn associate with each other to form the so-called *basic hydrates*, with its basic cavities fully occupied by gas molecules and all linked cavities left empty. This process is described by the following complex chemical reaction:

$$H_2O + \lambda_2 G \rightarrow G_{\lambda_2} \cdot H_2O \tag{1}$$

where G denotes the gas species and λ_2 stands for the number of gas molecules per water molecule in the basic hydrate. During this step, empty cavities (the so-called *linked cavities*) are encased in the basic hydrate.

In the second step, small size gas molecules (e.g. Ar, N_2, O_2, CH_4, etc.) dissolved in water may move into the empty linked cavities (‘*adsorbed*’), resulting in the nonstoichiometric property of hydrates. However, this step will not occur for larger size gas molecules (e.g. ethane, propane, *n*-butane and i-butane), none of such molecules could enter the linked cavities, hence the final hydrate formed is just the stoichiometric basic hydrate formed in the first step. Thus basic hydrate is not hypothetical, it does exist physically.

It is reasonable to apply the *Langmuir adsorption theory* to describe the filling of the linked cavities by gas molecules.

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PII: S1385-8947(98)00126-0

3. Derivation of the thermodynamic model and parameter evaluation

3.1. Pure gas hydrates

Based on the two-step hydrate formation mechanism mentioned above, there should be two kinds of equilibrium existing in the system: the quasi-chemical equilibrium for the reaction occurred in the first step, and the physical adsorption equilibrium for the filling of gas molecules in the linked cavities during the second step.

For the reaction shown in Eq. (1), using the constraint of chemical equilibrium we have

$$\mu_B = \mu_w + \lambda_2 \mu_g \tag{2}$$

where μ_B is the chemical potential of the basic hydrate, μ_w and μ_g stand for the chemical potential of water and gas, respectively. Since the adsorption of the gas molecules into the linked cavities will lower the chemical potential of the basic hydrate, μ_B can be expressed as

$$\mu_B = \mu_B^0 + \lambda_1 RT \ln(1-\theta) \tag{3}$$

where θ represents the fraction of the linked cavities occupied by the gas molecules, μ_B^0 is the chemical potential of unfilled basic hydrate ($\theta = 0$), and λ_1 denotes the number of linked cavities (small cavities) per water molecule in the basic hydrate. Based on the Langmuir adsorption theory, θ is calculated as follows:

$$\theta = \frac{Cf}{(1+Cf)} \tag{4}$$

where f denotes the fugacity of the gas species, and C is the Langmuir constant.

From basic thermodynamic relations, the chemical potential of gas species μ_g can be expressed as

$$\mu_g = \mu_g^0(T) + RT \ln f \tag{5}$$

where $\mu_g^0(T)$ represents the chemical potential of the ideal gas state. Combining Eqs. (2)–(5) yields the following expression:

$$\mu_B^0 + \lambda_1 RT \ln(1-\theta) = \mu_w + \lambda_2[\mu_g^0(T) + RT \ln f] \tag{6}$$

Define

$$f^0 = \exp\left[\frac{\mu_B^0 - \mu_w - \lambda_2 \mu_g^0(T)}{\lambda_2 RT}\right] \tag{7}$$

Eq. (6) can then be rearranged to the following form:

$$f = f^0(1-\theta)^\alpha \tag{8}$$

where $\alpha = \lambda_1/\lambda_2$, $\alpha = 1/3$ for structure I and $\alpha = 2$ for structure II. As indicated by Eq. (7), f^0 is not only a function of T, P and a_w (activity of water, refer to Eq. (11)), but also characterized by the properties of the basic hydrate former. When $\theta = 0$, Eq. (8) becomes

$$f = f^0 \tag{9}$$

Hence, in fact f^0 denotes the fugacity of gas phase in equilibrium with the unfilled basic hydrate ($\theta = 0$).

The $(\mu_B^0 - \mu_w)$ term in Eq. (7) can be expressed in terms of the following thermodynamic relations:

$$\mu_B^0 = A_B^0 + PV_B^0 \tag{10}$$

$$\mu_w = A_w + PV_w + RT \ln a_w \tag{11}$$

$$\mu_B^0 - \mu_w = \Delta A + P\Delta V - RT \ln a_w \tag{12}$$

where A denotes the molar Helmholtz free energy (which mainly depends on the system temperature), and the molar volume difference, ΔV, can be taken as a constant. Eq. (7) can then be expressed as the product of three factors, representing the contributions of T, P and a_w, respectively:

$$f^0 = f^0(T) f^0(P) f^0(a_w) \tag{13}$$

In Eq. (13)

$$f^0(P) = \exp\left(\frac{\beta P}{T}\right) \tag{14}$$

where $\beta = \Delta V/\lambda_2 R$ can be taken as a constant, β equals to 0.4242 K/bar for structure I, and 1.0224 K/bar for structure II, respectively.

$$f^0(a_w) = a_w^{-1/\lambda_2} \tag{15}$$

where λ_2 equals to 3/23 for structure I, and 1/17 for structure II, respectively.

In this work, $f^0(T)$ was correlated as a function of temperature through the following Antoine-type equation:

$$f^0(T) = A' \exp\left(\frac{B'}{T - C'}\right) \tag{16}$$

As most pure gases form only one hydrate structure, the Antoine constants, A', B' and C' can be determined by fitting the pure gas hydrate formation data for a particular structure only. The constants for the alternate structure (to be used in mixture hydrate calculations) should be determined by double-hydrate formation data. The regressed constants for typical gas species are given in Table 1.

In case the hydrate is formed from ice, the constants listed in Table 1 are still valid, but Eq. (16) should be corrected as follows

$$f^0(T) = \exp\left(\frac{D(T - 237.15)}{T}\right) \times A' \exp\left(\frac{B'}{T - C'}\right) \tag{17}$$

The constant D in Eq. (17) equals to 22.5 for structure I, and 49.5 for structure II, respectively.

In applying Eq. (8) to the general case ($\theta \neq 0$), θ is calculated by Eq. (4). The Langmuir constants involved were evaluated by integration of the two-parameter Lennard–Jones potential function, the details of the rigorous evaluation of Langmuir constants are referred to Sloan [4].

For engineering applications, it is convenient to correlate the Langmuir constant C as a function of temperature. In this work, the Antoine-type equation was again selected for

Table 1
Antoine constants for calculating $f^0(T)$ in Eqs. (16) and (17)

Gas	Structure I			Structure II		
	$A' \times 10^{-10}$	B'	C'	$A' \times 10^{-23}$	B'	C'
Ar	58.705[a]	−5393.68[a]	28.81[a]	7.3677	−12889	−2.61
Kr	38.719[a]	−5682.08[a]	34.70[a]	3.1982	−12893	4.11
N_2	97.939[a]	−5286.59[a]	31.65[a]	6.8165	−12770	−1.10
O_2	62.498[a]	−5353.95[a]	25.93[a]	4.3195	−12505	−0.35
CO_2	9.6372	−6444.50	36.67	3.4474[a]	−12570[a]	6.79[a]
H_2S	4434.2	−7540.62	31.88	3.2794[a]	−13523[a]	6.70[a]
CH_4	1584.4	−6591.43	27.04	5.2602[a]	−12955[a]	4.08[a]
C_2H_4	48.418	−5597.59	51.80	0.0377[a]	−13841[a]	0.55[a]
C_2H_6	47.500	−5465.60	57.93	0.0399[a]	−11491[a]	30.4[a]
C_3H_6	0.9496	−3732.47	113.6	2.3854	−13968	8.78
C_3H_8	100.00[a]	−5400[a]	55.50[a]	4.1023	−13106	30.2
n-C_4H_{10}	1.00	0.00	0.00	3.5907[a]	−12312[a]	39.0[a]
i-C_4H_{10}	1.00	0.00	0.00	4.5138	−12850	37.0

[a] Determined from double-hydrate data.

Table 2
Antoine constants for calculating the Langmuir constants in Eq. (18)

Gas	$X \times 10^6$	Y	Z
Ar	5.6026	2657.94	−3.42
Kr	4.5684	3016.70	6.24
N_2	4.3151	2472.37	0.64
O_2	9.4987	2452.29	1.03
CO_2	1.6464	2799.66	15.90
H_2S	4.0596	3156.52	27.12
CH_4	2.3048	2752.29	23.01

correlation:

$$C = X \exp\left(\frac{Y}{T - Z}\right) \tag{18}$$

The constants X, Y and Z were determined against the rigorous Langmuir constants C calculated from the Lennard–Jones potential function. The fitted X, Y, and Z values for typical gas species are listed in Table 2. It should be noted that according to the proposed hydrate formation mechanism, the adsorption of gas molecules occurs only in the linked cavities (assumed to be small cavities, 5^{12}).

3.2. Gas mixture hydrates

In dealing with the hydrate formation of gas mixtures, a concept of *basic hydrate component* was introduced in [2]. The basic hydrate mixture is taken as a solid solution composed of a number of *basic hydrate components*, which are characterized by the basic hydrate former. The overall properties of a mixture hydrate depend also on the filling of gas molecules in the linked cavities.

Since the molar volumes of different basic hydrates with same structure are close, the excess volume and excess entropy of the basic hydrate mixture should be very close to zero. Hence, it is reasonable to regard the basic hydrate mixture as a regular solution. If the cross-interactions between different guest molecules are neglected (it is equivalent to assume an ideal solution), the following expressions can be established for a mixture hydrate

$$f_i = x_i f_i^0 \left(1 - \sum_j \theta_j\right)^{\alpha} \tag{19}$$

$$\sum_j \theta_j = \frac{\sum_j f_j C_j}{1 + \sum_j f_j C_j} \tag{20}$$

$$\sum_j x_i = 1.0 \tag{21}$$

where f_i denotes the fugacity of gas component i – calculated using the Patel–Teja equation of state [5]; θ_j denotes the fraction of linked cavities occupied by gas component j; x_i denotes the mole fraction of basic hydrate i, and f_i^0 for each component is evaluated by Eq. (13).

Compared to the conventional vdW-P type hydrate model, the calculation of the chemical potential difference between water and empty hydrate lattice ($\Delta\mu^{\mathrm{w}}$) is not directly involved, and the confusion in selecting a suitable basic parameter set for evaluating $\Delta\mu^{\mathrm{w}}$ is therefore, avoided.

If the interactions between the guest molecules in the linked cavities and in the basic cavities are taken into account, Eq. (16) for evaluating f_i^0(T) should be corrected as follows:

$$f_i^0(T) = \exp\left(\frac{-\sum_j A_{ij}\theta_j}{T}\right) \times \left[A' \exp\left(\frac{B'}{T - C'}\right)\right] \tag{22}$$

where A_{ij} are the *binary interaction parameters* specifying the guest–guest interaction between components i and j ($A_{ij} = A_{ji}$ and $A_{ii} = A_{jj} = 0$). The A_{ij} values determined for typical binary pairs by regression of the corresponding hydrate formation data are given in Table 3

Table 3
Recommended values for the cross-parameter A_{ij}^{a} (structure II)

Component	C_2H_6	C_3H_8	i-C_4H_{10}	*n*-C_4H_{10}
CH_4	154	292	530	100
N_2	50	155	297	67
CO_2	165	352	560	100
H_2S	450	790	1500	879

[a] When the C_4-content is given in total, set $A_{ij}=0$ for C_4-pairs, and take the C_4 as i-C4 in the Langmuir constant calculation.

3.3. Determination of the Antoine constants for components in a mixture hydrate

Since the structure of a mixture hydrate could be different from the structure of its constituents in the pure state, the Antoine constants A', B' and C' in Eqs. (16) and (22) should be determined for both structure I and structure II. As mentioned in the previous section, in case the structure of mixture hydrate differs from the structure of gas components in pure state, double-hydrate formation data must be used to determine the Antoine constants corresponding to the structure of mixture hydrate. Following procedures were adopted for typical gas components in natural gas mixtures:

1. The hydrate formation data of C_2H_6–C_3H_8 binary system were used to determine the Antoine constants for both C_2H_6 (when the mixture forms structure II hydrate) and C_3H_8 (when the mixture forms structure I hydrate).
2. The formation data of the CH_4–Ar binary system were used to determine the Antoine constants for both CH_4 (when the mixture forms structure II hydrate) and Ar (when the mixture forms structure I hydrate).
3. For H_2S and CO_2, when either one is mixed with propane, structure II hydrate will be formed, and the corresponding formation data were used to determine the structure II Antoine constants of H_2S and CO_2.

The Antoine constants for the alternate hydrate structure thus determined are also listed in Table 1.

4. Calculation procedure

The calculation procedure for determining the hydrate formation conditions of a gas mixture with given composition is summarized in the schematic flow diagram shown in Fig. 1. For simple gas hydrates (formed by pure gas), a similar procedure can be applied.

5. Calculation results

5.1. Binary and ternary gas hydrates

The comparisons of the calculated and experimental formation/dissociation pressures of 14 binary and ternary gas hydrate systems are listed in Table 4. For the Ar–N_2, Ar–CH_4, CH_4–H_2S, CH_4–CO_2, C_2H_4–C_2H_6, C_2H_6–C_3H_8 binary systems, all A_{ij}s were set equal to zero. While for other systems the cross-parameters A_{ij} were incorporated in the calculations.

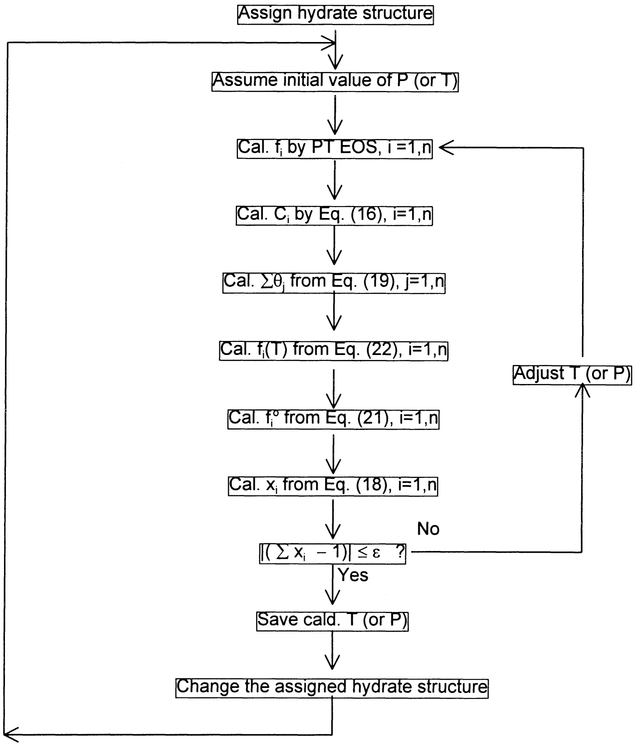

Fig. 1. The flow diagram of hydrate formation condition calculation for gas mixtures.

5.2. Natural gas hydrates

The multicomponent natural gas mixtures usually form structure II hydrates and the formation of the basic hydrate is dominated by the heavier gas components. The guest–guest interactions must be considered, the A_{ij} values used are listed in Table 3. For those pairs A_{ij} values are not available, set $A_{ij}=0$.

The comparison of the predicted results with those reported by Barkan and Sheinin [6] (based on a modified Parrish–Prausnitz model [7]) is given in Table 5. The improvement achieved by the new hydrate model is impressive.

Table 6 lists the prediction results on the hydrate formation temperature / pressure of another 21 natural gas mixtures. The average absolute deviations of predictions indicate that the new hydrate model is promising for engineering applications.

6. Discussions

6.1. About the change of hydrate structure

It was well known that when methane is mixed with a small amount of propane (e.g.<5%) the hydrate structure

Table 4
Average deviations of the predicted hydrate formation pressure for 14 binary and ternary gas mixtures[a]

Gas mixture	*T*-range (*K*)	*P*-range (bar)	Structure	N_p	AADP (%)[b]
$Ar + N_2$	275–290	144–613	II	7	5.5
$N_2 + C_3 H_8$	274–287	2.5–180	II	28	4.4
$CH_4 +$ Ar	273–299	31–1137	I	28	3.5
$CH_4 + CO_2$	277–286	28–70	I	17	6.6
$CH_4 + H_2S$	277–292	20–67	I	15	11.6
$CH_4 + C_2H_6$	273–289	7.3–136	I + II	32	2.2
$CH_4 + C_3H_8$	274–304	2.6–689	II	28	4.5
$CH_4 +$ i -C_4H_{10}	274–293	1.6–100	II	67	3.6
$CH_4 +$ n-C_4H_{10}	273–301	3.4–684	II	36	3.3
$C_2H_4 + C_2H_6$	273.9	5.8–9.2	I	10	5.9
$C_2H_6 + C_3H_8$	273–281	4.4–20	I + II	58	3.3
$C_3H_8 + CO_2$	273–285	3.0–42	I + II	33	4.6
$CH_4 + C_2H_6 +$ C3H8	276–300	12–544	I + II	18	4.5
$CH_4 + H_2S + C_3H_8$	276–301	3.8–43	II	13	5.9

[a] Data source: Sloan [4].

[b] AADP (%) is defined as $\mathrm{AADP}(\%) = 1/N_p \sum_j^{N_p} |(P_{cal} - P_{exp})/P_{exp}|_j \times 100$.

Table 5
Comparison of the hydrate formation temperature predictions for natural gases with those data reported by Barkan and Sheinin [6]

Gas mixture	*T*-range (K)	N_p	AADT (%)[a]		Data source
			This work	Barkan and Sheinin	
$C_1 + C_2 + C_3 +$ *n*-$C_4 + C_5$	277–297	12	0.30	0.48	[8]
$C_1 + C_2 + C_3 +$ i-$C_4 +$ *n*-$C_4 + N_2$	279–298	9	0.09	0.45	[8]
$C_1 + C_2 + C_3 + CO_2 + N_2$	278–297	15	0.11	0.31	[8]
$C_1 + C_2 + C_3 + C_4 + CO_2 + N_2$	274–282	6	0.13	0.32	[9]
$C_1 + C_2 + C_3 + C_4 + CO_2 + H_2S$	285–297	7	0.19	0.58	[10]
$C_1 + C_2 + C_3 +$ i-C_4	294–303	7	0.23	0.50	[11]
$C_1 + C_2 + C_3 +$ *n*-$C_4 +$ *n*-$C_5 + CO_2 + N_2$	279–293	5	0.07	0.11	[12]

[a] AADP (%) is defined as $\mathrm{AADP}(\%) = 1/N_p \sum_j^{N_p} |(T_{cal} - T_{exp})/T_{exp}|_j \times 100$.

Table 6
Predicted results on the hydrate formation conditions for 21 natural gases

Gas No.	*T*-range (K)	*P*-range (bar)	N_p	AADP (%)	AADT (%)	Data source
1	277–297	12.1–265.5	12	7.85	0.30	[8]
2	279–298	12.5–273.2	9	5.92	0.09	[8]
3	278–297	16.0–275.0	16	2.87	0.11	[8]
4	274–294	6.2– 85.4	9	4.9	0.13	[9]
5	273–286	6.0–28.6	9	7.3	0.19	[9]
6	273–283	7.2–22.1	8	4.5	0.12	[9]
7	273–282	7.5–21.0	6	4.4	0.12	[9]
8	275–289	9.4–52.5	4	9.1	0.23	[9]
9	273–292	7.6–93.9	8	8.1	0.17	[9]
10	273–291	7.5–77.3	6	5.7	0.14	[9]
11	274–282	7.5–21.3	5	2.7	0.07	[9]
12	273–280	7.9–18.1	4	1.6	0.04	[9]
13	273–291	8.8–83.8	23	3.9	0.10	[9]
14	274–286	10.7–45.9	6	2.9	0.08	[9]
15	285–296	14.7–55.2	4	11.1	0.19	[11]
16	293–303	135.5–628.5	7	10.5	0.11	[12]
17	277–295	14.7–196.7	7	5.4	0.11	[12]
18	279–292	18.6–136.5	5	4.7	0.09	[10]
19	281–291	17.6–58.3	5	10.6	0.25	[13]
20	275–282	17.2–52.4	4	4.0	0.12	[14]
21	273–282	7.5-21.0	4	8.7	0.29	[15]

will change from I to II, however, the reason of the structure change was not explained previously. The calculations based on the new model indicate that although the methane percentage in the gas mixture is very high (~95%), its basic hydrate content [$x\mathrm{CH}_4$ in Eq. (19)] is very small. This implies that the formation of the mixture hydrate is dominated by propane, methane plays a role of help gas only. From Eq. (19), it can be seen that f_i is very sensitive to the value of $\sum_j \theta_j$. For propane, the value of θ is equal to zero, and $f_i = f_i^0$. However, for a (methane + propane) mixture, as methane has a high occupancy of the linked cavities, this results in lowering the hydrate formation partial pressure of propane dramatically. For example, when the fraction of filling by methane in the small linked cavities equals to 0.8, the partial pressure of propane required to form structure II hydrate will become nearly 0.04 times the pressure required in the case of pure propane. Hence, even the concentration of propane is small, its partial pressure is enough for the formation of structure II hydrates, while the mole fraction of basic methane hydrate is very small. Based on the above analysis, the so-called '*hydrate structure change of methane*' is somewhat misleading.

6.2. About the guest–guest interactions

The guest–guest interactions may be divided into three parts: (1) the interactions of guest molecules in the basic hydrate, (2) the interactions between guest molecules in the basic hydrate and those filled in the linked cavities, and (3) the interactions between the guest molecules adsorbed in the linked cavities. In this work, Part 1 and Part 3 are neglected. Part 2 is considered in Eq. (22).

6.3. About the effect of $f^0(a_\mathrm{w})$ term in Eq. (13)

From Eq. (15) we have $f^0(a_\mathrm{w}) = a_\mathrm{w}^{-7.67}$ for structure I hydrate, and $f^0(a_\mathrm{w}) = a_\mathrm{w}^{-17}$ for structure II hydrate. This implies that the formation pressure is very sensitive to the activity of water, a slight decrease in water activity may increase the formation pressure significantly. However, for the systems containing pure water and gas species with low solubility, $x_\mathrm{w} \to 1.0$, $\gamma_\mathrm{w} \to 1.0$, and $a_\mathrm{w} \cong x_\mathrm{w}$, thus Eq. (15) can be expressed as

$$f^0(a_\mathrm{w}) \approx [1 - x_\mathrm{g}]^{-1/\lambda_2} \approx 1 + x_\mathrm{g}/\lambda_2 \qquad (23)$$

where x_g denotes the total mole fraction of gas species dissolved in the aqueous phase. When $x_\mathrm{g} = 10^{-3}$, $f^0(a_\mathrm{w})$ equals to 1.00768 for structure I, and 1.017 for structure II, respectively. As the mole fraction of natural gas in water is, in general, less than 10^{-3}, $f^0(a_\mathrm{w})$ can be taken as unity without significant error.

On the other hand, for the systems containing gases with considerable solubility (e.g. CO_2 and $\mathrm{H}_2\mathrm{S}$), and salt/polar inhibitor, the contribution of $f^0(a_\mathrm{w})$ to the formation conditions becomes not negligible. For such systems, the contribution of $f^0(a_\mathrm{w})$ term can be readily considered by incorporating a suitable phase equilibrium model based on equation of state or activity coefficient approach. The extension of the present model to such systems is in progress.

7. Conclusions

1. Based on the proposed two-step hydrate formation mechanism and the related basic concepts introduced in a previous paper [2], a new approach to hydrate modelling has been established.
2. The algorithm involved in the hydrate formation/dissociation calculation is simplified, as the direct calculation of $\Delta\mu^\mathrm{w}$ and the rigorous evaluation of Langmuir constant C, as well as the arbitrary selection of suitable parameter sets for evaluating $\Delta\mu_\mathrm{w}$ and C are avoided.
3. The structure change of methane hydrate when mixed with a small amount of propane can be physically explained.
4. The test results indicate that the proposed new hydrate model is adequate for engineering applications, especially for natural gas mixtures.

Acknowledgements

Financial support received from the China National Natural Science Foundation and the China National Petroleum Corporation are gratefully acknowledged.

Appendix

Nomenclature

A	molar Helmholtz free energy
A'	Antoine constants for calculating $f^0(T)$ in Eq. (16)
A_{ij}	cross interaction parameter
a	activity
B'	Antoine constant for calculating $f^0(T)$ in Eq. (16)
C	Langmuir constant
C'	Antoine constants for calculating $f^0(T)$ in Eq. (16)
f	fugacity of gas species
f^0	fugacity of gas species in equilibrium with the unfilled basic hydrate
n	number of components in a mixture
P	pressure
T	temperature
V	molar volume
X	Antoine constant for calculating Langmuir constant, Eq. (18)
x	mole fraction of basic hydrate
Y	Antoine constant for calculating Langmuir constant, Eq. (18)

Z	Antoine constant for calculating Langmuir constant, Eq. (18)

Greek letters

α	structural parameter, $\alpha = \lambda_1/\lambda_2$
β	structural parameter, $\beta = 0.4242$ K/bar for structure I hydrate, $\beta = 1.0224$ K/bar for structure II hydrate
γ	activity coefficient
Δ	difference
ε	allowable deviation
θ	fraction of the linked cavities occupied by guest molecules
λ_1	number of linked cavities per water molecule
λ_2	number of gas molecules per water molecule in basic hydrate
μ	chemical potential

Subscripts

B	basic hydrate
g	gas species
i	species i
j	species j
w	water

Superscript

0	reference state or pure state

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