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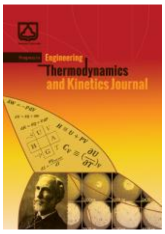

Research Article

Thermodynamic Modeling of Clathrate Hydrate Stability Conditions in Methane + 1-Methylpiperidine/2-Methylpiperidine + Water System

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ABSTRACT

There are three typical thermodynamic models to determine the stability conditions of structure H (sH) hydrate, i.e., the van der Waals-Platteeuw-based model developed by Mehta and Sloan, the Chen-Guo model introduced by Chen and Guo, and the Klauda-Sandler model applied by Sinehbaghizadeh et al. and other researchers. These thermodynamic models are typically used for water-immiscible or slightly soluble sH hydrate formers, e.g., methylcyclopentane, methylcyclohexane, 2,2-dimethylbutane, etc. However, some sH clathrate hydrate formers are soluble in water, such as 1-methylpiperidine, 2-methylpiperidine, 3-methylpiperidine, 4-methylpiperidine, and hexamethyleneimine. In this study, the Chen-Guo and Mehta-Sloan models were employed to model the stability conditions of sH hydrate for 1-methylpiperidine/2-methylpiperidine with methane as a help gas. The behavior of aqueous phase containing 1-methylpiperidine/2-methylpiperidine is explored using the NRTL activity coefficient model. Although both Chen-Guo and Mehta-Sloan models show errors of less than 1%, Mehta-Sloan model results are in a better agreement with the experimental data with 0.10% average absolute error in comparison with Chen-Guo model results with 0.38% average absolute error for 1-methylpiperidine, however, there is not much difference for 2-metylpiperidine when using both models in which %AAD for both models are approximately the same, i.e. 0.79%.

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1. Introduction

Clathrate hydrates, also known as gas hydrates, are solid solutions. In these compounds, water molecules connected by hydrogen bonding form cavities, which can be referred to as host lattices that capture various large molecules, known as guest molecules. Furthermore, no chemical bonding occurs between the host water molecules and the caged guest molecule [1]. Two well-known hydrate' structures, i.e., structure-I (sI) and structure-II (sII), have been examined extensively. The structure-H (sH) hydrate, as a member of the clathrate hydrate family, was introduced by Ripmeester et al. in 1987 [2].

The principal equations for the prediction of hydrate phase equilibrium/dissociation/stability conditions were derived by van der Waals and Platteeuw [3] using Lennard-Jones Devonshire cell theory. Mehta and Sloan [4] used the prediction technique for four structure H forming systems to determine sH hydrate phase equilibria based on Kihara potential parameters. They used the van der Waals-Platteeuw approach [3].

The calculation of hydrate phase equilibrium pressures for methane + single sH hydrate former + water systems was done for 20 heavy hydrocarbon hydrate formers by Chen and Guo [5]. The results were compared with the results of the Mehta-Sloan model. They demonstrated a satisfactory agreement between the experimental data and the model-determined values.

A thermodynamic model was presented by Sinehbaghizadeh et al. [6] to determine sH hydrate stability conditions with Methane as a help gas based upon an extension of the Klauda and Sandler fugacity model [7], while they applied the Peng-Robinson equation of state [8] for modeling water-hydrocarbon phase behavior with Wong-Sandler mixing rule [9] and UNIFAC model [10] to calculate excess Gibbs free energy of the mixture and corresponding activity coefficient.

Water-soluble sH hydrate formers with the determined solubility have been proposed [11],[12]. Shin et al. introduced some water-soluble sH hydrate formers, including 1-methylpiperidine or normal methylpiperidine (NMPD) and 2-methylpiperidine [13].

Considering this literature review, there is no thermodynamic model to predict or correlate hydrate equilibrium conditions for water-soluble sH hydrate formers. Therefore, in this work, Chen-Guo [5] and Mehta-Sloan [4] models were used to correlate sH hydrate dissociation data for 1-methylpiperidine and 2-methylpiperidine with methane as a help gas. The model parameters are evaluated, and the results are compared to experimental data.

2. Thermodynamic Model

2.1. Fluid Phase Models

For the gas phase, the Peng-Robinson equation of state [8] is used, while for the aqueous phase, the Non-Random-Two-Liquid (NRTL) model is applied. The NRTL equation [14] is given as follows:

$$\frac{G^E}{RT}=\sum_{i=1}^{nc} x_i \frac{\sum_{j=1}^{nc}\tau_{ji}G_{ji}x_j}{\sum_{j=1}^{nc}G_{ji}x_j}, G_{ij}=\exp\left(-\alpha''_{ij}\tau_{ij}\right), \quad G_{ii}=G_{jj}=0 \tag{1}$$

and

$$\begin{cases} \tau_{ij}=a''_{ij}+\frac{b''_{ij}}{T}+\frac{c''_{ij}}{T^2}+d''_{ij}\ln\left(T\right)+e''_{ij}T \\ \alpha''_{ij}=f''_{ij}+g''_{ij}\left(T-273.15\right) \\ \tau_{ii}=\tau_{jj}=0 \\ \alpha''_{ii}=\alpha''_{jj}=0 \end{cases} \tag{2}$$

The parameters of the NRTL model are given in Table 2 [15].

In equation (1), G^E is Gibbs free energy and T is temperature in K.

2.2. Chen and Guo Hydrate Model

The thermodynamic model of Chen and Guo for calculating the stability conditions of structure H hydrate with methane as a help gas is on basis of the calculation of the minimum fugacity of M required for hydrate formation with help gas, i.e., f_M and the value of $f(P)$ determined from the characteristics of the basic sH hydrate former and system pressure [3], in which f_M is given as [3]:

$$f_M=\exp\left(\frac{\mu_\beta^0-\mu_w-\lambda_3\mu_M^0(T)}{\lambda_3 RT}\right)(1-\theta_1)^{\lambda_1/\lambda_3}(1-\theta_2)^{\lambda_2/\lambda_3} \tag{3}$$

where

$$\theta_k=\frac{C_{ki}f_i}{1+\sum_{i=1}^{nc}C_{ki}f_i}, \quad k=1,2 \tag{4}$$

λ is the number of cavities per water molecule in the structure H hydrate. For sH hydrate lattice structure, $\lambda 1/\lambda 3 = 3$, $\lambda 2/\lambda 3 = 2$. Parameters of θ_1 and θ_2 are the fractions of the smallest and medium cavities occupied by help gas molecules, respectively. f_i is the fugacity of help gas species i and C_{ki} represent the Langmuir constant of help gas species i in type k linked cavity, which can be easily denoted through the Antoine-type equation as [5]:

$$C_k = X_k \exp\left(\frac{Y_k}{T - Z_k}\right), \quad k = 1,2 \tag{5}$$

in which 1 and 2 are for the small and the medium cavities, respectively [5]. X_k , Y_k , Z_k are the Langmuir constants which have been brought in Table 3.

Then, f_M^0 described as the minimum fugacity of M required for hydrate formation without the help of small gas species is evaluated as [5]:

$$f_M^0 = \exp(\frac{\mu_\beta^0 - \mu_w - \lambda_3 \mu_M^0(T)}{\lambda_3 RT}) \tag{6}$$

where $\mu_\beta^0 - \mu_w$can be estimated by [5]:

$$\mu_\beta^0 - \mu_w = \Delta A + P\Delta\upsilon - RT \ln\left(a_w\right) \tag{7}$$

where ΔA is the difference in molar Helmholtz free energy as a function of temperature, and $\Delta\upsilon$ represents the difference in molar volume. The activity of water is represented by a_w. Hence, f_M^0 can be expressed briefly as [5]:

$$f_M^0 = f(T)f(P)f(a_w) \tag{8}$$

where $f(T)$ as the characteristics of basic sH hydrate former and system temperature can be taken by the Antoine-type equation [5]:

$$f\left(T\right) = A'\exp\left(\frac{B'}{T - C'}\right) \tag{9}$$

Parameters A', B', and C' are determined by fitting the hydrate dissociation conditions data of the corresponding pure basic hydrate. The value of $f(P)$ is easily expressed as [5]:

$$f\left(P\right) = \exp\left(\frac{\beta' P}{T}\right) \tag{10}$$

in which β' can be taken as a constant that equals 2.2288 K/bar for sH hydrate [5].

$$f(a_w) = a_w^{-34} \tag{11}$$

where

$$a_w = \gamma_w x_w \tag{12}$$

3. Mehta-Sloan Hydrate Model

In this method, the equality of the difference in the chemical potential of water in the empty hydrate lattice, i.e. $\Delta\mu_w^H$ and water in liquid water or ice $\Delta\mu_w^L$ is considered as follows [4],[6]:

$$\Delta\mu_w^{\beta-H} = \Delta\mu_w^L \tag{13}$$

where

$$\Delta\mu_w^{\beta-H} = -RT\sum_{k=1}^{Ncav} v_k \ln\left(1-\sum_{i=1}^{nc}(1-\theta_{ki})\right) \tag{14}$$

in which v_k is the number of type k cavities per water molecule in the unit hydrate cell. The parameter θ_{ki} represents the fractional occupation of a type k cavity by a type i guest molecule shown as [4],[6]:

$$\theta_{ki} = \frac{C_{ki}f_i}{1+\sum_{i=1}^{nc} C_{ki}f_i} \tag{15}$$

The fugacity of the guest molecule f_i can be calculated as [4],[6]:

$$f_i = \varphi_i\, y_i\, P \tag{16}$$

in which φ_i is the fugacity coefficient, y_i represents the mole fraction of component i and P is pressure. The Langmuir constant C_{ki} for a guest molecule i in a type k cavity is only a function of temperature, which describes the guest-water interactions inside the cage given by [4],[6]:

$$C_{ki} = \frac{4\pi}{kT}\int_0^R exp\left[\frac{-\omega(r)}{kT}\right] r^2\,dr \tag{17}$$

where T is the absolute temperature, k represents the Boltzmann's constant, r stands for the radial distance from the center of the cavity, and $\omega(r)$ is the spherically symmetrical cell potential shown as [4],[6]:

$$\omega(r) = 2z\epsilon\left[\frac{\sigma^{12}}{R'^{11}r}\left(\delta^{10}+\frac{a'}{R'}\delta^{11}\right)-\frac{\sigma^6}{R'^5 r}\left(\delta^4+\frac{a'}{R'}\delta^5\right)\right] \tag{18}$$

where

$$\delta^N = \frac{1}{N}\left[(1-\frac{r}{R'}-\frac{a'}{R'})^{-N}-(1+\frac{r}{R'}-\frac{a'}{R'})^{-N}\right] \tag{19}$$

N is equal to 4, 5, 10, and 11, z represents the coordination number of the cavity, R' stands for the radius of the cavity, which is 3.91, 4.06, and 5.71 $^{\circ}A$ for small, medium, and large ones, respectively [4],[6]. $\Delta\mu_w^L$ is given as:

$$\frac{\Delta\mu_w^L}{RT} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T}\left(\frac{\Delta h_w}{RT^2}\right)dT + \int_0^P\left(\frac{\Delta v_w}{RT}\right)dP - ln\gamma_w x_w \tag{20}$$

where $\Delta\mu_w^0$ is the reference chemical potential difference between water in the empty hydrate lattice and pure water in the ice phase, at an arbitrary reference temperature T_0=273.15 K and absolute zero pressure.

For evaluation of molar enthalpy, i.e. Δh_w, it can be given by [4],[6]:

$$\Delta h_w = \Delta h_w^0 + \int_{T_0}^{T}\Delta C'_{pw}dT \tag{21}$$

as Δh_w^0 is the reference molar enthalpy and $\Delta C'_{pw}$ is the difference in molar heat capacity that is given by [4],[6]:

$$\Delta C'_{pw} = \Delta C'^{0}_{pw} + b(T-T_0) \tag{22}$$

4. Results and discussion

In this section, the required hypotheses and parameters for modeling are initially described, followed by the presentation of the modeling results.

In the calculations, two hypotheses are taken into account. Firstly, the solubility of help gas in the aqueous solution is neglected, and secondly, the gas phase is considered as pure methane.

Experimental data of vapor pressures of 1-methylpiperidine (NMPD) and 2-methylpiperidine are given in Table S1 [16],[17] and Table S2 [18], respectively.

These experimental vapor pressure data were fitted using the Antoine equation, and the coefficients are presented in Table 1.

$$\log_{10} Psat / Pa = A'' - \frac{B''}{T + C''/K} \tag{23}$$

The objective function (OF) was calculated by the sum of the average absolute relative deviations in vapor pressure:

$$OF = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{Psat_i^{cal} - Psat_i^{exp}}{Psat_i^{exp}}\right| \tag{24}$$

Table 1. Parameters A", B" and C" and Average Absolute Deviation (AAD%) between experimental data and Antoine vapor pressure for 1-methylpiperidine and 2-methylpiperidine (Eq. (23))

Component	Temperature/K	A"	B"	C"	AAD%
1-methylpiperidine	273.4 to 379.03	21.2338	3246.1582	-43.4899	0.38
2-methylpiperidine	324.62 to 430.64	20.5857	2929.5622	-68.0353	0.07

$AAD\% = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{Psat_i^{exp} - Psat_i^{cal}}{Psat_i^{exp}}\right| \times 100$, in which N represents the number of experimental data.

The parameters of the NRTL model for the 1-methylpiperidine/2-methylpiperidine + water system are taken from [15] and are reported in Table 2. These parameters are used to calculate the activity coefficients of water and 1-methylpiperidine/2-methylpiperidine in the aqueous phase.

Table 2. NRTL binary parameter values for 1-methylpiperidine(1)-water(2) and 2-methylpiperidine(3)-water(2) in Eq.(1, 2) [15]

Parameter	1-methylpiperidine		2-methylpiperidine	
	12	21	32	23
a"	-1.8862309	168.51859	-1.7965896	167.39657
b"	389.60375	-13066.792	295.7578	-12198.144
c"	-56856.407	707852.42	-37031.217	491023.74
d"	0.24311981	-22.985245	0.24343123	-22.991251
e"	0	0	0	0
f"	-15.110399	0.19247733	-15.746035	0.34515729
g"	0	0	0	0

The parameters needed to calculate the Langmuir constants of methane in small and medium cavities of structure H hydrate are reported in Table 3.

It should be noted that in the Chen-Guo model [5], equation (5) is used to calculate the Langmuir constant of methane, and in the Mehta-Sloan model [4], Kihara potential parameters are used to calculate the methane Langmuir constant.

Table 3. Characterizing parameters for calculating the methane Langmuir constant in small and medium cavities of the sH in Chen-Guo [5] and Mehta-Sloan [4] models

Methane	Chen-Guo model [3]				Mehta-Sloan model [2]		
	Cavity Type	$X_k \times 10^6$ (bar^{-1})	Y_k (K)	Z_k (K)	a' (^0A)	σ (^0A)	ε/k (K)
	Small Cavity	2.3048	2752.29	23.01	0.3834	3.165	154.54
	Medium Cavity	14.33	2625.04	19.93	0.3834	3.165	154.54

The parameters required to calculate the difference in chemical potential of water in the empty hydrate lattice and the aqueous phase are given in Table 4, which were used in this work.

Table 4. Reference Parameters in Mehta-Sloan Hydrate model in Eq. (20,21,22) [4]

$\Delta\mu_w^0$ (J/mol)	$\Delta C'^{0}_{p,w}$ (J/mol.K)	Δh_w^0 (J/mol)	Δv_w^0 (cm^3/mol)	b
914.38	38.12	-5165.78	5.45	0.141

In the Chen-Guo model [5], the model parameters are the same as the parameters in equation (9). The function f(T) for the structure H hydrate former in this model is not known, as it is obtained by fitting the experimental data. In the Mehta-Sloan model [4], the Kihara potential parameters for calculating the Langmuir constant of structure H hydrate former in large cavities of sH hydrate are not known. However, in this model, these parameters are obtained by fitting the experimental data. The optimized parameters of the Chen-Guo [5] and Mehta-Sloan [4] models are given in Table 5.

Table 5. Optimized model parameters for sH hydrate formers (i.e., 1-methylpiperidine and 2-methylpiperidine) obtained in this work (used in Eq. (9), (18))

Component	Mehta-Sloan [2]			Chen-Guo [3]		
	a' (^0A)	σ (^0A)	ε/k (K)	A'	B'	C'
1-methylpiperidine	0.3112	4.6418	302.99	1.4267×10^{17}	-3929.6	177.78
2-methylpiperidine	0.3067	4.6139	311.24	1.2459×10^{17}	-3897.7	180.23

Altogether, both models are well-suited to the experimental data within the limited temperature and pressure ranges applicable to sH hydrate dissociation conditions. The AAD% in calculated hydrate dissociation pressures using Mehta-Sloan [4] and Chen-Guo [5] models for the methane + 1-methylpiperidine + water system are 0.1% and 0.38%, respectively. This shows that the Mehta-Sloan model [4] correlates hydrate dissociation conditions for 1-methylpiperidine better than the Chen-Guo model [5]. However, AAD% for the methane + 2-methylpiperidine + water system is 0.79% when using both models, i.e., Mehta-Sloan [4] and Chen-Guo [5].

Hydrate dissociation conditions for methane + 1-methylpiperidine + water and methane + 2-methylpiperidine + water systems are reported in the literature [13] for NMPD and 2-methylpiperidine mole fractions equal to 0.029. The experimental data and modeling results, based on the Chen-Guo [5] and Mehta-Sloan [4] models for each system, are shown in Figures 1 and 2, respectively. As can be seen in these figures, both models correlate experimental data very well.

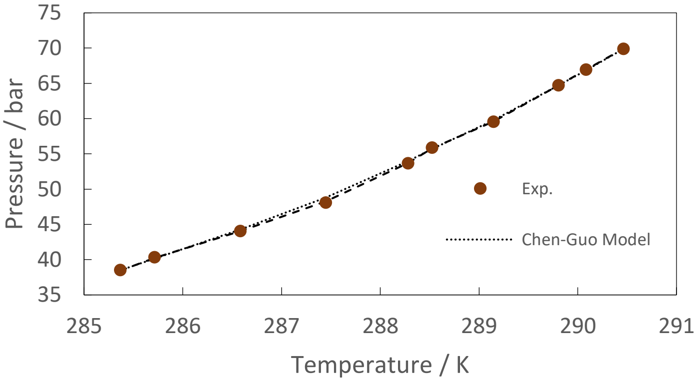

Figure 1. Correlated and experimental hydrate dissociation conditions in the methane + 1-methylpiperidine + water system, experimental data (●) [13], (….: Chen-Guo model [5] results), (----: Mehta-Sloan model [4] results)

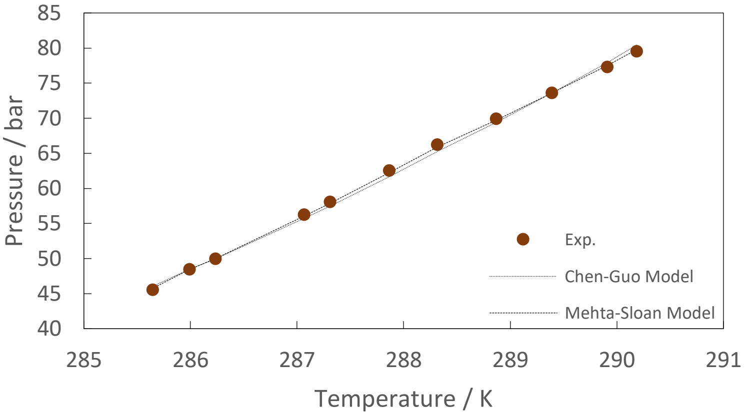

Figure 2. Correlated and experimental hydrate dissociation conditions in methane + 2-methylpiperidine + water system, experimental data (●) [13], (….: Chen-Guo model [5] results), (----: Mehta-Sloan model [4] results

5. Conclusions

Two thermodynamic models for calculating hydrate dissociation conditions of methane + 1-methylpiperidine/2-methylpiperidine (water-soluble sH hydrate formers) + water systems were introduced based upon Mehta-Sloan [4] and Chen-Guo [5] approaches. The fugacity of the help gas is calculated using the Peng-Robinson equation of state, while the NRTL activity coefficient model was applied for evaluation of the activity coefficients of water and sH hydrate formed in the aqueous phase. Assuming the gas phase was pure methane and the solubility of methane in the aqueous phase was negligible, two models were applied to calculate hydrate dissociation conditions for methane + 1-methylpiperidine/2-methylpiperidine + water systems. Parameters of the two models were optimized, and their results were successfully compared with the available experimental data. The results showed that both models correlate with experimental data very well.

Nomenclature

A	Helmholtz energy
A'	Parameter for equation (9)
A''	The parameter in the Antoine equation (23)
a	Activity
a'	The radius of the spherical core
a''	Parameter used in NRTL equation (2)
B'	Parameter for equation (9)
B''	The parameter in the Antoine equation (23)
b	Constant in equation (22)
b''	Parameter used in NRTL equation (2)
C	Langmuir constant in equations (4,5)
C'	Parameter for equation (9)
C'_p	Molar heat capacity
C''	The parameter in the Antoine equation (23)
c''	Parameter used in NRTL equation (2)
d''	Parameter used in NRTL equation (2)
e''	Parameter used in NRTL equation (2)
f	Fugacity in equation (3)
f''	Parameter used in NRTL equation (2)
G	Gibbs free energy in equation (1)
G_{ii}	NRTL parameter in equation (1)
g''	Parameter used in NRTL equation (2)
H	Molar enthalpy
N	Number of experimental data

Ncav	Number of types of cavities
Nc	Number of components
P	Pressure
Psat	Vapor pressure
R	Universal gas constant
R'	Free cavity radius
T	Absolute temperature
X	Used in Langmuir equation (5)
x	Mole fraction
Y	Used in Langmuir equation (5)
Z	Used in Langmuir equation (5)
y	Mole fraction
z	Coordination number
Greek letters	
α''	NRTL parameter
β'	Constant in equation (10)
γ	Activity coefficient
Δ	Difference
δ	The parameter in equation (18)
ε	Maximum attractive potential
θ	Fractional occupancy of the cavity
κ	Boltzmann's constant
λ	Number of cavities per water molecule in sH hydrate
μ	Chemical potential
ν	Number of cavities per water molecule in the hydrate structure
σ	The core distance at zero potential
τ	NRTL parameter
υ	Molar volume
φ	Fugacity coefficient
$\omega(r)$	The spherically symmetrical cell potential
Superscript	
cal	Calculated
E	Excess
exp	Experimental
H	Hydrate
L	Liquid water
0	Standard state
Subscript	
i	Component i
j	Component j
k	The cavity of type k

M	Minimum
w	Water
β	Empty hydrate lattice

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Supporting Information:

Table S1. Experimental vapor pressure of NMPD

T/K	P/Pa
379.03	101325
376.92	98258.3
298.14	4799.619
273.40	1238.17
273.40	1238.04
283.42	2216.33
283.42	2217.64
293.45	3813.42
293.45	3814.74
298.47	4928.56
303.49	6304.46

303.49	6305.78
313.53	10024.4
313.53	10023.1
323.52	15488.6
333.56	23085.8
333.56	23086.5
343.63	33490.5
343.63	33491.2
353.61	47331.0
353.61	47319.5
353.61	47329.3

Table S2. Experimental vapor pressure of 2-methylpiperidine

T/K	P/Pa
391.13	101325
391.13	99991.5
324.62	9581.88
327.51	10884.44
330.41	12334.99
333.33	13949.52
336.27	15740.04
339.21	17725.21
342.18	19919.7
348.14	25007.28
354.16	31160.1
360.23	38547.5
366.35	47358.77
372.54	57803.25
378.77	70108.9
385.06	84525.05
391.41	101325
397.81	120798.1
404.26	143268.2
410.77	169066.1
417.34	198530.3
423.96	232087.6
430.64	270111.1