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## RESEARCH NOTES

## Thermodynamic Model for Predicting Liquid Water–Hydrate Equilibrium of the Water–Hydrocarbon System

Amir H. Mohammadi and Dominique Richon\*

*Mines Paris / ParisTech, CEP-TEP, CNRS FRE 2861, 35 Rue Saint Honoré, 77305 Fontainebleau, France*

With the objective of estimating the solubility of a pure hydrocarbon hydrate former in pure water in equilibrium with gas hydrates, a simple thermodynamic model has been developed, based on the equality of water fugacity in the liquid water and hydrate phases. The solid solution theory of van der Waals–Platteeuw has been applied to calculate the fugacity of water in the hydrate phase. The Henry's law approach and the activity coefficient method have been used to calculate the fugacities of the hydrocarbon hydrate former and water in the liquid water phase, respectively. The results of this model are compared with some selected experimental data from the literature. Acceptable agreements between the model predictions and experimental data demonstrate the reliability of the model developed in this work. Finally, the possible errors sources in model predictions are discussed.

## 1. Introduction

Gas hydrates are icelike structures in which water molecules, under pressure, form structures composed of polyhedral cages that are surrounding gas molecule “guests” such as methane and ethane.<sup>1</sup> The most common gas hydrate structures are those of structure I (sI) and structure II (sII), where each structure is composed of a certain number of large and small cavities formed by water molecules.<sup>1</sup> For a molecule to enter a cavity, its size should be smaller than a certain value. Large molecule guests, which can enter only a limited number of large cavities, require smaller “help gas” molecules to mainly fill some smaller cavities sufficiently to stabilize hydrate crystals.<sup>1</sup> It has been proved that gas hydrates occur in staggering abundance in cold subsea, sea floor, and permafrost environments, where the temperature and pressure conditions ensure their stability. The natural gas trapped in these deposits represents a potential source of energy many times greater than that of all known classical natural gas reserves.<sup>1</sup> Gas hydrates can also form in undersea piping and above-ground pipelines, where they pose a major (and expensive) problem for the petroleum industry.<sup>1</sup> On the other hand, hydrate technology has been proposed as a means for CO<sub>2</sub> separation from industrial flue gases and sequestration in the deep ocean for reducing the emission of greenhouse gases.<sup>1,2</sup> Hydrates are also being regarded as an alternate means of gas transportation and storage.<sup>1</sup> It is believed that the potential storage of gas in hydrate form is comparable to the storage of gas in the form of liquefied natural gas (LNG) and compressed natural gas (CNG).<sup>3</sup>

Knowledge of the liquid water–hydrate (L<sub>W</sub>–H) equilibrium is necessary in the design of gas transportation and storage process, and the equilibrium should be destined for proposed CO<sub>2</sub> sequestration schemes.<sup>1,3</sup> These factors, and the potential widespread abundance of gas hydrates in the cold subsea, sea

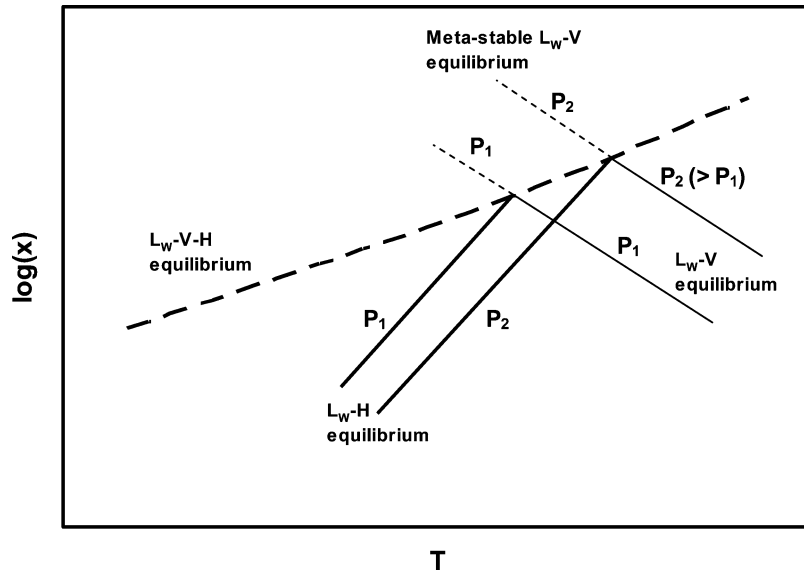
floor, and permafrost environments,<sup>1–3</sup> warrant an understanding of the L<sub>W</sub>–H equilibrium.

Figure 1 shows a typical solubility–temperature ( $x$ – $T$ ) diagram for a water–pure hydrate former (limiting reactant) system. As can be seen, the temperature and pressure dependencies of the pure hydrate former solubility in pure water, when in the liquid water–vapor (L<sub>W</sub>–V) equilibrium region, are different from the corresponding dependency in the L<sub>W</sub>–H equilibrium region. The L<sub>W</sub>–V equilibrium is a strong function of temperature and pressure, whereas the L<sub>W</sub>–H equilibrium is a strong function of temperature but a very weak function of pressure.<sup>1,3–12</sup> On the other hand, the pure hydrate former solubility in pure water, when in the L<sub>W</sub>–V equilibrium region, increases as the temperature decreases at a given pressure, while the corresponding solubility in pure water being in the L<sub>W</sub>–H equilibrium region decreases as the temperature decreases at the same pressure.<sup>1,3–12</sup> Furthermore, the metastable L<sub>W</sub>–V equilibrium may extend into the gas hydrate formation zone.<sup>1,3–12</sup>

The experimental works done to describe the L<sub>W</sub>–H equilibrium are limited, mainly because of two factors: the possible extension of the metastable L<sub>W</sub>–V equilibrium into the gas hydrate formation region and the experimental restraint that the existing analysis methods require modifications.<sup>1,3–8</sup> Literature surveys reveal the availability of few sets of experimental data for the L<sub>W</sub>–H equilibrium.<sup>4–8</sup> Consequently, few reliable models are available in the literature for calculating the L<sub>W</sub>–H equilibrium.<sup>3–5,8–12</sup> However, these models require considerable efforts to fit experimental data.

The objective of this work is to develop a simple model based on the equality of water fugacity in the liquid water and hydrate phases for determining the solubility of a pure hydrocarbon hydrate former in pure water, when in equilibrium with gas hydrates. The fugacity of water in the hydrate phase is calculated using the solid solution theory of van der Waals and Platteeuw.<sup>13</sup> The hydrocarbon hydrate former fugacity and water fugacity in the liquid water phase are calculated using the Henry's law

\* To whom correspondence should be addressed. Tel.: +(33) 1 64 69 49 65. Fax: +(33) 1 64 69 49 68. E-mail address: richon@ensmp.fr.



**Figure 1.** Typical solubility–temperature ( $x$ – $T$ ) diagram for the water–single (pure) hydrate former (limiting reactant) system. Legend: L<sub>w</sub>, liquid water; H, hydrate; V, vapor; and  $P$ , pressure. Bold solid lines denote the L<sub>w</sub>–H equilibrium, solid lines denote the L<sub>w</sub>–V equilibrium; dashed lines denote the metastable L<sub>w</sub>–V equilibrium, and bold dashed line denotes the L<sub>w</sub>–V–H equilibrium.

approach and the activity coefficient method, respectively. The reliability of this model is investigated for methane and ethane by comparing its predictions with selected experimental data from the literature. It is shown that the results are in acceptable agreement, which demonstrates the capability of the model developed in this work for estimating the solubility of a pure hydrocarbon hydrate former in pure water, when in equilibrium with gas hydrates.

## 2. Liquid Water–Hydrate Equilibrium

The L<sub>w</sub>–H equilibrium of a system is calculated by equating the fugacities of water in the liquid water phase ( $f_w^L$ ) and in the hydrate phase ( $f_w^H$ ):<sup>1</sup>

$$f_w^L = f_w^H \quad (1)$$

The fugacity of water in the hydrate phase ( $f_w^H$ ) is related to the chemical potential difference of water in the filled and empty hydrate cage by the following expression:<sup>1</sup>

$$f_w^H = f_w^{MT} \exp\left(\frac{\mu_w^H - \mu_w^{MT}}{RT}\right) \quad (2)$$

where  $f_w^{MT}$  is the fugacity of water in the hypothetical empty hydrate phase, and the term  $\mu_w^H - \mu_w^{MT}$  represents the chemical potential difference of water in the filled ( $\mu_w^H$ ) and empty ( $\mu_w^{MT}$ ) hydrate.  $R$  represents the universal gas constant.

The solid-solution theory of van der Waals and Platteeuw<sup>13</sup> can be applied to calculate  $(\mu_w^H - \mu_w^{MT})/RT$ :<sup>1</sup>

$$\frac{\mu_w^H - \mu_w^{MT}}{RT} = - \sum_i v'_i \ln(1 + \sum_j C_{ij} f_j) = \sum_i \ln(1 + \sum_j C_{ij} f_j)^{-v'_i} \quad (3)$$

where  $v'_i$  is the number of cavities of type  $i$  per water molecule in a unit hydrate cell,<sup>1</sup>  $C_{ij}$  represents the Langmuir constant for

the interaction of the hydrocarbon hydrate former with each type cavity, and  $f_j$  is the fugacity of the hydrate former.

The fugacity of water in the empty lattice can be expressed as<sup>1</sup>

$$f_w^{MT} = P_w^{MT} \varphi_w^{MT} \exp \int_{P_w^{MT}}^P \frac{v_w^{MT}}{RT} dP \quad (4)$$

where  $P_w^{MT}$ ,  $\varphi_w^{MT}$ ,  $v_w^{MT}$ , and  $P$  are the vapor pressure of the empty hydrate lattice, the correction for the deviation of the saturated vapor of the pure (hypothetical) lattice from ideal behavior, the partial molar volume of water in the empty hydrate<sup>1,14</sup> and pressure, respectively. The exponential term is a Poynting-type correction.

Equation 4 may be simplified by two assumptions: (1) assuming that the hydrate partial molar volume is equal to the molar volume and is independent of pressure and (2) assuming that  $P_w^{MT}$  is relatively small (on the order of  $10^{-3}$  MPa), so that  $\varphi_w^{MT} = 1$ .<sup>1</sup> Therefore,<sup>1</sup>

$$f_w^{MT} = P_w^{MT} \times \exp\left(\frac{v_w^{MT}(P - P_w^{MT})}{RT}\right) \quad (5)$$

Using the aforementioned expressions, the following equation is obtained for the fugacity of water in the hydrate phase:

$$f_w^H = P_w^{MT} \exp\left[\frac{v_w^{MT}(P - P_w^{MT})}{RT}\right] \times [(1 + C_{small} f_{HC}^L)^{-v'_{small}} \times (1 + C_{large} f_{HC}^L)^{-v'_{large}}] \quad (6)$$

where  $f_{HC}^L$  is the fugacity of the hydrocarbon hydrate former in the liquid-water phase.

The Poynting correction term can be ignored up to intermediate pressures; therefore, the following equation can be obtained to calculate the fugacity of water in the hydrate phase:

$$f_w^H = P_w^{MT} \times [(1 + C_{small} f_{HC}^L)^{-v'_{small}} \times (1 + C_{large} f_{HC}^L)^{-v'_{large}}] \quad (7)$$

The fugacity of water in the liquid water phase can be expressed by<sup>15</sup>

$$f_w^L = x_w^L \gamma_w^L P_w^{\text{sat}} \quad (8)$$

where  $x_w^L$  and  $\gamma_w^L$  are the water mole fraction and the activity coefficient of water in liquid water phase, when in equilibrium with gas hydrates, respectively. In the intermediate pressure range, the liquid water is an incompressible fluid and the hydrocarbon hydrate former solubility is very small, in comparison to unity, and the activity coefficient of water can be approximated to unity<sup>15</sup> (however, one must be careful, because it is not the same as the case at high pressures,<sup>15</sup> where the nonideality of the liquid-water phase and solubility become important). Therefore, eq 8 can be satisfactorily written as below:

$$f_w^L \cong P_w^{\text{sat}} \quad (9)$$

Using eqs 7 and 9, the following expression is obtained:

$$P_w^{\text{sat}} = P_w^{\text{MT}} \times [(1 + C_{\text{small}} f_{\text{HC}}^L)^{-\nu'_{\text{small}}} \times (1 + C_{\text{large}} f_{\text{HC}}^L)^{-\nu'_{\text{large}}}] \quad (10)$$

or

$$1 - \left( \frac{P_w^{\text{MT}}}{P_w^{\text{sat}}} \right) \times [(1 + C_{\text{small}} f_{\text{HC}}^L)^{-\nu'_{\text{small}}} \times (1 + C_{\text{large}} f_{\text{HC}}^L)^{-\nu'_{\text{large}}}] = 0 \quad (11)$$

where the fugacity of the hydrocarbon hydrate former in the liquid-water phase up to intermediate pressures can be calculated using the following equation:<sup>15</sup>

$$f_{\text{HC}}^L = x_{\text{HC}}^L H'_{\text{HC-w}} \quad (12)$$

where  $H'_{\text{HC-w}}$  represents Henry's constant for hydrocarbon hydrate former–water system. Therefore, the following final expression is obtained for estimating the solubility of a pure hydrocarbon hydrate former in liquid-water phase, when in equilibrium with gas hydrates:

$$1 - \left( \frac{P_w^{\text{MT}}}{P_w^{\text{sat}}} \right) \times [(1 + C_{\text{small}} x_{\text{HC}}^L H'_{\text{HC-w}})^{-\nu'_{\text{small}}} \times (1 + C_{\text{large}} x_{\text{HC}}^L H'_{\text{HC-w}})^{-\nu'_{\text{large}}}] = 0 \quad (13)$$

Our model, which has led to eq 13, allows easy calculation of the solubility of a pure hydrocarbon hydrate former in the liquid water, when in equilibrium with gas hydrates. Its main advantages are (i) the availability of necessary input data and (ii) the simplicity of the calculations, because the calculations can be done using Microsoft Excel spreadsheets. Furthermore, as can be observed in eq 13, almost all terms are temperature-dependent, which indicates that the solubility of a pure hydrocarbon hydrate former in liquid-water phase, when in equilibrium with gas hydrates, is a strong function of temperature and only a weak function of pressure.

**2.1. Model Parameters.** In eq 13, the following values of  $\nu'_i$  for structure-I hydrates can be used:<sup>1</sup>

$$\nu'_{\text{small}} = \frac{1}{23} \quad (14a)$$

$$\nu'_{\text{large}} = \frac{3}{23} \quad (14b)$$

The Langmuir constants (they are generally functions of temperature, pressure, composition, and hydrate structure, whereas the effect of pressure is normally ignored<sup>16</sup>), which account for the interaction between the hydrate former and water molecules in the cavities, were reported by Parrish and Prausnitz<sup>17</sup> for a range of temperatures and hydrate formers. However, the integration procedure was already followed in obtaining the Langmuir constants for wider temperature ranges, using the Kihara<sup>18</sup> potential function with a spherical core, according to the study by McKoy and Sinanoğlu.<sup>19</sup> In this work, the Langmuir constants for the interaction of the hydrate former with each type of cavity have been determined using the equations of Parrish and Prausnitz.<sup>17</sup>

For pentagonal dodecahedra (small cavity):

$$C_{\text{small}} = \frac{a}{T} \exp\left(\frac{b}{T}\right) \quad (15)$$

For tetrakaidecahedra (large cavity):

$$C_{\text{large}} = \frac{c}{T} \exp\left(\frac{d}{T}\right) \quad (16)$$

where  $T$  is in Kelvin and  $C$  has units of  $\text{MPa}^{-1}$ . Constants  $a$ – $d$  are reported in Table 1.

The concept of having a universal empty hydrate vapor pressure for each structure—prompted Dharmawardhana et al.<sup>20</sup> to calculate the  $P_w^{\text{MT}}$  value from several simple hydrate three-phase ice–vapor–hydrate equilibria. By equating the fugacity of water in the hydrate phase to that of pure ice at the three-phase line, Dharmawardhana et al.<sup>20</sup> obtained the following equation for the vapor pressure of the empty hydrate structure-I:<sup>1</sup>

$$P_w^{\text{MT}} = 0.1 \exp\left(17.440 - \frac{6003.9}{T}\right) \quad (17)$$

where  $P_w^{\text{MT}}$  is given in units of  $\text{MPa}^{-1}$  and  $T$  is in Kelvin.

The following values for Henry's constant of the hydrocarbon hydrate former–water system can be used:<sup>21</sup>

$$H'_{\text{HC-w}} = (10^{A+B/T+\bar{C} \times \log(T)+D \times T}) \times 0.1 \quad (18)$$

where  $T$  is in Kelvin and  $H'_{\text{HC-w}}$  is given in units of MPa. The constants  $A$ ,  $B$ ,  $\bar{C}$ , and  $D$  are given in Table 2.

### 3. Results and Discussion

Among the  $L_w$ –H equilibrium data reported in the literature for the hydrocarbon + water systems, those reported by Servio and Englezos<sup>7</sup> and Kim et al.<sup>8</sup> for methane solubility in pure water being in equilibrium with gas hydrates seem to be the most reliable. They are reported in Tables 3a and 3b, respectively. As can be seen, the temperature range is 274.15–281.7 K, and the pressures go up to 14.4 MPa. The experimental data of Yang et al.<sup>5</sup> for methane solubility in pure water, when in equilibrium with gas hydrates, have not been considered in this work, because they are not consistent with other literature data.<sup>7,8</sup> Tables 3a and 3b also show the predictions of the model developed in this work and the absolute deviations (ADs). As can be seen, eq 13 (without any adjustable parameter) shows

**Table 1. Constants  $a$ – $d$  Used in eqs 15 and 16<sup>a</sup>**

hydrate former	$a$ (K MPa <sup>-1</sup> )	$b$ (K)	$c$ (K MPa <sup>-1</sup> )	$d$ (K)
methane	0.0037237	2708.8	0.018373	2737.9
ethane	0	0	0.006906	3631.6

<sup>a</sup> Data taken from ref 17.**Table 2. Constants  $A$ – $D$  Used in eq 18<sup>a</sup>**

hydrocarbon	$A$	$B$	$\bar{C}$	$D$	$T_{\min}$ (K)	$T_{\max}$ (K)
methane	147.788	-5768.3	-52.2952	0.018616	273.15	373.15
ethane	146.901	-5768.3	-51.8593	0.017410	273.15	343.15

<sup>a</sup> Data taken from ref 21.**Table 3. Experimental and Predicted Solubility of Methane in Pure Water Being in Equilibrium with Gas Hydrates (Liquid Water–Hydrate Equilibrium)**

temperature, $T$ (K)	pressure, $P$ (MPa)	Methane Solubility		AD% <sup>a</sup>
		experimental	predicted	
(a) Using Experimental Data from Servio and Englezos <sup>7</sup>				
274.35	3.5	$1.170 \times 10^{-3}$	$1.260 \times 10^{-3}$	7.7
275.45	3.5	$1.203 \times 10^{-3}$	$1.340 \times 10^{-3}$	11.4
274.15	5.0	$1.190 \times 10^{-3}$	$1.250 \times 10^{-3}$	5.0
277.35	5.0	$1.360 \times 10^{-3}$	$1.500 \times 10^{-3}$	10.3
275.25	6.5	$1.201 \times 10^{-3}$	$1.330 \times 10^{-3}$	10.7
280.15	6.5	$1.567 \times 10^{-3}$	$1.770 \times 10^{-3}$	13.0
(b) Using Experimental Data from Kim et al. <sup>8</sup>				
276.2	5	$1.33 \times 10^{-3}$	$1.40 \times 10^{-3}$	5.3
277.9	5.1	$1.59 \times 10^{-3}$	$1.55 \times 10^{-3}$	2.5
279.9	5.1	$1.75 \times 10^{-3}$	$1.75 \times 10^{-3}$	0.0
280.5	5.1	$1.86 \times 10^{-3}$	$1.81 \times 10^{-3}$	2.7
276.4	10.1	$1.33 \times 10^{-3}$	$1.41 \times 10^{-3}$	6.0
278.7	10.2	$1.59 \times 10^{-3}$	$1.42 \times 10^{-3}$	10.7
280.1	10.2	$1.75 \times 10^{-3}$	$1.77 \times 10^{-3}$	1.1
280.7	10.2	$1.86 \times 10^{-3}$	$1.84 \times 10^{-3}$	1.1
276.7	12.7	$1.33 \times 10^{-3}$	$1.45 \times 10^{-3}$	9.0
278.9	12.7	$1.59 \times 10^{-3}$	$1.65 \times 10^{-3}$	3.8
280.4	12.7	$1.75 \times 10^{-3}$	$1.80 \times 10^{-3}$	2.9
281.1	12.7	$1.86 \times 10^{-3}$	$1.88 \times 10^{-3}$	1.1
276.9	14.3	$1.33 \times 10^{-3}$	$1.46 \times 10^{-3}$	9.8
279.2	14.4	$1.59 \times 10^{-3}$	$1.68 \times 10^{-3}$	5.7
280.6	14.3	$1.75 \times 10^{-3}$	$1.82 \times 10^{-3}$	4.0
281.7	14.3	$1.88 \times 10^{-3}$	$1.94 \times 10^{-3}$	3.2

<sup>a</sup> AD = |(experimental value – predicted value)/experimental value|.**Table 4. Experimental and Predicted Solubility of Ethane in Pure Water Being in Equilibrium with Gas Hydrates (Liquid Water–Hydrate Equilibrium)**

temperature, $T$ (K) <sup>b</sup>	pressure, $P$ (MPa)	Ethane Solubility		AD%
		experimental <sup>a</sup>	predicted	
277.3	10.1	$4.37 \times 10^{-4}$	$4.90 \times 10^{-4}$	12.1
277.8	15.1	$4.37 \times 10^{-4}$	$5.12 \times 10^{-4}$	17.2
278.5	20.1	$4.37 \times 10^{-4}$	$5.43 \times 10^{-4}$	24.3

<sup>a</sup> Data taken from Kim et al.<sup>8</sup> <sup>b</sup> Experimental gas solubility is not absolutely temperature-dependent; consequently, the corresponding experimental data cannot be considered to be reliable.

encouraging results. The predictions show <13% absolute deviation and the average absolute deviation (AAD) among all the experimental and predicted data is <6%.

Limited information is available for the L<sub>w</sub>–H equilibrium of the ethane + water system. Kim et al.<sup>8</sup> measured ethane solubility in pure water, when in equilibrium with gas hydrates. These data, along with the predictions of eq 13 and the AD values, are shown in Table 4. As can be seen, the temperature range is 277.3–278.5 K and the pressures go up to 20.1 MPa. The predictions show <25% absolute deviation and the AAD value among all the experimental and predicted data is <18%. As can be observed, the temperature change has no effect on the experimental gas solubility data,<sup>8</sup> which indicates unreliability of the experimental data that was reported by Kim et

al.<sup>8</sup> on ethane solubility in pure water, when in equilibrium with gas hydrates.

In addition to the quality of the experimental data reported in the literature, the deviations may also be attributed to other factors: The Langmuir constants and the vapor pressures of the empty hydrate lattice are consistent with initial data on the liquid water/ice–vapor–hydrate equilibrium. However, because the experimental conditions go far below the initial hydrate formation conditions, the assumptions that are evidently valid at the initial hydrate formation conditions may not be valid elsewhere.<sup>1</sup> Accurate determination of the fugacity has also an important effect on the predictions. The Henry's law approach for calculating the fugacity of pure and heavy hydrocarbon hydrate former may not be very accurate, as the Henry's constants are normally determined based on the L<sub>w</sub>–V equilibrium data and measuring these data for heavy hydrocarbon hydrate formers especially near the hydrate formation region may not be easy.

Finally, note that the use of this model is not recommended for acid gases (CO<sub>2</sub> and H<sub>2</sub>S), because the assumptions that have been made to obtain eq 9 are conservative for these systems. That is, the acid gas solubility in the liquid-water phase is not small, compared to unity, and therefore, the water activity coefficient cannot be taken to be unity and the nonideality of the liquid-water phase becomes important.

#### 4. Conclusions

A thermodynamic model that is based on the equality of fugacity concept was developed to estimate the hydrocarbon hydrate former solubility in pure water, when in equilibrium with gas hydrates. The model applied the solid-solution theory of van der Waals and Platteeuw<sup>13</sup> to calculate the fugacity of water in the hydrate phase, whereas the Henry's law approach and the activity coefficient method were used to calculate the hydrocarbon hydrate former fugacity and water fugacity, respectively, in the liquid-water phase. The main advantage of this model is the availability of input data and the simplicity of the calculations. The reliability of the model was tested for two hydrocarbon hydrate formers: methane and ethane. Acceptable agreements were achieved between the results of this model and some experimental data reported in the literature. The study showed a need to generate reliable experimental data for the liquid-water–hydrate equilibrium of the heavy hydrocarbon hydrate former + water systems. The deviations of the model predictions were attributed to different factors, especially the quality of the experimental data, correlations used for the Langmuir constants and the vapor pressures of the empty hydrate lattice, and finally the expressions applied for the components fugacities.

#### Nomenclature

##### Abbreviations

AAD = average absolute deviation;  $AAD = 1/N \sum_i |(\text{experimental value} - \text{predicted value})/\text{experimental value}|$

AD = absolute deviation;  $AD = |(\text{experimental value} - \text{predicted value})/\text{experimental value}|$

CNG = compressed natural gas

H = hydrate

L = liquid

LNG = liquefied natural gas

V = vapor



*Parameters/Variables*

$A$  = parameter of Henry's constant correlation (eq 18)

$B$  = parameter of Henry's constant correlation (eq 18)

$\bar{C}$  = parameter of Henry's constant correlation (eq 18)

$C$  = Langmuir constant ( $\text{MPa}^{-1}$ )

$D$  = parameter of Henry's constant correlation (eq 18)

$H'$  = Henry's constant

$N$  = number of experimental data

$P$  = pressure (MPa)

$R$  = universal gas constant ( $\text{MPa m}^3 \text{ kg-mol}^{-1} \text{ K}^{-1}$ )

$T$  = temperature (K)

$a, c$  = parameters of the Langmuir constant correlation ( $\text{K MPa}^{-1}$ )

$b, d$  = parameters of the Langmuir constant correlation (K)

$f$  = fugacity (MPa)

$v$  = molar volume ( $\text{m}^3 \text{ kg-mol}^{-1}$ )

$v'$  = number of cavities of type  $i$  per water molecule in a unit hydrate cell

$x$  = mole fraction in the liquid phase

*Greek Letters*

$\phi$  = correction for the deviation of the saturated vapor of the pure (hypothetical) lattice from ideal behavior

$\mu$  = chemical potential

$\gamma$  = activity coefficient

*Superscripts*

MT = hypothetical empty hydrate

H = hydrate

L = liquid

sat = saturation condition

*Subscripts*

HC = hydrocarbon hydrate former

max = maximum value

min = minimum value

w = water

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