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Thermodynamic Modelling of Gas Hydrate Formation in the Presence of Inhibitors and the Consideration of their Effect

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Gas hydrates formation is considered as one the greatest obstacles in gas transportation systems. Problems related to gas hydrate formation is more severe when dealing with transportation at low temperatures of deep water. In order to avoid formation of Gas hydrates, different inhibitors are used. Methanol is one of the most common and economically efficient inhibitor. Adding methanol to the flow lines, changes the thermodynamic equilibrium situation of the system. In order to predict these changes in thermodynamic behavior of the system, a series of modelings are performed using Matlab software in this paper. The main approach in this modeling is on the basis of Van der Waals & Plateau's thermodynamic approach. The obtained results of a system containing water, Methane and Methanol showed that hydrate formation pressure increases due to the increase of inhibitor amount in constant temperature and this increase is more in higher temperatures. Furthermore, these results were in harmony with the available empirical data.

Keywords: Gas hydrates, thermodynamic inhibitor, modelling, pipeline blockage

INTRODUCTION

Natural gas hydrates are solid crystal substances which are formed of water and gas composition and are considered as a member of Clathrates family. Guest gas molecules are trapped inside water network pores (host), which are formed due to the hydrogen bonds among water molecules. Of the dominant members of these gas molecules are materials smaller than pentane in natural gas including Methane, Propane and Carbon dioxide. Gas hydrates can be made of pure gas or of a composition of gases including one or two components. Clathrates are known as solid liquids in which guest gas molecules and hydrate former gases become entrapped in host network (water). Thus, gas hydrate is known as a non-stoichiometric solid. There is a strong hydrogen bond between water molecules in hydrate structures, while there is no chemical interaction between host-guest molecules and they are only kept together with Van der Waals forces (Sloan, 1998).

Hydrogen bonds among water molecules create a network structure, which lead to formation of pores. This network structure, known as empty hydrate network, is unstable. The presence of light hydrocarbon and non-hydrocarbon gases (as guest) having smaller molecule diameters than that of the pores, the network structure can become a stable structure. Hydrate crystal stability is affected by the hydrogen bond among host molecules and Van der Waals forces which are present between host-guest molecules. Today has been known as an important energy source to substitute other kinds of fuels and also it is formation considered as a cheaper natural gas transportation method (Sloan, 1998).

Oil and gas industries' fast developments especially in North America have increased the importance of hydrate gas industry. Regarding the fact that gas hydrate exists in temperatures higher than freezing temperature of water, it can result in the blockage in pipelines, nozzles, distillations, tower trays, and other installations. For the first time, Hammer Schmidt reported that hydrate formation in gas transfer network caused pipeline blockages. Afterwards, many researchers became interested in investigating this phenomenon in oil and gas industry. Most of the studies in this field have been concentrated on temperature and pressure conditions for hydrate formation. The inhibiting methods of hydrate formation include reducing water volume in the mixture, keeping the temperature high, lowering system's pressure, and injecting inhibitors to the system. These are materials that cause hydrate formation in lower temperatures in specific pressure. Alcohols, Glycols hand Salts are among these materials (Mahmoodaghdam, 2001).

The aforementioned methods move thermodynamic equilibrium condition of hydrate formation and are known as thermodynamic inhibition methods, because they disarrange stability of the system by changing composition, temperature or operational pressure, and hydrates will not be formed until the system is far from its stable conditions. Another method to prevent hydrate formation is to use synthetic inhibitors. These substances allow the system to stay under stable thermodynamic conditions; they, however, will inhibit hydrate crystal growth (Mahmoodaghdam, 2001).

Thermodynamic Model to Predict Hydrate Formation Conditions

Various procedures have been innovated to predict hydrate formation conditions (or its dissociation). These procedures can be divided into two categories: 1- empirical models and 2- thermodynamic models (Englezos & Bishnoi, 1988). Empirical models used to be employed in the industry sector in the past; they, however, are less common due to the development of modeling methods (Demirbas, 2010).

Almost all the recent operations on hydrate crystal formation conditions have been based on chemical thermodynamic sciences. The suggested models all have similar assumptions. Contrary to empirical models, thermodynamic models have stronger theoretical bases; these approaches involve intermolecular effects in the model. The available thermodynamic models in predicting hydrate formation conditions are based on what Plateau& Van der Waalsmodel (1959) have stated, that is on classic statistical thermodynamics. Parrish & Prausnitz (1972) developed this model and the model became simpler by Holder & Kerbin. In the following, Van der Waals' thermodynamic model is first introduced and then, this model is modified for systems including inhibitor substances.

Van der Waals - Plateau Thermodynamic Model

Van der Waals & Plateau (1959) have suggested fundamental equations based on classic thermodynamics for gas hydrates in which the equilibrium temperature and pressure of hydrate formation have been related with chemical potential differences between the empty hydrate network and the filled network. The basic assumptions of this model are:

1- Guest gas molecules become trapped inside spherical pores.
2- Each pore only places 0 or 1 guest gas molecule in it.
3- No interaction exists among gas molecules inside the next pores.
4- It is assumed that guest gas molecules are small enough and their presence does not change hydrate network form.(Nguyen, 1986)

Thermodynamically speaking, hydrate is formed when hydrate state is more stable than non-hydrate state (liquid water or ice) in terms of energy. Water transformation from non-hydrate to hydrate state is divided into two stages:

1- Liquid water or ice (α) →empty hydrate network (β)
2- Empty hydrate network (β)→ filled hydrate network(H)

α ،β and H refer to each of these three states; β is a hypothetical state and is used just in hydrate computations; between H or α states, the one with a lower energy level is the better. The difference between water chemical potential in hydrate network state H and pure water state α has been stated as follows (Pedersen, Christensen, & Azeem, 2006):

$$\mu_w^H - \mu_w^\alpha = \left(\mu_w^H - \mu_w^\beta\right) + (\mu_w^\beta - \mu_w^\alpha) \quad (1)$$

In an equilibrium state, water's chemical potential in hydrate phase is equal to water's chemical potential in liquid phase. Therefore, it can be said that:

$$\mu_w^H = \mu_w^\alpha \rightarrow \mu_w^\beta - \mu_w^H = \mu_w^\beta - \mu_w^\alpha \rightarrow \Delta\mu_w^{\beta-H} = \Delta\mu_w^{\beta-\alpha} \quad (2)$$

In the following lines, the procedures of calculating the two potential differences of $\Delta\mu_w^{\beta-\alpha}$&$\Delta\mu_w^{\beta-H}$ are presented.

The Calculation of Potential Differences between the Water in Empty and Filled Hydrate Networks ($\Delta\mu_w^{\beta-H}$)

According to Van der Waals & plateau model (1959), the potential difference between water in empty hydrate network (β) state and the stable hydrate network (H), i.e. $\Delta\mu_w^{\beta-H}$, refers to the stabilization effect of gas molecules' absorption inside hydrate network and is calculated as follows:

$$\Delta\mu_w^{\beta-H} = \mu_w^\beta - \mu_w^H = RT\sum_{i=1}^{NCAV} v_i\left(1-\sum_{k=1}^{N} Y_{ki}\right) \quad (3)$$

Table 1. Geometrical Characteristics of the Pores (Sloan, 1998)

Hydrate structure	**I**		**II**		**H**		
Type of pore	**Small**	**Big**	**Small**	**Big**	**Small**	**Big**	**Big**
Pore per each water molecules	$\frac{1}{23}$	$\frac{3}{23}$	$\frac{2}{17}$	$\frac{1}{17}$	$\frac{3}{34}$	$\frac{2}{34}$	$\frac{1}{34}$
Mean radius of the pore(Å)	3.95	4.33	3.93	4.73	3.94	4.04	5.79
Coordination number (z)	20	24	20	28	20	20	36

Where

- $\boldsymbol{v_i}$ refers to the number of type i pores in water's molecule;
- $\boldsymbol{Y_{ki}}$ refers to the probability of type i pores' occupation by type k gas molecules;
- **NCAV** refers to the number of pores types for hydrate structure which for I &II structure is equal 2 and for structure H is equal 3; and
- **N** refers to the number of gas components which can penetrate the hydrate network (Sloan 1998).

Pore occupation fraction value is calculated using Langmuir's structure absorption theory:

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

Where f_k is fugacity of component K , C_{ki}denotes Langmuisr's absorption constant of pore type I for component K and denotes gas – water interactions inside the pore. Using Leonard-Jones – Devonshire theory, Vander waals & plateau proposed the following equation to calculated Langmuir constant:

$$C_{ki} = \frac{4\pi}{kT} \int_0^{R-a} \exp\left(\frac{-\varpi(r)}{kT}\right) r^2 dr \tag{5}$$

Where

- **K** is Boltzmann constant: 1.3806488*10$^{(-23)}$ (J/K);
- $\boldsymbol{\varpi(r)}$ is symmetric spherical pore's potential function which is subordinate to cell radius, coordination number and the type of guest-host interactions;
- **r** refers to the radial distance from pore's center to the guest molecule's center[m];
- **R** refers to hydrate spherical pore radius [m]; and
- **a** refers to the guest molecule radius [m].

Using Kihara's potential function with spherical core in this model, parameters are calculated as follow:

$$\varpi(r) = 2z\varepsilon\left(\frac{\sigma^{12}}{R^{11} r}\left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma^6}{R^5 r}\left(\delta^4 + \frac{a}{R}\delta^5\right)\right) \tag{6}$$

$$\delta^N = \frac{1}{N}\left[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-N}\right] \tag{7}$$

Table 2. Kihara's Parameters (Sloan, 1998)

Gas Compositions	ε/k (K)	σ (Å)	a (Å)
Methane	154.54	3.165	0.3834
Ethane	176.4	3.2641	0.5611
Propane	203.31	3.2041	0.6520
Nitrogen	125.15	3.0124	0.2526
Dioxide carbon	168.77	2.9818	0.6850

Z denotes coordination number and R is pore's radius; their values for various pores have been presented in table 1(Nguyen1986). Kihara's parameters have also been presented in table 2 for gas compositions forming hydrates.

In Equation (4), the fugacity of pore's occupying components in hydrate Structure are seen which must be calculated. Thus, since in Equation (5) Langmuir constant is calculated in Pa^{-1}, the fugacity should be calculated in Pa. Three parameter state equations such as Soave - Redlich – Kwong (SRK) or Peng – Robinson (PR) are used in order to calculate the components' fugacity in gas phase. Finally, calculating all the required parameters in the afore-mentioned equations and using Equations (3) to (5), (6) and (7), the value of $\Delta\mu_w^{\beta-H}$ is calculated.

The Calculation of Chemical Potential Difference between Water in liquid-phase and Empty Hydrate Network ($\Delta\mu_w^{\beta-\alpha}$)

Parrish & Prausnitz have stated that the chemical potential difference between a hypothetical empty hydrate network and water in liquid state is calculated based on Gibbs - Helmholtz equation and temperature and pressure changes as follow:

$$d\left(\frac{\Delta\mu_W}{RT}\right) = -\left(\frac{\Delta h_W}{RT^2}\right)dT + \left(\frac{\Delta V_W}{RT}\right)dP \qquad (8)$$

In above equation, $\Delta h_W \& \Delta V_W$ are enthalpy and volume difference between water and empty hydrate network. Integrating the above equation, the following statement is obtained from classic thermodynamic:

$$\left(\frac{\Delta\mu_W}{RT}\right) - \left(\frac{\Delta\mu_W}{RT}\right)_{T_0} = -\int_{T_0}^{T}\left(\frac{dh_W}{RT^2}\right)dT + \int_{P_0}^{P}\left(\frac{dV_W}{RT}\right)dP \qquad (9)$$

The above equation has been written for a condensate water phase like ice or water in liquid state without any solvent. If the condensate water phase is not pure, activity coefficient of water will not be 1, and equation 11 is calculated based on equation (10):

$$\mu_W = \mu_W^{pure} + RT\ln(x_W\gamma_W) \qquad (10)$$

$$\left(\frac{\Delta\mu_W}{RT}\right) - \left(\frac{\Delta\mu_W}{RT}\right)_{T_0} = -\int_{T_0}^{T}\left(\frac{dh_W}{RT^2}\right)dT + \int_{P_0}^{P}\left(\frac{dV_W}{RT}\right)dP - \ln(x_W\gamma_W) \qquad (11)$$

Such that x_W is the composition of water percentage in liquid phase and γ_W is water activity coefficient of this phase, and x_W will be calculated by the following equation:

$$x_W = 1 - \sum x_k \tag{12}$$

where x_k denotes gas component k composition in water phase of the gas – hydrate - water system, which is calculated as below. At first, at 1atm pressure and low concentration of component i in liquid phase and using Henry's Law for solutions at infinite dilution we will have:

$$H_{kw}(T) = \frac{1}{x_k(T)} \tag{13}$$

Which $x_k(T)$ will be calculated by the following equation:

$$R \ln x_k = H_{kw}^{(0)} + \frac{H_{kw}^{(1)}}{T} + H_{kw}^{(2)} \ln T + H_{kw}^{(3)} T \tag{14}$$

The values of $H_{kw}^{(i)}$ have been presented in Table 3 for hydrate former components.

The following equation has been presented in calculating Henry's constant of component K at higher pressures:

$$\ln H_{kw}(T,P) = \ln H_{kw}(T) + \frac{\bar{V}_k^\infty}{RT}(P-1) \tag{15}$$

Consequently, the solubility of gas components in higher pressures is calculated as follows:

$$x_k = \frac{f_k}{H_{kw} \exp\left(\frac{\bar{V}_k^\infty (P-1)}{RT}\right)} \tag{16}$$

$\bar{V}_k^\infty$ is the partial molar volume of component K at infinitely diluted water and it is assumed to be independent of temperature. In this equation, fugacity and temperature must be in atmosphere measurement. In the presented model by Parrish & Prausnitz (1972), the statement of $slope = \frac{\bar{V}_k^\infty}{R}$ has been used instead of direct use of parameter$\bar{V}_k^\infty$. This slope is equal to $\log_{10}\left(\frac{f_k}{x_k}\right)vsP/_T$ of the curve's slope and in P/T, while f_k is fugacity of the gas component in terms of atmosphere unit and x_k is a molar fraction of component K in water. The slope values for common hydrate former components have been presented in Table 4 (Nguyen, 1986).

Table 4. The Required slope to Calculate Henry's constant in high pressures (Parrish & Prausnitz, 1972)

Gas Composition	Slope
Methane	0.17
Ethane	0.24
Propane	0.24
Nitrogen	0.14
Carbon dioxide	0.17

Table 3. The Required Parameters for Henry's Constant's Calculation (Sloan, 1998)

Gas Composition	$H_{kw}^{(0)}$	$H_{kw}^{(1)}$	$H_{kw}^{(2)}$	$H_{kw}^{(3)}$
Methane	-365.183	18016.7	49.7554	0.0000285
Ethane	-533.125	26565.0	76.624	0.000254
Propane	-628.866	31638.4	88.0808	0.0
Nitrogen	-327.124	16757.6	42.84	0.16765
Carbon Dioxide	-317.526	17371.2	43.0677	-0.00291

Table 5. The Required Thermodynamic Parameters for Water's Chemical Potential Difference (Sloan, 1998)

Parameters	Structure I	Structure II	Structure H
$\Delta\mu_w^0(J/mol)$	1297	937	914.38
$\Delta h_w^0(J/mol)$	1389	1025	846.57
$\Delta v_w^0(cc/mol)$	3	3.4	3.85
$\Delta C_p(J/mol)$	$-38.12-0.0336\times(T-273.15)$		

In Equation (11), under conditions where no soluble material exists in liquid phase, water's activity coefficient in liquid phase can be assumed equal to 1 without any significant error. Water's activity coefficient in liquid phase must be calculated using common models such as UNIFAC, if any additives such as inhibitors or improver exist in the system. (Reid, Prausnitz, & Poling, 1987). The empirical parameters required for solving Equation (11) have been presented to calculate the value of$\Delta\mu_w^{\beta-\alpha}$. Values presented in Table 5 have been used in this study (Sloan, 1998).

The value of Δh_w^0 must be modified in the expected temperature as follows:

$$\Delta h_w = \Delta h_w^0 + \int_{T_{ref}}^{T} \Delta C_p dT \tag{17}$$

METHODHOLOGY

Thermodynamic Model Modification in Presence of Additive Materials

In this study, it is assumed that temperature, weight percentage of Methanol in water phase, and input gas composition are known and the goal is to find hydrate formation pressure under these conditions. If methanol exists, water's activity coefficient will no longer be equal to 1 and will be calculated by UNIFAC model. On the other hand, the solubility of gas components such as Methane and carbon dioxide depends on Methanol concentration in water phase and it has been changed regarding its state in relation to pure water state in the system. Therefore, solubility changes in components of water phase will significantly affect hydrate formation conditions. The following equation has been suggested to predict natural gas components solubility in water – methanol mixture (Ngsuyen, 1986).

$$\ln x_i = A + C\ln T + DT + EX_{met} + FX_{met}^2 + G\ln X_{met} \tag{18}$$

Constants' values have been presented in Table 6.

The Calculation of the Activity Coefficient

UNIFAC model is employed based on different groups share for liquid phase to calculate the components' activity coefficient in water. Activity coefficient of component i in the mixture is considered as the sum of the two parts of combinatorial and residual:

$$\ln\gamma_i = \underset{combinatorial}{\ln\gamma_i{}^c} + \underset{residual}{\ln\gamma_i{}^R} \tag{19}$$

Table 6. The Required Parameters for Components' Solubility in Water-Methanol Calculations (Nguyen, 1986)

Gas Components	A	C	D	E	F	G
Methane	547.2	-119.76	0.4082	11.6	-8.7	-0.9860
Ethan	49.14	-3.943	-0.1161	-4.247	-5.304	0.3786
Propane	-4957.1	1161.1	-4.679	-132.65	132.61	0.515
Carbon Dioxide	86.12	-18.89	0.0349	9.729	-3.009	-1.236
Hydrogen Sulfide	672.15	-137.30	0.3684	-18.43	9.670	2.883

For other gas components, gas solubility coefficient is equal to the values presented for pure water system.

Combinatorial part is calculated as follows:

$$\ln \gamma_i{}^c = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (20)$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad ,\mathrm{z} = 10 \quad (21)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (22)$$

Pure components' properties are used in the calculation of the combinatorial part in equation (20). r_i and q_i parameters are as the total volume and group area of Ri & Qi whose values have been presented in reference (Reid et al., 1987) and have been taken from this reference, concerning the available groups in the system.

$$r_i = \sum_k v_k^{(i)} R_k \;\; and \; q_i = \sum_k v_k^{(i)} Q_k \quad (23)$$

$v_k^{(i)}$denotes the number of type K in type i molecule and is always a natural number. Residual term is calculated as follows:

$$\ln \gamma_i{}^R = \sum_{\substack{k \\ all\ groups}} v_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (24)$$

Γ_k is the group's residual activity coefficient and $\Gamma_k^{(i)}$is residual activity coefficient of group K in the reference solution which only contains molecule type i, and is expressed as follows (Poling, Prausnitz, & John Paul, 2004):

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \Psi_{mk} \right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}} \right] \quad (25)$$

θ_m represents group m's volume percentage and is calculated like θ_i:

$$\theta_m = \frac{Q_m \mathrm{X}_m}{\sum_n Q_n \mathrm{X}_n} \quad (26)$$

X_m is group m's composition percentage in the mixture. The Interaction parameter Ψ_{mn} among the groups is calculated as follows:

Table 7. The Calculation of the Reference Hydrate Pressure Constants (Nguyen, 1986)

Gas Composites	A_r	B_r	C_r	Temperature Range
Methane	-1212.2	44344.0	187.719	273-300
Natural Gas Compound	-1023.14	34984.3	159.923	273-291
Natural Gas Compound	4071.61	-193428.8	-599.755	291-303

$$\Psi_{mn} = \exp\left(-\frac{a_{mn}}{T}\right) \tag{27}$$

Using the above mentioned equations, water activity coefficient can be calculated in presence of additive materials and soluble gas components in water phase (Poling et al., 2004).

The Calculations of the Prediction Algorithm for Gas Hydrate Formation Conditions

Using Gibbs' Law of phases, three-phase equilibrium temperature can be determined and vice versa in the fixed pressure and composition of gas mixture; it means that if temperature and composition are determined, the pressure will be determined, too. The simplest procedure for phase equilibrium calculation of hydrate formation is pressure determination at fixed temperature and composition. Prediction calculation algorithms for hydrate formation have been presented below on the basis of the mentioned equations.

1- In the temperature in question for gas mixture, the number of components in gas phase and their composition percentage, critical properties, and other needed parameters for calculations are read.
2- If temperature is higher than quadrate points of gas components, hydrate will not be formed.
3- Using Kihara parameters for each component, Langmuir constant in each pore for either of the structures is calculated using the given numerical integrating in equations 5 to 7.
4- A pressure is estimated for the three-phase conditions at the given temperature. For better and faster convergence, this pressure is usually selected the same as hydrate reference pressure which is calculated by the equation.

Reference Pressure

Parrish & Prausnitz suggested this pressure as a function of temperature and hydrate structure as follows:

$$\ln P_r = A_r + \frac{B_r}{T} + C_r \ln T \tag{28}$$

A_r,B_r and C_r are constants that are different for various hydrate structures.

5- Gas phase's fugacity for each component in the given temperature and the estimated pressure can be calculated by a suitable state equation.

6- Under conditions that natural gas components which form structure II hydrate (nitrogen, propane isobutane and heavier components) do not exist in the mixture, structure I is formed; these components, however, usually exist in natural gas mixtures and structure II will be formed. This condition will be checked in the final stage, but the type of the structure must be first selected to make the proper selection and usage of the parameters' values depending on the structure possible.

7- Pore occupation fraction is calculated by equation 4; by which, the primary value for the chemical potential deference of water by the equation in the given temperature and the estimated pressure is calculated.

8- Water composition percentage is computed in liquid phase. If necessary, water activity coefficient will be calculated using a suitable procedure.

9- Performing the available numerical integration in equations (11) & (17), secondary chemical potential difference of water will be calculated by equation 11.

10- According to equation, the potential differences' values in stage 7 & 9, must be equal. At this stage, these values are compared; if there is a considerable difference between them, the pressure value will be calculated by Newton – Raphson method; the calculations will be repeated from stage 4 until the error value becomes negligible, using this new pressure.

The following equations have been used in correcting the equilibrium pressure for hydrate formation using Newton – Raphson method:

$$P_{k+1} = P_k - \frac{F(P)}{\acute{F}(P)} \tag{29}$$

$$F(P) = \Delta\mu_W(T,P_r) - RT \sum_{i=1}^{NCAV} \nu_i \left(1 + \sum_{k=1}^{N} C_{ki} y_i P\right) - RT \ln x_w \tag{30}$$

$$\acute{F}(P) = -RT \sum_{i=1}^{NCAV} \nu_i \left(\frac{\sum_{k=1}^{N} C_{ki} y_i \varphi_i}{1 + \sum_{k=1}^{N} C_{ki} y_i P}\right) \tag{31}$$

Conducting above mentioned calculations for chosen Structures, stage 6 to 10 must be repeated for other structures. Crystal structure formation with lower pressures is more probable thermodynamically. If formation pressure is equal in both structures (which rarely happens), both structures are created next to each other (Sloan1998).

A part of physical properties of the available components in the system used in the model such as the critical temperature, critical pressure, eccentric coefficient, and quadrate points temperature of hydrate former components has been provided in a program as a database for 11 common hydrate former compositions. The values of these parameters have been derived from Green &Perry (2007) reference. In the computer program, a special number is allocated to each component such that the stored information related to required component can be read, entering the indicated numbers.

RESULTS AND DISCUSSION

In this study, the accuracy of the model for pure system and system containing inhibitor is checked, in addition to the investigation of the effect of an industrial inhibitor on the prevention of gas hydrate formation. In the following lines, the results of the model for a gas system including pure Methane along with industrial Methanol inhibitor are compared with the available empirical data. The empirical data have been reported by Daaton & Frost (1946).

In order to compare the results of modeling with the empirical data, the absolute error average has been used as follows:

$$\text{Average Absolute Deviation} = \frac{\sum_{\#data} \left|P_{model} - P_{exp}\right| / P_{exp}}{\#data} \times 100 \qquad (32)$$

In the present research, no correction has been made in the prediction model of hydrate formation condition in the pure system and in presence of inhibiting substances; the results have only been stated for the efficiency of the prediction model.

As can be seen, the model has been successful in presenting good predictions in relation to empirical results. Minimum error is at 280.4F and is equal to 0.18 % and the maximum error is related to 285.9F temperature and is equal to 3.88%, and as can be seen in the table, the errors are more in temperature over 280.4F temperature.

All alcohols (all compositions whose molecular chain end with Bothanol) make hydrogen bond with water and their solubility in water is high. This property is the reason for their high influence on hydrate formation process (Cieslesicz1981).

Among alcohols, Methanol is the most common inhibitor due to its cost and efficiency rate. The inhibiting power of alcohols reduces as follows: Methanol<Ethanol<isopropanol (Sloan & Kohl, 2007). Nielsen & Bucklin (1983) have shown that using Methanol in comparison with other materials is cheaper and their separation at the end of transportation operation is more economic relative to other inhibitors.

Compared to alcohols, Glycols own higher hydrogen bonds with water, but have higher molecular weight in relation with their counterparts; therefore, they are more costly than alcohols and need more complex installations for separations in recovery gas transportation operations. Among inhibitors, salts, alcohols and glycols, alcohols are the best inhibitors and Methanol is the most common inhibitor among alcohols (Nguyen, 1986; Nielsen & Bucklin, 1983; Sloan &kohl, 2007). Besides, in this section, the absolute average error calculation has been shown by equation (32). The empirical results in this section of the research have been borrowed from Ng & Robinson's (1985) article. As can be seen (Table 8 and Table 9), the model has presented good predictions, although error rate is higher in comparison with the non-inhibitor state. The least error amount is at 250.9 K in weight percentage of 35 Methanol and is equal to 0.42%, while the highest error amount is at 233.1 K temperature in weight percentage of 50 Methanol and is equal to 17.1%.

Table 8. Comparison between the empirical and modeling results

Temperature (k)	**Bar**	
	Empirical results Presented by Daaton & Frost (Sloan & Koh, 2007)	**Model results**
273.7	27.6	27.7
274.3	29.0	22.2
275.4	32.4	32.1
275.9	34.2	34.0
277	38.1	38.3
279.3	47.7	47.5
280.4	53.5	53.4
280.9	57.3	55.8
280.5	60.6	59.1
282.6	67.7	66.0
284.3	81.2	78.5
285.9	97.8	94.0
The Absolute Error Mean Percentage		1.47

Figure 1 demonstrates the summary of results for water – methane and methanol system. Noticing this diagram, the following points are obtainable, in addition to a good comparison:

- The increase of inhibitor concentration at a given temperature results in hydrate formation in a higher pressure. Other parameters such as cost and separation of methanol from the transferred gas mixture can affect the optimal concentration of the inhibitor. Additionally, it must be noted that the addition of a great amount of the inhibitor substance to pipe lines will result in the usage of a great number of theses pipe lines in the transportation of this material, and this is the biggest problem of thermodynamic inhibitors in the industry.
- The efficiency rate of these substances is more in higher temperatures. As can be seen in the figure, the trend of changes is slower in low temperatures in a specific concentration. In higher temperatures, however, the slope of the curve has significantly increased.

Table 9. Comparison of the modeling results with empirical data.

Methanol Weight Percentage	**Temperature (K)**	**Pressure (bar)**	
		Ng & Robinson, 1985 (empirical)	**Model**
10	266.23	21.4	21.2
	271.24	34.1	33.4
	275.87	56.3	55.0
	280.31	90.7	87.4
	283.67	133.2	126.7
	286.40	188.2	175.6
The Absolute Error Mean Percentage			3.41
20	263.34	28.3	28.1
	267.51	42.0	41.2
	270.08	56.1	55.1
	273.55	84.1	81.3
	277.56	133.0	127.6
	280.17	187.5	176.6
The Absolute Error Mean Percentage			2.93
35	250.9	23.8	23.7
	256.3	36.9	42.1
	260.3	68.1	65.6
	264.6	101.6	97.2
	267.8	136.8	131.2
	268.5	172.2	145.0
	270.1	205.1	205.6
The Absolute Error Mean Percentage			6.1
50	233.1	14.7	12.2
	240.1	29.5	27.6
	247.4	72.4	63.3
	250.4	105.4	88.3
	255.3	169.8	150.9
The Absolute Error Mean Percentage			12.69

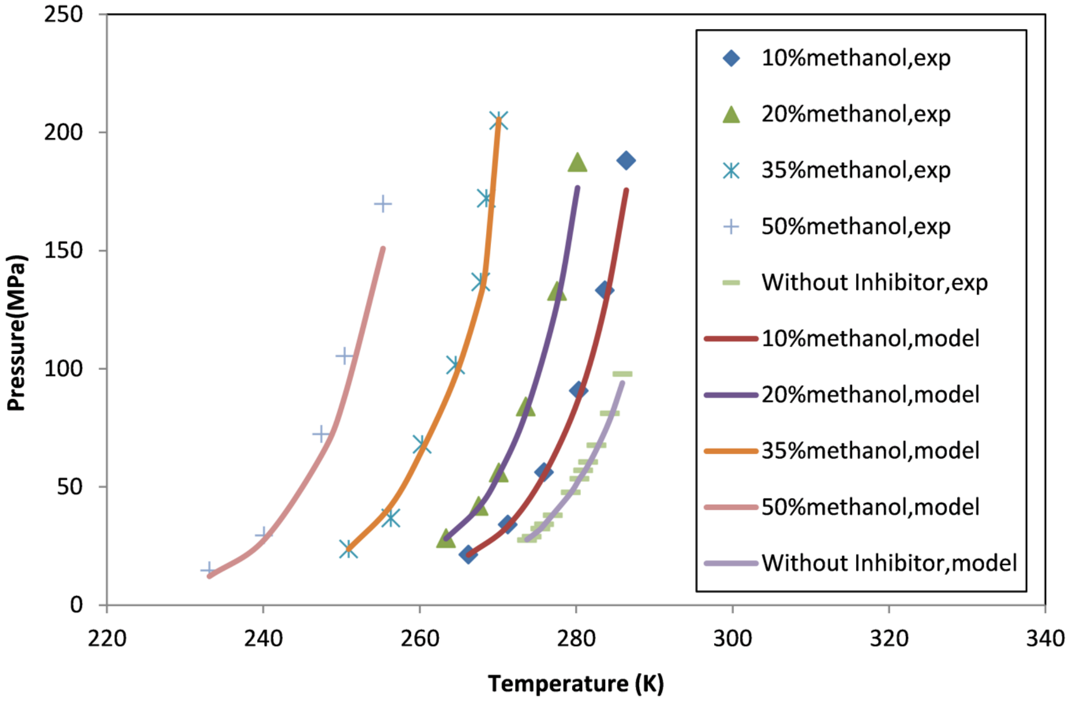

Fig. 1: Phase diagrams for different percentage of inhibitors.

CONCLUSIONS

This study concerned with formation of gas hydrates in severe thermodynamic situations in gas production and transportation systems. The presence of additive substances such as inhibitors affects liquid phase behavior and changes it from an ideal solution. It has been shown that Van der Waals & Plateau's (1959) thermodynamic model for prediction of pure water – gas system conditions operates very well; UNIFAC model for the model corrections and the study of liquid phase behavior along with inhibitor (methanol) presence are efficient as well.

The inhibitor effect on hydrate formation conditions is such that hydrate formation pressure increases due to the increase of inhibitor concentration in the system in a specific temperature; this increase continues more in higher pressures. Consequently, concerning the costs of the inhibitors and its separation at the end of the pipe lines, the inhibitor's optimum level can be determined.

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