Prediction of Gas Hydrate Formation in Industries

Alireza Bozorgian[1], Zahra Arab Aboosadi*[1], Abolfazl Mohammadi[2], Bizhan Honarvar[1], Alireza Azimi[3]

[1]*Department of Chemical Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran*

[2]*Department of Chemical Engineering, University of Bojnord, Bojnord, Iran*

[3]*Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran*

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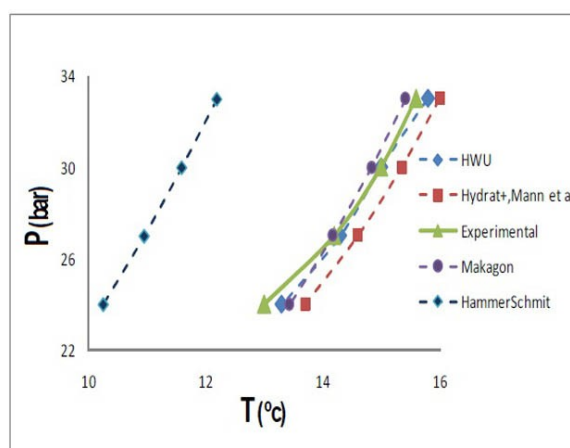
A B S T R A C T

Natural gas and crude oil in natural underground reservoirs are in contact with water. Stability of these compounds at the presence of both components and complete dependence on the host molecules by forming holes in their guest molecules are replaced. There are many gases such as methane, ethane, propane, carbon dioxide, hydrogen sulphides that can play the role of guest molecules. The natural gas hydrate formation in different sectors of the oil and gas industry in downstream processes causes the production to stop or decrease. Therefore, the need to know the causes and conditions of hydrate formation is strongly felt. In this study, Van der Waals and Platteeuw model was used to predict hydrate formation conditions. The prediction of hydrate formation conditions needs equilibrium fugacity of gaseous components, and for the equilibrium molar component of water. Also Van der Waals and Platteeuw model was used to predict hydrate formation conditions. The prediction of the hydrate formation conditions needs equilibrium fugacity of gaseous components and the equilibrium molar component of water.

Introduction

Natural gas and crude oil in natural underground reservoirs are in contact with water. Stability of these compounds at the presence of both components and complete dependence on the host molecules by forming holes in their guest molecules are replaced. There are many gases such as methane, ethane, propane, carbon dioxide, hydrogen sulphide that can play the role of guest molecules. **Fig. 1** penetration of gas into the hollow cavities which ultimately can lead to formation of hydrate crystals can be seen.

The three necessary conditions for the hydrate formation are as following.

1- Water as liquid or ice phase

2- The presence of small gas molecules such as Methane, Ethane, Propane and Argon

3. High pressures and low temperatures

Various methods have been used to predict the formation conditions of hydrate crystal. These methods can be divided into two categories:

➢ Experimental methods
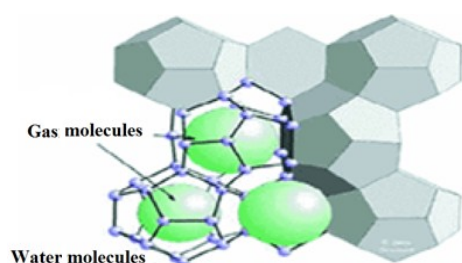➢ Thermodynamic models

Figure 1. Host molecules (water) and guests (Gas) [1-3].

In this study, Van der Waals and Platteeuw model was used to predict hydrate formation conditions. The prediction of the hydrate formation conditions needs equilibrium fugacity of gaseous components and the equilibrium molar component of water. A cumulative state equation was used. Water molecules create a network-like structure due to their strong hydrogen bonds by developing holes. The gas molecules (guest) due to interaction between the guest and host molecules that create a stable structure. Various methods have been devised to predict hydrate crystal formation conditions (or decompose). The methods can be divided into two categories:

1- Experimental methods

2- Thermodynamic models.

Experimental Methods

Experimental methods (that are mentioned below) are mainly used in the industry, but their usage has been decreased over the last decade.

➢ Using relative gas weight curves;
➢ Diffraction of distribution coefficients;
➢ Experimental relationship of Stronger thermodynamic models;

Many studies have been conducted on predicting the hydrate crystal formation conditions that are based on the science of chemical thermodynamics. These models all have similar assumptions. Unlike the experimental models, thermodynamic models have stronger theoretical foundations. Hence can

incorporate intermolecular effects into the model. For equilibrium calculations we need to calculate quantities such as fugacity and fugacity coefficient. We know that

$$f_{ij} = x_{ij}\, \varphi_{ij} P \qquad (1)$$

Where f_{ij} is fugacity and φ_{ij} is the fugacity coefficient part i in the phase P, and j is the pressure of the system. For the gas and liquid phase, a same state equation can be used, and for the solid phase of the hydrate, Van der Waals and Platteeuw model can be implemented [2, 3]. In this study, a new cumulative equation for gas and liquid phases was used, and for the hydrate phase the Van der Waals and Platteeuw model was employed.

Van der Waals and Platteeuw Model

The basis of the existing thermodynamic models in the field of predicting the hydrate formation conditions such as Van der Waals and Platteeuw model is based on classical statistical thermodynamics. Parrish and Prausnitz developed these models in 1972, and later it was simplified by Holder, Carbin et al. This has enabled the model to have acceptable predictions for hydrate formation conditions. The Van der Waals-Plateau uses to make corrections [4-7]. The model is based on the assumption that there is a similarity between the hydrate phase formation and isothermal absorption. The hypothesis of the model is as following.

1- Each hole in the crystal lattice can accept a molecule as a guest.
2- Ideal gas splitting is applicable to guest molecules.

3- The intermolecular forces of the guest and the water molecules are expressed by a potential function and each spherical cavity is considered.
4- The forces between the guest gas molecules in the network are ignored.
5- There is only force between the gas molecule in the cavity and the water molecules that surround it.
6- The free energy distribution of water molecules is independent of how the crystal lattice is occupied by the molecules. Thermodynamically, hydrates form when the hydrate state is more energy-intensive than the non-hydrate state (liquid or ice water). The transition from non-hydrate to hydrate is divided into two stages:

• Liquid water or ice (α) → empty hydrate network (β)

• Empty carbohydrate network β→ Filled carbohydrate network (H)

α, β, and H are to specify each of the three states. The β state is a hypothetical state and is only used in hydrate calculations.

Among the α or H modes, the most favourable state is the one with the lowest energy level. The difference between the chemical potential of water in the H-hydrate network state and the liquid or solid state of water, α, is described below [8-11].

$$\mu_w^H - \mu_w^\alpha = (\mu_w^H - \mu_w^\beta) + (\mu_w^\beta - \mu_w^\alpha) \qquad (2)$$

At equilibrium, the chemical potential of water in the hydrate phase is equal to the chemical potential of water in the liquid phase. So we can write:

$$\underset{w}{\mu} H = \underset{w}{\mu} \alpha \tag{3}$$

$$(\mu_w^\beta - \mu_w^H) = (\mu_w^\beta - \mu_w^\alpha) \tag{4}$$

$$\Delta\mu_w^{\beta-H} = \Delta\mu_w^{\beta-\alpha} \tag{5}$$

Based on the WP model, the water fugacity in the hydrate phase is obtained from Equation 6.

$$f_w^H = f_w^\beta \, exp[-\frac{\Delta\mu_w^{\beta-H}}{RT}] \tag{6}$$

Also, u_m^{B-H} shows the stabilizing effect of adsorption of gas molecules in the hydrate network and is calculated using the Equation 7.

$$\Delta\mu_w^{\beta-H} = \mu_w^\beta - \mu_w^H = RT \sum_{m=1}^{Ncavity} V_m (\ln (1+\sum_{j=1}^{NH} C_{jm} \, f_j)) \tag{7}$$

The parameters of these two relationships are:

> Water fugacity in the hydrate phase
> Fugacity of water molecules if are filled in an hydrate empty network
> Chemical potential of water molecules if are filled in an hydrate empty network
> Chemical potential of water molecules in hydrate phase
> The number of m-type holes in each water molecule in the hydrate crystalline network
> a number of components that can enter the hydrate phase

The type of cavities in the hydrate unit network is respectively 2, 2, and 3 for structures I, II and H. The Langmuir absorption coefficient of component j in the m type cavity indicates the interaction between the water and gas molecules in the cavity [12]. The value of the occupied fraction of m type cavity by the gas component i is represented by θ_{im}, which is calculated using Langmuir absorption theory:

$$\theta_{im} = \frac{C_{im} f_i}{1+\sum_{j=1}^{NH} c_{jm} f_j} \tag{8}$$

Van der Waals and Platteeuw used the Lennard-Jones-Duncan theory and showed that the Langmuir coefficients are derived from the relation [13-16]

$$C_{jm} = \frac{4\pi}{KT} \int_0^R exp[-\frac{\omega(r)}{KT}]r^2 \, dr \tag{9}$$

Where we have:

K: Fixed Boltzmann

W (r): Spherical potential function

r: The radial distance from the centre of the cavity to the center of the guest molecule

R: The radial distance from the centre of the cavity to the center of the guest molecule

A: The radius of the guest molecule [17-20]. As can be seen, the Langmuir coefficient is merely a function of temperature. In this model, we use the k energy potential function for two molecules:

$$\Gamma(r) = \begin{cases} 4\varepsilon[\left(\frac{\sigma}{r-2\alpha}\right)^{12} - \left(\frac{\sigma}{r-2\alpha}\right)^6] & r < (a+a_w) \\ \infty & \\ & r < (a+a_w) \end{cases} \tag{10}$$

Where in

$\Gamma(r)$: Energy potential function

σ: Impact diameter (a value of r that equals the potential value of zero)

a: Radius of the Guest Molecule Radius in Hard Sphere Theory

ε: Depth of Energy Well (Energy Characteristic)

Equation expresses the interaction between gas molecules and water molecules in the cavity. Researchers using the above relationships have obtained the following relation for w (r) [21].

$$\omega(r) = 2Z\varepsilon[\frac{\sigma^{12}}{R^{11}r}(\sigma^{10} - \frac{a}{R}\sigma^{11}) - \frac{\sigma^6}{R^5 r}(\sigma^4 + \frac{a}{R}\sigma^5)] \qquad (11)$$

Where Z is the neighbourhood number of each cavity (the number of oxygen molecules in per cavity) and R is the mean radius of the cavity the average radius of the cavity $^N\delta$ is obtained from the relationship [13].

$$\delta^N = \frac{1}{N}[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-N}] \qquad (12)$$

Where N can take values of 10, 5, 4, and 11, and a is the rigid radius of the sphere.

Some researchers have proposed the following empirical relationship to obtain

$$C_{im}:C_{im} = \frac{A_{im}}{T} exp(\frac{B_{im}}{T}) \qquad (13)$$

i: Index for Components

m: index for the cavity

Where A and B are constants that are dependent on the type of gas and the type of hole.

Theory of Cumulative State Equation

Anderko (1991) [22] has reported that, in systems containing a cumulative component, the state equation can consist of two separate components, the chemical part and the physical part. For the first time, Lambert (1953) [23] divided the second virial coefficient into two physical and chemical. To find the corresponding state of this view, the equation of the disrupted viral state after the second sentence is written as follows.

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} \qquad (14)$$

Where B is the second viral coefficient and according to B we have two physical and chemical parts:

$$Z = 1 + \frac{B}{v} = 1 + \frac{B^{ch} + B^{ph}}{v} = (1 + \frac{B^{ch}}{v}) + (1 + \frac{B^{ph}}{v}) - 1 = Z^{ch} + Z^{ph} - 1 \qquad (15)$$

The Z^{ph} portion does not react with the equation of state of the monomeric species, and the Z^{ch} equals with the inverse mean cumulative number, χ, which is defined as:

$$\chi = \frac{n_0}{n} = \frac{1}{Z^{ch}} \qquad (16)$$

The mean cumulative number, χ, is the number of monomeric moles per a cumulative mole. n_0 is the number of monomeric moles defined as cumulative moles in non-cumulative state and n is the total number of moles in cumulative state. Thus the Z^{ch} portion is derived only from the accumulation and depends only on the accumulation constant and not on the parameters that explain the physical interactions. In this work we use the cumulative equation presented by Vafaie *et al.* [24-30].

$$Z^{ch} = \frac{1}{[1+(K/P^0)(RT/v)]} \qquad (17)$$

$$LnK = [\Delta H^0(T_0) + \Delta C_p^0]/RT + 1/R[\Delta S^0(T_0) - \Delta C_p^0 - \Delta C_p^0 \ln T_0] + (\Delta C_p^0/R)\ln T \qquad (18)$$

Results of Prediction of Hydrate Formation Conditions for Water System

Fig. 2 demonstrates the equilibrium curve of the hydrate formation conditions for CO_2 using the above software. **Fig. 2** reveals a comparison of the two models presented in this paper.
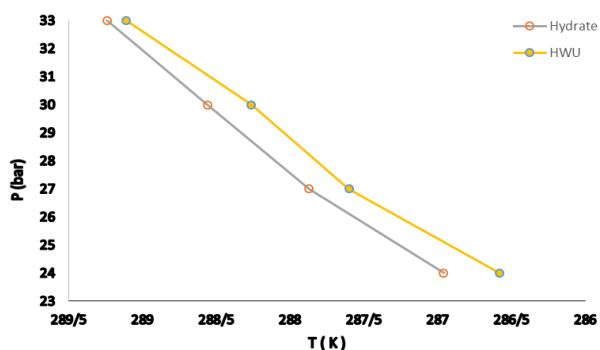

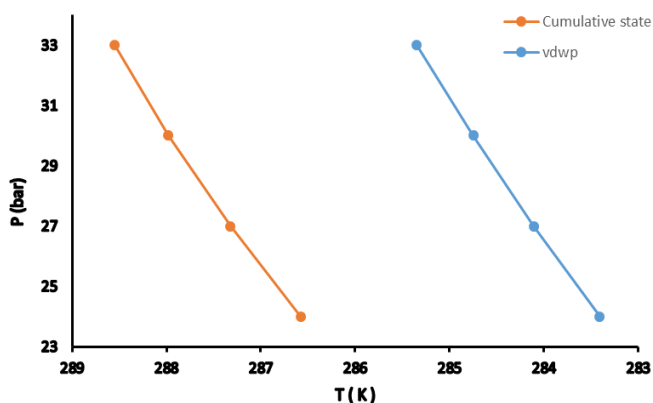**Fig. 2.** Prediction graph of equilibrium conditions of hydrate formation by software.

Fig. 2. Prediction graph of equilibrium conditions of hydrate formation by equations Van der Waals and Platteeuw and Cumulative state.
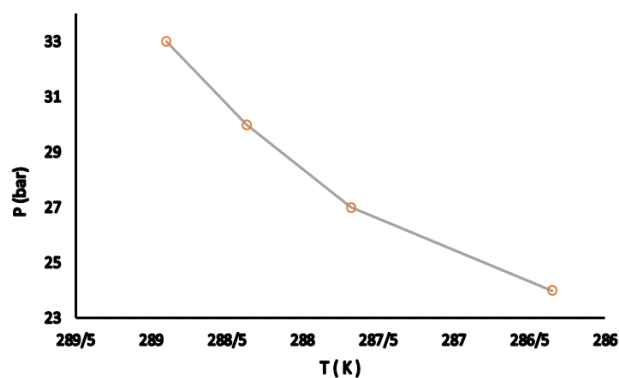

Fig. 3. The results of experimental.

To obtain the equilibrium graph of the formation of CO_2 gas hydrates at different equilibrium pressures, the experimental results are depicted in **Fig. 3.**

Results and Discussion

It seems that the use of a cumulative term in the equation of state of prediction of the fugacity of the hydrate constituent's gas well predicted the hydrate formation pressures. So that, comparison of the thermodynamic conditions of the hydrate formation for CO_2 revealed that, the experimental results are in good agreement with the Hydrate and HWU integration models.
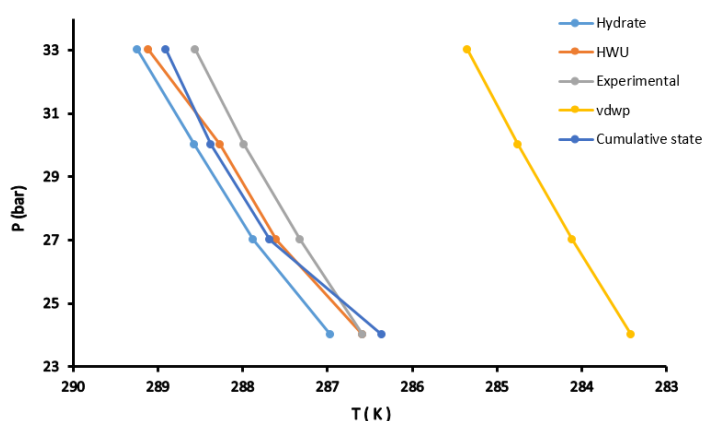

Fig. 4. Diagram of laboratory results with predicted equilibrium points of gas hydrate formation temperature.

Conclusion

The natural gas hydrate formation in different sectors of the oil and gas industry in downstream processes causes the production to stop or decrease. Hence, the need to know the causes and conditions of hydrate formation is strongly felt. In this study, Van der Waals and Platteeuw model was used to predict hydrate formation conditions. The prediction of hydrate formation conditions needs equilibrium fugacity of gaseous components, and for the equilibrium molar component of water.

Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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