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Modeling Of Methane Hydrate Formation In The Presence Of Thermodynamic Inhibitors

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Abstract: **Present study is dedicated to hydrate, a dilemma in the oil and gas industry. It is formed in the conditions of low temperature and high pressure when there is water in the system and because of its solid ice-like bulk, it prevents the continuation of oil and gas and even drilling mud flow. According to the importance of hydrate formation, scientists are investigate its nature and the ways to deal with its formation in the operating system and to this day many compounds have been studied and are used in this field such as alcohols and salts. Determination of thermodynamic equilibrium conditions for hydrate formation will be the topic of the present study and methanol and sodium chloride additives as well as mixtures thereof with the weight percentage of between 5% and 20% are used which makes changes in the thermodynamic conditions of problem including temperature and pressure and also the pressure of methane gas hydrate formation will be higher than such pressure in a state without additives. MATLAB and Hydoff software are used to solve equations and their corresponding results. The results indicate that the proposed model is able to predict the conditions for pure methane hydrate formation with high accuracy. Also for ensuring the authenticity of the results, the results were compared with experimental data and laboratory results in this context that the results indicate that the accuracy of the model is greatly desirable and it can be used with high confidence level in the mentioned conditions and process. The highest percentage of error was 5% and the lowest was 1.55% for the results comparing to experimental data.**

***Keywords: Gas Hydrate, Methane, Hydoff, Thermodynamic Inhibitors*.**

I. Introduction

Gas hydrates are crystalline solids compounds that are considered part of the clathrate family. Clathrate is a simple combination of a molecule of a substance (guest molecule) trapped in the network made of molecules of another substance (host molecules). Clathrate water is called hydrates.

Network-like structure is formed in their structure due to the hydrogen bond of water molecules that create some holes. This is an unstable network known as hydrates empty network at a specific temperature and pressure (low temperature and high pressure) in the presence of different gas components with the appropriate size and shape that can be converted into a stable structure.

In this type of crystals, no kind of chemical bonds are formed between water molecules and trapped gas molecules and the only factor for stability of crystals is the formation of hydrogen bonds between the host molecules (water molecules) and van der Waals forces created between host molecules and guest molecules (gas molecules) [1]. Hydrate structure is similar to ice structure with this difference that hydrate crystals can be stable at a higher temperature than the melting point of ice and don't melt when the pressure is higher than the ambient pressure.

Additional items causing similarity between hydrate and ice crystals are increasing the volume and heat release during its formation.

Gas hydrates are basically a combination of light gases such as methane, ethane or carbon dioxide under specific conditions of temperature and pressure that combine to water molecules to form ice-like substance.

Four basic factors play a role in the process of hydrate formation: The crystal structure of water molecules as the main factor, the guest molecules to complete crystal structure, low temperature and high pressure.

To prevent hydrate formation some changes should be applied in one or more of these factors so that the conditions for hydrate formation are not appropriate.

In the pressure control method, system is designed in such a way that the operating pressure is less than the pressure of hydrate formation from thermodynamic point of view. This method in many cases, especially when high-pressure gas transmission system is mandatory, is not efficient.

II. Hydrate structure

The structure of hydrate contains 85% water on average and many of its mechanical properties are similar to ice. So, we need to be explained a little about the water molecule and its structure. The most common form of solid water is Ih ice that its molecular structure is shown in Figure 1.

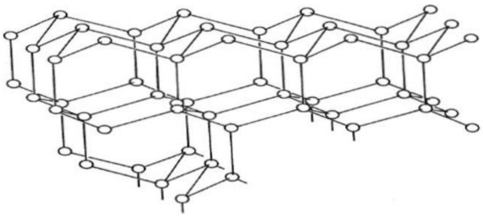

Figure 1- Basic crystal structure of Ih ice [4].

A. Structure I

Structure I is formed usually by smaller molecules such as methane, carbon dioxide, ethane, etc. In this structure, two 5^{12} holes (small holes) and six $5^{12}6^{2}$ holes (large holes) make up this space together by sharing sides due to repeated network in space.

Therefore, this structure contains 46 water molecules per unit cell and has eight holes for gas molecules that among them two holes are small and six holes are large and the structure is cubic. Thus, there are 46 water molecules for eight gas molecules in this structure. Structure I has four percent deviation from spherical form [2].

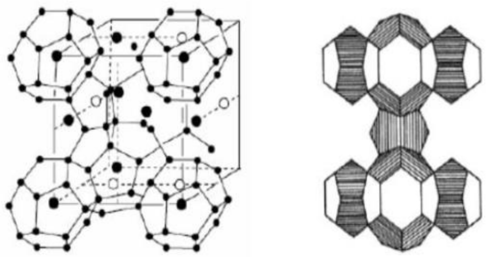

Figure 2- Structure I view.

B. Structure II

Molecules with a diameter of between 5 to 7.6 angstroms which cannot be placed in the structure I just can occupy the structure II. Thus, this structure is formed by larger molecules such as propane and isobutane. In this structure, Sixteen 5^{12} holes (small holes) and eight $5^{12}6^{2}$ holes (large holes) make up the space by sharing the surfaces. Therefore, this structure contains 136 water molecules per unit cell and has 24 holes for the gas molecules that among them eight holes are small and sixteen holes are large. So, in this structure, there are 136 water molecules per 24 molecules of gas. Structure II has ten percent deviation from spherical form. Therefore, it has the most spherical structure among the hydrate structures. This structure is suitable for water sweetening [2].

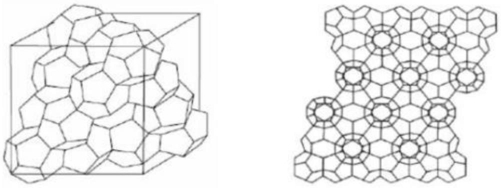

Figure 3 -Structure II view.

C. Structure H

This structure was unknown until 1987 and is still known less than the two previous structures. This structure of is formed by the combination of three 5^{12} holes (small holes), two $4^{3}5^{6}6^{3}$ holes (medium holes) and one $5^{12}6^{8}$ hole (large hole). Therefore, this structure contains 34 water molecules per unit cell and has six holes for gas molecules that among these holes, three holes are small, two holes are medium and one hole is large. Thus, in this structure 34 water molecules are available per six molecules of gas.

This structure does not exist when there are the components of natural gas such as propane and isobutane. H structure is known as a dual structure and a small molecule like methane and a large molecule such as methyl cyclohexane should be available for the formation of it to stabilize its structure.

The most important mechanical property of structure H is low formation pressure and high storage capacity [2].

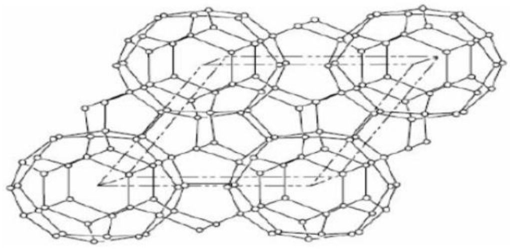

Figure 4- Structure H view.

III. The effects of additives on the formation of hydrates

Additives are divided into four categories in a general division:

- Inhibitors
- Additives that stable hydrates in one of the structures I, II or H (Hydrate Formers)
- Thermodynamic Additives (Thermodynamic Promoters)
- Kinetics Additives (Kinetics Promoters)

IV. Modeling

Many thermodynamic models are available to predict the formation of hydrates that have been obtained by various changes and modifications in the Vdwp model (provided the van der Waals and Platteeuw) [1]. Authors and researchers recently have suggested that alternate static mechanisms are the basis of the formation of hydrates. The basis and objective of vdw-p model is the assumption of similarity between the formation of hydrates and Langmuir adsorption.

Although the mechanism of adsorbing has the ability to interpret the properties and non-stoichiometric states of hydrates however there is a huge difference between the two processes.

In 1959, van der Waals and Platteeuw presented basic equations for gas hydrates based on classic thermodynamics that in these equations, equilibrium pressure and temperature of hydrate formation is related to the potential difference between hollow and filled hydrate network. The basic assumptions of this model are:

1. Guest gas molecules are trapped within spherical holes.
2. Each hole places only zero or one guest gas molecule in self.
3. There is no interaction between gas molecules in the adjacent holes.
4. It is assumed that guest gas molecules are small enough and their presence does not deform the hydrate network.

The difference between the chemical potential of water in hydrate network case H and pure water case α is expressed as follows:

$$\mu_W^H - \mu_W^\alpha = \left(\mu_W^H - \mu_W^\beta\right) + (\mu_W^\beta - \mu_W^\alpha) \qquad (1)$$

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:

$$\mu_W^H = \mu_W^\alpha \rightarrow \mu_W^\beta - \mu_W^H = \mu_W^\beta - \mu_W^\alpha \rightarrow \Delta\mu_W^{\beta-H} = \Delta\mu_W^{\beta-\alpha} \qquad (2)$$

Based on the Van der Waals and Platteeuw model, the potential difference between the water in the hollow hydrate network (β) and stabilized hydrate network (H) ($\Delta\mu_W^{\beta-H}$) represents a stabilizing impact of gas molecules adsorption within the hydrate network. it is calculated as follows:

$$\Delta\mu_W^{\beta-H} = \mu_W^\beta - \mu_W^H = RT\sum_{i=1} V_i(1 - \sum_{i=1}^N Y_{ki}) \qquad (3)$$

$$Y_{ki} = \frac{C_{ki}f_k}{1+\sum_{j=1}^N C_{ji}f_j} \qquad (4)$$

Van der Waals and Platteeuw provided the following equation using Lennard-Jones theory to calculate the Langmuir constant:

$$C_{ki} = \frac{4\pi}{kT}\int_0^{R-a} \exp(\frac{-\omega(r)}{kT})r^2 dr \qquad (5)$$

Fugacity of hydrate gas constituent components in the gas phase can be obtained by the following equation:

$$f_i = y_i\varphi_i P \qquad (6)$$

A. Peng-Robinson equation of state (PR)

Fugacity coefficient of hydrate gas constituent component in the gas phase is calculated using the Peng Robinson equation as follows:

$$z^3 + (B-1)Z^2 + (A - 2B - 3B^2)Z + (B^2 - AB + B^3) = 0 \qquad (7)$$

$$A = \frac{aP}{(RT)^3} \qquad (8)$$

$$B = \frac{bP}{RT} \qquad (9)$$

For pure components a and b are calculated as follows:

$$a = \frac{0.45724R^2T_c^2}{P_c}\alpha(T) \qquad (10)$$

$$\alpha(T) = (1 + \xi(1 - \left(\frac{T}{T_c}\right)^{0.5}\Big))^2 \qquad (11)$$

$$\xi = 0.37464 + 1.54226 - 0.26992\omega^2 \qquad (12)$$

$$b = \frac{0.07780RT_c}{P_c} \qquad (13)$$

Fugacity coefficient of component i in a gas mixture is defined as follows:

$$ln\varphi_i = \frac{b_i}{b_m}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{2}{A}\sum_j (a_i a_j)^{0.5}(1-\delta_{ij})y_i - \frac{b_i}{b_m}\right)\ln(\frac{Z+B(1+\sqrt{2}}{Z+B(1-\sqrt{2}}) \qquad (14)$$

Parrish and Prausnitz have suggested that the chemical potential difference between hydrate network and water in a saturated liquid state is calculated as follows based on Gibbs – Helmholtz equation according to changes in temperature and pressure:

$$d\left(\frac{\Delta\mu_w}{RT}\right) = -\left(\frac{\Delta h_g}{RT^2}\right)dT + \left(\frac{\Delta V_w}{RT}\right)dP \qquad (15)$$

In the above equation, ΔV_w and $\Delta\mu_w$ is the volume between water and hydrate network and enthalpy difference, respectively. The following equation is obtained by integrating the above equation:

$$(\frac{\Delta\mu_w}{RT}) - \left(\frac{\Delta\mu_w}{RT}\right)_{T0} = -\int_{T0}^{T}\left(\frac{dh_g}{RT^2}\right)dT + \left(\frac{dV_w}{RT}\right)dP \qquad (16)$$

The above equation is written for the condensed organic phase such as ice or water in liquid phase with no solute. If the aqueous condensed phase is not pure, water activity coefficient will be different from the one and as a result we have:

$$\mu_w = \mu_w^{pure} + RTln(x_w\gamma_w) \qquad (17)$$

By substituting the above equation, we have:

$$\frac{\Delta\mu_w}{RT}) - \left(\frac{\Delta\mu_w}{RT}\right)_{T0} = -\int_{T0}^{T}\left(\frac{dh_g}{RT^2}\right)dT + \left(\frac{dV_w}{RT}\right)dP - ln(x_w\gamma_w) \qquad (18)$$

Where x_w is the composition of the water in the liquid phase and γ_w is water phase activity coefficient. The composition of the water in the liquid phase can be calculated as follows:

$$x_w = 1 - \sum x_k \qquad (19)$$

x_k is the composition of the gas component in the water phase in a water - hydrate - natural gas system which is calculated as follows:

At atmospheric pressure and low concentration of component i in the liquid phase using Henry's law for solutions with infinite dilution we have:

$$H_{kw}(T) = \frac{1}{x_k(T)} \qquad (20)$$

$$Rlnx_k = H_{kw}^0 + \frac{H_{kw}^1}{T} + H_{kw}^2 lnT + H_{kw}^3 T \qquad (21)$$

Table 1. Experimental parameters required to calculate the water chemical potential difference.

References	Structure II		structure I	
	$\Delta h_w^0(\frac{J}{mol})$	$\Delta \mu_w^0(\frac{J}{mol})$	$\Delta h_w^0(\frac{J}{mol})$	$\Delta \mu_w^0(\frac{J}{mol})$
van der Waals and Platteeuw	0	820	0	699
Child	837	795	753	1255
Parrish and Prausnitz	808	-	1150	1264
Darmavand Hannah, Parrish and Sloan	1025	937	1389	1297
John, Papadopoulos and Holder	1400	1714	931	1120
Ci. et al.	764	1068	931	1287

Peng-Robinson equation of state to obtain the fugacity of pure component is as follows:

$$Ln\varphi = Z - 1 - Ln(Z - B) - \frac{A}{2\sqrt{2}B} Ln(\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}) \qquad (22)$$

For mixtures, the above equation can be rearranged as follows:

$$Ln\varphi = (BB)_i(Z-1) - Ln(Z-B) - \frac{A}{2\sqrt{2}B}((AA)_i - (BB)_i Ln\left(\frac{Z+(1+\sqrt{2})B}{Z—1+\sqrt{2}} B\right) \qquad (23)$$

$$(AA)_i = \frac{2}{(\alpha\alpha)_m}[\sum_j^N (\alpha\alpha)_{ij} \qquad (24)$$

$$(BB)_i = \frac{b_i}{b_m} \qquad (25)$$

V. Solve equations:

Modeling has been performed using MATLAB and Hydoff software and hydrate formation experimental data such as temperature, pressure and composition of gas components are required to predict hydrate formation conditions. All the experimental data were derived from natural gas hydrates book that is the only authoritative reference book in this field. All the hydrate formation experimental data for methane and carbon dioxide gases with various compositions of gas components were obtained from this reference and gas hydrate formation pressure is calculated using the software in processing conditions.

VI. Results

Results are divided into four general categories: pure methane system without inhibitors, pure methane including methanol inhibitors with different weight percentages, pure methane with sodium chloride inhibitor and a system including pure methane and carbon dioxide with a mixture of methanol inhibitors with weight percentages between 5% and 20%. So far extensive studies are conducted by different researchers on the conditions of hydrate formation and some modifications have been applied by them on the basic model of van der Waals and Platteeuw so that the van der Waals and Platteeuw model are now able to predict the thermodynamic conditions including temperature and pressure of hydrate formation with high accurately. In the present model results are presented merely to determine the performance of the model predictions.

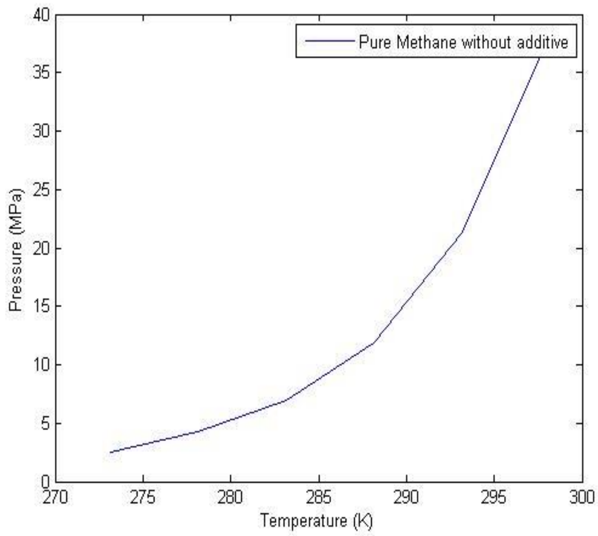

Figure 5- The results of the pure methane hydrate formation without additives.

Table 2. Comparison of experimental and software results for pure methane without additives.			
error	Experimental pressure of hydrate formation	Pressure of hydrate formation (modeling)	Temperature (K)
3.2%	1.648	1.702	259.1
0.2%.	2.64	2.647	273.2
5%	5.85	5.54	280.9
7%	10.63	9.878	286.5
4.3%	10.8	11.267	286.7
error average =3.9%			

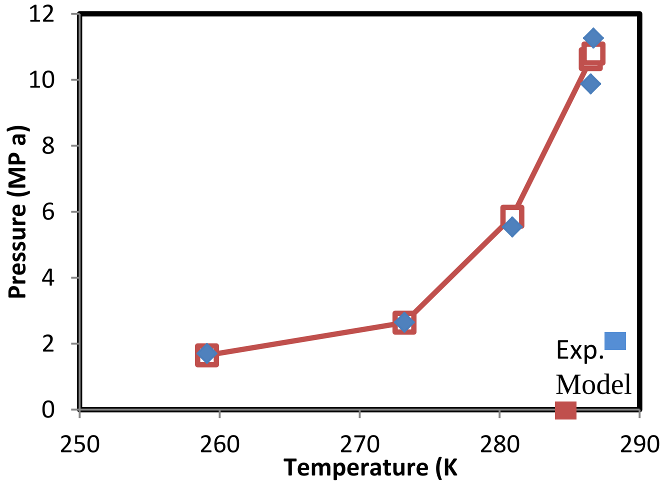

Figure 6- Comparison of experimental and software results for pure methane without additives.

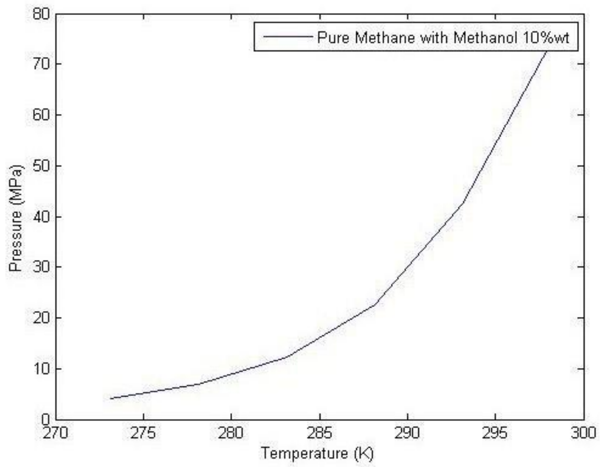

Figure 7- Results of pure methane formation pressure with the addition of methanol (10% by weight).

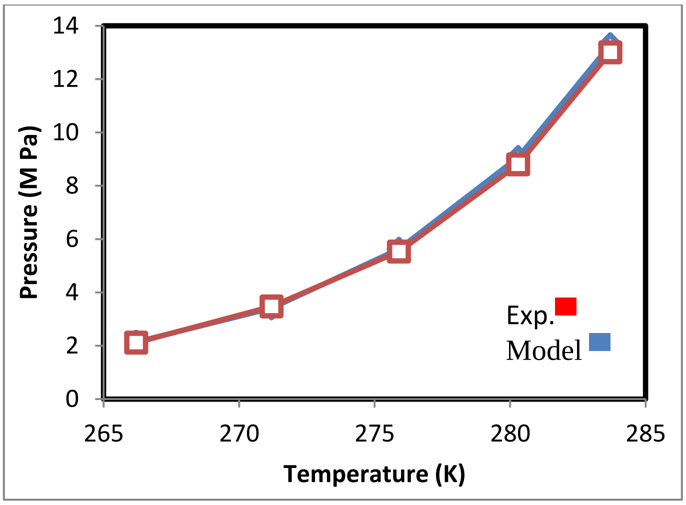

Figure 8- Comparison of experimental results of hydrate formation for pure methane with 10% methanol inhibitor.

Table 3. Comparison of experimental results of hydrate formation of pure methane with 10% methanol inhibitors with the software results.			
Temperature(K)	Experimental pressure of hydrate formation	Pressure of hydrate formation (modeling)	Error
266.2	2.14	2.115	1.1%
271.2	3.41	3.476	1.9%
275.9	5.63	5.531	1.7%
280.3	9.07	8.803	2.9%
283.7	13.3	13.003	2.2%
error average = 1.96%			

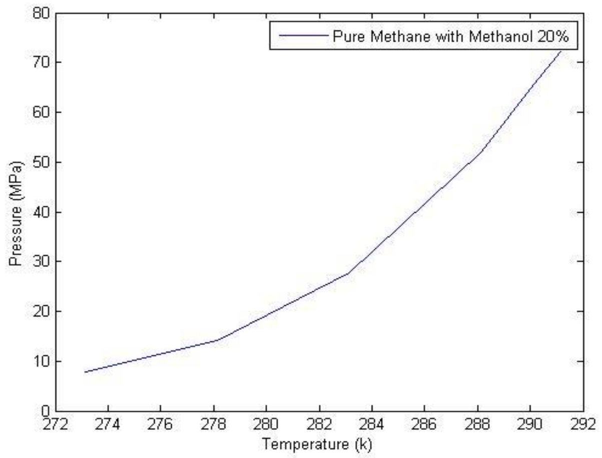

Figure 9- Results of pure methane hydrate formation with 20% methanol Inhibitor.

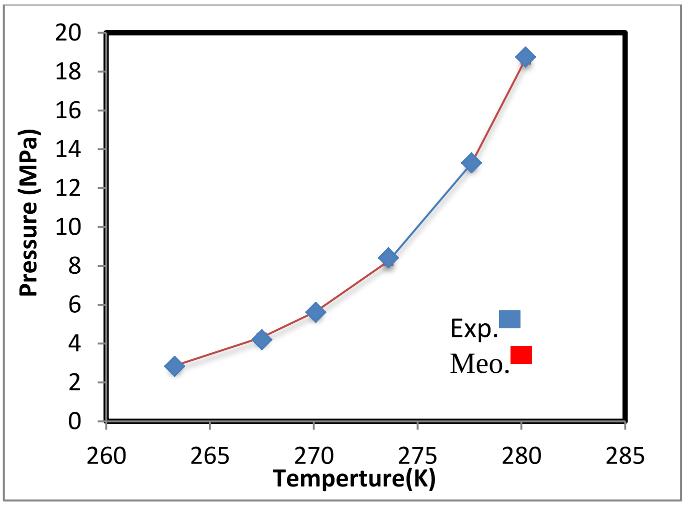

Figure 10- Comparison of experimental and software results for pure methane with 20% methanol Inhibitor.

Table 4: Comparison of experimental and software results for pure methane with 20% methanol.

Temperature(K)	Experimental pressure of hydrate formation	Pressure of hydrate formation (modeling)	Error
263.3	2.83	2.861	1.90%
267.5	4.2	4.325	2.90%
270.1	5.61	5.648	0.60%
273.6	8.41	8.248	1.90%
277.6	13.3	13.276	0.18%
280.2	18.75	18.641	0.50%
error average = 1.55%			

The results of the plotted figures can be explained as follows:

With increasing concentrations of inhibitors in the system, at a specified temperature, hydrate is formed at higher pressures. The methanol concentration is higher; the rate of pressure increase is more at a certain temperature. Other parameters such as cost and separation of methanol from the mixture are influential in determining the optimum concentration of inhibitor. Also the inhibitor cannot be added in any amount to the system because it causes spend a lot of system performance for transporting the inhibitor substance.

The effect of inhibitors is greater at higher temperatures and as can be seen from the figures, the trend is slower at lower temperatures in a certain concentration but at higher temperatures the slope is increased significantly.

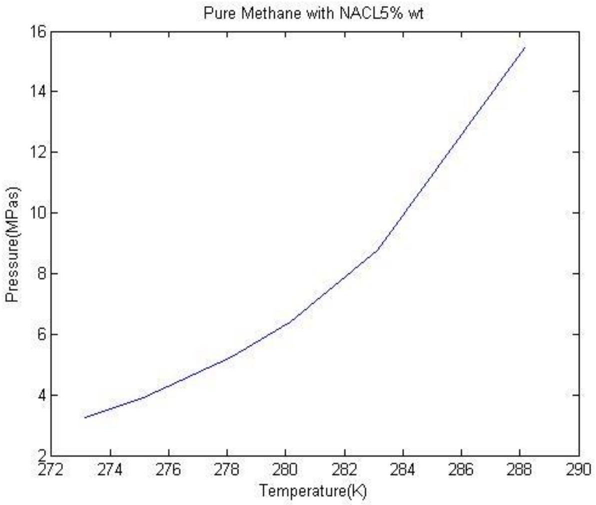

Figure 11- Pure methane hydrate formation conditions in the presence of 5 wt% sodium chloride inhibitor.

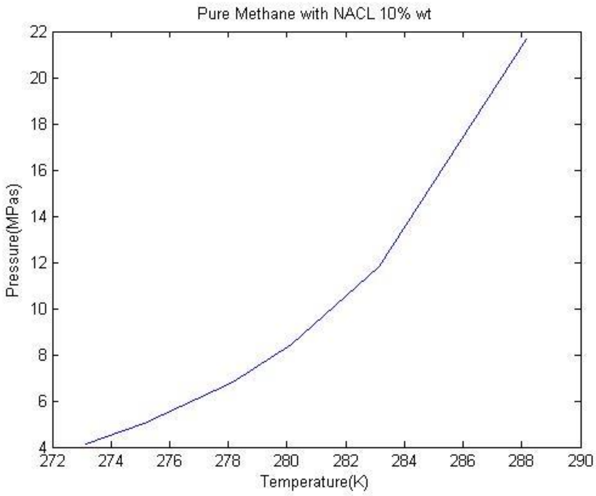

Figure 12- Pure methane hydrate formation conditions in the presence of 10 wt% sodium chloride inhibitor.

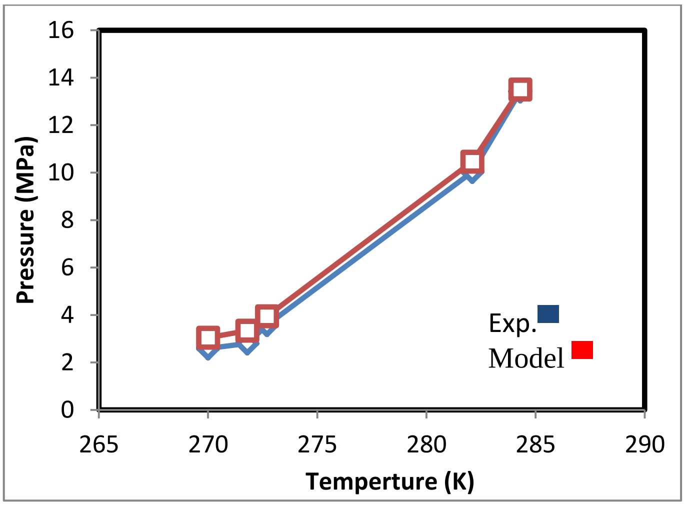

Figure 13- Comparison of experimental and software results for methane with 10% sodium chloride.

Table 5. Comparison of experimental and software results for methane with 10% sodium chloride.

Temperature (K)	Experimental pressure of hydrate formation	Pressure of hydrate formation (modeling)
270	2.59	3.043
271.8	2.8	3.341
272.7	3.58	3.949
282.1	10.03	10.46
284.3	13.42	13.5

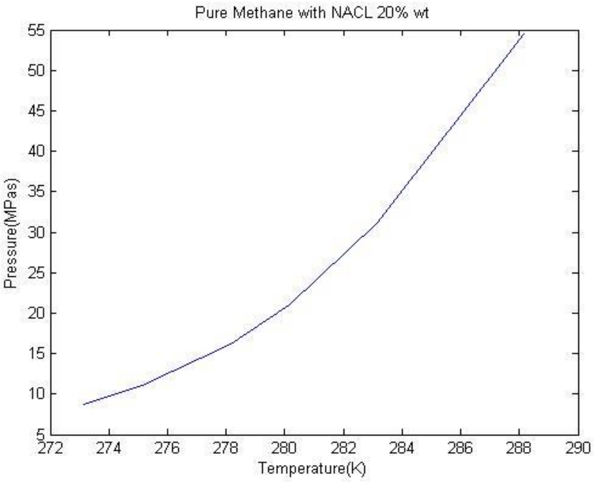

Figure 14- Pure methane hydrate formation conditions in the presence of 20% wt inhibitor of sodium chloride.

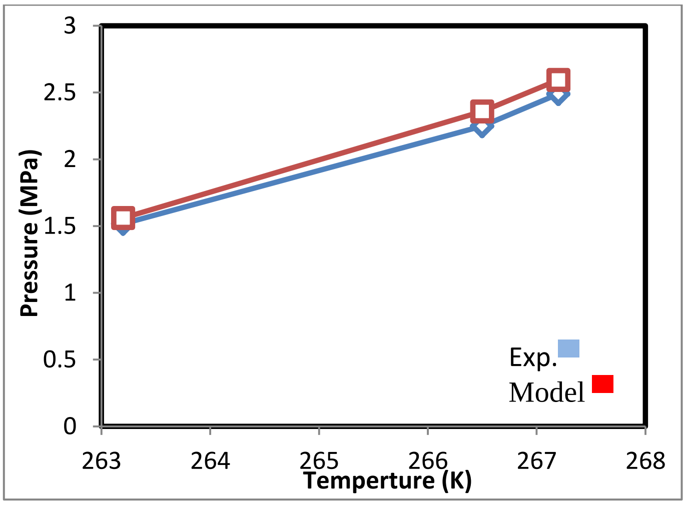

Figure 15- Comparison of experimental and software results for methane with 20% sodium chloride.

Table 6. Comparison of experimental and software results for methane with 20% sodium chloride.

Temperature(K)	Pressure of hydrate formation (Experimental)	Pressure of hydrate formation (modeling)	Error
265.9	3.78	4.064	7.50%
267.8	4.63	4.928	6.40%
275.7	11.09	11.856	6.90%
276.3	13.66	12.76	6.50%
Error average% =6.8			

The reason of inhibitory of these compounds can be assigned to their salt property. Comparison of thermodynamic effect of two ionic liquids on hydrate of carbon dioxide indicates that ionic liquid inhibitor is stronger.

Ionic substances used in carbon dioxide hydrate show enhancer behavior that the reason for this behavior can be attributed to the solubility of carbon dioxide in ionic liquids. Generally, dissolution of acid gases such as carbon dioxide in ionic liquids is high that causes the accelerated kinetics of formation and enhancer behavior of these liquids in hydrate of carbon dioxide.

In another study the system includes pure carbon dioxide with a mixture of methanol inhibitors and sodium chloride with different wt% was analyzed. As is clear from the figures obtained in this case, the hydrate formation pressure rises sharply by increasing the concentration of both inhibitors that is the result of a combined effect of inhibitors.

Salts act in solution by absorbing dipoles of water molecules. These molecules tend to be combined with ions rather than forming a network around the gas molecules in solution. Thus, in a certain pressure, the formation of hydrate network of water molecules requires lower temperature and therefore the solubility of gas in water is reduced.

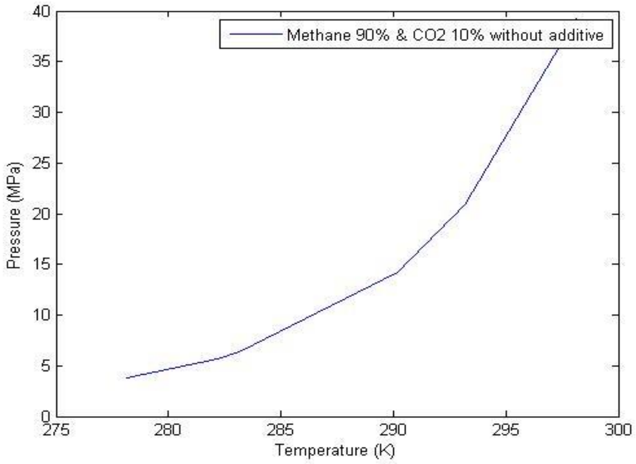

Figure 16- Hydrate formation conditions for 90% methane and 10% carbon dioxide without Inhibitor.

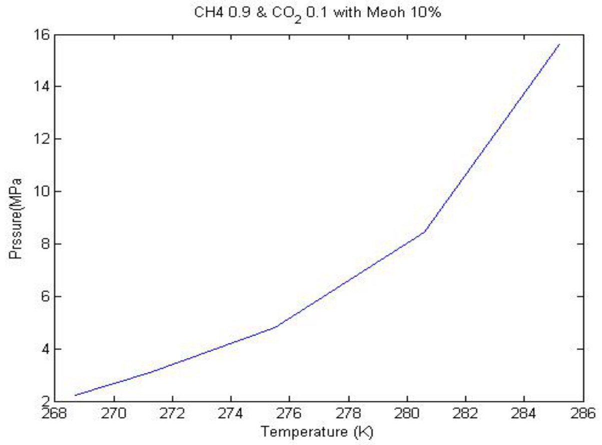

Figure 17- Hydrate formation conditions for 90% methane and 10% carbon dioxide with 10% methanol Inhibitor.

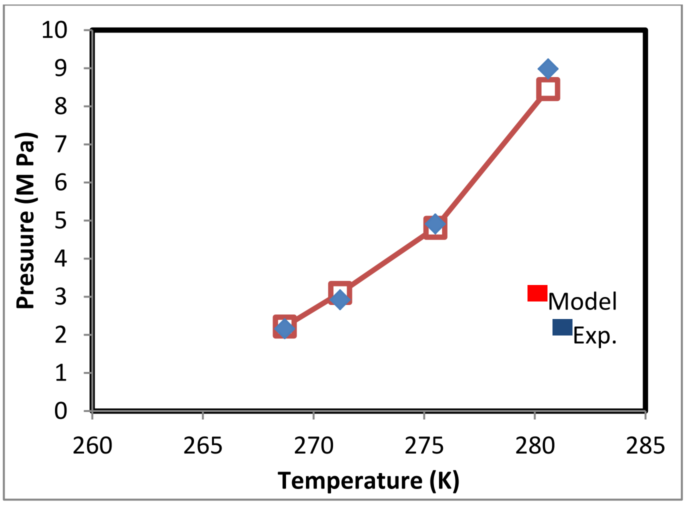

Figure 18- Comparison of experimental and software results for 90% methane and 10% carbon dioxide with 10% methanol Inhibitor.

Table 7.Comparison of experimental and software results for 90% methane and 10% carbon dioxide with 10% methanol Inhibitor.

Temp.(K)	Pre.(Exp)	Pre.(Model)	Error
268.7	2.16	2.217	2.6%
271.2	2.92	3.1	6%
275.5	4.91	4.81	2%
280.6	8.98	8.451	5%
285.2	15.28	15.63	1.4%
Error average=3.4%			

VII. Conclusion

Four factors play a role in the process of hydrate formation: water molecules, guest molecules, low temperature and high pressure that to prevent hydrate formation some changes should be applied in one or more of these factors so that the conditions for hydrate formation is not appropriate.

Chemical inhibitors that include three categories: thermodynamics, Synthetic and are anti-agglomerant; play the most important role in preventing hydrate formation.

In this study we tried to investigate the conditions of carbon dioxide and methane hydrate formation in the presence and absence of inhibitors with different concentrations and compare the results with experimental data available in this field. Therefore, the van der Waals and Platteeuw model and Peng Robinson equation are used.

Thermodynamic inhibitors alter fluid chemical potential when adding to it and shift hydrate equilibrium curve toward a lower temperature and higher pressure.

The most important advantages of traditional inhibitors (thermodynamically) are optimal efficiency and availability of distinctive relations for their accurate performance estimation.

The presence of additives such as inhibitors influenced the behavior of the liquid phase making it a non-ideal solution. In this study the hydrate formation pressure at different temperatures were compared with experimental results in this field for pure systems in the presence and absence of inhibitors to demonstrate the accuracy of results that the result reflects the fact that the present model is well able to predict the conditions so that the results can be used with high confidence level.

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