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Thermodynamic modeling of inhibitors' role in preventing from gas hydrate formation in the pipelines

Fateme Sadat Mosavi Kakavand[1], Reihaneh Asachi[1]

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

Abstract

The existence of water beside gas has led to the creation of gas hydrate formation phenomenon in these pipelines. The phenomenon causes to basic financial and operational problems in the system. For this reason, the flow purpose of the present study was to simulate the formation condition in a specific flow and thermodynamic conditions and finally to provide the best possible solution to this problem. The Van Der Waals & Plague equation was used to thermodynamic modeling in the terms of temperature and pressure and the computer coding was carried out by MATLAB software. In addition, the results of Green & Perry study were used to utilize from physical characteristics, such as critical temperature, critical pressure, acentric factor and the temperature of quadruple points of elements forming hydrate .the results of this study indicated that increasing the concentration of inhibitor in system at the specified temperature, delay the hydrate formation. Moreover, temperature rising can also increase the effect of solvents. Therefore, two parameters of ambient temperatures in hot seasons or using heaters for pipelines can reduce the risk to a minimum in critical (sensitive) points. Finally, the used model in this design which has had some changes in variables properly can see the needs and meanwhile it is usable for other similar changes by a brief change.

Keywords: *Gas pipelines, gas hydrate, Van Der Weal's & Plague equation, MATLAB software.*

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1 Introduction

Natural gas hydrate is a crystalline solid compound that is occurred by the combination of water and gas and is considered as a part of Catharses family. The guest gas molecules trapped into pore of water system (the host), which created by hydrogen bonding between water molecules. The typical sample of these gas molecules are compounds existed in natural gas which are smaller than pentane, such as methane, Ethane, propone and carbon dioxide [1].

The rapid development of oil and gas industry, particularly in North America has increased the industrial importance of gas hydrate. Since gas hydrates are existed in temperature higher than water freezing temperature, so it can cause to clogging in the pipelines, nozzles, valves, tray of distillation tower and other related equipment. The trends to studding this phenomenon in the oil and gas industry was increased after Hammer Schmidt (1934) has stated that hydrate formation in gas transmission network has led to the congestion of pipelines. Most of studies in this area have been done to data gathering about temperature and pressure conditions of hydrate formation.

The ways of preventing from hydrate formation includes:

Reducing the amount of water in the mixture, keeping the temperature low, reducing the pressure of system and injecting inhibitors to system; the compounds are materials which in specified pressure lead to the matter that hydrate is formed at lower temperatures. Alcohols, glycolic and salts are example of these compounds [2]. The gas hydrate can be formed by pure gas or gas mixture consisting of two or more components. Catharses are considered as a solid solution in which guest gas molecules and hydrate- forming gases are in contact with the host network (water). Therefore, gas hydrates are non- stoichiometric solids. In hydrate structure there are strong hydrogen bonds between molecules of water, while there is no chemical interaction between guest-host molecules and they are kept to each other only by Van Der Waals forces [3].

In the presence of free water, hydrates are formed when the temperature is lower from a certain level (the temperature of hydrate formation). The temperature of hydrate formation is lower or equal to the dew point temperature of hydrate maker gas. The appearance of gas hydrate crystals is like to ice or water snow [4]. Generally, the characteristics which hydrate exhibit depend on gas composition, temperature and pressure. The main component of their structure (80% by volume) is water. Gas hydrates have a number of unique features. For example a cubic meter of water maybe locked by 207 cubic meters of methane in order to form 1.26 meters solid hydrate, while is absence of gas, a cubic meter of water is freeze to 1.09 cubic meter of ice [5].

The purpose of this study was to investigate the thermodynamic relationships governing the phenomenon of deposit formation and also to find a proper percent of current condition by considering the role of inhibitors in preventing from these materials formation by using the least chemical composition and the most sever operating condition. In fact, the main purpose of the study was to investigate the required condition of preventing deposits formation in pipelines, rather than to removing created deposits.

A certain conditions should be beard in mind in this study, when the flow of oil and gas in produced pipeline, without a doubt there is water with them. Therefore, there are usually three phases:

Liquid hydrocarbons, liquid water and gas; since there is no uniform model to the hydrate formation, so the problem has been explained by dividing into four models which included [6:[

1 Mainly oil system
2 Mainly gas system
3 Gas condensates systems
4 Systems with high presence of water (by volume).

2 Literature Review

The rapid development of oil gas industry, particularly in North America has increased the industrial importance of gas hydrates. Since, gas hydrates are existed in temperature higher than water freezing temperature, so it can cause to clogging in the pipelines, nozzles, values, tray of distillation tower and other related equipment. The trends to studying this phenomenon in the

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oil and gas industry was increased after Hammer Schmidt (1934) had stated that, hydrate formation in gas transmission network has led to the congestion of pipelines. Most of studies in the area, have been done to gatherings data about temperature and pressure conditions of hydrate formation [1].the way of preventing from hydrate formation include: reducing the amount of water in the mixture ,keeping the temperature low, reducing the pressure of system and injecting inhibitors to system. The compounds are materials which in specified pressure lead to the matter that, hydrate is formed at lower temperature. Alcohols, glycolic and salts are examples of these compounds [8].

The mentioned methods change the thermodynamic equilibrium of hydrate formation and are known as thermodynamic inhibitor methods, because they keep the system far from thermodynamic stability by changing the level of composition, temperature or operational pressure and the hydrate will not be formed, until the system is far from stable condition [9]. Another method to prevent from hydrate formation is utilizing from Kinetic inhibitors. These materials allow the system to remain under thermodynamic stability, but prevent from hydrate crystals growing and don't the crystals to grow [10].

Historically, the studies have been done on gas hydrates can be classified into the following three important periods [1].

-the first period since discovery in 1810 to the present

In this period hydrates have been studied as an unknown phenomenon, in which water and gas are transmitted into a solid network.

-the second period, since 1934 until now: in this period, the hydrate phenomenon has been investigated in the gas transmission Industry.

-the third period, since 1960 until now: this period was started with the discovery of underground resources of hydrates in the depth of the oceans and frozen areas in depth of the earth.

For a first time, Sir Humphrey Davy founded the chlorine hydrate formation, when he was cooling a saturated aqueous solution of chlorine test at the temperature of 40 F [12].

Since 1810 to 1934, the studies have been performed on hydrates, emphasized on following two main matters [13].

1 Identifying all compounds that can form hydrates

2 The quantitative description of compounds in the terms of composition arête physical properties

3 The studies on hydrates has trend to find methods for preventing from the phenomenon formation is gas transmission pipelines, since 1934. Because at that time, Hammer Schmidt found that pipelines clogging is due to the hydrate formation. Rather than freezing, strange and transmission of natural gas by means of hydrate method firstly has been introduced in 1942 by Binche. After that, it was also proposed by Miller & Strong in 1946, parented in 1946 and Dobinin and Ginkon in 1979 [14].

4 It is necessary to use more than a model in order to describe the phase behavior of gas hydra

EOS equation is a way to describe the hydrate behavior. Satio et al have proposed a method for an ideal solution (Raoult's law) to describe the water-rich fluid. The solubility of gas in water wasn't considered in their supposition. but the existed events criticize this when it is need to calculate the hydrate formation preventing, the calculation should be carried out based on mente method and also modifying the Raoult's law by an activity coefficient in order to more accuracy. The results of this method are reliable and provide relatively good estimate about the distribution of the inhibitor in the solution. Another method to solve the problem was introduces in 1986 by Anderson and Brabont; where they used the combination of UNIQUAC equation and Henry law to calculate the fugacity of solid lubricating particles. These methods are not stable for complex problems and hardly become converge. In addition, they don't have high accuracy for analyzing stability problems [15].

Englezos et al and Avlonities et al have provided a model for all phases of fluid based on the single-mood equation. The first one uses a third degree equation with 4 parameters and the last on use from 3 parameters and mixtures law.

3 Methodology

The relations of Van De Waals & Platue alongside the procedure existed in Sloan (1998)

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were used to thermodynamic modeling of temperature are pressure conditions of hydrate formation. Some physical properties of element of system which were used in the model, such as critical temperature, critical pressure, acentric factor and temperature of four points of components of hydrate formation were inserted in the program in the form of a data base for eleven common compositions forming hydrate. An index number was allocated to each composition in computer program which the component of each composition can be read from data base by inserting the index number of desired composition.

4 Results

The results of model for a gas system include pure methane gas and industrial inhibitors of methanol were comprised with the experimental data of Daaton and Frost (1946). The following average absolute Deviation was used to this purpose:

$$\text{Average Absolute Deviation} = \frac{\sum_{\#data} \left|P_{model} - P_{exp}\right| / P_{exp}}{\#data} \times 100$$

In above equation, the predicted pressure by model was taken from the empirical results of articles and the denominator is the number of experimental points used in each case.

In present study, no modifications has been done on prediction model of hydrate formation condition is pure system and with present of inhibitor materials and the results has been presented in only for the efficiency of model.

As it can be seen, the model display better predictions compare to experimental results. The minimum error was related to the temperature of 4.280 and equal to 18.0 percent and the maximum one was related to the temperature of 9.285 equal to 88.3 percent. In addition, the error in temperature higher than 4.280 is more than lower temperature.

The compositions of the process formation are their properties [16]. Among alcohols, methanol is most common inhibitors due to the low cost and high efficiency. The inhibition capability of alcohols reduced as follows: Methanol> Ethanol > Isopropanol [17]. They have showed that utilizing from methanol is cheaper than other materials and also, its separation at the end of transferring operation is more economic than other inhibitors.

Table (1): The conditions of hydrate forming for water_ methane system

Pressure (bar)		Temperature (K)
Model Results	**Experimental Results** (Sloan & Koh, 2007)	
27.7	27.6	273.7
29.9	29.0	274.3
32.1	32.4	275.4
34.0	34.2	275.9
38.3	38.1	277.0
47.5	47.7	279.3
53.4	53.5	280.4
55.8	57.0	280.9
59.1	60.6	2814.5
66.0	67.7	282.6
78.5	81.2	3284.3
94.0	98.7	285.9
1.47	The percentage of absolute error average	

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Table (2): The conditions of hydrate forming for water_ methane _ methanol system

Pressure (bar)		**Temperature (K)**	**Weight percent of methanol**
Model Results	**Experimental Results** (Ng & Robinson, 1985)		
22.1	21.4	266.33	10
33.4	34.1	271.24	
55.0	56.3	275.87	
87.4	90.7	280.31	
126.7	133.2	283.67	
175.6	188.2	286.40	
3.37	The percentage of absolute error average		
28.1	28.3	263.34	20
41.2	42.0	267.51	
55.1	56.1	270.08	
81.3	84.1	273.55	
127.6	133.0	277.56	
176.6	187.5	280.17	
2.90	The percentage of absolute error average		
23.7	23.8	250.9	35
35.9	36.9	256.3	
65.6	68.1	260.3	
97.6	101.6	264.6	
128.2	136.8	267.8	
161.8	172.2	268.5	
190.9	205.1	270.1	
4.31	The percentage of absolute error average		
14.4	14.7	233.1	50
28.3	29.5	240.1	
69.1	72.4	247.4	
0.1	105.4	250.4	
0.07157	169.8	255.3	
754.0	The percentage of absolute error average		

Glycols from more hydrates bones with water compare to alcohols, but in the other side they have higher molecular weight than their corresponding alcohol and therefore, they are more expensive n the retrieval operation of gas transmission compare to alcohols and need to more complex separation equipment. Among common inhibitors, i.e., salts, alcohols and glycols are the best inhibitors and among them, methanol is introduced as the most common inhibitor [18], [19]. In this section, the average absolute error by equation (32) has been shown.

The experimental results of this part have been given by the article of Ng & Robinson (1985) [18].

As it can be seen, the methanol also has presented the better predictions in this part, compare to empirical results. However the level of error is higher than the case without inhibitor. The minimum amount of error was related to the

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temperature of 250.9 in mean weight of 35 for methanol and was equal to 0.42 percent and the maximum one was related to the temperature of 255.3 in mean weight of 50 for methanol and was equal to 7.13.

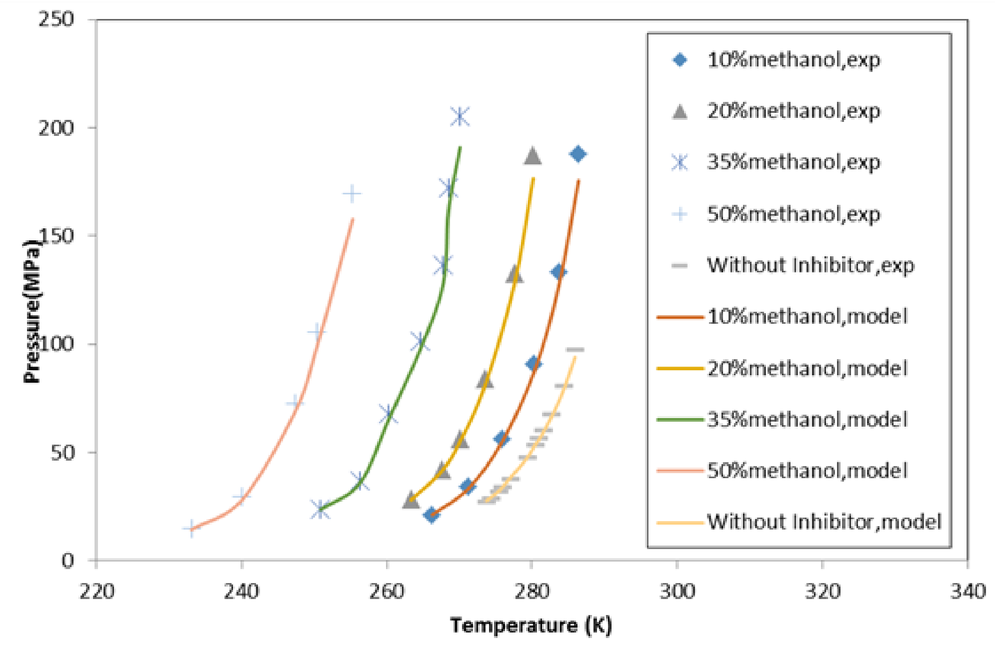

Figure (1): The results of model

5 Conclusions

The results of the present study are as follows:

- Increasing the concentration of inhibitor in system and the specified temperature can make delay in hydrate forming. Therefore, i.e. is possible to create more pressure differences in the system and hasten the transmission process. Of course in this case, the lateral parameters such as the additional costs of creating more pressure and as well as the cost of methanol isolation from transferred gas mixture should be considered. Moreover it should be noted to reasonable rate of solvent and gas transferring process in economic view point.
- Temperature rising can increase the effect of solvents. Therefore two parameters of environmental temperature in hot seasons and utilizing from heaters in pipelines can minimize the risk in critical (sensitive) points .
- The used model in this plan with changes in variable could properly see the needs and meanwhile, it can be used for other similar cases with some brief change.

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