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Phase equilibrium for hydrate formation in the Methane and Ethane system and effect of inhibitors

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ABSTRACT

Gas hydrates form at various facilities related to the natural gas and process equipment in oil and gas fields, refineries, petrochemical and facilities in the chemical industry, in the presence of both natural gas and water, at high pressure and low temperature. In the present study, the equilibrium conditions of gas hydrate mixture formation including methane and ethane and also pure ethane are investigated. The conditions for binary hydrate formation without the presence of inhibitors have been used and the empirical research available in the field has been used to evaluate the accuracy of the present modeling. Hydoff software was used for modeling and the hydrate formation pressure was calculated. In order to evaluate the accuracy of the modeling, the values related to the calculation error were calculated from the existing experimental research and the results showed that there are 11%, 14% and 0.08% errors with Deaton & Frost, McLeod & Campbell, Holder & Grigoriou research, respectively. Therefore, it can be concluded that the best case for modeling according to the experimental results is Holder & Grigoriou, and therefore a mathematical model is presented to estimate the formation conditions of the binary mixture of methane and ethane, which can be used with very high accuracy. Pure ethane was also tested with potassium chloride, sodium chloride and 5% methanol inhibitors and also without inhibitors and the results showed that the effect of adding methanol is greater than sodium chloride and potassium chloride, respectively, and ethane hydrate is formed at higher pressures.

1. Introduction

Hydrate formation in gas transportation lines is considered a serious threat to reduce the useful life of the pipeline. If there is enough time after the initial stages of nucleation and formation of hydrate crystals, hydrate plugs will form, leading to blockage of the flow path and even rupture of the pipeline. A two-step mechanism of hydrate formation has been proposed. Stage One: stoichiometric alkaline hydrates during a semi-chemical reaction. Second step: The adsorption of gaseous molecules through a series of alkaline hydrate chains during a non-stoichiometric process of hydrates. There are three factors involved in the formation of gaseous hydrates, very low temperature, very high pressure, and the existence of moisture. In gas refining processes, the first two factors are almost always present; because for easier storage of gas, it is tried to increase its pressure to reduce its volume. Also, due to safety considerations, the temperature in the process is often very low. In such cases, in order to remove the gas hydrate, the third factor must be removed or ineffective. It should be such that the residual moisture in the gas is so low that there is no potential for hydrate formation in the gas.

Hydrates have another useful aspect that makes the study of their formation very important. The hydrate property can also be used to transfer gas. The conditions for hydrate formation are appropriate pressure and temperature, the presence of water molecules, and the presence of gas molecules. Gaseous hydrates are formed naturally at ambient temperatures and pressures of ocean floor sediments and in areas with a depth of more than

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500 m. At this pressure and at temperatures above the stable temperature of ice, the gas hydrate is quite stable. Reasons for the importance of gas hydrates is the high potential of gas hydrates in natural gas storage makes it attractive to use them for storage and transportation of natural gas and other gases as a competitor to liquefaction and condensation methods. Gaseous hydrates can be easily transported; Therefore, the technology of building ships carrying gas hydrates will be much less complex than ships carrying LNG, and gas production facilities can be designed much easier than LNG facilities. Gaseous hydrates can also be used in separation processes. Gaseous hydrates are composed of only a limited number of substances, and if a substance is separated from a mixture, including non-hydrate-forming substances, the use of the hydrate-forming property is considered an opportunity. Applications of this separation include concentrating water-rich streams, preparing drinking water from seawater, or separating gas streams. It is worthy to note that hydrate formation can be beneficial in some limited cases such as le in the CCS industry for the safe storage of carbon dioxide albeit it is a challenge as there are several impurities that can impact on hydrate formation curve and its equilibrium [1]. The impact of impurities on the formation of CO2 hydrate has been addressed elsewhere by Peletiri et al. and is not in the scope of this article [2,3]. The research was done by Porgar et al. to investigate the role of methanol and sodium chloride effect on CO2 hydrate formation and found that by increasing inhibitor's concentration, hydrate formation pressure was enhanced [4]. Muromachi studied the ammonium chloride effect on CH4, CO2, and C2H6 hydrates and stated that this inhibitor can reduce their solubility in water and as a result found that methanol has a better effect than ammonium chloride on hydrate formation [5]. Xu et al. investigated the basic structures involved in the formation of methane and ethane hydrates and experimentally studied the tetrahydrofuran effect on the triple system [6]. In another study, Menezes et al. at high pressure experimentally perused methane, ethane, and carbon dioxide hydrate system and finally compared their results with software. The rate of cooling and size of samples were parameters that were investigated and hydrate volume was estimated [7]. Salehfekr et al. examined hydrate formation conditions at the temperature range of 267 to 276 °C. Their results showed that by increasing ethane concentration, a more stable gas hydrate was formed, and also equilibrium pressure will have enhanced [8]. In Table 1 a study on clathrates formation condition was done.

Table 1- Hydrate formation results

Ref.	Tem. (°C)	Pressure (MPa)	Enthalpy (kJ.mol CH_4)
[9]	0	2.56	53.8
[10]	11.25 to 16.35	9.2 to 16	59
[11]	13,25,29,33	9.88,43.9,69.6,105	55.7,54.5,54.8
[12]	1 to 31	2.9 to 69.7	54.5
[13]	17	16	53.8

In hydrate system, the amount of cavity occupation fraction is calculated using Langmuir absorption theory:

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

In equation 1, f_k is fugacity and C_{ki} is the Langmuir absorption constant and expresses the interactions between water and gas in the cavity. Using Leonard Jones' theory, Van der walls and Platteeuw presented the following equation for Langmuir's constant calculation:

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

k is the Boltzmann constant and ω (r) is a function of the spherical symmetrical cavity potential, which is a function of the cell radius, the coordinate number, and the type of interaction. R is the radius of the spherical cavity and "a" is the radius of the guest molecule [4]. Other studies and reviews were done on hydrates formation and its mechanism [14,15].

2. Results and Discussion

In the present study, the binary methane-ethane system without any additives was compared with the experimental results **.**The hydrate formation pressure at different temperatures was calculated and their deviation was investigated with experimental results. In Figure 1, the results of the modeling are compared with the results of Deaton and Frost and the results are presented. Table 2 presents the results of the methane and ethane gas mixture modeling with different percentages of methane and compared them with the experimental results from Deaton and Frost.

Table2- Results for hydrate formation pressure: Reference for experimental data: Deaton and Frost [16]

%CH_4	Tem. (K)	Pres. (kPa)-Exp.	Pres. (kPa)-Mod.	Devi.	%CH_4	Temp.(K)	Pres. (kPa)-Exp.	Pres. (kPa)-Mod.	Devi.
56.4	277.6	1289	1179.1	8.526	97.1	274.8	2158	2565.33	15.878
56.4	280.4	1758	1596.88	9.165	97.1	277.6	2958	3382.748	12.556
56.4	283.2	2434	2174.699	10.653	97.1	280.4	4034	4486.598	10.088

90.4	274.8	1524	1870.752	22.753	97.1	274.8	2365	2565.33	7.809
90.4	277.6	2096	2492.471	18.916	97.8	277.6	3227	3516.882	8.243
90.4	280.4	2889	3340.111	15.615	97.8	280.4	4413	4655.161	5.202
90.4	283.2	3965	4519.019	13.973	97.8	282.6	5668	5837.042	2.896
95	274.8	1841	2292.919	24.547	97.8	283.2	6088	6221.382	2.144
95	274.8	1841	2292.919	24.547	98.8	274.8	2861	2842.293	0.658
95	277.6	2530	3037.25	20.049	98.8	277.6	3806	3728.436	2.080
95	280.4	3447	4047.11	17.410	98.8	280.4	5088	4918.475	3.447

Average error = 11.2%

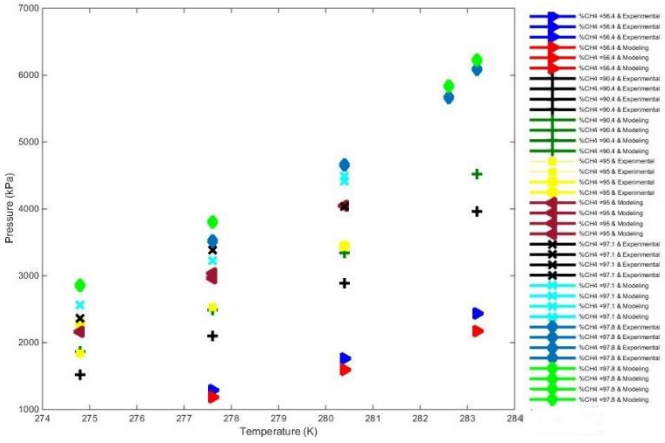

Fig. 1-Comparison pressure result of modelling with Deaton and Frost research

Obtained results from modeling also compared with McLeod and Campbell results from the temperature of 284.9 to 304.1 K and average deviation of 14% was obtained that this amount of error at lower temperatures compared to higher temperatures showed less difference with laboratory values. The results were summarized in Table 3.

Hydrate pressure formation for methane at concentrations of 94.6% and 80.9% at different temperatures were plotted in Fig.2 and Fig.3 respectively. By increasing temperature, the pressure also increases for both modeling and experimental results that for 80.9%, by enhancing temperature from 288.8 to 304.1 K, the equilibrium pressure increased from 6.6 to 56.5 Mpa while for 94.6% concentration, the pressure was changed from 6.4 to 53.3 Mpa.

Table 3- Results for hydrate formation pressure: Reference for experimental data: McLeod and Campbell [16]

%CH_4	**Temp. (K)**	**Pres. (MPa)-Exp.**	**Pres. (MPa)-Mod.**	**Devi.**	**%CH_4**	**Tem. (K)**	**Pres. (MPa)-Exp.**	**Pres. (MPa)-Mod.**	**Dev.**
94.6	302	68.43	53.37	22.0	80.9	304.1	68.57	56.57	17.496
94.6	301.2	62.23	48.95	21.3	80.9	303.1	61.95	50.87	17.874
94.6	299.1	48.23	38.54	20.1	80.9	301.3	48.64	41.44	14.797
94.6	296.6	34.44	28.35	17.7	80.9	299	35.61	30.95	13.080
94.6	293.6	24.24	19.13	21.1	80.9	296.4	23.48	21.271	9.405
94.6	289.7	13.89	11.44	17.6	80.9	293.3	13.89	12.88	7.217
94.6	287.9	10.45	9.155	12.4	80.9	291.7	10.45	9.98	4.490
94.6	284.9	6.93	6.456	6.8	80.9	288.8	7	6.61	5.604

Average error = 14%

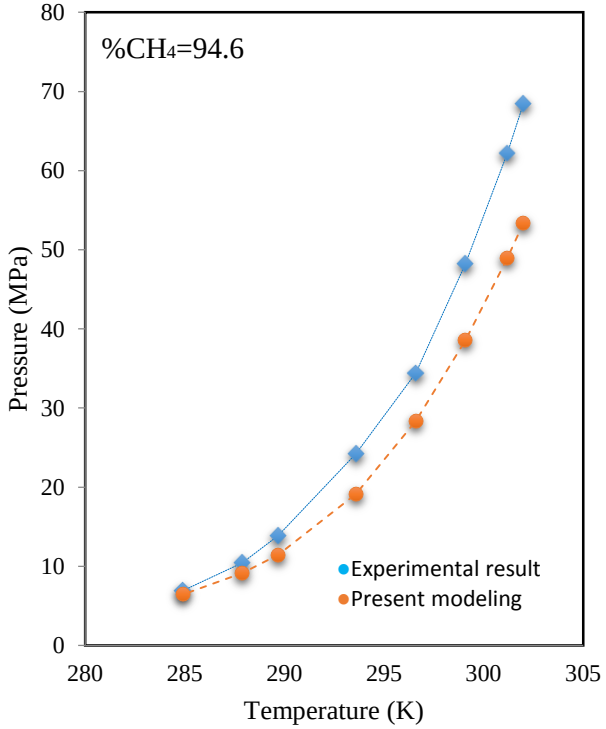

Fig.2-Comparison pressure result of modelling with McLeod and Campbell research @ %CH_4=94.6 [16].

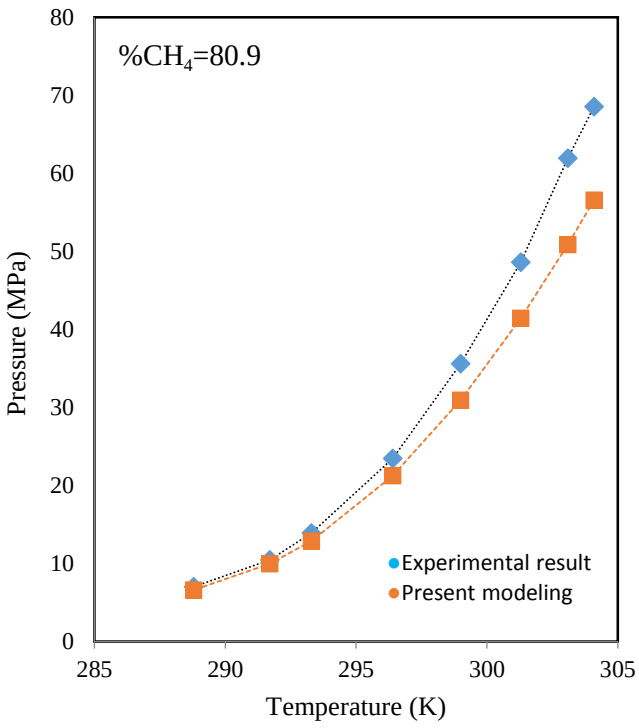

Fig.3-Comparison pressure result of modelling with McLeod and Campbell research @ %CH_4=80.9 [16].

In substances like methane that have a structure I, hydrate forms at higher pressures than materials that have structure II and in identical compounds of several mixtures, the higher the methane content, the pressure of hydrate formation is higher. This model was presented by a team led by Dr. Sloan in 1998. Its infrastructure is based on the Van der Waals-Platteeuw and Parish-Praznitz model. Of course, there have been changes in the values of the parameters used and the form of the equations to eliminate some of the model constraints. For example, instead of using chemical potential equivalence, the equation of water fugacity in phases is used.

Table 4- Results for hydrate formation pressure: Reference for experimental data: Holder and Grigoriou [16]

%CH_4	Tem. (K)	Pres. (kPa) -Exp	Pres. (kPa)- Mod	Devi.	%CH_4	Temp. (K)	Pres. (kPa)- Exp	Pres. (kPa)- Mod	Dev.
1.6	283.9	1810	1687.04	0.068	4.7	286.4	2510	2335.886	0.069
1.6	285.7	2310	2145.339	0.071	4.7	287.6	2990	2763.547	0.076
1.6	286.6	2710	2433.133	0.102	17.7	281.6	1420	1319.093	0.071
1.6	287.8	3080	2910.036	0.055	17.7	283.3	1770	1610.669	0.090
4.7	279.4	990	967.678	0.023	17.7	284.8	2140	1927.43	0.099
4.7	281.5	1340	1248.678	0.068	17.7	286.2	2660	2288.371	0.140
4.7	283.3	1710	1560.819	0.087	17.7	287	3000	2530.252	0.157
4.7	285.3	2170	2017.037	0.070	Average error=0.083				

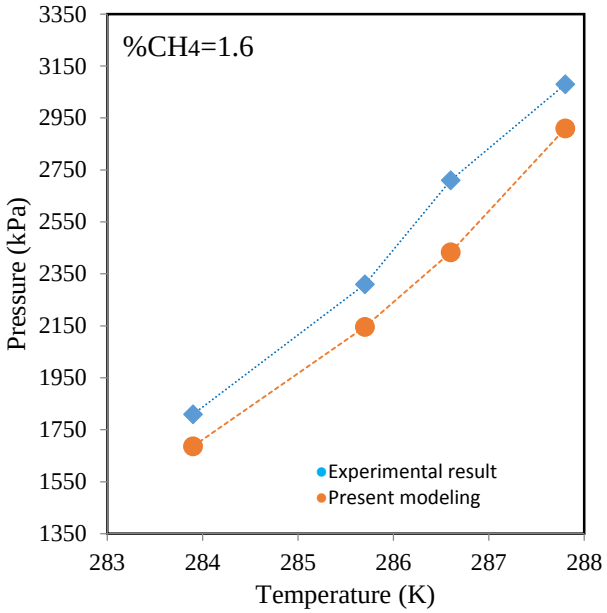

Fig. 4-Comparison pressure result of modelling with Holder and Grigoriou research @ %CH_4=1.6 [16].

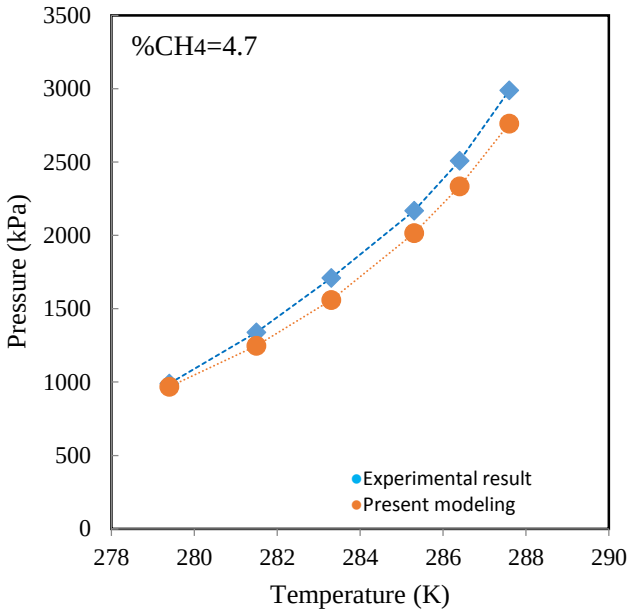

Fig. 5-Comparison pressure result of modelling with Holder and Grigoriou research @ %CH_4=4.7 [16].

Figures 4 to 6 were plotted in three different percentages of methane and Table 4 reports the results of the modeling with Holder and Grigoriou result and the average error is 0.083 which shows the best agreement with the experimental results and shows that the proposed model can predict the hydrate formation behavior with high confidence. For this reason, the mathematical model is presented for three different percentages of methane that can predict the pressure of methane-ethane gas mixture formation.

$P = 0.9023T^3 - 754.46T^2 + 210411T - 2E+07$ @%CH_4=17.7 (3)

$P = 1.0983T^3 - 918.24T^2 + 256015T - 2E+07$ @%CH_4=4.7 (5)

$P = 3.2928T^3 - 2795.1T^2 + 791117T - 7E+07$ @%CH_4=1.6 (4)

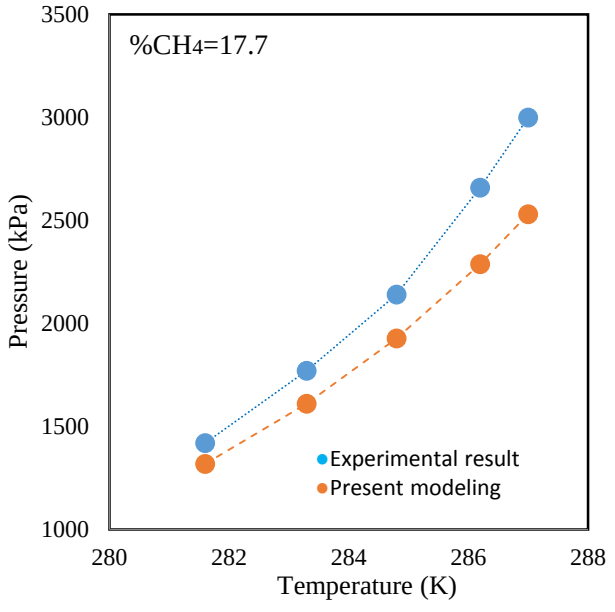

Fig.6-Comparison pressure result of modelling with Holder and Grigoriou research @ %CH_4=17.7.

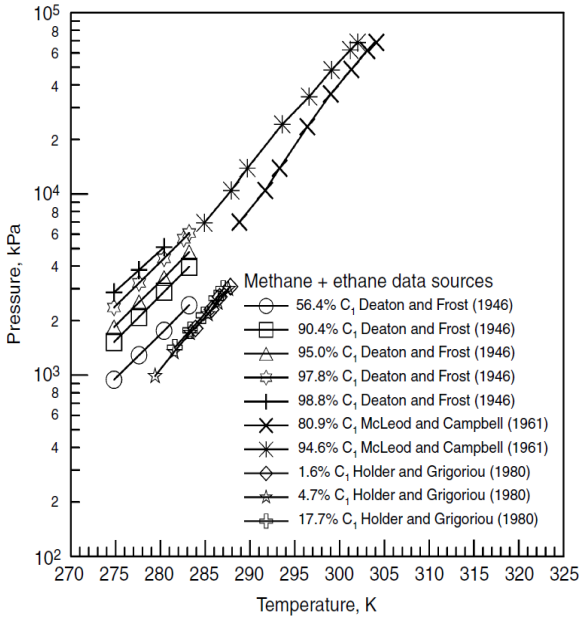

Fig.7- Methane + ethane mixture (LW–H–V) data [16].

In Figure 7, the experimental studies of methane-ethane hydrate formation were plotted. Hydrates formed in porous media are a function of temperature, pressure and pore size. At a specific pore size with decreasing temperature, equilibrium occurs at higher pressure and at constant temperature increases with decreasing pore size of equilibrium pressure. Therefore, it is important to know the equilibrium conditions of hydrate

decomposition to be extracted from these sources. Due to the solid nature of the hydrate phase, hydrate formation at higher pressures will be more intense than at lower pressures and eventually lead to increased mass transfer coefficients at pressures. In fact, the increase in pressure increases the condensing force and the rate of gas consumption, which increases the driving force to reduce the mass transfer coefficient, but increases the rate of gas consumption to increase the mass transfer coefficient.

In other section of the present study, pure ethane hydrate formation in two different modes was investigated, in the first case, ethane without additive was tested and then in order to evaluate the importance of using inhibitors, three inhibitors, methanol, sodium chloride and potassium chloride, were used at a concentration of 5% by weight. Ethane in the temperature range between 298.1 to 317.5 °C without additives showed an almost linear relationship that with increasing temperature also increased the amount of hydrate formation pressure. This trend was plotted in Fig.8.

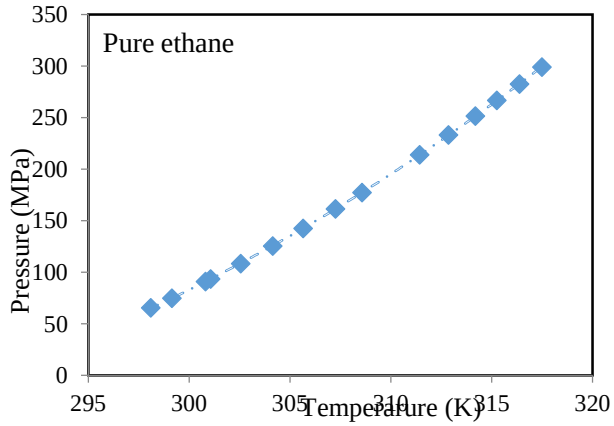

Fig.8. Equilibrium pressure changes for pure ethane without inhibitor versus to temperature changes.

To validate the research, the results were compared with the experimental results of Alvonitis and the corresponding graph was shown in Figure 9, which shows a good agreement with the laboratory results.

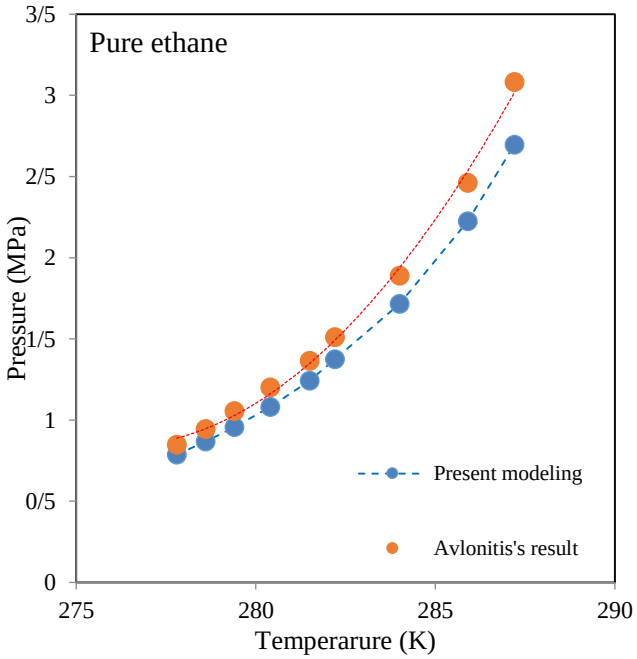

Fig.9. Comparison between present study with Alvonitis result [16].

The results of modeling the formation of ethane hydrate using Hydoff software in the temperature range between 277 to 317 °C are fully included in Table 5, which showed structure I in this temperature range, and with increasing temperature, the amount of pressure increased and also, the amount of molar percentage of water in equilibrium increased.

Table 5- Pure ethane result via using Hydoff software

Tempe. (K)	Equilibrium Hydrate :	Composition of Phases at Equilibrium (moles)				Equilibrium Pressure (kpa)	Fractional Occupancy of Cages	
		FEED	Water	Liquid	Hydrate		Small	Large
277.8	STRUCTURE I	1	0.0005	1	1	786.515	0	0.9894
278.6	STRUCTURE I	1	0.0005	1	1	866.792	0	0.9899
279.4	STRUCTURE I	1	0.0005	1	1	955.826	0	0.9904
280.4	STRUCTURE I	1	0.0006	1	1	1081.168	0	0.9909
281.5	STRUCTURE I	1	0.0006	1	1	1241.628	0	0.9915
282.2	STRUCTURE I	1	0.0006	1	1	1374.327	0	0.9919

284	STRUCTURE I	1	0.0007	1	1	1714.434	0	0.9927
285.9	STRUCTURE I	1	0.0008	1	1	2223.26	0	0.9935
287.2	STRUCTURE I	1	0.0009	1	1	2694.55	0	0.994
299.15	STRUCTURE I	1	0.0017	1	1	74941.234	0	0.9989
298.1	STRUCTURE I	1	0.0016	1	1	65468.148	0	0.9987
300.82	STRUCTURE I	1	0.0018	1	1	90871.4	0	0.9992
302.56	STRUCTURE I	1	0.002	1	1	108530.07	0	0.9994
304.15	STRUCTURE I	1	0.0021	1	1	125609.703	0	0.9996
305.65	STRUCTURE I	1	0.0022	1	1	142473.766	0	0.9997
307.26	STRUCTURE I	1	0.0023	1	1	161363.828	0	0.9998
308.57	STRUCTURE I	1	0.0024	1	1	177343.984	0	0.9998
301.07	STRUCTURE I	1	0.0019	1	1	93341.719	0	0.9993
311.44	STRUCTURE I	1	0.0027	1	1	214066.453	0	0.9999
312.86	STRUCTURE I	1	0.0028	1	1	233193.219	0	0.9999
314.2	STRUCTURE I	1	0.0029	1	1	251511.328	0	1
315.26	STRUCTURE I	1	0.003	1	1	266571.281	0	1
316.39	STRUCTURE I	1	0.0031	1	1	282416.406	0	1
317.49	STRUCTURE I	1	0.0032	1	1	298906.719	0	1

Finally, in order to investigate the role and effect of different inhibitors on equilibrium pressure, three different inhibitors, one methanol and the other two salt inhibitors including potassium chloride and sodium chloride at a weight concentration of 5% were used. The results showed that the use of inhibitor increases the amount of pressure, which was higher for methanol in the the amount of inhibitor used to prevent hydrate formation, it is necessary to predict the hydrate formation conditions in systems containing the inhibitor. In the salt-water system, the interaction of the ions from the salt ionization with the water dipoles is much stronger than the hydrogen bond and van der Waals forces between the water molecules and the guest molecules. This interaction prevents the formation of hydrates due to the adsorption of more water molecules to salt ions than the adsorption of water in the hydrate structure.

studied temperature range, which was more significant at higher temperatures that related graph was plotted in Fig.10.

The results indicate that the addition of salts such as NaCl and KCl to organic inhibitors increases the efficiency of inhibitors. In order to describe

Salts act as a thermodynamic inhibitor by lowering the temperature of hydrate formation. The following two reasons can be suggested for the improving effect of these liquids. The first reason is the effect of these liquids on surface tension. Adding ionic liquid to water decreased the surface tension between phases, which is a good phenomenon for two-phase contact and increases the nucleation possibility in the interface of liquid and gas. The second reason is related to the salt effect of ionic liquids, which increases the rate of water transfer for the growth of hydrates by adding these liquids.

Table 6 shows complete results of methanol inhibitor on ethane hydrate formation that water content decreased with increasing temperature. The mechanism of alcohols is such that form a hydrogen bond with water by hydroxyl group, and on the other hand, the hydrocarbon atoms of the alcohol molecules direct the water molecules towards the formation of clusters.

Methanol delays the participation of water molecules in the formation of the hydrate structure and maintains them in the fluid phase. The more inhibitors are added to the structure, the fewer molecules of water are formed in the structure of the hydrate, and therefore the lower the temperature and the higher the pressure required to forming the hydrate.

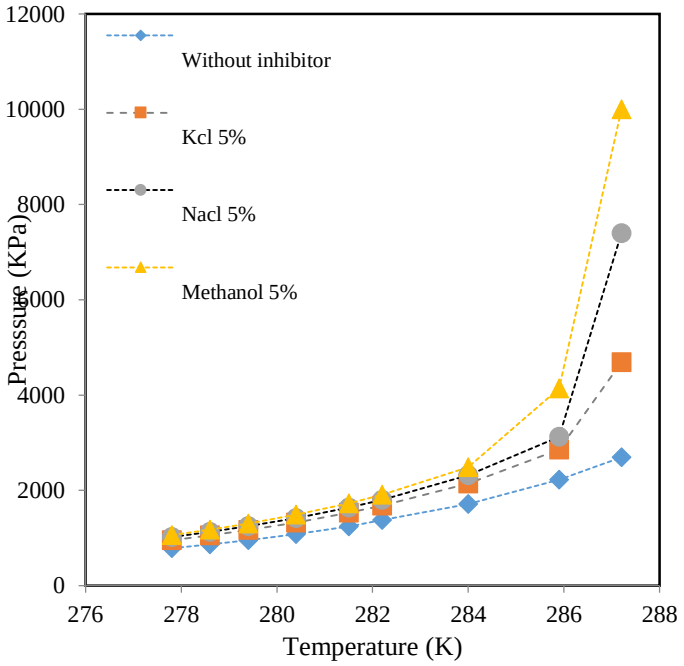

Fig.10. Effect of various inhibitors on ethane hydrate formation.

Table 6- Pure ethane formation with Methanol 5%

Tempe. (K)	Equilibrium Hydrate :	Composition of Phases at Equilibrium (moles)				Equilibrium Pressure (kpa)	Fractional Occupancy of Cages	
		FEED	Water	Liquid	Hydrate		Small	Large
277.8	STRUCTURE I	1	0.0119	1	1	1057.631	0	0.9919
278.6	STRUCTURE I	1	0.0117	1	1	1173.127	0	0.9923
279.4	STRUCTURE I	1	0.0116	1	1	1302.686	0	0.9927
280.4	STRUCTURE I	1	0.0114	1	1	1487.847	0	0.9931
281.5	STRUCTURE I	1	0.0111	1	1	1727.584	0	0.9936
282.2	STRUCTURE I	1	0.011	1	1	1906.797	0	0.9939
284	STRUCTURE I	1	0.0106	1	1	2484.281	0	0.9945
285.9	STRUCTURE I	1	0.0102	1	1	4137.688	0	0.9952
287.2	STRUCTURE I	1	0.0096	1	1	9997.062	0	0.9959

Inhibitors are more effective at higher temperatures and, as can be seen from the figures, at a specific concentration, the process of change is slower at lower temperatures, but at higher temperatures, the slope shows a large increase. Kcl inhibitor effect on formation was summarized in Table 7.

Table 7- Pure ethane formation with Kcl 5%

Tempe. (K)	Equilibrium Hydrate	Composition of Phases at Equilibrium (moles)				Equilibrium Pressure (kpa)	Fractional Occupancy of Cages	
		FEED	Water	Liquid	Hydrate		Small	Large
277.8	STRUCTURE I	1	0.0006	1	1	955.631	0	0.9911
278.6	STRUCTURE I	1	0.0006	1	1	1055.177	0	0.9915
279.4	STRUCTURE I	1	0.0006	1	1	1167.321	0	0.9919
280.4	STRUCTURE I	1	0.0007	1	1	1325.453	0	0.9924
281.5	STRUCTURE I	1	0.0007	1	1	1528.302	0	0.9929
282.2	STRUCTURE I	1	0.0008	1	1	1676.335	0	0.9932
284	STRUCTURE I	1	0.0009	1	1	2145.462	0	0.9939
285.9	STRUCTURE I	1	0.001	1	1	2856.422	0	0.9946
287.2	STRUCTURE I	1	0.0011	1	1	4691.5	0	0.9951

Methanol is a volatile substance and therefore when injected into the condensate (liquefied) phase or into a natural gas stream, only part of it enters the phases. Methanol is commonly used to prevent hydrate formation in pipelines and process equipment. But methanol has the opposite effect on the subsequent process of hydrocarbon flow. For example, a process problem associated with methanol is that methanol is concentrated in liquefied petroleum gas and liquefied petroleum gas (LPG). LPG is composed of large amounts of propane and butane mixtures. Propane + methanol and butane + methanol mixtures form azeotropes. These azeotropes mean that it is possible to separate two components from each other by the distillation method. This may be the reason why there are unacceptable amounts of methanol in LPG products, which even leads to a decrease in thermal value. Pure ethane formation with Nacl 5% was mentioned in Table 8.

Table 8- Pure ethane formation with Nacl 5%

Temp. (K)	Equilibrium Hydrate :	Composition of Phases at Equilibrium (moles)				Equilibrium Pressure (kpa)	Fractional Occupancy of Cages	
		FEED	Water	Liquid	Hydrate		Small	Large
277.8	STRUCTURE I	1	0.0006	1	1	1018.207	0	0.9916
278.6	STRUCTURE I	1	0.0006	1	1	1126.145	0	0.992
279.4	STRUCTURE I	1	0.0007	1	1	1246.139	0	0.9924
280.4	STRUCTURE I	1	0.0007	1	1	1416.952	0	0.9928
281.5	STRUCTURE I	1	0.0008	1	1	1637.015	0	0.9933
282.2	STRUCTURE I	1	0.0008	1	1	1798.348	0	0.9936
284	STRUCTURE I	1	0.0009	1	1	2314.759	0	0.9942

285.9	STRUCTURE I	1	0.0011	1	1	3125.331	0	0.9949
287.2	STRUCTURE I	1	0.0011	1	1	7396.086	0	0.9956

3. Conclusion

The phenomenon of hydrate formation in different parts of the oil and gas industry in downstream processes causes the production to stop and reduce production, so the study of how it occurs and also the conditions for hydrate formation is important and vital. The importance of the study in this field goes back to the issue of transfer of natural gas as a hydrate in order to reduce costs, increase the volume of transferred gas and suitable thermodynamic conditions.

In the present study, the conditions for the formation of methane and ethane hydrates at different temperatures were investigated and the results were compared with experimental data in this field. At first hydrate formation without inhibitor was studied and then methanol and salt inhibitor effect on hydrate formation was investigated. The results showed that with increasing temperature and adding inhibitors to the hydrate structure, the amount of equilibrium pressure increases for all states.

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