Research Article

THE FORMATION OF GAS HYDRATES AND THE EFFECT OF INHIBITIORS ON THEIR FORMATION PROCESS

M. J. Choobineh[1*], M. Abdollahbeigi[2], B. Nasrollahzadeh[3]

[1]Department of Chemical Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran

[2]Department of Chemical Engineering, Faculty of Engineering,   North Tehran Branch, Islamic Azad University, Tehran, Iran

[3]Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

ABSTRACT

Natural gas hydrate is a solid crystalline compound produced by combining water and gas and it is considered as the clathrates. Guest gas molecules are stuck insider the pores of water networks produced by hydrogen bonds between molecules of water. There are different ways to analyze the hydrate formation operating conditions (temperature and pressure) including drawing the logarithm of pressure changes curve in terms of gas temperature which is one of the most common methods. In this case, the curve is straight line that is easy to analyze. The structure of hydrates in water-gas area is kept by molecules of the solution in aqueous phase area. As a result, H_2S and CO_2 accelerate the formation hydrates at high temperatures because they are more soluble in water than most hydrocarbons. The pressure leads to the formation of the network. In the case of pentane and larger molecules, pressure breaks the network and prevents the formation of stable hydrates.

Keywords: hydrates, hydrogen bonding, free water, methane, carbon dioxide.

Author Correspondence, e-mail: choobineh69@gmail.com

1. INTRODUCTION

Natural gas hydrate is a solid crystalline compound produced by combining water and gas and it is considered as the clathrates. Guest gas molecules are stuck insider the pores of water networks produced by hydrogen bonds between molecules of water. An obvious example is the gas molecules of compounds smaller than pentane existing in natural gas such as methane, ethane, propane and carbon dioxide [1]. Gas hydrates can be formed by pure gas or gas mixture including two or more components. Clathrates are considered as a solid solution in which the guest gas molecules of the gases forming the hydrates are in contact with the host network (water). Therefore gas hydrate is considered among the non-stoichiometric solids. There is a strong hydrogen bonding among water molecules in the hydrate structure, while there is no chemical interaction between the guest-host molecules and they are kept besides each other by van der Waals forces. Leatherhose et al studied the effect of some kinetic inhibitors on natural gas hydrate formation process in a series of tests and showed that the formation of hydrate is slowed down in the presence of sodium chloride and polyvinyl caprolactam. Visual observations in these tests showed that the obtained hydrate in the presence of sodium chloride has coarser crystals than hydrate obtained in the presence of PVCap [2]. Also according to Long and Quami model, the reason for the formation of hydrate at low temperatures and high pressures can be explained. By reducing the temperature the kinetic energy of the molecules of the liquid phase is reduced and a greater number of hydrogen bonds are created between the water molecules. The formation of these bonds increases the number of molecular aggregation at the surface. The increased number of these holes means that the number of sites to accept gas molecules to form hydrate per unit area is increased and the chance of trapping gas molecules in one of the holes by random collision increases. Also by increasing the pressure, the number of gas molecules per unit of water surface increases and the possibility of the placement of a gas molecule inside the cavity due to random motion increases and the possibility of hydrate formation will rise. According to leatherhose et al. it can be concluded that the inhibitors or sodium chloride can slow the hydrate formation process down or stop it by reducing the number of holes at the surface or blocking the holes similar to PVCap. To explain the inhabitation mechanism of sodium chloride it is possible to use the similarity of this phenomenon with water

freezing. Pure water starts freezing at zero degree centigrade. For this purpose it is necessary to form molecular aggregation of water by hydrogen bonding. These aggregations are the building blocks of an ice crystal. The sodium chloride is quickly ionized through solution in water and its positive and negative ions are dispersed in the liquid phase. These ions have a high charge density that can establish strong absorptions with polar water molecules [3]. With the establishment of absorption between cations and anions with water molecules, each ion is quickly surrounded by six water molecules. Thus, the presence of cations and anions keeps the water molecules apart from each other to form suitable molecular arrangements for the formation of ice crystals. On the other hand hydration is a highly exothermic process. The released energy breaks some hydrogen bonds formed between water molecules and eliminates molecular aggregations that are already created, the consequences of which is the lower rate and speed of hydrate formation process. This mechanism can be used to explain the effect of sodium chloride on hydrate formation. Accordingly, the level of sodium chloride's inhibition depends on the charge on the ions and free ions' radius. Given the lower number of hydrogen bonds in the aggregations with lower water molecules, less energy is required to break the bonds and absorption to the positive and negative ions, so the small holes are removed earlier. However, higher number of the bonds in aggregations with more molecules requires higher energy to be broken. Therefore, we expect to observe coarser hydrate crystals due to the loss of small holes in the presence of sodium chloride [4].

2. THE PROPOSED HYDRATE FORMATION MECHANISM

A two-stage mechanism of hydrate formation is proposed as follows:

The first step is the formation of stoichiometric alkaline hydrates in a semi-chemical reaction.

The second step is the absorption of gas molecules among a mass of alkaline hydrate chains in a non stoichiometric process.

In the first stage according to Long and Stoan we assume that gas molecules are dissolved in water which is done by surrounding molecules surrounded by several water molecules. In this surrounding, which is performed continuously and they are called alkaline hydrates the alkaline side of these molecules is occupied by gas molecules and the other side of the chain remains

intact [5].

This process is described by the following complex process:

$$H_2o + \lambda_2 G \rightarrow G_{\lambda 2} . H_2o \qquad (1)$$

Where, G is the specific gravity of the gas and $_2$ is the number of gas molecules and the number of water molecules in the alkaline hydrates. During this step, the intact areas (in the chain) are covered by other alkaline hydrates. In the second step the small molecules such as (Ar, N_2, O_2, CH_4, etc.) that are soluble in water move toward the ring chains (absorption process) which is the result of the non-stoichiometric property of hydrates. But here this will not happen for the larger size molecules (such as ethane, propane, -n butane and-i butane) and for the molecules that are able to removed from the chain. Therefore the final form of the stoichiometric alkaline hydrates will form in the first step. So it can be assumed that the alkaline hydrates are not hypothetical and they are physically available. They were rational reasons that are used in Langmuir absorption theory to explain to saturation of chain rings by gas molecules [6].

2.1. Analyzing the operating conditions for hydrate formation

There are different ways to analyze the hydrate formation operating conditions (temperature and pressure) including drawing the logarithm of pressure changes curve in terms of gas temperature which is one of the most common methods. In this case, the curve is straight line that is easy to analyze. The structure of hydrates in water-gas area is kept by molecules of the solution in aqueous phase area. As a result, H_2S and CO_2 accelerate the formation hydrates at high temperatures because they are more soluble in water than most hydrocarbons. The pressure leads to the formation of the network. In the case of pentane and larger molecules, pressure breaks the network and prevents the formation of stable hydrates. Hydrates increase like crystals. They form sediment. In fact, high pressure and low temperature in places like the cap of a tube on perforated plates and valves form sediments that the maximum force on the part of variable flow can prevent the formation of these hydrates in these areas. Therefore, high turbulence can change their actual structure easily. Hydrocarbon fluids help this process by a vigorous washing. These structures are related to the size of the spaces in the network. This space could easily accommodate methane, ethane, H_2S and CO_2 and similar molecules. It means that the alternative molecule should have the right size so that it could enter the water

gap. [7].

2.2. Thermodynamic origins of the model and the evaluation of special hydrate gas parameters

According to the two-stage mechanism of hydrate formation described above, there are two types of equilibriums in the system: A quasi- chemical equilibrium reaction that occurred in the first step, and balanced physical absorption in which gas molecules have saturated around the chain rings during the second step. For the reaction we noted in formula (1), if we use chemical equilibrium constants, we have:

$$\mu_B = \mu_w + \lambda_2 \mu_g \tag{2}$$

Where μ_B is the chemical potential of alkaline hydrates, μ_w and μ_g are water and gas standard chemical potential respectively. After the absorption of gas molecules in the chain rings, the chemical potential of the alkaline hydrates will

$$\mu_B = \mu^o_B + \lambda_1 \, RT\ln (1\text{-}\theta) \tag{3}$$

Where θ represents a fraction of chain rings surrounded by gas molecules and μ^o_B represents the unsaturated chemical potential of alkaline hydrates (θ=0) and λ_1 refers to the number of chain rings of small chains on water molecules in alkaline hydrates. Based on the theory of Langmuir, θ is calculated as follows.

$$\theta = \frac{Cf}{(1+ Cf)} \tag{4}$$

Where f denotes the fugacity of special gas and C refers to Langmuir constants. Using the general and fundamental thermodynamics, the special chemical potential of gas is calculated as follows.

$$\mu_g = \mu^o_g \, (T) + RT \, Lnf \tag{5}$$

Where, $\mu^o_g(T)$ represents the chemical potential of the ideal gas. The result of subtracting the equations (2) - (5) are presented in Eq.6:

$$\mu^o_B + \lambda_1 RT \, Ln \, (1\text{-}\theta) = \mu_w + \lambda_2 \, [\mu^o_g \, (T) + RT \, lnf] \tag{6}$$

According to the definition:

$$f\circ = \exp\left[\frac{\tilde{\mu}^o_B - \tilde{\mu}_w - \lambda_2 \tilde{\mu}^o_g(T)}{\lambda_2 RT}\right] \tag{7}$$

Equation (6) can then be turned to the following equation:

$$f = f° (1- \theta)^{\alpha} \tag{8}$$

Where $\alpha = \lambda_1/\lambda_2$, $r = \dfrac{1}{3}$ for the compound I and $\alpha = 2$ for compound II. In the Equation 7, $f°$ is

not only a function of T, P and αw of water activity (see equation (11)) but also presents a

quality of alkaline hydrate. When $\theta = 0$, equation (8) will be as follows:

$$f = f° \tag{9}$$

In this case $f°$ exactly represents fugacity of the gas phase in equilibrium while an alkaline

hydrate is unsaturated. ($\theta = 0$). The part ($\mu^o_B - \mu_w$) in equation (7) can be calculated by numerous

thermodynamic relations.

$$\mu_w = A_w + PV_w + RT \ln aw \tag{11}$$

$$\mu^o_B - \mu_w = \Delta A + P\Delta V - RT \ln a_w \tag{12}$$

Where, A represents the number of Helmholtz free energy moles (which is essentially related to

the system energy) and the number of ΔV moles the constant value of which can be calculated.

Equation (7) is the result of three factors and accordingly the share of each component T, P and

aw is displayed as follows:

$$f° = f° (T) f° (P) f° (a \tag{13}$$

In equation (13)

$$f°(P) = \exp(\frac{sP}{T})$$

Where $s = \dfrac{\Delta V}{\}_2 R}$ obtained by the constant value, β is equal to 0.4242 k/bar for compound I and

1.0224 k/bar for compound II respectively.

$$f° (aw) = aw^{-1/\lambda 2} \tag{15}$$

The number of λ_2 equals 3.23 for compound I and 1.17 for compound II.

$$f°(T) = A' \exp(\frac{B'}{T - C'}) \tag{16}$$

In a specific and pure compound that is composed of a material, Antoine constants, A′, B′ and

C′ can be obtained in proper constant and amount of forming hydrate gas that are the specific

values of the same material. This constant value for alternate compounds is obtained by measuring a two hydrate compound. These constant values that have a downward trend can be observed for special gases in the relevant table. In the case that the hydrates are formed in cooling mode, the listed constants in the table will remain unsettled, but the equation (16) is corrected as follows:

$$f^{\circ}(T) = \exp\left(\frac{D(T-273.15)}{T}\right) \times A' \exp\left(\frac{B'}{T-C'}\right) \tag{17}$$

Where, the constant D is equal to 22.5 and 49.5 for compound I and II respectively.

In order to apply equation (8) under the condition ($\theta \neq 0$), θ may be obtained by equation (4). To investigate Langmuir constants it is possible to determine integrating Lennard-Jones, and the results indicate that secondary Langmuir constants are close to Sloan values. It is important for the applied engineering to relate Langmuir constant C with temperature. In this regard Antoine equation is used to determine the value.

$$C = X \exp(\frac{X}{T-Z}) \tag{18}$$

Constants X, Y and Z used in Langmuir constant C are calculated by Lennard-Jones potential functions. The constant measured values for these numbers indicate that in order to suggest hydrate formation mechanism, gas absorption is performed by the chain rings.

3. EVELUTION OF HYDRATE FORMATION IN GAS MIXTURES

The behavior and operation of hydrate formation that are composed of gas mixtures is discussed as alkaline hydrates above. Alkaline hydrate mixtures behave similar to solid solutions called alkaline hydrates combination. The general properties of hydrate mixtures merely depend on the saturation of gas molecules around the ring chains. In alkaline hydrates the only difference of which is in their volume with similar composition, the extra volume and entropy of alkaline hydrate mixtures should be close to zero. Therefore, it is reasonable to consider the alkaline hydrate mixture as a real solution. If we ignore the number of molecules in solution that have minimal influence on each other (ideal solution assumption) the following relations are considered for hydrate mixture:

$$\sum_{j} O_{j} = \frac{\sum j \, f_{j} \, G_{j}}{1 + \sum j \, F_{j} \, G_{j}} \tag{20}$$

$$\sum_{j} x_{i} = 1.0 \tag{21}$$

Where, f_i is related to fugacity of component i calculated by equation Patel- Tega. θ_j refers to the part of chain rings occupied by gas j. x_i refers to the mole fraction of alkaline hydrate.

Determining the type and model of hydrate will no be performed based on contract Vdw-p that considers it under the effect of chemical potential difference between water and hydrate networks ($\Delta\mu$w). If the factors determining the model of hydrates between the molecules around the ring as alkaline group, equation (16) to calculate $f_i^\circ(T)$ is corrected as follows:

$$fi^\circ(T) = \exp\left(\frac{-\sum j \, Aij \,_{,,}j}{T}\right) \times \left[A' \exp\left(\frac{B'}{T - C'}\right)\right] \tag{22}$$

Where Aij is a two part parameter between the components i and j $A_{ij} = A_{ji}$. , $A_{ii} = A_{jj} = $ o.

4. THE RESULTS OF COLCULATING TWO AND MULTICOMPONENT GAS HYDRATES

Comparing the calculated results and the experienced formation values under pressure in two and multicomponent systems is separately present in gas hydrate systems. For two component systems Ar-N_2, Ar-CH_4, CH_4-H_2S, C_2H_4-C_2H_6, C_2H_6-C_3H_8, all A_{ij}s options will be equal to zero. But for other systems the crossover and return A_{ij} parameter is calculated in the system.

If the effect of mixture molecules on each other is considered for each pair of A_{ij} the amount and level of which is not available, the value is considered zero. The mean absolute prediction error indicates that the new models of hydrate on applied engineering have a promising future.

According to Equation 15 we have $f^\circ(aw) = aw^{-7.67}$ for hydrate compound I and $f^\circ(aw) = aw^{-17}$ for hydrate compound II. This means that product formation pressure is very sensitive to water activity and a slight reduction of water activity may lead to significant increase in system pressure. For the system that are formed of water and different types of water and gas with solubility $X_w \rightarrow 1.0 \, \gamma_w \rightarrow 1.0$ and $\alpha_w \approx x_w,$ thus Equation 15 can be shown as follows:

$$f^\circ(aw) \approx [1-xg]^{-1/\lambda 2} \approx 1 + xg /\lambda_2 \tag{23}$$

Where, xg presents the molar fraction of the gas species dissolved in the aqueous phase. When $f°(aw)$, $xg = 10^{-13}$ is equal to 1.00768 and 1.017 for compound I and II. On the other hand for systems containing gases with relatively high solubility in water, e.g. (H_2S, CO_2) and bipolar sodium chloride inhibitor, the share of $f°(aw)$ is not insignificant to be formed. For other compounds, the share of $f°(aw)$ can be analyzed a suitable compound of equilibrium gases presented by equation of state and available activity coefficients [9].

5. CONCLUSION

1. Based on the proposed two-stage mechanism for the formation of hydrates and concepts described in the previous pages, new models of hydrate will be available.

2. The complicated algorithm of hydrate formation, simplifying the calculations, the direct calculation of $\Delta\mu w$ and complex evaluations based on Langmuir C, plus the choosing optional parameters the assessment of $\Delta\mu w$ and C will not be possible.

3. The change of methane hydrate composition can be physically addressed when mixed with a small amount of propane.

4. The results of various experiments show that proposing new hydrate models is suitable for engineering applications especially when natural gas compositions are intended.

6. REFERENCES

[1] Makogon, Y. F., Holditch, S. A., Makogon, T. Y., (2007). Natural gas-hydrates -A potential energy source for the 21st Century, Journal of Petroleum Science and Engineering, 56(3), 14-31.

[2] Afchangi, A., Predicting hydrate formation in the pipeline, Masters degree thesis in Chemical Engineering, Tarbiat Modarres University in 1997.

[3] Azari, Homeira, Honarvar, Bizhan, Samimi, Amir, "Investigating Ways of Hydrate Formation Prevention by the Use of Certain Substances in Gas Industry," Australian Journal of International Social Research, Australia, Vol.3, 2015

[4] Lederhouse, R., Finke, M., & Scriber, J. (1982). The contributions of larval growth and pupal duration to protandry in the black swallowtail butterfly, Papilio polyxenes. Oecologia, 53(3), 296-300.

[5] Eltejaei, H., Analyzing methane penetration in hydrate cavities, a Master's thesis. TMU, 2000.

[6] Samimi, Amir, "Preventing Hydrate Formation in Gas Transporting Pipe Lines with Synthetic Inhibitors", International Journal of science and investigations, France, pp.48-50, 2012

[7] Selim, M., Sloan, E. D., (1990). Hydrate dissociation in sediment, SPE Reservoir Engineering, 5(2), 245-251.

[8] Izadpanah, A.A., Kinetics of hydrate formation using natural thermodynamic path in the kinetics of chemical reactions, dissertations, Tarbiat Modarres University, 2006.

[9] Khoddami, Seyed Ali, Esfandiary, Ali, Samimi, Amir, "Investigating the Process of Separation from Gas Mixtures Using Gas Hydrate," Australian Journal of International Social Research, Australia, Vol.4, 2015

[10] Østergaard, K. K., Masoudi, R., Tohidi, B., Danesh, A., & Todd, A. C. (2005). A general correlation for predicting the suppression of hydrate dissociation temperature in the presence of thermodynamic inhibitors. Journal of Petroleum Science and Engineering, 48(1), 70-80.

[11] Zarinabadi, Soroush, Samimi, Amir," Problems of hydrate formation in oil and gas pipes deals," Australian journal of basic and applied science, 2011

[12] Sadeghi, A., Hydrate formation modeling in system consisting of a combination of improved building lime, master's thesis, University of Isfahan, 2009.

[12] Patel, N., Teja, A., (1982). A New Cubic Equation of State, Chemical Engineering Science, 37(2), 463-473.

[14] Samimi, Amir, "Offer a New Model to Prevent Formation of Hydrate in Gas Pipeline in Gas Refinery", International Journal of Innovation and Applied Studies, ISSN 2028-9324, 2012

[15] Esfandiyari, Ali, Khoddami, Seyed Ali, Samimi, Amir, "The Investigation of Methods of Preventing Gas Hydrate Formation in Gas Pipelines," Australian Journal of International Social Research, Australia, Vol.4, 2015