A Fugacity Approach for Prediction of Phase Equilibria of Methane Clathrate Hydrate in Structure H

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In this communication, a thermodynamic model is presented to predict the dissociation conditions of structure H (sH) clathrate hydrates with methane as help gas. This approach is an extension of the Klauda and Sandler fugacity model (2000) for prediction of phase boundaries of sI and sII clathrate hydrates. The phase behavior of the water and hydrocarbon system is modeled using the Peng-Robinson equation of state (PR-EoS) with Wong-Sandler mixing rule, while the excess Gibbs free energy of the mixture is calculated using the UNIFAC activity model. The van der Waals-Platteeuw (vdWP) solid solution theory is used to model the hydrate phase. Results are compared with the results of the models proposed by Mehta and Sloan (1996) and Chen *et al*. (2003) for prediction of dissociation conditions of structure H hydrates. According to the results, the overall average absolute deviation of dissociation temperatures between experiments and predictions are 0.18 (K), depending on the promoter, and the accuracy of the model proposed in this study is found to be better than the accuracies of the aforementioned models.

Keywords: Clathrate hydrate, Structure H, Promoter, Thermodynamic model, Gas hydrate

INTRODUCTION

Clathrate hydrates, or gas hydrates, are crystalline structures composed of gases and/or some volatile liquids (guests) + water mixtures in which water molecules (hosts) are bonded to each other, through hydrogen bonds, where guest molecules are trapped in water cavities leading to stable lattice [1]. Clathrate hydrates can be divided into three typical crystalline structures [1]: Before the discovery of sH hydrates, it was assumed that the clathrate hydrates include two kinds of cubic structures known as sI and sII while molecules larger than normal butane cannot occupy the crystalline lattice due to their large size [2]. Later,

Ripmeester *et al*., (1987) found out a new class of clathrate hydrates known as structure H hydrates [3]. Unlike other two structures, in this structure, three types of cavities exist: small, medium and large. Gas molecules like methane, and hydrogen sulfide can fill small and medium cavities and sH hydrate former molecules like methylcyclopentane, methylcyclohexane and neohexane fill large cavities and stabilize clathrate hydrate structures. Ripmeester and Ratcliffe, (1990) identified about 25 guest heavy hydrocarbons capable of forming structure H clathrate hydrates with xenon as a help gas [4]. Some heavy molecules belonging to isoalkanes, cycloalkanes, alcohols and ketones with molecular diameters of about 7 to 8.6 Å may form sH hydrates. However, it is believed that some larger molecules like ethylcyclohexane with a molecular

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diameter of 9.82 Å are also capable of forming this structure [1]. These molecules are generally considered insoluble or slightly soluble in water and in terms of size, are generally larger than guest molecules forming sII hydrates and form hydrates at lower pressures than those required for stability of sI clathrate hydrates [1].

After the discovery of sH clathrate hydrates, the first phase equilibrium data of sH hydrate for methane + adamantane system was reported by Lederhos *et al.* [5]. The sH hydrates in nature are much less than the other two structures discovered naturally by Sassen and MacDonald [6]. They suggested that a range of hydrocarbons can form sH hydrates in pipelines. In the recent years, other researchers conducted studies to identify more hydrocarbon molecules which may form the same structure and therefore phase equilibrium data were measured for a series of methane + liquid hydrocarbon systems [7,8]. Measurements were also undertaken for sH hydrates stabilized with other help gases like nitrogen [9,10], carbon dioxide [11], xenon [12] and hydrogen [13].

Despite Hammerschmidt's idea (1934) that gas hydrates can cause blockage of petroleum pipelines and process equipment and then direction of studies shifted to prevent hydrate formation [14], in next years, many researchers suggested that clathrate hydrates can be used to store some gases. Gudmundsson *et al.* showed that sII clathrate hydrates can be fully maintained for 15 days at -15 °C under atmospheric pressure [15]. During a feasibility study on the possibility of transferring of natural gas in hydrate form, Borrehaug and Gudmundsson, showed about 24% cost saving for gas transport in hydrates compared to liquefied natural gas (LNG) from the northern North Sea to Central Europe [16]. Later, Khokhar *et al.* verified methane storage capacity in sH clathrate hydrates [17]. Recently, Javanmardi *et al.* (2005) proposed a process for conversion of natural gas to gas hydrates. Moreover, the economic evaluation of the transportation of natural gas hydrate as an alternative was investigated [18].

So far, several thermodynamic models have been proposed, by considering interactions between guest and host molecules, to calculate the chemical potential difference in empty hydrate lattice and stabilized hydrate lattice after adsorption of gas molecules inside the cavities to predict dissociation conditions of sH clathrate hydrates

[1].

Mehta and Sloan developed a thermodynamic model based on the van der Waals and Platteeuw (vdWP) solid solution theory and optimized the thermodynamic values and Kihara potential parameters of molecules forming sH clathrate hydrates [7,19].

The reference chemical potential in this model was assumed to be constant and this parameter is set at the ice point of water. Thus, the model close to the ice point of water performs well, while the deviation in prediction of sH hydrates phase equilibria can be increased at conditions far away from this point.

Chen *et al.* extended their model for sH clathrate hydrates [20], which was previously proposed to predict formation of sI and sII hydrates based on the two-step hydrate formation mechanism [21,22]. The latter model does not require thermodynamic properties of empty hydrate lattice [20].

It should be mentioned that due to the fitted parameters of this model based on Antoine equation, the inaccuracy of model over extended temperature ranges can be expected. Moreover, presentation of a complete occupation of all large cavities as an assumption of this model has not been performed experimentally yet [23].

Martin and Peters proposed a thermodynamic model to predict the dissociation conditions of hydrogen hydrates by considering secondary interactions [24,25]. They proposed a similar model to predict the dissociation conditions of sH hydrogen clathrate hydrates [26]. Based on their models, the occupation of hydrate cavities by several hydrogen molecules was considered and in addition to interactions between guest-host molecules, the interactions between guest-guest molecules were also taken into account. To calculate the fugacity of fluid phases, the CPA (cubic plus association) equation of state was used [26].

A similar thermodynamic model was later proposed by Babaee *et al.* for prediction of sH hydrogen hydrate phase equilibria with different promoters [27].

Klauda and Sandler, proposed a thermodynamic model based on equality of water fugacity between hydrate and aqueous phases to predict dissociation conditions of sI and sII hydrates [23]. In their model, there is no need for reference properties in vdWP-type models. Furthermore, similar to John *et al.* [28] model, secondary interactions

were considered for the calculations of the potential function. Moreover, the Kihara spherical core potential parameters are used from viscosity and second Virial coefficient data [29], while in the vdWP-type models these parameters are obtained by fitting to the experimental data. Within the next years, they also developed their models for multiple gas component clathrate hydrates [30,31,32].

As mentioned earlier, models of Mehta and Sloan and Chen *et al.* are capable of predicting the phase boundaries of the methane sH hydrate. In this communication, the thermodynamic approach based on the Klauda and Sandler model for sI and sII clathrate hydrates has been extended for estimating sH hydrate dissociation conditions with methane as help gas and the comparisons with the aforementioned models have been performed to clarify the capability of the model. Moreover, using the Wong Sandler mixing rule causes the more accurate prediction of the gas phase compositions, especially in the presence of heavy sH hydrate former. Details of the model are presented as follows.

THERMODYNAMIC MODEL

The thermodynamic model for estimating the dissociation conditions of structure H methane hydrates is based on equality of fugacity between hydrate and aqueous phases. At equilibrium, the fugacity of water in the hydrate and aqueous phases are equal [23]:

$$f_w^H(T,P) = f_w^L(T,P) \tag{1}$$

The fugacity of water in the hydrate phase is calculated as follows [33]:

$$f_w^H = f_w^\beta \exp\left(\frac{-\Delta\mu_w^{\beta-H}(T,P)}{RT}\right) \tag{2}$$

The fugacity of water in aqueous phase, f_w^L, and the hypothetical and empty hydrate lattice, f_w^β are evaluated as follows [23]:

$$f_w^L(T,P) = x_w(T,P)\gamma_w(x_w,T)P_w^{sat,L}(T)\exp\left(\frac{V_w^L(T,P)\left(P-P_w^{sat,L}(T)\right)}{RT}\right) \tag{3}$$

$$f_w^\beta(T,P) = P_w^{sat,\beta}(T)\exp\left(\frac{V_w^\beta(T,P)\left(P-P_w^{sat,\beta}(T)\right)}{RT}\right) \tag{4}$$

where $P_w^{sat,L}(T)$ is the vapor pressure in the aqueous phase in units of Pa. [23]:

$$\ln\left(P_w^{sat,L}\right) = \left(4.1539\ln(T) - \frac{5500.9332}{T} + 7.6537 - 16.1277\times10^{-3}T\right) \tag{5}$$

The empty hydrate lattice vapor pressure $P_w^{sat,\beta}(T)$, based on the investigation of researchers depends on the guest molecules [23]. Hence, in the current work, the following form for this parameter for sH hydrates of methane with different promoters are proposed [23]:

$$\ln\left(P_w^{sat,\beta}\right) = \left(A\ln(T) + \frac{B}{T} + 2.7789 + DT\right) \tag{6}$$

where T and P are the system temperature and the pressure in K and Pa, respectively. The optimized values of the parameters A, B and D for sH are given in Table 1.

Due to the low solubility of heavy molecules forming sH hydrates in aqueous phase, this term is ignored and the methane solubility in water phase is estimated using the Henry's law approach as follows [23]:

$$x_i^{guest(s)} = \frac{f_i}{H_i(T)\exp\left(Z_i^\infty\right)} \tag{7}$$

where Z_i^∞ is the infinite dilution compressibility factor. To calculate the Henry's law constant, the following temperature dependence equation is used [23]:

$$-\ln\left(\frac{H_i(T)}{101325}\right) = -183.786 + \frac{9112.582}{T} + 25.0405\ln(T) - 0.00015T \tag{8}$$

The unit for $H_i(T)$ and T are Pa^{-1} and K, respectively.

The difference between the chemical potential of water in the empty hydrate lattice and the hydrate phase in Eq. (2) is determined as follows [34]:

Table 1. Vapor Pressure Constants for the Empty Hydrate Lattice in Eq. (6)

Promoter	A	B	$D \times 10^3$
2-Methylbutane	38.1018	-26143.1912	-416.6586
2,2-Dimethylbutane	24.6231	-17702.4931	-252.7757
2,2-Dimethylpentane	36.1236	-24893.0436	-393.4375
2,3-Dimethylbutane	34.7221	-24123.9028	-374.0982
3,3-Dimethylpentane	24.0152	-17216.7327	-246.7680
2,2,3-Trimethylbutane	23.6376	-17104.6751	-240.5623
Methylcyclopentane	34.0009	-23688.2957	-365.2308
Ethylcyclopentane	50.6504	-34672.8597	-559.9892
Methylcyclohexane	32.3511	-22727.0502	-344.3528
Cycloheptane	29.4058	-20768.4272	-309.7910
Cycloheptene	15.8123	-11958.0052	-148.6967
Cyclooctane	35.4360	-24704.9003	-381.0192
Cis-cyclooctene	21.1520	-15424.6049	-211.8914
1,1-Dimethylcyclohexane	32.8530	-23284.4813	-347.4761
1,2-Dimethylcyclohexane	33.2490	-23292.4671	-355.4793
1,3-Dimethylcyclohexane	38.1973	-26347.6641	-416.0899
1,4-Dimethylcyclohexane	31.5412	-22157.1357	-335.5657
2,3-Dimethyl-1-butene	26.2903	-18600.3650	-274.9777
3,3-Dimethyl-1-butene	25.7763	-18419.3538	-267.1849
3,3-Dimethyl-1-butyne	31.3956	-21865.0721	-336.4130
Adamantan	14.7562	-11555.2044	-134.5352

$$\Delta\mu_w^{\beta-H} = \mu_w^{\beta} - \mu_w^{H} = RT \sum_{i=1}^{NCAV} v_i \left(1 + \sum_{j=1}^{NHYDF} C_{ij} f_j \right) \qquad (9)$$

$$C = \frac{4\pi}{kT} \int_0^{R'-a} \exp\left(\frac{-\omega(r)}{kT} \right) r^2 dr \qquad (10)$$

where v_i denotes the number of cavities of type i per water molecule in the unit cell, f_j is the fugacity of the hydrate former j and C denotes the Langmuir constant, which is calculated using the following expression [34]:

where R' is the radius of cage, $\omega(r)$ is the cell potential and k is the Boltzmann's constant.

The crystallographic data for the second and third shell (cavity) parameters of sH clathrate hydrates have not been reported in the literature. Hence, to determine the Langmuir

Table 2. The Critical Properties and the Acentric Factors of Hydrate Formers [19,40]

Promoter	T_C (K)	P_C (MPa)	ω
Methane	190.6	4.599	0.008
2-Methylbutane	460.4	3.38	0.227
2,2-Dimethylbutane	488.8	3.08	0.232
2,2-Dimethylpentane	520.5	2.77	0.287
2,3-Dimethylbutane	500.0	3.13	0.247
3,3-Dimethylpentane	537.4	2.91	0.296
2,2,3-Trimethylbutane	531.2	2.95	0.250
Methylcyclopentane	532.7	3.78	0.231
Ethylcyclopentane	569.5	3.40	0.271
Methylcyclohexane	532.7	3.78	0.236
Cycloheptane	604.2	3.81	0.237
Cycloheptene	598.3	3.95	0.231
Cyclooctane	647.2	3.56	0.236
Cis-cyclooctene	641.4	3.62	0.246
1,1-Dimethylcyclohexane	591.0	2.96	0.238
1,2-Dimethylcyclohexane	606.0	2.96	0.236
1,3-Dimethylcyclohexane	591.1	2.94	0.237
1,4-Dimethylcyclohexane	598.1	2.94	0.231
2,3-Dimethyl-1-butene	501.0	3.24	0.221
3,3-Dimethyl-1-butene	490.0	3.25	0.121
3,3-Dimethyl-1-butyne	490.8	3.41	0.133
Adamantine	680.0	2.81	0.297

constant, the assumption of a single layer was considered and the Kihara potential function was utilized to describe the guest-host interactions. The details of estimation of the Langmuir constant have been given elsewhere [34]. The values of the Kihara potential parameters were obtained from correlations optimized based on the viscosity and second virial coefficient presented by Tee *et al.* [29]. These parameters are determined from the following combining rules [27,28]:

$$\sigma = \frac{\sigma_g + \sigma_w}{2}, \quad \varepsilon = \sqrt{\varepsilon_g \varepsilon_w}, \quad a = \frac{a_g + a_w}{2} \tag{11}$$

Table 3. The Kihara Potential Parameters of Hydrate Formers [23,29]

| Promoter	α (Å)	σ (Å)	ε/k (K)
Methane	0.3834	3.505	232.2
2-Methylbutane	0.9859	5.2454	698.2495
2,2-Dimethylbutane	1.0472	5.5151	746.8082
2,2-Dimethylpentane	1.2122	5.7862	859.5095
2,3-Dimethylbutane	1.0781	5.5147	780.7575
3,3-Dimethylpentane	1.2207	5.7450	898.2748
2,2,3-Trimethylbutane	1.1277	5.7365	833.0544
Methylcyclopentane	1.0047	5.3020	812.6845
Ethylcyclopentane	1.1391	5.5823	919.9675
Methylcyclohexane	1.0140	5.2980	818.6640
Cycloheptane	1.0566	5.5096	929.9031
Cycloheptene	1.0291	5.4309	912.7635
Cyclooctane	1.1038	5.7669	994.6299
Cis-cyclooctene	1.1140	5.7092	1000.1158
1,1-Dimethylcyclohexane	1.1429	5.9480	910.9142
1,2-Dimethylcyclohexane	1.1483	5.9996	931.3129
1,3-Dimethylcyclohexane	1.1435	5.9626	909.7613
1,4-Dimethylcyclohexane	1.1353	5.9915	912.4584
2,3-Dimethyl-1-butene	1.0166	5.4766	753.0756
3,3-Dimethyl-1-butene	0.7767	5.5120	626.5361
3,3-Dimethyl-1-butyne	0.7960	5.4178	640.7811
Adamantine	1.3376	6.2852	1138.1602
Water	0.000	3.564	102.134

where, subscript g and w denote the guests and water molecules, respectively. The critical constants and the Kihara potential parameters of hydrate formers are reported in Tables 2 and 3, respectively.

To determine the molar volume of pure water in Eq. (3), the relation proposed by Jager *et al.* was used [35]. The

**Table 4.** Parameters for Volume of Water ($m^3 \ mol^{-1}$) (Eq. (12)) [35]

|	n = 0	n = 1	n = 2	n = 3
a_{1n}	31.1251	-1.14154×10^{-1}	3.10034×10^{-4}	-2.48318×10^{-7}
a_{2n}	-2.46176×10^{-7}	2.15663×10^{-9}	-6.48160×10^{-12}	6.47521×10^{-15}
a_{3n}	8.69425×10^{-16}	-7.96939×10^{-18}	2.45391×10^{-20}	-2.51773×10^{-23}
a_{4n}	-6.03348×10^{-25}	5.57791×10^{-27}	-1.72577×10^{-29}	1.77978×10^{-32}
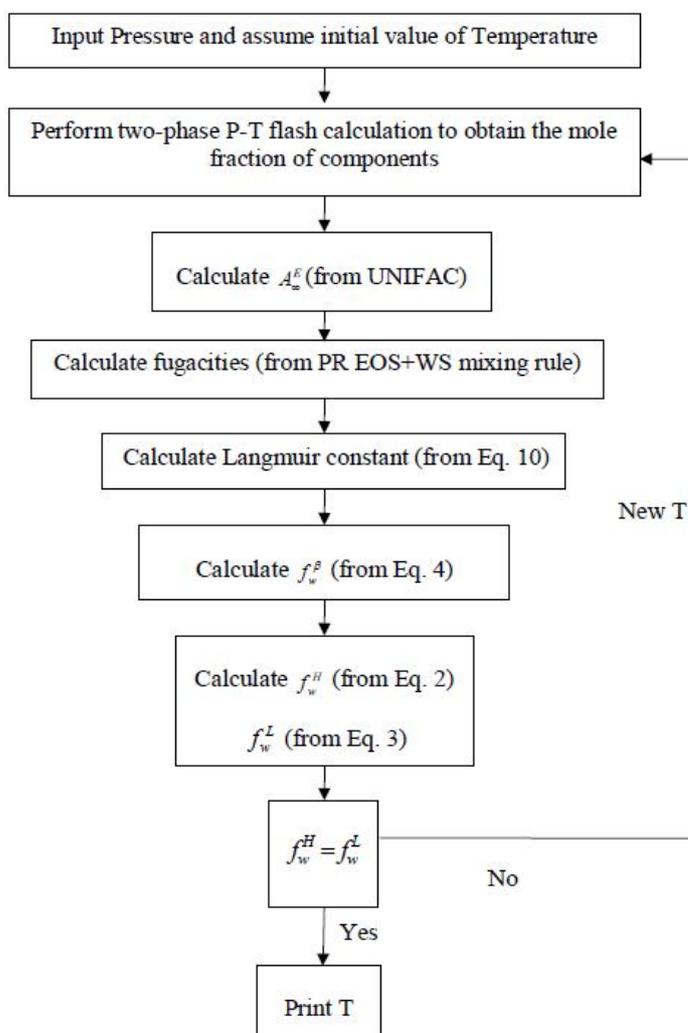
Fig. 1. Flow chart of computational algorithm for calculating the dissociation temperature of sH hydrate at a given pressure.
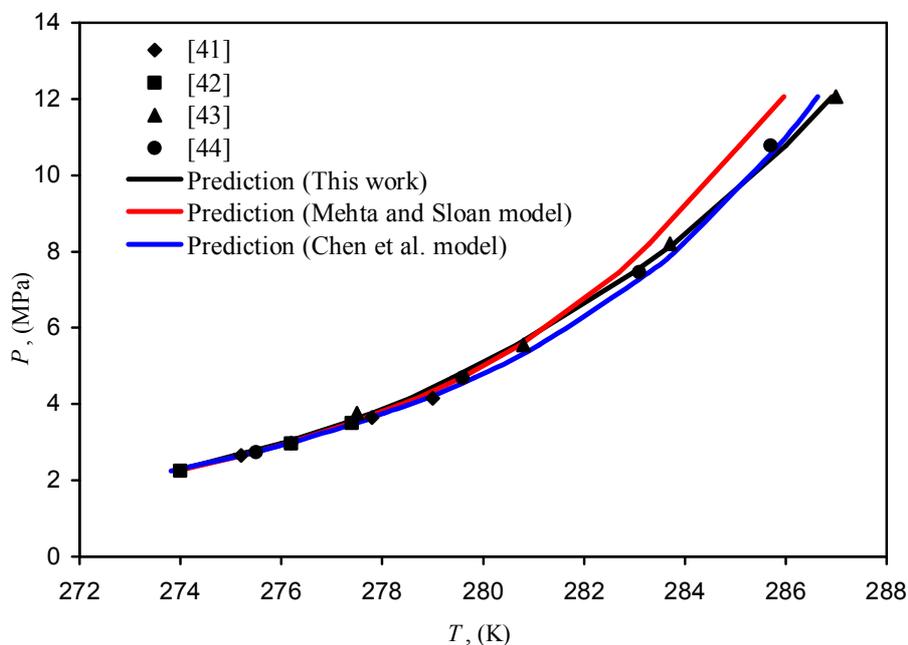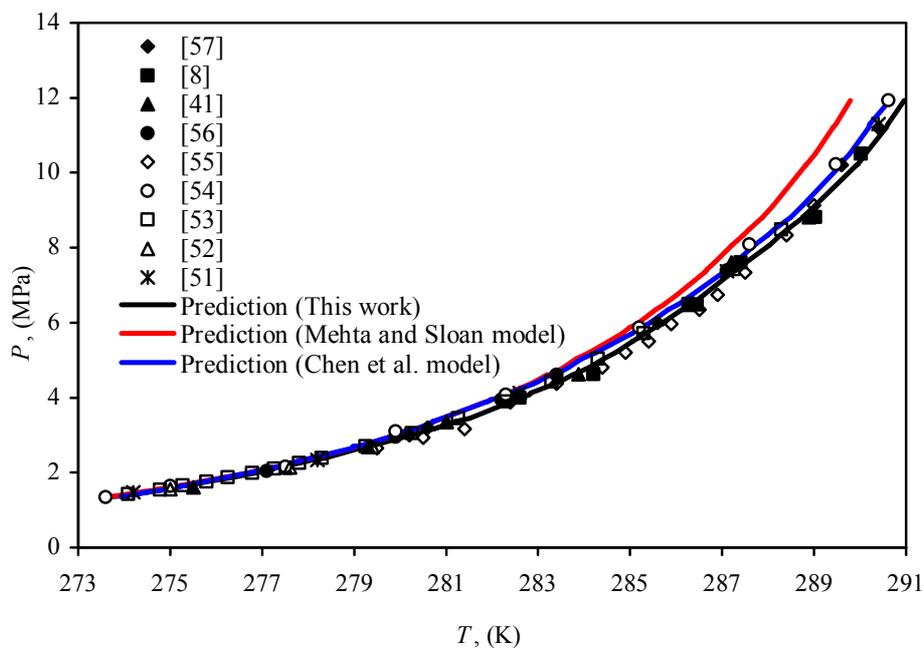
Fig. 2. Predicted and experimental methane structure H hydrate dissociation conditions in the presence of 2-methylbutane.
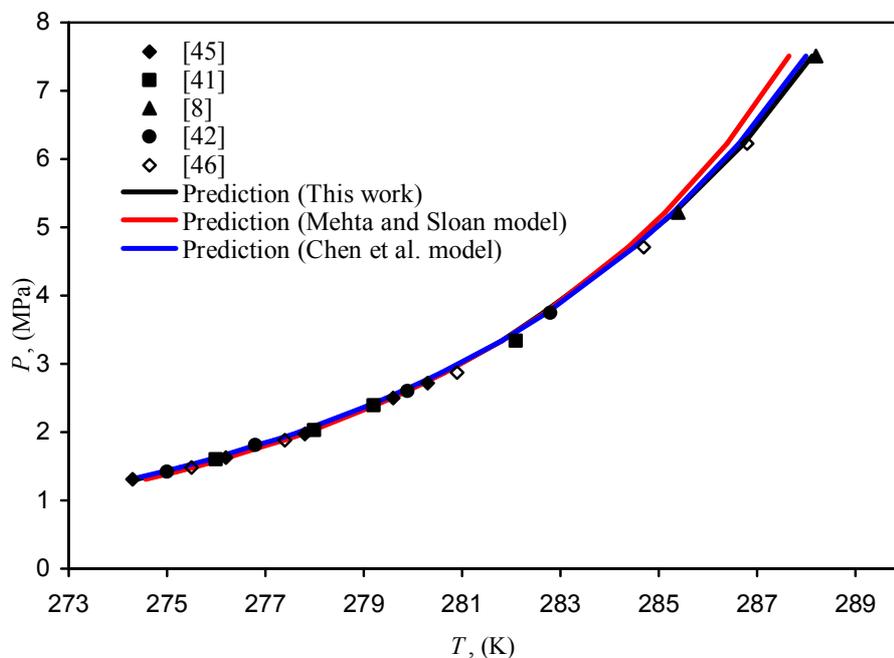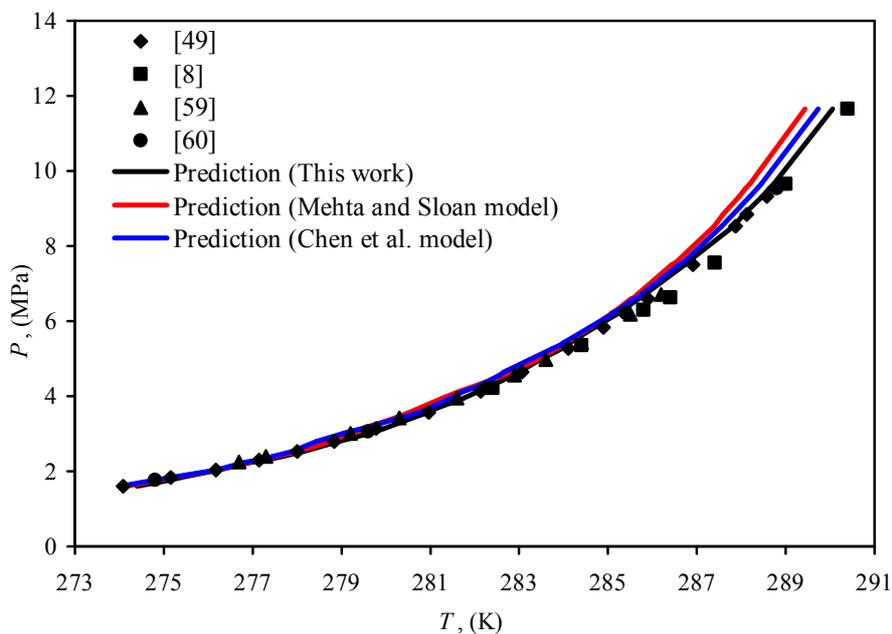

Fig. 3. Predicted and experimental methane structure H hydrate dissociation conditions in the presence of 2,2-dimethylbutane.
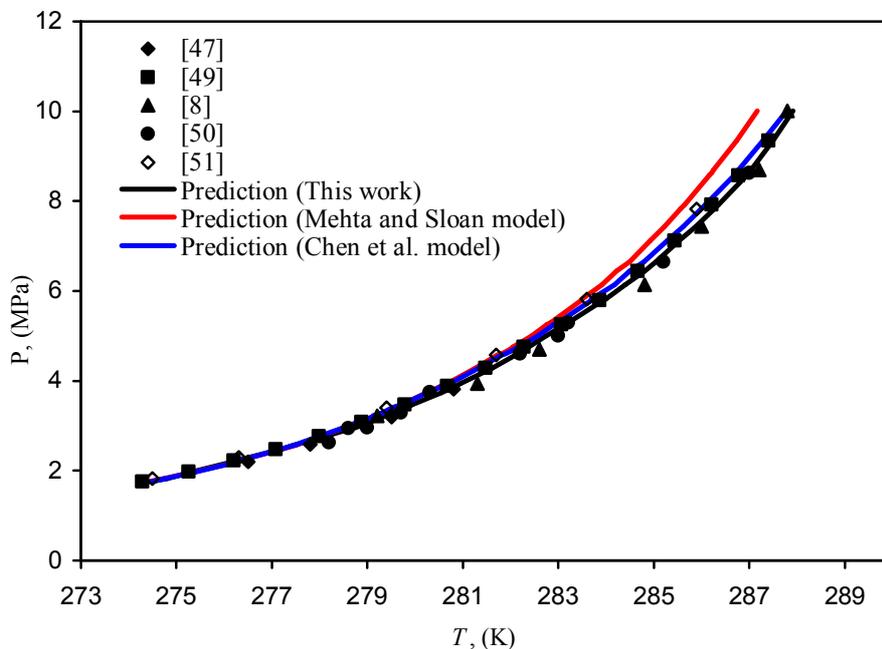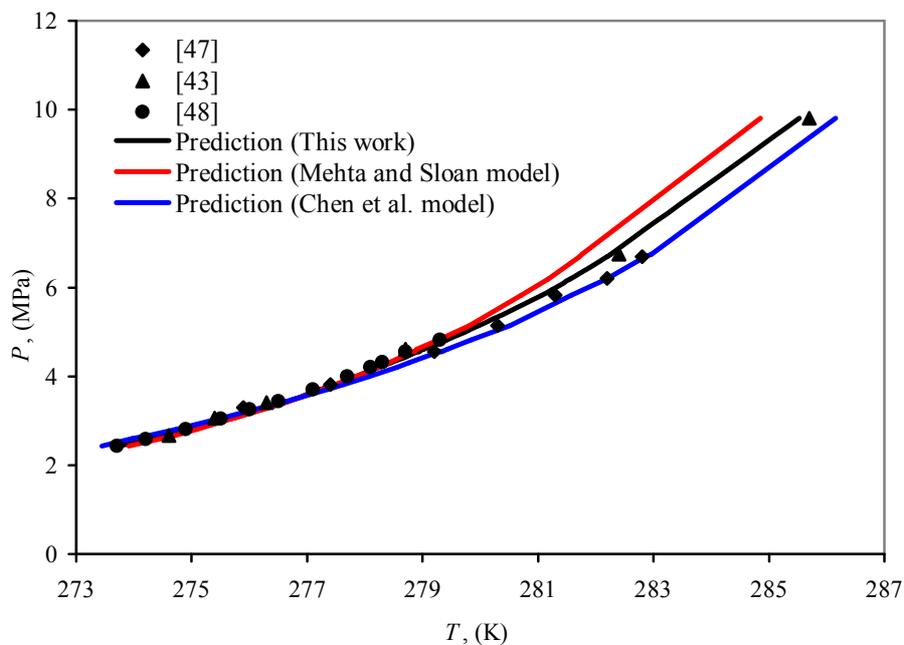
Fig. 4. Predicted and experimental methane structure H hydrate dissociation conditions in the presence of methylcyclopentane.

Fig. 5. Predicted and experimental methane structure H hydrate dissociation conditions in the presence of methylcyclohexane.

Fig. 6. Predicted and experimental methane structure H hydrate dissociation conditions in the presence of Cyclooctane.

Fig. 7. Predicted and experimental methane structure H hydrate dissociation conditions in the presence of 2,2-dimethylpentane.

parameters are reported in Table 4.

$$V_w^L = \sum_{n=0}^{3} \left(a_{1n} + a_{2n}P + a_{3n}P^2 + a_{4n}P^3 \right) T \times 10^{-6} \qquad (12)$$

where V_w^L is in (m^3 mol^{-1}), P is in Pa and T is in K.

Molar volume of the empty sH clathrate hydrate lattice in Eq. (4), as a function of temperature and pressure is expressed as follows [26]:

$$V_w^\beta = \frac{3^{1.5}}{2} \left(12.268 + 0.697 \times 10^{-3}(T-80) + 1.33 \times 10^{-6}(T-80)^2 \right)^2$$
$$\left(9.997 - 0.332 \times 10^{-3}(T-80) + 4.30 \times 10^{-5}(T-80)^2 \right)$$
$$\frac{10^{-30}N_A}{N_w^H} \exp\left(-1.05 \times 10^{-10}(P-101325) \right) \qquad (13)$$

Here N_A and N_w^H represent the Avogadro's number and number of water molecules per unit cell, respectively. In this equation, V_w^β is in m^3 mol^{-1} and T and P are the system temperature and the pressure in K and Pa, respectively.

To calculate the fugacity of the hydrate formers in Eq. (9), the effect of the heavy components on the gas phase is not negligible and their mole fractions should be considered [7,26]. Also, in the ice point vicinity, the effect of the presence of water on the hydrocarbon phase behavior is inappreciable [20]; accordingly, to determine the fugacity of components, (help gas + heavy hydrocarbon) Pressure-Temperature flash calculation was performed using the Peng-Robinson equation of state [36] and the Wong-Sandler mixing rule [37]. Original WS mixing rule uses the NRTL activity model, but in the current work, in order to avoid fitting the binary interaction parameters required in the NRTL model, we have applied the UNIFAC activity model. The Appendix contains the Wong-Sandler mixing rule and its details.

RESULTS AND DISCUSSION

In this study, constants of Eq. (6) for each large guest component of sH hydrate in the presence of methane as a help gas were obtained by regression of 40% of available experimental data and using the following objective function:

$$F_{obj} = \sum_{n=1}^{NDP} \left(\frac{|T_{exp} - T_{cal}|}{T_{exp}} \right) \qquad (14)$$

where T_{xep} and T_{cal} are the experimental and the calculated dissociation temperatures of sH hydrate, respectively. The optimized values of parameters A, B and D are given in Table 1.

It should be noted that in the Mehta and Sloan model, the three parameters of Kihara potential function for each heavy guest molecule are optimized. The Chen *et al.* model also has three to six adjustable parameters per liquid hydrocarbons and help gas in the form of Antoine equation which are determined. Meanwhile, the present model requires three adjustable parameters just for each system. Furthermore, due to constant assumption of reference chemical potential parameter, error at high pressure ranges may be observed for activity coefficient based models.

Thus, fugacity based models as a new generation for gas hydrates prediction, have been proposed to create the increase of flexibility in prediction of hydrate phase equilibrium conditions. Additionally, EOS/G^E models are capable of predicting the vapor-liquid equilibria (VLE) for multicomponent mixtures over the entire pressure range. Thus, the main aim of this study was to combine the advantages of the two earlier descriptions (fugacity approach accompanied with EOS/G^E model) for estimation of the real phase equilibria of methane sH clathrate hydrate.

Figure 1 presents the flowchart for predicting sH hydrates equilibrium conditions based on equality of water fugacity between hydrate and aqueous phases. The results of this work as well as the models of Mehta and Sloan [19] and also Chen *et al.* [20] are compared with the experimental data in Figs. 2-7.

It should be mentioned that because of numerous experimental sH hydrate data, only some typical systems have been depicted in these figures. The number of data points, pressure ranges and average absolute deviations, AAD, are summarized in Table 5. As evident from obtained results, a good agreement between the model predictions and the available experimental data is observed.

Table 5. The Average Absolute Deviation Temperature (AADT) for Methane sH Hydrate Dissociation Conditions

Promoter	No. of data	P-Range (MPa)	AADT (K)			Data source
			This work	Chen *et al.* 2003	Mehta and Sloan 1996	
2-Methylbutane	15	2.24-12.06	0.15	0.18	0.23	[41,42,43,44]
2,2-Dimethylbutane	20	1.30-7.51	0.14	0.15	0.17	[8,41,42,45,46]
2,2-Dimethylpentane	25	2.43-9.81	0.21	0.29	0.37	[43,47,48]
2,3-Dimethylbutane	10	2.07-8.96	0.11	0.13	0.16	[9,47]
3,3-Dimethylpentane	7	1.73-7.28	0.07	0.10	0.15	[8,47]
2,2,3-Trimethylbutane	6	1.47-7.55	0.20	0.34	0.43	[8,47]
Methylcyclopentane	44	1.75-10.01	0.16	0.23	0.36	[8,47,49,50,51]
Ethylcyclopentane	6	3.59-9.13	0.11	0.26	0.29	[8]
Methylcyclohexane	76	1.35-11.93	0.19	0.29	0.42	[8,41,51,52,53,54, 55,56,57]
Cycloheptane	23	1.38-10.93	0.20	0.29	0.36	[8,58,59]
Cycloheptene	4	2.10-3.81	0.15	0.18	0.44	[47]
Cyclooctane	39	1.60-11.65	0.24	0.31	0.42	[8,49,59,60]
Cis-cyclooctene	4	2.08-3.56	0.07	0.12	0.21	[47]
1,1-Dimethylcyclohexane	20	1.07-11.50	0.16	0.24	0.27	[8,61]
1,2-Dimethylcyclohexane	24	1.57-11.32	0.15	0.26	0.30	[8,47,53]
1,3-Dimethylcyclohexane	10	3.07-6.35	0.10	0.19	0.25	[17]
1,4-Dimethylcyclohexane	20	1.62-9.13	0.16	-	0.41	[62]
2,3-Dimethyl-1-butene	4	2.53-4.80	0.06	0.07	0.11	[47]
3,3-Dimethyl-1-butene	12	2.01-6.50	0.11	0.17	0.25	[47,60]
3,3-Dimethyl-1-butyne	5	2.85-4.56	0.10	0.11	0.15	[19]
Adamantine	8	1.77-3.01	0.08	0.10	0.16	[5,42]
Overall	382	-	0.18	0.24	0.33	-

$$AADT, (K) = \frac{1}{NP} \sum_{n=1}^{NP} \left(\left| T_{\exp} - T_{cal} \right| \right)$$

CONCLUSIONS

A thermodynamic model based on equality of water fugacity for methane structure H hydrate in the presence of different heavy hydrate formers (promoters) was proposed. The values of Kihara cell potential parameters based on the viscosity and second virial coefficient data were obtained directly from the correlations given in the literature. The vapor pressure constants of the empty hydrate lattice for various sH hydrate formers were obtained by regression of experimental data. The fugacities of the species in all phases were calculated using the Peng-Robinson equation of state accompanied with the Wong-Sandler mixing rule combined with the UNIFAC activity model. The results of the present model were compared with the available experimental data in the literature where an acceptable agreement is observed.

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Appendix

The Peng Robinson equation of state is as follows [36]:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + 2bV - b^2} \tag{A1}$$

To apply Peng-Robinson equation of state to the mixtures, its parameters a_m, and b_m for mixtures can be expressed as follows using the Wong-Sandler mixing rule [37]:

$$a_m = b_m \sum_i x_i \frac{a_i}{b_i} - \frac{A_\infty^E}{0.62323} \tag{A2}$$

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - \frac{a}{RT})_{ij}}{1 - \sum_i x_i \frac{a_i}{b_i RT} + \frac{A_\infty^E}{0.62323 RT}} \tag{A3}$$

Here A_∞^E is the excess Helmholtz free energy of

mixing at infinite pressure and can be considered equal to the excess Gibbs free energy at low pressure [37]. To calculate A_∞^E, the UNIFAC activity model is applied [38]:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{A4}$$

where combinational part due to differences in size and shape of the molecules is given by [38]:

$$\ln \gamma_i^C = \left(\ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \right) - 5q_i \left(\frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right) \tag{A5}$$

where x_i is the mole fraction of component i, θ_i is the area fraction, and ϕ_i is the segment fraction which are defined as follows [38]:

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{A6}$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{A7}$$

where r_i and q_i are the volumes and molecular surface areas, respectively. These parameters are calculated using the group contribution method [38]:

$$r_i = \sum_k v_k^{(i)} R_k \tag{A8}$$

$$q_i = \sum_k v_k^{(i)} Q_k \tag{A9}$$

where $v_k^{(i)}$ is the number of groups of type k in molecule i. R_k and Q_k are the UNIFAC volume and surface area parameters, respectively. These parameters are given elsewhere, [38]. The residual term is expressed by:

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_i^{(i)} \right) \tag{A10}$$

where:

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \left(\sum_m \frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}} \right) \right] \qquad (A11)$$

$\ln \Gamma_k$ is the group residual activity coefficient and $\ln \Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i [38]. θ_m is the area fraction of group m and Ψ_{mn} is the group-interaction parameter [39]:

$$\psi_{mn} = \exp \left[- \left(\frac{a_{mn} + b_{mn}T}{T} \right) \right] \qquad (A12)$$

Here a_{mn} and b_{mn} are the parameters of main group CH_4-CH_2, which are given elsewhere, [39].

List of Symbols

A	Parameter in Eq. (6)
A_∞^E	Excess Helmholtz free energy
a	Guest core radius
$a(T)$	Equation of state "energy" parameter
a_i	Energy parameter of component i
a_m	Energy parameter of mixture
a_{mn}	Interaction parameter
B	Parameter in Eq. (6)
b	Excluded volume
b_i	Excluded volume of component i
b_m	Excluded volume of mixture
b_{mn}	Interaction parameter
C	Langmuir constant
D	Parameter in Eq. (6)
f	Fugacity
H	Henry's constant
N_A	Avogadro number
N_w^H	Number of H_2O molecules per unit cell in sH hydrates
k	Boltzmann's constant
P	Pressure
P_C	Critical pressure
P^{sat}	Saturation pressure
Q_k	UNIFAC surface area parameter
T	Temperature
T_C	Critical temperature
r	Integration variable
R	Universal gas constant
R'	Hydrate shell radius
R_k	UNIFAC volume parameter
v_i	Number of cavities of type per water molecule
V	Molar volume
x_i	Mole fraction of component i
X_m	Mole fraction of group m
z	Number of water molecules of each hydrate cage
Z_i^∞	Infinite dilution compressibility factor
$\Delta \mu_w^{\beta-H}$	Chemical potential of water difference between the empty and filled hydrate
σ	Collision diameter
β	Empty hydrate
$\omega(r)$	Potential function
γ	Activity coefficient
θ_i	Area fraction
ϕ_i	Segment fraction
Ψ	Group-interaction parameter
ε	Depth of the intermolecular potential well
Γ_k	Residual activity coefficient of group k in a solution

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