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Investigation of the Hydrate Formation Equilibrium Conditions of Natural Gas

Mohsen Kasaeezadeh[1*], Alireza Azimi[1]

Department of Chemical engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

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Abstract

One of the main problems in oil recovery via the gas injection is the formation of hydrates in the lines. In order to prevent the formation of hydrate in these lines, which leads to the blockage and sometimes explosion, at first, the equilibrium formation conditions must be determined and then to prevent its formation by changing the thermodynamic conditions or by adding the inhibitors. In this research, the hydrate formation for a natural gas sample has been studied under the various thermodynamic conditions. For this purpose, a gas sample was taken from the natural gas transmission lines. Then, the conditions for the formation of gas hydrates were determined from the experimental equations. Also, by constructing and launching a laboratory system, the experiments were carried out using the Isochoric method and the hydrate formation conditions were determined. The experiments were done at a temperature range of 264 to 300 K and a pressure range of 5 to 45 bar in the pure water. The results showed that, with increasing temperature, the equilibrium pressure of the hydrate formation increases and with increasing pressure, the equilibrium temperature of hydrate formation is reduced.

Keywords: *Gas Hydrate, Constant volume size, Equilibrium conditions.*

[*]***Corresponding author***: *Mohsen Kasaeezadeh, Department of Chemical engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran. Email: mohsen.kasaeezadeh@gmail.com.*

Introduction

Gas hydrate is a solid crystalline compound that is composed of a mixture of water and gas. This crystalline material is similar to ice. In this type of crystal, there is no chemical bond between water molecules and the enclosed gas molecules and the only factor in the stability of the crystals is the presence of a hydrogen bond between the water molecules and the van der Waals forces between the water and the gas guest molecules [1].World registered gas reserves up to the beginning of 2008, are estimated to be 177.36 trillion cubic meter and 27.8 trillion cubic meters of these reserves are located in Iran and Iran is ranked second with 15.7 percent of the world's gas after Russia (26.7) [2-4].The formation of hydrates in natural gas pipelines leads to an increase in the loss of flow pressure, blockage and sometimes the explosion of the transmission pipelines. Hence, it is important to have detailed information on the thermodynamic conditions of the natural gas hydrate formation. In 1810 Humphrey Davy discovered the first hydrate, a crystalline compound of chlorine and water. In 1882 Wroblewki reported the carbon dioxide hydrate [1]. Methane forms hydrates alone and in the vicinity of heavier hydrocarbons. The equilibrium conditions for the formation of these hydrates have been investigated and their equilibrium curves are determined [5]. Pinnelli et al. studied the hydrate formation of the mixtures of methane, butane and propane in the pure water [6]. Azimi et al. investigated the hydrate formation of methane, carbon dioxide and their mixture [7-9]. Delavar et al. presented a thermodynamic model for hydrate formation of the mixed gases in pure water as well as in the presence of inorganic inhibitors [10].

Experimental

Materials

A cylinder containing 20 liters of natural gas sample was obtained from the pipeline with a primary pressure of 960 psi with the percentage composition given in Table 1.

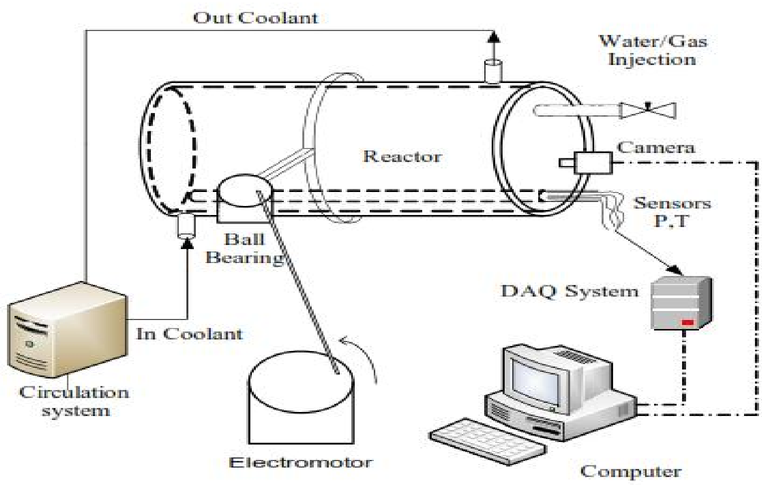
Details of Hydrate Formation apparatus

For experiments, a reactor with a stainless steel (SS-316) jacket has been used with a volume of 295 cc, which has an operating pressure of 80 bar. The internal chamber of this reactor is equipped with four valvesthe pressure capability of 6000 psi. A mixture of methanol and water is used as a cooling agent and in order to reduce the energy dissipation of the reactor, the formation of hydrate and all the connections and refrigerant fluid transfer pipes are well insulated. Using the temperature and pressure sensors, the operating conditions of the reactor are recorded in arbitrary intervals on the computer.

Table 1. Analysis of hydrocarbon compounds of natural gas sample.

Mole %	Composition
0.42	hydrogen sulfide
0.1	nitrogen
4.0	Carbon dioxide
75.70	methane
10.7	ethane
5.7	propane
0.66	iso-butane
1.45	N-butane
0.35	iso-pentane
0.4	N-pentane
0.43	hexanes
0.08	heptane
0.01	octane

In this system, a mixer is used to utilize the oscillating motions to do the mixing. In Figure 1, a schematic representation of the hydrate formation apparatus is shown.



Figur 1. A schematic diagram of the Hydrate Formation apparatus.

To record the temperature data in this system, a 100-PT type temperature sensor has been used. The sensor used in this system is made by Nafag Company, Switzerland. The accuracy of this sensor is ±0.1 bar. The electrical signal produced by the temperature and pressure sensors is transmitted by the DAQ system to the computer. Then, input data to the computer is stored by the Graph View software. In this software, in addition to display data at any moment, as well as to display data in the form of a graph (temperature-time and pressure-time), data can also be recorded at arbitrary intervals. It also has the capability to prepare data for analysis in Excel or other statistical software.

Experiment

To obtain equilibrium points, the isochoric method have been used (Figure 2). In this method, the temperature and pressure change and the reactor volume remains constant. Initially, the solution and gas are injected into the cells, the reactor temperature is set higher than the equilibrium temperature and then the solution temperature is slowly reduced. Due to the constant volume of the reactor, the pressure of the system decreases slowly with decreasing temperature. By decreasing the temperature of the system and at (point B), the hydration process starts and the pressure of the system drops with a large slope. After the pressure becomes constant and hydration is completed (point C), the temperature is slowly increased to decompose the hydrate. In the temperature-pressure diagram, the contact point of the cooling and heating curve (point D), is the hydrate decomposition point or the hydrate equilibrium point.

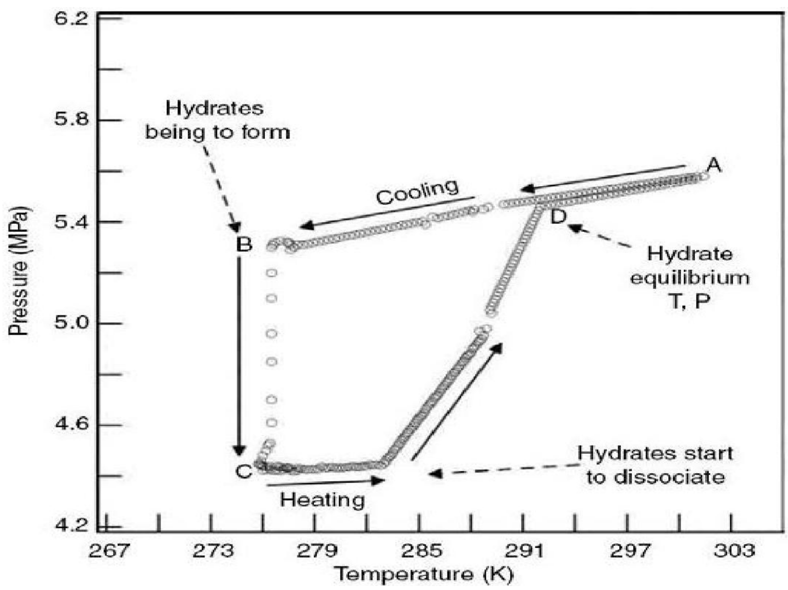


Figure 2. Determination of equilibrium points by isochoric method [1].

Theory

Ketz presented the simplest method for obtaining the pressure and temperature of the hydrate formation from a mixture [11]. To use this diagram, as shown in Fig. 3, the gas density is first calculated, and having one of the parameters of pressure or temperature, another parameter is determined for the hydrate formation point. The error rate is up to 40%. This method can be used to obtain initial approximation of the hydrate formation conditions [12].

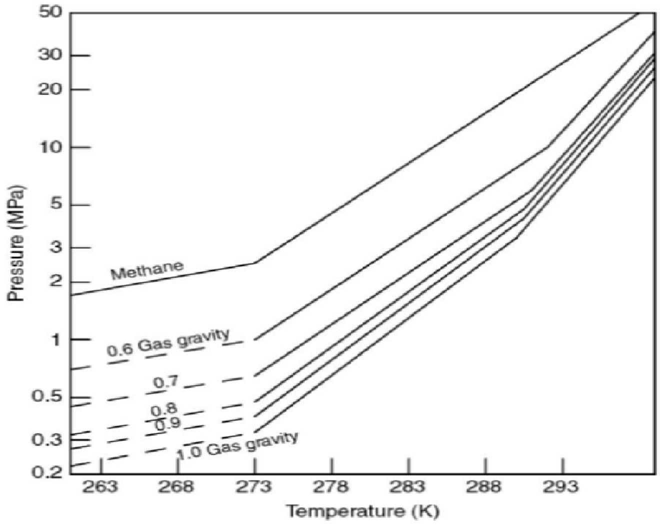


Figure 3. Gas gravity curves as temperature-pressure to predict the hydrate formation [11].

Hammer Schmit presents the temperature relation of the hydrate formation as follows [13]. The constants of this relation are shown in Table (2):

$$T = \alpha P^{\beta} \quad (1)$$

Table 2. Hammerschmit relation constants.

Coefficients	Value of coefficients
α	14.7593
β	0.2101

Macagon introduced a relation to obtain hydrate formation pressure with respect to gas density [14]. In this relation, the pressure is in Mpa and the temperature is in Celsius.

$$logP = \beta + 0.0497(t + kt^2) - 1 \quad (2)$$

$$\beta = 2.681 - 3.811\gamma + 1.679\gamma^2 \quad (3)$$

$$k = -0.006 + 0.011\gamma + 0.011\gamma^2 \quad (4)$$

Towier-Mokhatab obtained the following relation to determine the temperature of hydration formation based on the density and the gas pressure [15].

$$T = 13.47 \ln P + 34.27 \ln \gamma - 1.675 \ln P \ln \gamma - 20.35 \quad (5)$$

Using DWHC-HWU software (Distilled Water-HydrateCorrelation -HWU)

This software is provided at the University of Harriot-Watt and is mostly used to calculate the hydrate formation conditions in hydrocarbon reservoirs. Given the composition of the mixture, the software has the ability to determine the temperature of the hydrate formation at different pressures and also the hydrate formation pressure at different temperatures [17, 16].

Using Hydrate Off software

The Hydrate off software was provided by Sloan. This software has the ability to estimate the hydrate formation conditions for pure gases and mixtures of gases from C1 to C8 with N_2, CO_2 and H_2S. The advantage of this software is the use of inhibitors and the prediction of the effect of these additives on the hydrate formation conditions.

Results and discussion

In this study, the equilibrium conditions of the hydrate formation of the natural gas sample, were determined by thermodynamic equations and specialized hydrate software and then, using the experimental results, these values were evaluated and compared.

Estimation of the Hydrate Formation of Natural Gas Samples by the Experimental Relationships

One of the quick and easy methods to predict the hydrate formation conditions is to use the gas gravity diagram. Figure 4 shows the results of predicting equilibrium conditions for the hydrate formation of natural gas sample in pure water by the gas gravity method.

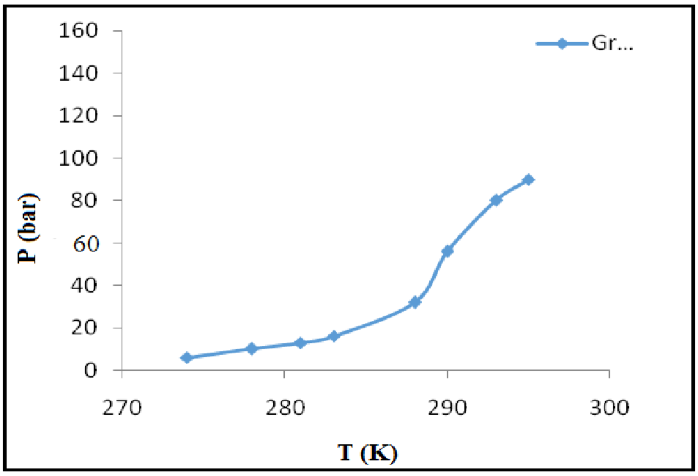


Figure 4.Predicting the equilibrium conditions for hydrate formation using the gravity method.

As shown in Figure 4, with increasing temperature, the equilibrium pressure of hydrate formation increases. As it is known, the gradient of the graph is above the temperature of 290 extreme Kelvin. Figure 5 shows the results of predicting equilibrium conditions for the hydrate formation of a natural gas sample in the pure water, using the Makagon method.

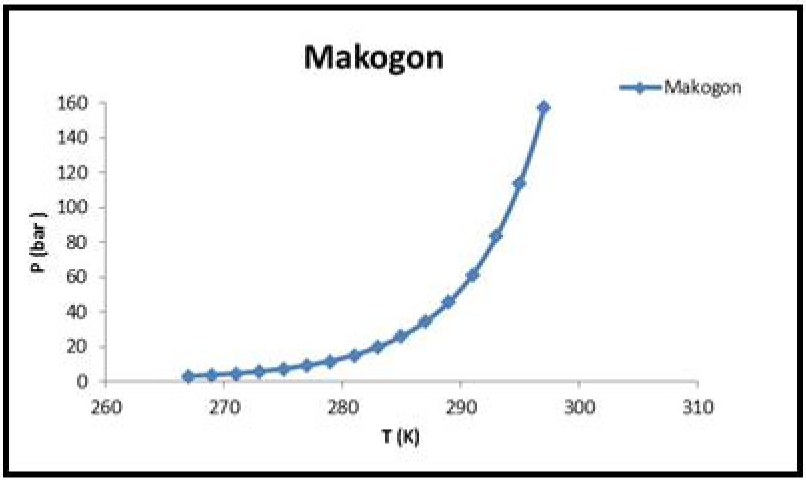


Figure 5.Predicting diagram of hydrate formation equilibrium conditions by Makagon relationships.

In Figure 6, the predicting diagram of hydrate formation equilibrium conditions by Hammer Schmit method is presented.

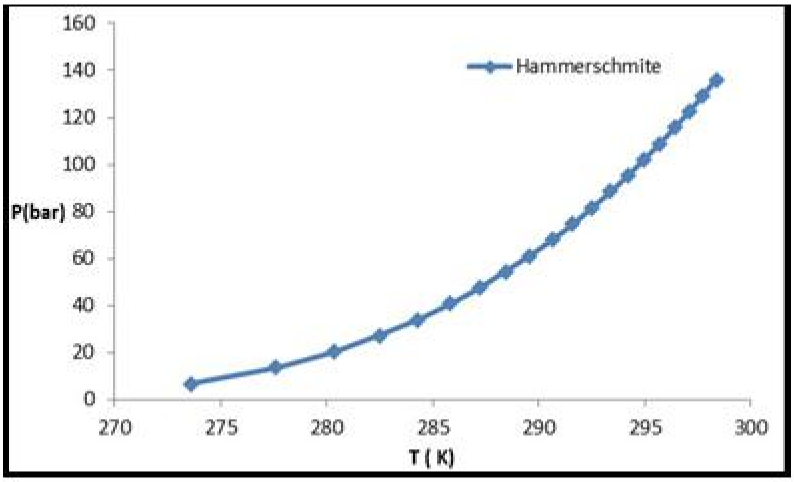


Figure 6. Predicting diagram of hydrate formation equilibrium conditions by Hammer Schmit relationships.

As shown in Figure 6, with increasing temperature, the hydrate formation pressure is steadily increasing with a steady gradient. In Figure 7, the predicting results of hydrate formation equilibrium conditions for the natural gas in pure water by Towier – Mokhatabmethod is presented.

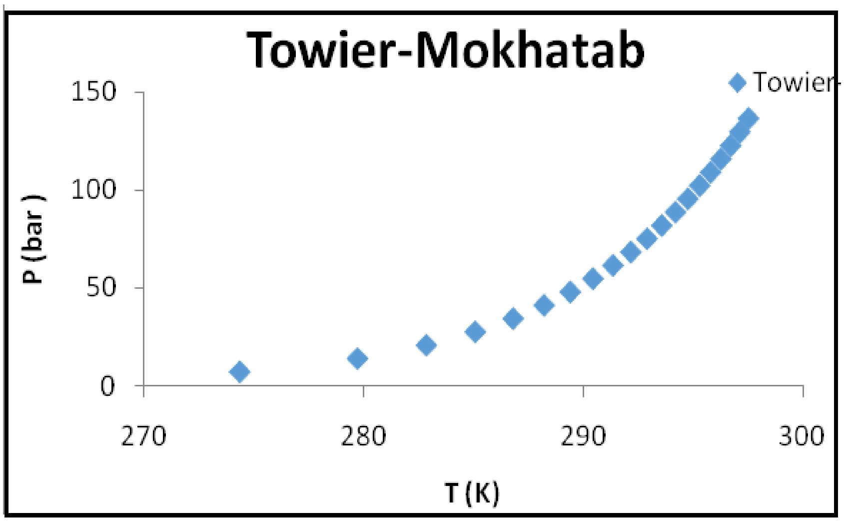


Figure 7.Predictingdiagram of hydrate formation equilibrium conditions by Towier – Mokhatab relationships.

According to Figure 7, the temperature gradient up to about 285 K, the increase in the hydrate formation pressure is low and then increases strongly. According to Figure 7, up to about 285 K, the temperature gradient increase is low with respect to the hydrate formation pressure, and then the gradient increases strongly. Figure 8 shows the comparison between different methods for predicting hydrate formation conditions. As can be seen, gas gravity methods and Hammer Schmit are highly error-prone. But the methods of Towier-Mokhatab and Makagon are well-suited for the fact that gas type (gas density) is involved in relationships.

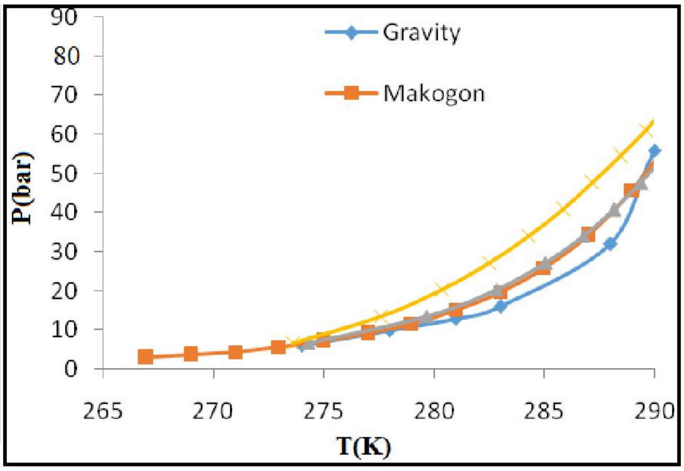


Figure 8. Comparison of prediction of hydrate formation equilibrium conditions by thermodynamic relations.

Estimation of the Hydrate Formation Conditions for the Natural Gas Sample Using Software

Prediction of equilibrium points for natural gas sample in the pure water, using the Hydrate + software by Mann et al. and Baillie-Wichert methods have been investigated. The simulation results are presented in Figures 9 and 10. As can be seen, the results of these two methods are in good agreement with each others.

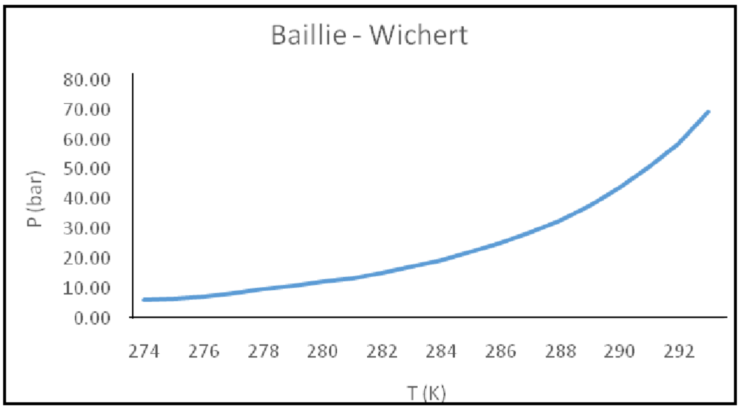


Figure 9. Prediction of Hydrate Formation Equilibrium conditions by Hydrate + Software through Baillie-Wichert method.

As shown in the diagram, the hydrate formation pressure up to 285 K is very slow and then shows a more intense increase.

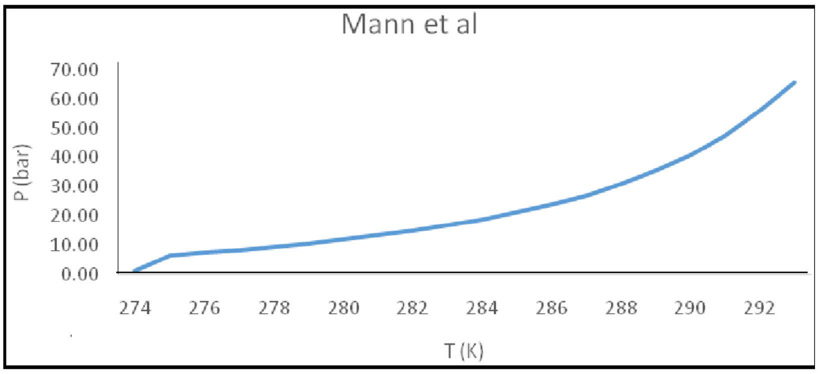


Figure 10. Prediction of Hydrate Formation Equilibrium conditions by Hydrate + Software through Mann et al. method.

According to the diagram, almost the same as in the previous method, the hydrate formation pressure up to 285 K is very slow and then shows a more intense increase.In this research, HWU-DWHC software is also used to predict thermodynamic conditions of hydrate formation. Figure 11 shows the hydrate formation diagram in this procedure.

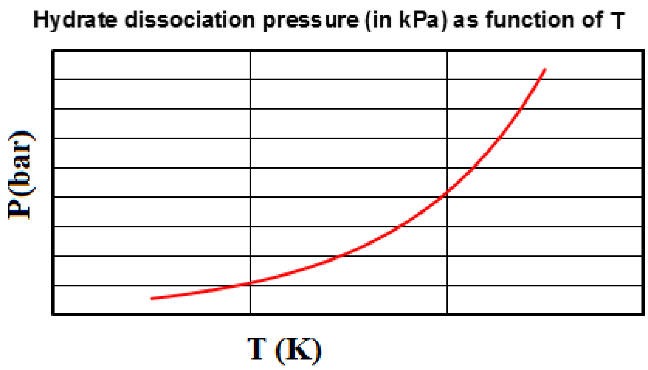


Figure 11. Prediction of the equilibrium conditions for the formation of gas hydrates by HWU-DWHC software.

The result of the simulation of hydrate formation of the natural gas sample, through the Hydrate Off software, is given in Figure 12.As can be seen, the results of the simulation are in good agreement with the HWU and Hydrate Off software.

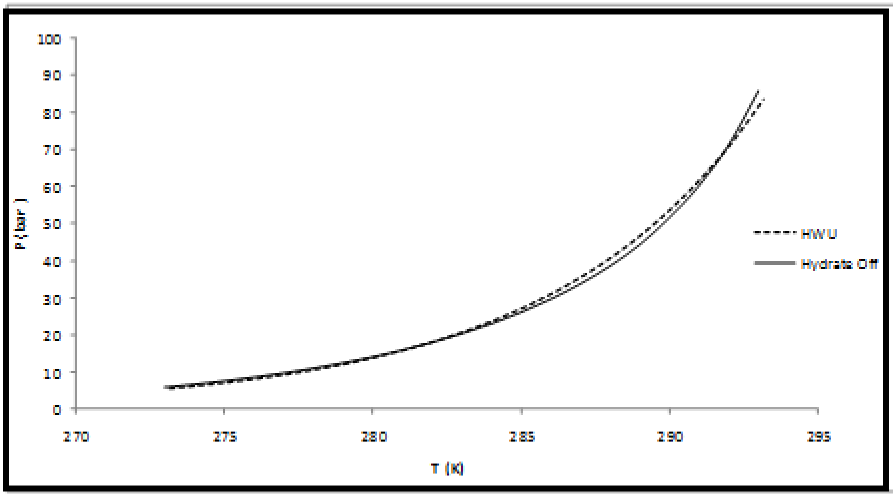


Figure 12.Prediction of the equilibrium conditions for hydrate formation by HWU and Hydrate Off software.

Experimental results

In order to obtain the equilibrium graph of the hydrate formation of the natural gas sample, the experiments were carried out in 100 cc pure water at different pressures and the hydrate formation equilibrium points have been obtained. The results of the experiments are as follows. In this study, 7 experiments were carried out using the Isochoric method. The overall results of the experiments are presented in Table 3 and Figure 13.

Table 3. Experimental results for hydrate formation equilibrium conditions of natural gas sample.

Experiment no.	**Equilibrium temperature (K)**	**Equilibrium pressure (bar)**
1	287.5	39.5
2	284.9	27.8
3	283.5	24
4	278	13.7
5	286.3	32
6	279.9	16.3
7	288.5	41.4

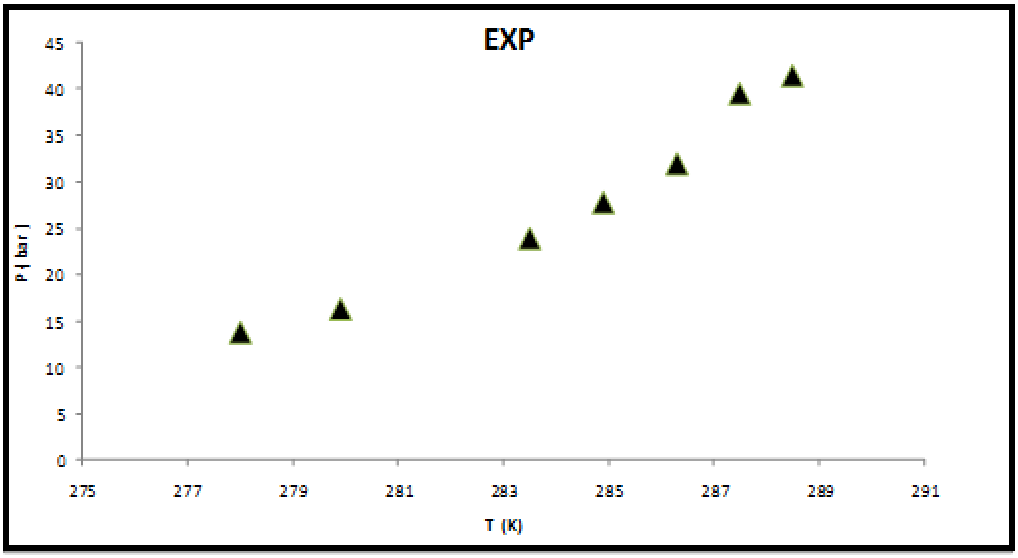


Figure 13. Experimental results of determining the equilibrium conditions for the hydrate formation of the natural gas sample.

In Figure 14, the experimental results have been compared and evaluated with the predicted points of the HWU-DWHC and Hydrate Off software.

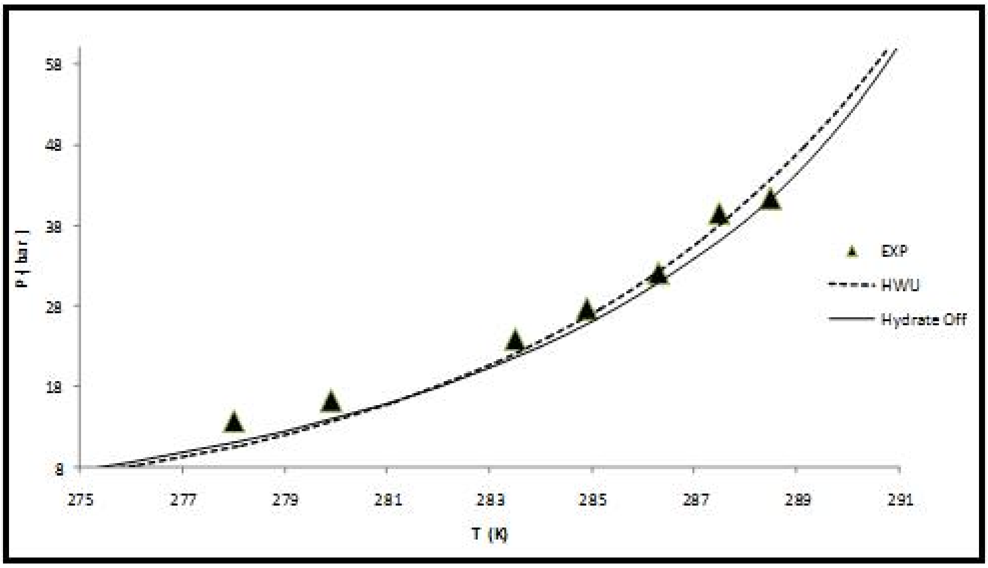


Figure 14. Comparison of the experimental results with the predicted points by Hydrate Off and HWU software.

Comparison of thermodynamic conditions of hydrate formation for this gas sample shows that the obtained results are in good agreement with the Hydrate Off and HWU software.

Conclusion

-The data on the hydrate formation of the natural gas sample were obtained by Isochoric method.

-The results of the experiments were compared and evaluated with different practical thermodynamic relationships.

-Equilibrium data for the formation of natural gas hydrates with the specialized Hydrate + software through Mann et al. and HWU-DWHC methods and Hydrate Off software were investigated. The thermodynamic conditions of the natural gas hydrate formation, which were determined from the simulating softwares, were in good agreement with the experimental results.

-Experimental results showed that, with increasing temperature, the equilibrium pressure of hydrate formation increased.

-Experimental results showed that with increasing pressure, the equilibrium temperature of hydrate formation decreased.

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