



Thermodynamic Model for Prediction of Phase Equilibria of Gas Hydrates in the Presence of Water-Insoluble Organic Compounds

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Abstract

A thermodynamic model for predicting pressure – temperature phase diagrams of structure II and structure H clathrate hydrates of methane, carbon dioxide, or hydrogen sulfide in the presence of "water-insoluble" organic compounds is presented. The model is based on equality of water fugacity in the aqueous and hydrate phases. The solid solution theory of van der Waals – Platteeuw (vdW-P) is used for calculating the fugacity of water in the hydrate phase. The Peng-Robinson (PR) equation of state (EoS) is employed to calculate the fugacity of the compounds in gas phase. It is assumed that the gas phase is water and promoter free and the organic compounds do not have considerable effects on water activity in liquid phase. The results of this model are finally compared to existing experimental data from the literature. Acceptable agreement is found between the model predictions and the investigated experimental data.

Keywords: Gas hydrate, Thermodynamic model, Van der Waals – Platteeuw theory, Phase equilibria, Water-Insoluble Organic Compounds

Research Highlights

- A thermodynamic model has been developed for predicting P–T phase diagrams of binary clathrate hydrates.
- The binary clathrate hydrates include methane, CO₂ or H₂S + various heavy hydrate formers.
- The model is based on the solid solution theory of van der Waals – Platteeuw combined with the PR-EoS.



1. Introduction

Clathrate hydrates are inclusion compounds, which are composed of H_2O and guest species [1]. They are stabilized by the guest molecules enclathrated in the hydrogen-bonded water cages. At relatively high pressures and low temperatures, water molecules form various crystalline structures generally depending on the size and shape of the guest molecule(s) [1]. Three common structures, structures I (sI), II (sII), and H (sH) are known to form, as a function of the size and shape of the guest molecules [1]. sI and sII contain two types of cavities (small and large) while sH contains three types of cavities (small, medium, and large) [1].

Recently, novel technologies utilizing gas hydrates have been proposed. These clathrate structures may be used as media for the storage and transportation of natural gas and even hydrogen [1-3]. Therefore, various experimental and theoretical investigations have been done so far to determine the phase equilibria of corresponding systems and the capacity of gas storage in hydrate structures.

Mooijer-van den Heuvel et al. [4] studied the formation of sII gas hydrates of cyclic organic compounds like tetrahydropyran (THP) and cyclobutanone (CB). Østergaard et al. [5] investigated the effects of cyclopentane, cyclohexane, neopentane, isopentane, methylcyclopentane, and methylcyclohexane at various concentrations on the phase behavior of methane clathrate hydrates. They concluded that sII clathrate hydrates can be a stable structure for the treated systems. They also found that these heavy hydrocarbons can have significant effects on the gas hydrate phase boundary of petroleum systems at high concentrations. Sun and coworkers [6] reported four-phase liquid water (L) + hydrate (H) + liquid hydrocarbon (LH) + vapor (V) equilibrium data for sII hydrates of methane + cyclohexane or cyclopentane systems. It was concluded that the hydrate dissociation pressure of the methane + cyclohexane or cyclopentane systems are lower than that of the system containing clathrate hydrate of pure methane at a given temperature.

Three sets of experimental data for the methane + cyclohexane, nitrogen + cyclohexane, and methane + nitrogen + cyclohexane over wide ranges of temperatures were reported by Tohidi et al. [7]. In addition, the solid solution theory of van der waals and Platteeuw [8], as implemented by Parrish and Prausnitz [9], was applied for thermodynamic modeling of the investigated systems. Later, Tohidi and coworkers [10] reported the hydrate dissociation data for the nitrogen and/or methane + cyclopentane/neopentane systems. The subsequent results showed that both of the mentioned heavy hydrocarbons are strong hydrate promoters. Mohammadi and Richon [11] reported experimental dissociation data for clathrate hydrates of the carbon dioxide + methyl cyclopentane, methyl cyclohexane, cyclopentane, or cyclohexane.

The phase behaviors of sH clathrate hydrate of 1,1-dimethylcyclohexane and 2,2-dimethylpentane stabilized by methane molecules have been studied by Hara et al. [12] and Kozaki and coworkers [13] in order to search for an effective additive for natural gas transportation system applying gas hydrate formation technology. Kang et al. [14] measured the four phase (sH hydrate + water-rich liquid + hydrocarbon-rich liquid + vapor) equilibria. They also provided a thermodynamic model for representation/prediction of the obtained data. However, one the most widely-used thermodynamic model for calculation/estimation of the phase equilibria of the aforementioned system is that proposed by Mehta and Sloan [15,16]. Recently, Eslamimanesh et al. [17,18] have presented two different approaches on the basis of the group contribution model and Quantitative Structure Property Relationship (QSPR) to



determine the phase behavior of the systems containing water-insoluble hydrocarbon promoters clathrate hydrates.

A concise literature survey indicates that almost all of the literature available models for calculation/estimation of the hydrate dissociation conditions of the systems including water-insoluble heavy hydrocarbons (except the two latter ones [17,18]) have been developed using the Holder model [19] as a basis of their theory. Therefore, the reference parameters for sII or sH clathrate hydrates are required for this purpose. Moreover, they have been generally developed for the systems containing methane as the help gas. In the present work, we propose a thermodynamic model for representation/prediction of clathrate hydrate (sII or sH) dissociation pressure for the methane, carbon dioxide, or hydrogen sulfide + water-insoluble heavy hydrocarbon systems.

2. Thermodynamic Model

2.1. Developing the equations

The equality of fugacity of water in liquid phase to that in hydrate phase at equilibrium has been taken into account for phase equilibrium calculations as follows:

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

where f is fugacity, subscript W refers to water and superscripts L and H refer to liquid water phase and hydrate phase, respectively. The fugacity of water in the hydrate phase is related to the chemical potential difference of water in the filled and empty hydrate lattice ($\Delta\mu_w^{MTH}$) using the following expression [20-23]:

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

In Eq. 2, the superscript MT represents the empty hydrate, R and T are universal gas constant and temperature, respectively. The fugacity of the hypothetical empty hydrate lattice, f_w^{MT} , is given by the following equation [20-23]:

$$f_w^{MT} = P_w^{MT} \phi_w^{MT} \exp\left(\int_{P_w^{MT}}^P \left(\frac{v_w^{MT}}{RT} - \frac{1}{P}\right) dP\right) \quad (3)$$

where P stands for pressure, ϕ and v are fugacity coefficient and molar volume, respectively, P_w^{MT} is the vapor pressure of water in empty hydrate lattice. The fugacity coefficient of water in empty hydrate, ϕ_w^{MT} , is taken to be unity because the vapor pressure of water is low. The partial molar volume of water in the empty hydrate lattice, v_w^{MT} in the Poynting correction term of the preceding equation is assumed to be pressure independent. Therefore, Eq. 3 can be rewritten in the following from [20-23]:

$$f_w^{MT} = P_w^{MT} \exp\left(\frac{v_w^{MT}(P - P_w^{MT})}{RT}\right) \quad (4)$$

In Eq. 2, $\Delta\mu_w^{MTH}$ is calculated using the van der Waals and Platteeuw model [1,8,19-22]:

$$\frac{\mu_w^H - \mu_w^{MT}}{RT} = \left[\sum_i v_i \ln \left(1 - \sum_k Y_{ki} \right) \right] \quad (5)$$

where v_i is the number of cages of type i per water molecule in a unit hydrate cell. Y_{ki} (the fractional occupancy of the hydrate cavity i by guest molecule of type k) is expressed using the following equation [1,8,19-22]:

$$Y_{ki} = \frac{C_{ki} f_k}{1 + \sum_k C_{ki} f_k} \quad (6)$$

where f_k is the fugacity of the hydrate former and C_{ki} stands for Langmuir constant. Substituting Eq. 6 in Eq. 5 results in [1,8,19-23]:

$$\frac{\mu_w^H - \mu_w^{M,T}}{RT} = - \left[\sum_i v_i \ln \left(1 + \sum_k C_{ij} f_j \right) \right] = \sum_i \ln \left(1 + C_{ij} f_j \right)^{-v_i} \quad (7)$$

It is assumed that, small and medium cavities are occupied by gases and large cavities are occupied by the heavy hydrocarbon hydrate formers. As a consequence, Eq. 7 can be rewritten as follows for sII clathrate hydrate:

$$\frac{\mu_w^H - \mu_w^{M,T}}{RT} = \ln \left[\left(1 + C_{small} f_g^V \right)^{-v_{small}} \left(1 + C_{large} f_{oc}^L \right)^{-v_{large}} \right] \quad (8)$$

and for sH clathrate hydrate:

$$\frac{\mu_w^H - \mu_w^{M,T}}{RT} = \ln \left[\left(1 + C_{small} f_{HC}^V \right)^{-v_{small}} \times \left(1 + C_{medium} f_{HC}^V \right)^{-v_{medium}} \times \left(1 + C_{large} f_{oc}^L \right)^{-v_{large}} \right] \quad (9)$$

where the superscripts V and L represent gas and liquid phases, g and oc represent gas and organic components (heavy hydrocarbon hydrate former), respectively.

In eq.1, the fugacity of water in the aqueous phase (f_w^L) can be calculated using the following equation:

$$f_w^L = x_w^L \gamma_w P_w^{s,a,L} \exp \left(\frac{v_w^L (P - P_w^{s,a,L})}{RT} \right) \quad (10)$$

where x_w^L , γ_w , $P_w^{s,a}$ and v_w^L represent mole fraction of water in the aqueous phase, activity coefficient of water, water vapor pressure, and molar volume of liquid water, respectively. Activity coefficient of water is assumed to be unity because non-solubility of promoters in water and no interactions between the dissolved help gas and water in the liquid phase. Furthermore, x_w^L can be obtained using the following equation:

$$x_w^L = 1 - x_g^L \quad (11)$$

To calculate solubility of methane in the aqueous phase (x_g^L), the Krichevsky-Kasarnovsky equation can be applied [24]:

$$x_g^L = \frac{f_g^G}{H_{g-w} \exp\left(\frac{v_g^\infty}{RT} (P - P_W^{sat})\right)} \quad (12)$$

where H_{g-w} is Henry's constant of gases in water, and the superscript ∞ represents infinite dilution condition. By substituting the above equations in Eq.1, the following expression is finally obtained:

For clathrate hydrate sII:

$$\left[\frac{P_w^M \exp\left(\frac{v_w^M (P - P_w^M)}{RT}\right)}{x_w^L P_w^{sat} \exp\left(\frac{v_w^L (P - P_w^{sat})}{RT}\right)} \right] \times \left[(1 + C_{small} f_g^L)^{-V_{small}} \times (1 + C_{large} f_{oc}^L)^{-V_{large}} \right] - 1 = 0 \quad (13)$$

For clathrate hydrate sH:

$$\left[\frac{P_w^M \exp\left(\frac{v_w^M (P - P_w^M)}{RT}\right)}{x_w^L P_w^{sat} \exp\left(\frac{v_w^L (P - P_w^{sat})}{RT}\right)} \right] \times \left[(1 + C_{small} f_{HC}^L)^{-V_{small}} \times (1 + C_{medium} f_{HC}^L)^{-V_{medium}} \times (1 + C_{large} f_{oc}^L)^{-V_{large}} \right] - 1 = 0 \quad (14)$$

The hydrate dissociation pressure (P) at a given temperature (T) is obtained by solving the latter equations.

2.2. Model parameters

The values of the Langmuir constants are calculated using the following expression [25] with the parameters (a_{ij} and b_{ij}) reported in Table 1:

$$C_{ij} = \frac{a_{ij}}{T} \exp\left(\frac{b_{ij}}{T}\right) \quad (15)$$

Table 1. The values of a_{ij} and b_{ij} parameters in Eq. 15 for gases and organic compounds, which form clathrate hydrate structure II [25].

Hydrate former	Small cavity		Large cavity	
	$a_{ij} (\times 10^3 \text{ K.bar}^{-1})$	$b_{ij} (\text{K})$	$a_{ij} (\times 10^3 \text{ K.bar}^{-1})$	$b_{ij} (\text{K})$
CH ₄	0.2207	3453	0	0
CO ₂	0.0845	3615	0	0
CH*	0	0	0.3403	6045
CB*	0	0	1.2397	6440
CP*	0	0	2.1559	5950
THP*	0	0	1.9073	6200

* Adjusted values.

Because of the orders of magnitude of small and medium cavities sizes, their Langmuir constants parameter values in Eq. 15 have been assumed to be equal. In addition, the optimal values of the corresponding parameters for large cavities of sII clathrate hydrate and those of small and medium cavities of sH have been obtained using tuning against the existing phase equilibrium data. The following relation is applied for calculation of the Langmuir constants for large cavities in sH clathrate hydrate [26] and in table 2 parameters of Eq. 15 and 16 for gases and organic compounds are shown:

$$C_{i,j} = \frac{a_{i,j}}{T} \exp\left(b_{i,j} \left(\frac{1}{T} - \frac{1}{273.15}\right)\right) \quad (16)$$

Table 2. The values of a_{ij} and b_{ij} parameters in Eq. 15 and 16 for gases and organic compounds, which form clathrate hydrate structure II [26].

Hydrate former	Small and medium cavities		Large cavity	
	a_{ij} (K.bar ⁻¹)	b_{ij} (K)	a_{ij} (K.bar ⁻¹)	b_{ij} (K)
CH ₄ *	0.1619	1568.6076	0	0
CO ₂ *	0.09565	1730.34	0	0
H ₂ S*	0.01505	3128.8239	0	0
MCH	0	0	9681	3604
2,3-DMB	0	0	940	3608
MCP	0	0	1584	4024
CHP	0	0	41840	5050
1,1-DMCH	0	0	74330	4089
NH	0	0	1794	3175
CO	0	0	61010	4135

* Adjusted values.

The saturated vapor pressure of water in empty hydrate (P_w^*) is calculated using the method of Dharmawardhana *et al.* for structures I and II [27]:

For structure I:

$$P_w^* = 0.1 \exp\left(17.44 - \frac{6003.9}{T}\right) \quad (17)$$

For structure II:



$$P_w^{M,T} = 0.1 \exp\left(17.332 - \frac{6017.6}{T}\right) \quad (18)$$

Additionally, the following equation is obtained for calculation of $P_w^{M,T}$ of structure H clathrate hydrate through adjusting of the parameters against the corresponding phase equilibrium data:

$$P_w^{M,T} = 0.1 \exp\left(18.4014 - \frac{6284.32}{T}\right) \quad (19)$$

where the units of $P_w^{M,T}$ and T are, respectively, MPa and K.

$v_w^{M,T}$ for structures I and II are obtained using the following expressions [20]:

$$v_w^{M,T} [sI] = (11.835 + 2.217 \times 10^{-5} T + 2.242 \times 10^{-6} T^2) \frac{10^{-30} N_A}{N_w^{M,T}} - 8.006 \times 10^{-9} P + 5.448 \times 10^{-12} P^2 \quad (20)$$

$$v_w^{M,T} [sII] = (17.13 + 2.249 \times 10^{-4} T + 2.013 \times 10^{-6} T^2 + 1.009 \times 10^{-9} T^3) \times \frac{10^{-30} N_A}{N_w^{M,T}} - 8.006 \times 10^{-9} P + 5.448 \times 10^{-12} P^2 \quad (21)$$

and it is calculated using the following equation for structure H [28]:

$$v_w^{M,T} [sH] = (24.2126 \exp(3.57549 \times 10^{-4} (T - 273.15)) + 6.29439 \times 10^{-7} (T - 273.150)^2 - 3 \times 10^{-7} (P - 0)) \quad (22)$$

where N_A is Avogadro's number and $N_w^{M,T}$ stands for the number of water molecules per hydrate cell. The unit of pressure in Eqs. 20 through 22 is MPa, and the unit of temperature is K. The following equations are applied to evaluate the molar volume of the help gas at infinite dilution [29]:

$$\left(\frac{P_{c,i} v_i^\infty}{RT_{c,i}}\right) = 0.095 + 2.35 \frac{TP_{c,i}}{c T_{c,i}} \quad (23)$$

$$c = \frac{\Delta U_w}{v_w^{s,i}} \quad \Delta U_w = \Delta H_w - RT \quad (24)$$

$$v_w^{s,i} = \frac{RT_c}{P_c} (0.2905 - 0.08775 \cdot \omega)^{(1+(1-T_c)^{2/7})} \quad (25)$$

Moreover, the following quantities are applied to evaluate the number of cages of type i per water molecule in a unit hydrate cell [1]:

for sI: $v_{small}=1/23$, $v_{large}=3/23$

for sII: $v_{small}=2/17$, $v_{large}=1/17$

for sH : $v_{small}=3/34$, $v_{medium}=2/34$ and $v_{large}=1/34$

Fugacity of gases in the gas phase is calculated using the Peng-Robinson equation of state (PR-EoS) [30]. Due to the low concentrations of water and hydrate promoters in the gas

phase, it is assumed that the it consists of pure gases (help gases) [31,32]. Table 3 summarizes the rest of parameters required in this model.

Table 3. The required parameters of the developed model [20, 33, 34, 35].

Parameter	Expression	Units	Ref.*
v_w^L	$-10.9241 + 2.5 \times 10^{-4} (T - 273.15) - 3.532 \times 10^{-4} (P - 0.101325) + 1.559 \times 10^{-7} (P - 0.101325)^2$	cm ³ /mol and MPa, K	[34,35]
$P_w^{s,a}$	$10^{-6} \exp(7.6537 - \frac{5500.9332}{T} + 4.1539 \ln(T) - 0.0161277 \times T)$	MPa, K	[20,33]
H_{CH_4-w}	$0.1 \times (10^{14.77885763/T + 5.22951206} + 0.0186\pi^5)$	MPa, K	[35]
H_{CO_2-w}	$\exp(159.868 - \frac{8742.426}{T} - 21.6712 \times \ln(T) - 0.0011 \times T)$	MPa, K	[20]
H_{H_2S-w}	$\exp(149.5510 - \frac{8227.328}{T} - 20.2327 \times \ln(T) - 0.00129 \times T)$	MPa, K	[20]

* References of the equations.

3. Results and Discussion

The representations/predictions of the hydrate dissociation conditions of methane + heavy hydrocarbon hydrate former systems including cyclohexane (CH), cyclopentane (CP), cyclobutane (CB), or tetrahydropyran (THP) are shown in Figure 1.

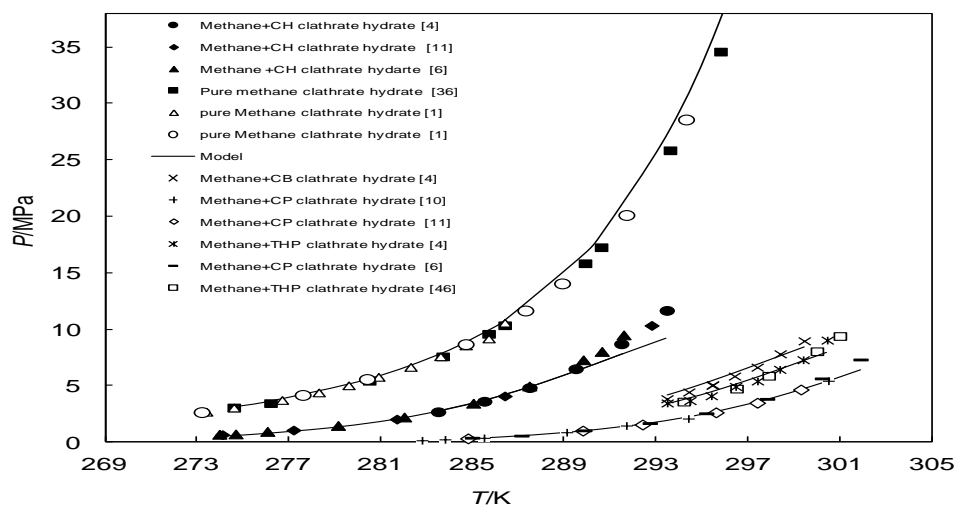


Fig 1. Experimental [1, 4, 6, 10, 11, 36, 46] and represented/predicted dissociation conditions of CH₄ clathrate hydrates in the absence/presence of CH, CB, CP or THP heavy hydrocarbon hydrate formers.

Acceptable agreement between the model results and existing experimental phase equilibrium data is observed. It can be seen that the aforementioned heavy hydrate formers contribute to promotion effects that can change hydrate dissociation pressure values to lower ones and the temperature values to higher ones. In other words, these promoters shift the phase boundary of the investigated systems to the right. For a comparison purpose between the promotion effects of the studied heavy hydrocarbon hydrate formers, the corresponding phase behavior calculations along with the experimental data have been shown in Figure 1.

The determined hydrate dissociation conditions for the carbon dioxide + (CH, CP, CB, or THP) systems are shown in Figure 2 along with the selected experimental data from the literature. Reasonable deviations of the model results from the experimental values are observed. In addition, it is interpreted that these hydrate promoters show the same promotion effects priority with respect to the related phase equilibria of methane hydrates (Figure 1).

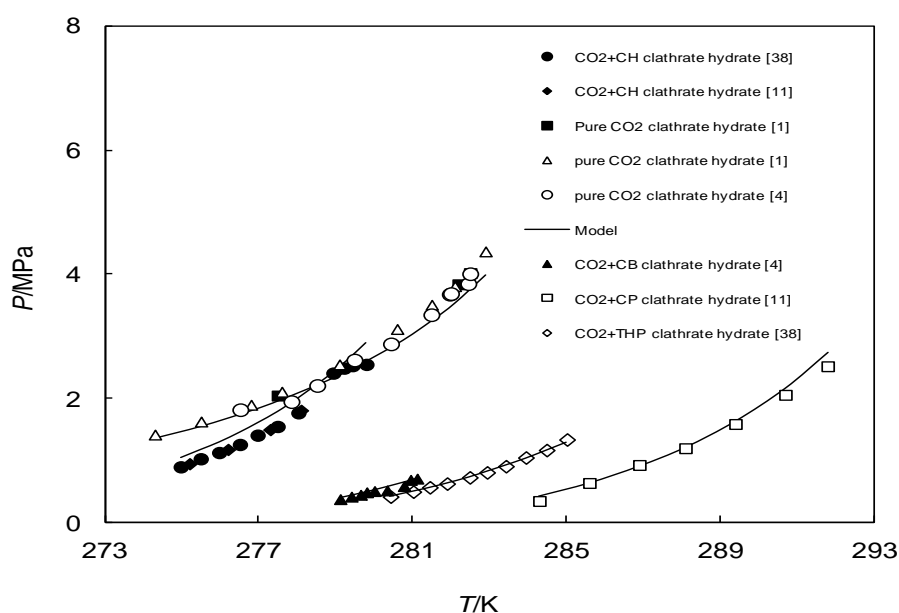


Fig 2. Experimental [1, 4, 11, 38] and represented/predicted dissociation conditions of CO₂ clathrate hydrates in the absence/presence of CH, CB, CP or THP heavy hydrocarbon hydrate formers.

However, cyclohexane exhibits negligible effects on clathrate hydrate phase behavior of the CO₂ containing systems compared to the other hydrate promoters. It is also assumed that the later systems form clathrate hydrates of structure II. Moreover, there exists intercross of the CO₂ hydrate dissociation conditions curve and CO₂+CH hydrate dissociation conditions curve indicating CH shows inhibition effect rather than promotion effect after the intersection [4]. Figure 3 reports the capability of the proposed model to calculate/estimate hydrate dissociation conditions for methane + methylcyclohexane (MCH), methylcyclopentane (MCP), cycloheptane (CHP), dimethylcyclohexane (DMCH), neohexane (NH) or cuclooctane (CO) systems. The highest promotions effects are detected for DMCH, NH, MCH, CHP, CO and MCP, respectively. Negligible promotion effects of MCH, CHP, or CO on the hydrate dissociation conditions of carbon dioxide are shown in Figure 4. These low effects can also be identified using the developed thermodynamic model.

Beside the acceptable accuracy of the presented thermodynamic model to represent/predict the phase behaviors of the studied systems, it is worth it to know that there is no need to use the clathrate hydrates reference parameters as applied in the previous models [e.g., 16,47]. In addition, the calculation procedure of the developed model is generally easy and straightforward.

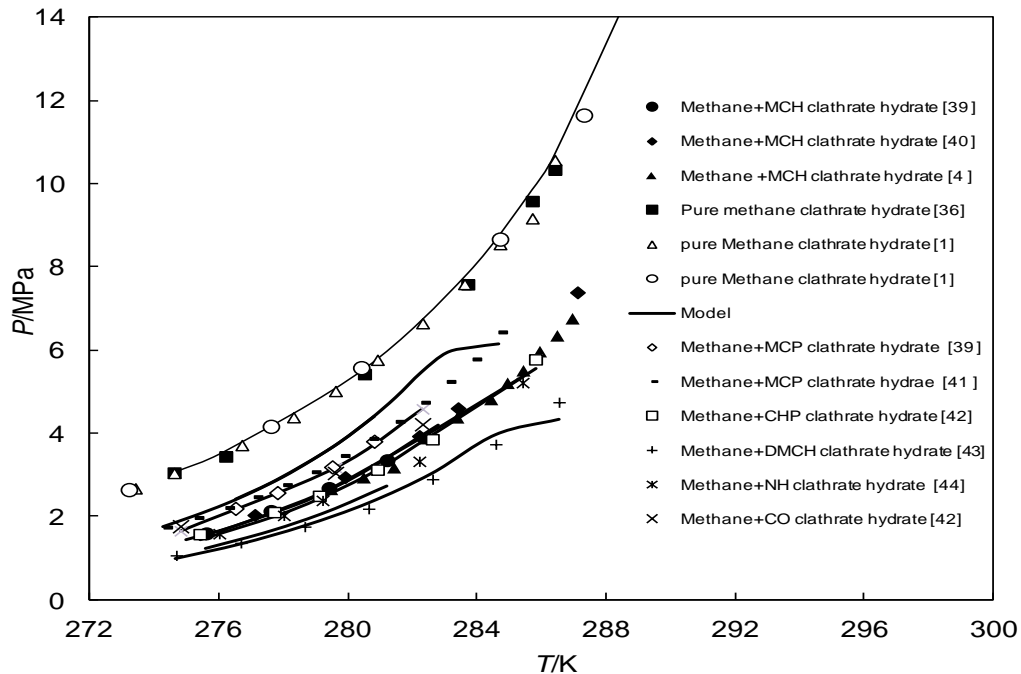


Fig 3. Experimental [1, 4, 36, 39-44] and represented/predicted dissociation conditions of CH₄ clathrate hydrates in the absence/presence of MCH, MCP, CHP, DMCH, NH or CO heavy hydrocarbon hydrate formers. There exists an inflexion and the curve become flat for methane + MCP and methane + DMCH systems at high pressure and temperature. This is likely a numerical problem.

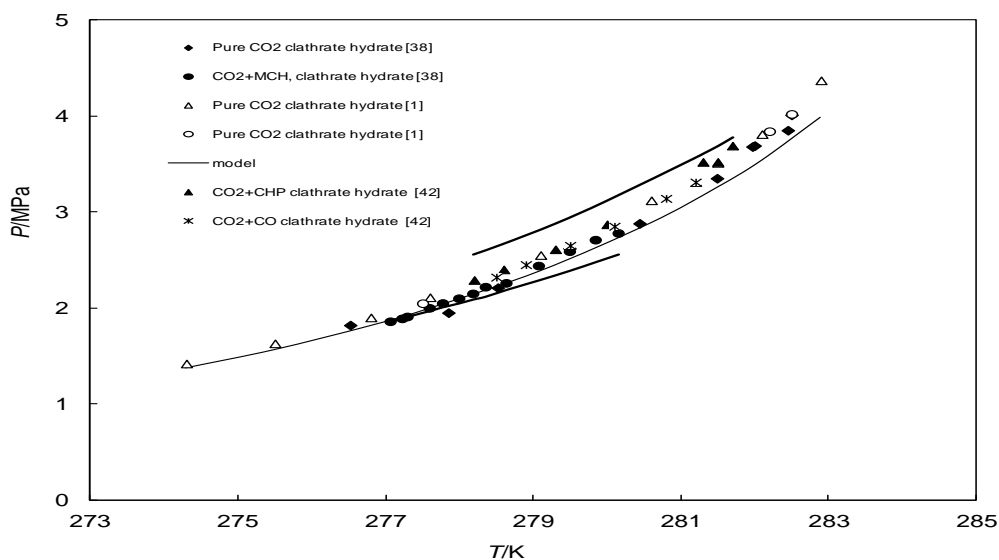


Fig 4. Experimental [1, 38, 42] and represented/predicted dissociation conditions of CO₂ clathrate hydrates in the absence/presence of MCH, CHP or CO heavy hydrocarbon hydrate formers.



4. Conclusions

In this work, we proposed a thermodynamic model for representing/predicting hydrate phase boundaries of methane, carbon dioxide, or hydrogen sulfide systems in the presence of heavy hydrocarbon hydrate formers. The effects of CH, CB, CP, THP, MCH, MCP, CHP, DMCH, NH or CO on the corresponding phase behaviors were investigated to present a comprehensive study. The solid solution theory of vdW-P [8] was applied to deal with the hydrate phase while the PR-EoS [30] was used to determine the fugacity of hydrate formers in the gas and liquid phase.

Acceptable agreement of the model results with the existing experimental hydrate dissociation conditions from the literature demonstrates its reliability and accuracy. It was also found that CH (which form structure II) and all of structure H hydrate formers show slight effects on the phase behavior of clathrate hydrate of CO₂. The advantages of the model compared to the available ones in the literature can be stated as: no requirement of the clathrate hydrates reference parameters; easy-to-use calculation algorithm; extension to CO₂ and H₂S containing systems.

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