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Research Article

Investigating and Modeling the Thermo-dynamic Impact of Electrolyte Solutions of Sodium Chloride and Sodium Sulfate on Prevention of the Formation of Methane Hydrate

M. Manteghian, H. Ahmadi, M. Rahimi and M. Ghorbani Bejgerdi
Department of Chemical Engineering, Tarbiat Modares University, National Iranian Gas Company, Iran

Abstract: Devising methods to prevent hydrate formation is of the important issues in natural gas industry. Since a great deal of money is annually spent on using hydrate inhibitors, identification of new inhibitors with higher degrees of efficacy is economically justifiable. Bearing in mind the significant role of hydrate inhibitors in prevention of natural gas pipelines' getting blocked, the present study attempts to investigate two compounds of NaCl and Na_2SO_4 as inhibitors of hydrate methane's formation so as to respond to "what is the inhibitive thermo-dynamic impact of electrolyte compounds of NaCl and Na_2SO_4 on the formation of methane hydrate?" To do so, this study not only measures the equilibrium temperature and pressure of methane hydrate formation in the presence of electrolyte solutions of NaCl and Na_2SO_4 and compares the results obtained with the state lacking such inhibitors, but it also assesses the regression and mathematical modeling are utilized within a basic virtual environment in order to propose a model for prediction of thermo-dynamic equilibrium temperature and pressure of methane hydrate formation.

Keywords: Electrolyte solutions, methane hydrate, sodium chloride, sodium sulfate, thermodynamic inhibitor

INTRODUCTION

Gas hydrate is a compound, which is formed in the presence of water and the guest molecule under the condition of low temperature and high pressure. After being formed, this stable and tough compound leads to creation of a blockage in natural gas pipelines (Sloan, 1998). In 1810 Devi, an English chemist, for the first time found out the formation of gas chloral hydrate while cooling an aqueous solution of chlorine in the temperature of 10°C (Sloan, 1990). In 1934, Homer and Schmitt found that the hydrate formed created a blockage in gas pipelines. Thenceforth, Diatom and Frost were of the early scientists who conducted and reported on empirical experiments on hydrate formation (Sloan, 1998; Carl, 2002). More serious studies on these molecules were carried out regarding their crystal structure, properties and formation conditions as well as ways to inhibit their formation (Katz, 1942). To predict the pressure and temperature conditions under which hydrate forms, two major methods, known as Gas Gravity and K-factor, were proposed by Katz (1942) as manual ways to do so. Gas Gravity was presented by Katz (1942) and Kurnosov *et al.* (2004). Furthermore, another set of manual calculations has been presented by Bialy and Vichert that is of less utilization compared to the said two methods. First model to calculate hydrate formation was proposed by Van der Waals and Platteeuw (Sloan, 1998). This model cannot be generalized to mixture gas systems, so Parrish and Prausnits (1972) proposed a model for multi-compound systems applying VDWP model. The model was presented based on VDWP with the distinction that Ciara potential function was utilized to calculate spherically symmetric cell potential rather than Lenard-Jones potential function (Parrish and Prausnits, 1972). Taking into account and modifying some of the VDWP's assumptions, Lee and Holder (2002) presented their new model. The model proposed by Gue-Chen was based on the hydrate's formation mechanism by Sloan (1998) and Chen and Gue (1996, 1998). New conceptualizations of local stability, linked pores, main hydrate and combination of main hydrates (in mixture) were applied by this model. Owing to the limitation of laboratory data to explore formation conditions of hydrate, different thermo-dynamic models were offered (Englezos, 1993; Sloan, 1998; Duan and Sun, 2006). For an instance, Vlahakis *et al.* (1972) investigated the conditions under which hydrate formed in the presence of electrolyte NaCL molecules. In addition, Englezos and Bishnoi (1988) presented a regressive method to predict hydrate formation conditions in the presence of electrolyte solutions. In their study, Ahmed and Ali (1999) devised a neural network model to predict temperature and pressure conditions. They also presented another model which demonstrated the amount of inhibitor as a function of consumed gas, pressure and temperature depression

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Corresponding Author: M. Manteghian, Department of Chemical Engineering, Tarbiat Modares University, Iran

Fig. 1: Laboratory unit of methane hydrate formation

Fig. 2: Laboratory unit of methane hydrate formation

(Ahmed and Ali, 1999). With consideration of complexity of thermo-dynamic models, the present study applies a 10-v1 riable thermo-dynamic model to predict conditions of hydrate formation in the presence of electrolyte solutions of NaCl and Na_2SO_4.

Methods to inhibit hydrate formation were classified (Pickering *et al*., 2001) as the following: pressure control, temperature control, removing the water existing within the fluid, Direct Electrical Heating System (DEHS), water injection method, cold flow method (SØrheim and Gudmundsson, 2005) and injection of inhibitors. Among the methods proposed for inhibition of hydrate formation, the most scientific one is the fourth method i.e., injection of inhibitors (Shabani *et al*., 1383). Chemical hydrate inhibitors are classified into three categories: thermodynamic, kinetic and anti-conglomerate inhibitors (Sefidroodi *et al*., 2011).

Inhibitors of the second and third types recently have drawn a great deal of attention because even little injection of them is capable of inhibiting hydrate formation. However, Thermo-dynamic Inhibitors (THIs) postpone hydrate formation via changing thermo-dynamic equilibrium condition. When added to the fluid, THIs change its chemical potential and drive the curve of thermo-dynamic equilibrium towards a lower temperature and a higher pressure (Sloan, 1998). The present study makes efforts to investigate the impact of NaCl and Na_2SO_4 electrolytes on the inhibition of gas methane hydrate's formation; therefore, a laboratory unit is used to conduct the relevant experiments. After obtaining the required empirical data, one thermo-dynamic model is developed for hydrate formation. Next section deals with the laboratory unit, methods and materials.

Experiment:

Laboratory unit: The laboratory unit used by the study consists of a milliliter reactor, which is cooled down with water of circulator. The gas methane is prepared from a gas capsule which is connected to the laboratory unit. The computer records rector temperature and pressure, specifically the use of sensors that are connected to the system. The laboratory unit is shown by Fig. 1 and 2.

METHODOLOGY

To examine the impact of thermo-dynamic conditions on the described laboratory unit, the researcher uses NaCl and Na_2SO_4. Accordingly, equilibrium conditions of hydrate formation are recorded for the molal densities of 0.5, 2.5, 3.5, 4.5 and 5 of NaCl. The experiment is replicated for sodium sulfate with the same molal densities and again values of equilibrium temperature and pressure are recorded.

RESULTS AND DISCUSSION

The impact of NaCl and Na_2SO_4 electrolytes on thermo-dynamics of methane hydrates formation:
The impact of the electrolyte of sodium chloride on thermo-dynamics of methane hydrates formation: In this stage, 5 different molalities of NaCl (0.5, 2.5, 3.5, 4.5 and 5) are injected to the laboratory unit and formation conditions of methane hydrate according to the pressure variation are recorded on the unit's monometers. The results obtained are presented by the Fig. 3.

The impact of the electrolyte of sodium sulfate on thermo-dynamics of methane hydrates formation: Similar to the examination of sodium chloride, sodium sulfate was studied. To conduct a better comparison, the same molalities are used in this stage. The obtained data for equilibrium temperature and pressure of hydrate formation in the presence of sodium sulfate are presented in Fig. 4.

Comparative thermo-dynamic impact of NaCl and Na_2SO_4 electrolytes on methane hydrate formation: Previously we presented the separate impact of each electrolyte on equilibrium temperature and pressure of hydrate formation. Now, we try to compare these two electrolytes and their equilibrium data in the absence of inhibitors. To do so, five diagrams corresponding to five under examination molalities are presented that provide equilibrium data of hydrate formation in the absence of inhibitors and in the presence of either NaCl or Na_2SO_4. The following Fig. 5 presents these five curves.

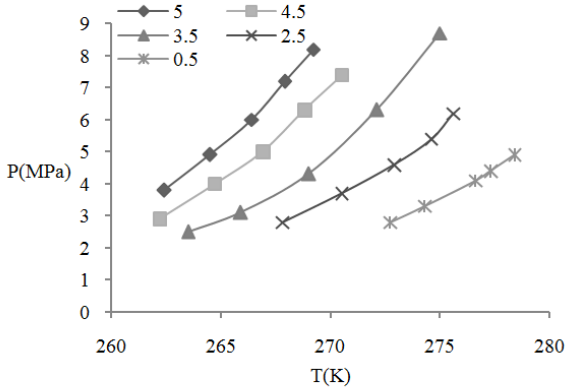

Fig. 3: Data on equilibrium temperature and pressure of methane hydrate formation in the presence of sodium chloride of different molalities

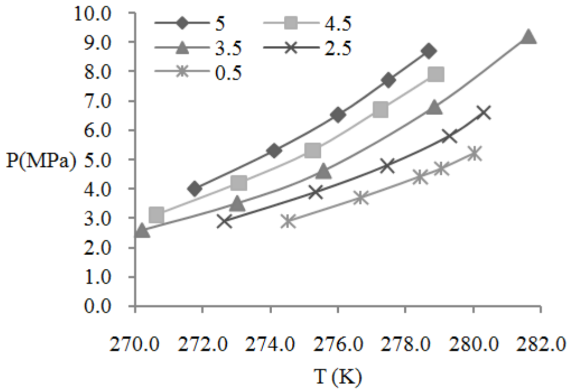

Fig. 4: Data on equilibrium temperature and pressure of methane hydrate formation in the presence of sodium sulfate of different molalities

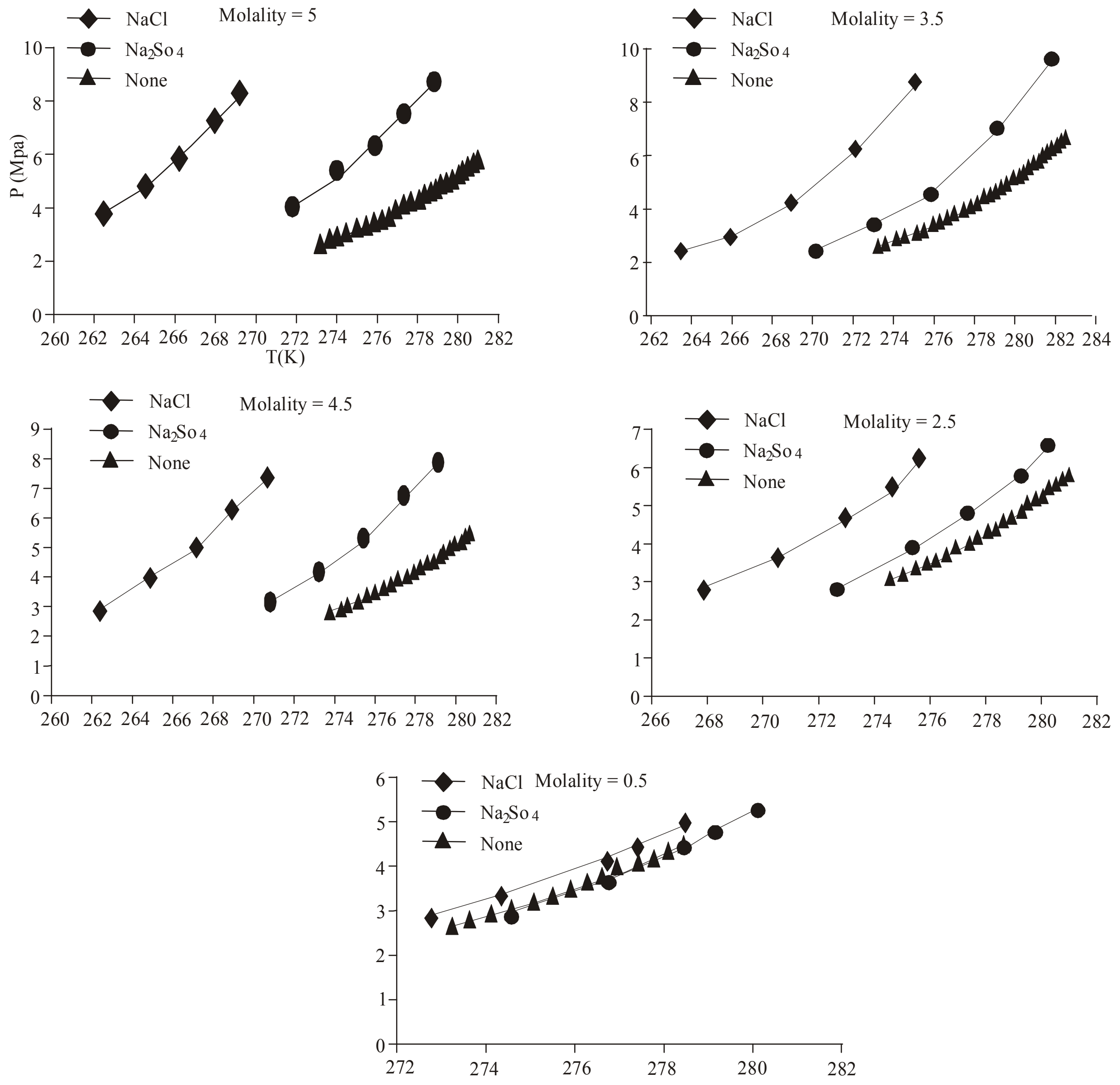

Fig. 5: Comparative thermo-dynamic impact of NaCl and Na_2SO_4 electrolytes on methane hydrate formation

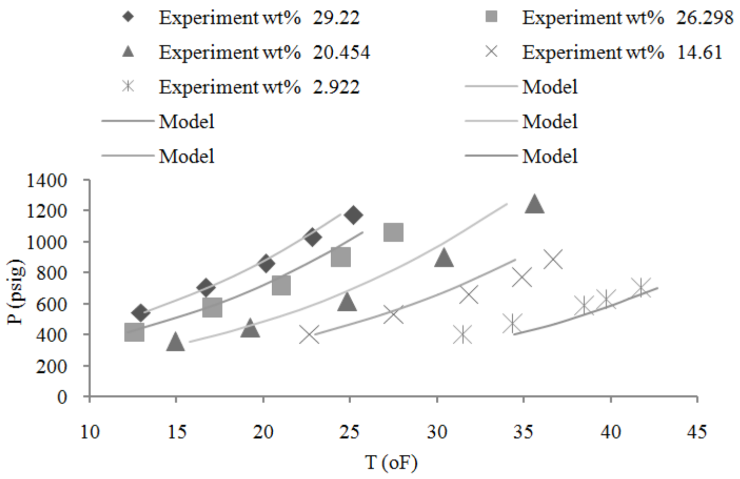

Fig. 6: Comparison of the date on equilibrium temperature and pressure of hydrate formation in the presence of sodium chloride with the estimation model

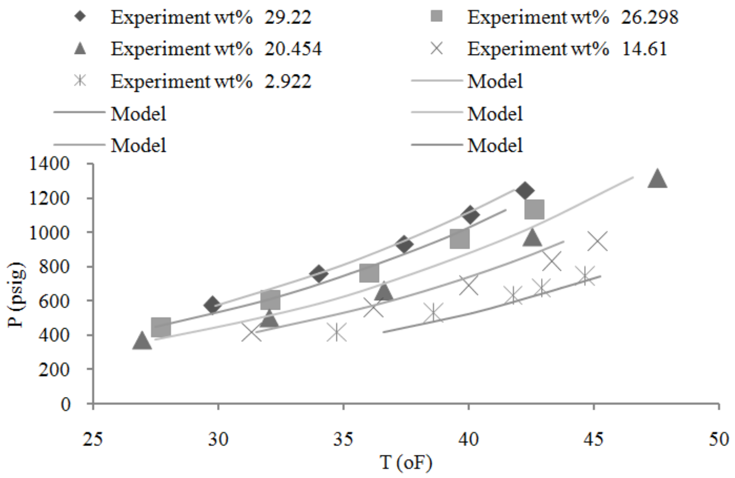

Fig. 7: Comparison of the date on equilibrium temperature and pressure of hydrate formation in the presence of sodium sulfate with the estimation model

As shown in the presented figures, at a low density (e.g., 0.5 molality) no significant difference is observed between the impacts of two electrolytes. However, higher densities (e.g., 5 molality) a considerable difference is created, that is to say, both electrolytes reveal an inhibitive impact on hydrate formation but the effect of sodium chloride outperforms that of sodium sulfate. The higher the density of these electrolytes, the greater the difference between their impacts on inhibition of methane hydrate formation.

Regressive model: The study utilizes a regressive model to be able to predict equilibrium temperature of hydrate formation, without any need for complicated calculation, only through having pressure and density of the electrolyte. The regressive model proposed by the study is as follows:

$$\ln(Tpr) = b_0 + b_1(lnp)^2 + b_2\frac{C_{nacl}}{\gamma} + b_3\gamma^2$$
$$+b_4\frac{(1-C_{nacl})}{\gamma^3} + b_5\frac{ln\gamma}{lnp} + b_6\frac{ln\gamma}{(lnp)^4} + b_7\frac{lnp}{\gamma}$$
$$+b_8\frac{(lnp)^2}{\gamma} + b_9\frac{(lnp)^3}{\gamma} + b_{10}\frac{(lnp)^4}{\gamma} + b_{11}\ln(pr)$$
$$+b_{12}(lnpr)^2$$

The model is assessed for the equilibrium thermodynamic data presented above and coefficients $\{b_o - b_{12}\}$ is measured via regression. Values obtained for the coefficients are shown in the following:

$[b_0]$ = 3.1113797464
$[b_1]$ = -0.06121811
$[b_2]$ = -0.034581592
$[b_3]$ = -0.161387206
$[b_4]$ = 0.0004644864

$[b_5] = -0.193610096$
$[b_6] = 0.00019320793$
$[b_7] = 0.1324677497$
$[b_8] = -0.078512137$
$[b_9] = 0.009232805$
$[b_{10}] = -0.000232276$
$[b_{11}] = 0.8054836679$
$[b_{12}] = 0.0063403148$

Finally the model is coded within a basic virtual environment and presented as an executive program within the EXCEL environment. To examine the results estimated by the model, one can refer to the Fig. 6 and 7. They present empirical values of equilibrium temperature and pressure for five different densities in the form of dots and, further, the model-estimated values are presented via a curve. Figures reveal that the estimation model proposed by the study is of high ability to determine the values of equilibrium temperature and pressure of methane hydrate formation in the presence of sodium chloride and sodium sulfate.

CONCLUSION

Compared to sodium sulfate, sodium chloride exerts a greater influence on thermo-dynamic equilibrium of methane hydrate formation and its influence enhances with the increase of sodium chloride density. At low density (e.g., 0.5 molality), no difference was observed between these two electrolytes, but at higher densities (5 molality), a considerable difference is created, that is to say, both electrolytes reveal an inhibitive impact on hydrate formation but the effect of sodium chloride outperforms that of sodium sulfate. The higher the density of these electrolytes, the greater their inhibitive impact and also the bigger the difference between their impacts on inhibition of methane hydrate formation. In the second stage of the study, a ten-variable linear regressive model was proposed for the thermo-dynamic model of methane hydrate formation in the presence of electrolytes. The estimation model proposed by the study is of high ability to determine the values of equilibrium temperature and pressure of methane hydrate formation in the presence of sodium chloride and sodium sulfate.

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