The thermodynamics effect of sodium chloride and sodium sulfate on the prevention of methane hydrate formation and offering its thermodynamics model by using neural networks

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Abstract: In this work, we have studied the thermodynamics effect of sodium chloride and sodium sulfate on the prevention of methane hydrate formation, and have offered its thermodynamics model. Gaseous hydrates are crystalline compounds which form at low temperature and high pressure in the presence of and guest molecule, in which water molecules are placed at the center of the hydrate structure will embay the guest molecule with a hydrogen bound network. Gaseous hydrate compounds are stable and hard after formation and can cause obstruction in natural gas transport pipes. In this study, we have investigated the effect of sodium chloride and sodium sulfate in the prevention of the formation of hydrates. The method which has been used in this work modeling the equilibrium condition for the formation of hydrates and the amount of pressure and temperature are recorded in different concentrations (0.5, 2.5, 3.5, 4.5, and 5 molal) of sodium chloride and sodium sulfate. Regression and mathematical programming in visual basics were used for modeling to offer a mathematical model for thermodynamic equilibrium of hydrate formation and prediction of the equilibrium temperature. The results showno appreciable difference between two electrolytes at low concentrations, but raising the concentration significant difference will be observed between the two electrolytes. In higher concentrations, both electrolytes prevented the hydrate formation, but sodium chloride showed greater prevention power. The more the concentration of the electrolytes, the greater the prevention power. However, the assumption model of the study possessed a high ability for expressing the equilibrium temperature and pressure for methane hydrate formation in the presence of the sodium chloride and sodium sulfate electrolytes. In this paper we do a modeling for experimental results by the learning ability of neural networks in modeling nonlinear andcomplex relationships, a model is provided to predict effect of sodium chloride and sodium sulfate on the prevention of methane hydrate formation . The input parameters of the network include element are temperature,concentrations. Model is based on supervised learning algorithm and in terms of topology is from type of backpropagation. According to this model,the correlation coefficient is more than 0.99, So could trusted model for simulation and modeling in hydrate formation of methane and confirm certitude of the experimental results.

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1. Introduction

Gaseous hydrates which are also called hydrate caltrate are generally formed from small gaseous molecules (≤0.9 nm) like methane or carbon dioxide at low temperature (≤300 K) and high pressure (≥0.6 MPa) in the presence of water. Water molecules act as host and form networks containing different cavity sizes by hydrogen bonding, which can trap gaseous guest molecules. Repulsive forces between guest molecules form polyhedral structures with different sizes compared with water molecules (Dendy Sloan, 2003). The structures are not stable, unless molecules with appreciable size and proportionally nonpolar character occupy suitable fractions of the cavities (Jager& Sloan,2003). Polyhedral cages can be determined by the position of water molecule's oxygen atom, and Hydrogen atoms in the molecules are extended along the sides of this polyhedral structures. The guest molecules can only occupy one or a small number of the cavities regarding the size of the cavities (Jeffrey, 1991).

Filling the cavities is proportional to pressure, temperature and the nature of the guest molecule components. The formed structures can therefore be regarded as nonstoichiometric hydrates, while filling all of the cavities is unlikely (Struzhkin et al, 2006).

There are a number of methods for predicting the condition of hydrate formation. In gas gravity method, the gaseous specific gravity is calculated by the molecular weight of the gas, M, as following:

$$\gamma = \frac{M}{28.966} \qquad \text{Eq. 1}$$

While M is standard molecular weight of the air and equal to 28.966.

Having the gaseous gravity, γ, the corresponding pressure or temperature can be achieved from the diagram. The obtained pressure or temperature can be correlated to the hydrate formation equilibrium condition. If the pressure is more than equilibrium pressure at constant temperature, or temperature is more than equilibrium temperature at constant pressure, the condition is in hydrate formation condition. In K-factor method which was first expressed by Carson and Kats in 1942, the interphase composition of hydrate and gas is defined as:

$$K_i = \frac{y_i}{s_i} \qquad \text{Eq. 2}$$

While Y_i and S_i are mole fractions of compound I in hydrate and vapor phase respectively. Diagrams for each of the compounds in natural gas can be found in literature (Mokhatab, et.al, 2006). For the compounds which exist in gas phase, but are not able to form hydrate, K_i is regarded as ∞, which means the compound I does not exist in hydrate phase, or $S_i = 0$.

Baillie-Wichert method is another one, in which we consider the presence of hydrogen sulfate (about 50 mol %) and propane (about 10 mol%). The effect of the presence of propane is regarded as thermal correction, which is a function of pressure and H2S concentration.

In phase equilibrium method, the chemical potential of the components in equilibrium conditions should be equal. Nevertheless, most of the phase equilibrium calculations prefer fugacity equality instead if chemical potential equality, but in general, most of the hydrate formation equations are expressed based on chemical potential equality. However, a number of models are offered based on fugacity equality for predicting hydrate formation conditions. Two steps hydrate formation can be shown as below:

Pure water (a) → empty hydrate network (β) → filled hydrate network (H)

Any change in chemical potential can be expressed as:

$$\mu H - \mu a = (\mu H - \mu B) + (\mu B - \mu a)$$

In which μ is chemical potential and each of the superscripts represent numerous phases which exist symbiotic together in the hydrate formation. Most of the thermodynamics models which are used for predicting the formation or decomposition of hydrates are different generalizations of van der waals–Plative model (vdwp).

In general, methods for preventing hydrate formation can be classified as below:

-Preserving the flow pressure below the hydrate formation pressure in a definite temperature and composition;

-Preserving the flow temperature above the hydrate formation temperature in vapor phase definite pressure and composition using an oven or a heat transducer;

-Preventing the formation of water liquid phase in transport system by reducing the amount of the water in system by dehydrating the entrance gas;

-Injection of hydrate formation inhibitor compounds, such as alcohols, glycols, and other electrolytes to the entrance natural gas;

Among which, the forth method is more acceptable (Shabani and et.al. 2004)

Hydrate formation chemical inhibitors can be classified to Thermodynamic Inhibitors, Kinetic Inhibitors, and Anti-Agglomeration Inhibitors. Second and third inhibitors are interestingly investigated in recent years. Injection of little amounts of these compounds can inhibit the formation of hydrates, and therefore are called LDHI.

Thermodynamic inhibitors (THI) change the chemical potential with addition to the fluids, so that shifts the thermodynamic equilibrium diagram of hydrate to lower temperature and higher pressures. Molecular structure of these materials suggest that their strong hydrogen bonding causes the lower tendency of water molecules to hydrate formation. Methanol (MEOH), mono ethylene glycol (MEG), di ethylene glycol (DEG), and tri ethylene glycol (TEG) are of the best known thermodynamic inhibitors.

The ability of calculating the needed amounts to be injected by thermodynamic equations is one of the advantages of THIs, which can act according to the system conditions as below: needed weight percent of the inhibitor for preventing hydrate formation relates to the amount of needed subcooling, d˚f, and is shown with W, which can be obtained from Hammer-Schmirt equation.

$$w = \frac{(dM)(100)}{K+dM} \qquad \text{Eq. 3}$$

The inhibitor molecular weight = MK = constant (2335 for MEOH and MEG)

This equation shows the needed amount of the inhibitor more than the real amount (Sanjay Kumar, 1987).

Kinetic inhibitors (KHI) are studied in recent decay, while change the kinetic of the formation instead of changing the thermodynamic condition of hydrate formation. These compounds rebate both nucleation and crystal growth. The molecular mechanism and their interactions are not completely known yet, but two theorems which are obtained by molecular dynamics simulations are better accepted. The first theorem offers that the surface tension of these compounds on hydrate crystals causes disappearance or severe reduction of activated points, and therefore inhibits their growth. The second mechanism offers that the kinetic inhibitors molecules act as a barrier for diffusion of guest molecules and prevents the crystal evolution. The lack of an acceptable mechanism, complicates the calculations for predicting of the needed amount of inhibitors. Poly(vinylpyrolidine), poly(cinylcaprolactam) and a number of quaternary ammonium salts are some examples of KHIs. Using KHIs in industries can be seen in some cases (SØrheim&Gudmundsson, 2005).

KHIs efficiency decreases in subcooling temperatures (12 °C) which means that if the fluid temperature decreases more than 12 degrees from thermodynamic equilibrium temperature of hydrate formation, the hydrate formation will be more likely; but there is no limitation for the amount of moisture in the fluid.

An ant hunk (AA) inhibitors prevents aggregation or agglomeration of crystals instead of affecting thermodynamic or the growth rate of the crystals. Therefore, the hydrated crystals are not able to form larger masses to block the flow. The mechanism of these materials prevention is by surface tension on the hydrated crystals. However, lying the hydrophobic head in crystal can cause disorders in crystalline order, which is because of the difference of its size compared with the guest molecules.

Regarding the problems which hydrate formation can inflict gas transportation lines, and existence of large gas resources in Iran, finding methods for preventing the formation of hydrates is a very significant challenge in natural gas industries. Regarding the high cost which spends annually for hydrate inhibitors, finding convenient inhibitors which are more efficient can cause saving large amounts of money. In this study, the compounds NaCl and Na2SO4 have been investigated as thermodynamic and kinetic methane hydrate, with an insight to the significance of hydrate formation inhibitors.

Experimental:

Laboratory unit in this study contained a 22 meter long pipe with one inch diameter which was cooled by water circulation. The gas flow in this research contained 85% methane and 15% water, while methane gas was supplied with a gas cylinder which was connected to the laboratory unit using respective injections. Water was connected to the system using distilled water circulation.

However, the thermodynamic model for gaseous hydrate formation in presence of electrolyte is as following:

The system containing "vapor-hydrate" in equilibrium state for water component will be:

$$\mu_W^H = \mu_W^L \qquad \text{Eq. 4}$$

While $\Delta\mu_W^H$ and $\Delta\mu_W^L$ in the equation are chemical potential of water in liquid phase and hydrate network respectively. Let us demonstrate the chemical potential of empty space of the imaginary hydrate phase withμ_W^B, then we write the equation 4 as:

$$\Delta\mu_W^H = \Delta\mu_W^L \qquad \text{Eq. 5}$$

Then we will have $\Delta\mu_W^H = \mu_W^\beta - \mu_W^H$ and $\Delta\mu_W^L = \mu_W^\beta - \mu_W^L$. For calculating $\Delta\mu_W^H$ we use Van der Waals and Plative statistical theorem:

$$\frac{\Delta\mu_W^H}{RT} = \sum_{i,cavitis} v_i \ln\left(1+\sum_j C_{ij} f_j\right) \qquad \text{Eq. 6}$$

In which, V_i represents the number of cavities of type i for water molecules, f_i represents the fugacity of hydrate component which is equal in equilibrium condition in all hydrate, liquid and vapor phase, and C_{ii} is the Langmuir constant and is a function of temperature.

To calculate the fugacity for gas phase components, a state equation must be chosen, while SRK state equation is more preferable according to the gaseous phase of the methane hydrocarbon. We note that in hydrate formation conditions, the presence of water in vapor phase can be neglected. For calculating the Longmuir coefficients, we use the experimental equation offered by Parish and Prasnits (Eq. 4-3).

$$Cij = \frac{A_{ij}}{T} \exp \frac{B_{ij}}{T} \qquad \text{Eq. 7}$$

A_{ij} and B_{ij} are constant values offered by Parish and Prasnits for methane. The values are presented in table 1.

Table1. Parish and Prasnits equation parameter for Longmuir constant coefficient (Parish and Prasnits, 1972).

Parameter (unit)	Small cavity	Large cavity
$A_{ij}(K.MPa^{-1})$	0.036759	0.18136
$B_{ij}(K)$	2708.8	2737.9

For calculating $\Delta\mu_W^H$, we use Holder equation:

$$\frac{\Delta\mu_W^L}{RT} = \frac{\Delta\mu_W^o}{RT_o} - \int_{T_o}^{T} \frac{\Delta h_W}{RT^2} dT + \frac{\Delta V_W}{RT} P - \ln(a_w) \qquad \text{Eq. 8}$$

In equation 8, T_0 is the reference temperature which is 237.5 K, R is gas constant, T and P are temperature and pressure of hydrate formation, and $\Delta\mu_W$ and ΔV_W

are constant parameters whose quantity for I and II hydrate structures are offered by Parish and Prasnits which can be seen in the following table. The quantity of Δh_W is a function of temperature and can be demonstrated as below:

$$\Delta h_W = \Delta h_W^o + \int_{T_o}^{T} \Delta C_{PW} dT \qquad \text{Eq. 9}$$

$$\Delta C_{PW} = a_l + b_l (T - T_o) \qquad \text{Eq. 10}$$

Combination of all of the above equations we will have equation 11, which can give hydrate formation temperature for methane gas by solving it by temperature in definite concentration and pressure.

$$\frac{\Delta V_W}{RT} P + \Phi(T) - \sum_{i=1}^{2} v_i \ln[1 + C_{ki}(T) f_k(P, T)] - \ln(a_w) = 0 \qquad \text{Eq 11}$$

In which Φ is a function of temperature as can be seen in following:

$$\Phi(T) = \frac{\Delta\mu_o}{RT_o} + \frac{b_1}{2R}(T_o - T) + \frac{(a_1 + b_1 T_o)}{R} \ln\left(\frac{T_o}{T}\right) + \frac{(\Delta h_o + a_1 T_o + 0.5 b_1 T_o^2)}{R}\left\{\frac{1}{T} - \frac{1}{T_o}\right\} \qquad \text{Eq. 12}$$

Constant values in equation 12 is calculated by Parish and Prasnits, which can be seen in table 2.

Table 2. The amounts of quantities reported by Parish and Prasnits (Parish and Prasnits, 1972).

Quantity	Unit	Amount
$\Delta\mu_0$	j.mol-1	1264
Δh_0	j.mol-1	-4860
Δv_w	m3.mol -1	4.6*10-6
a1	j.mol-1.K-1	-38.13
b1	j.mol-1.K-2	0.141

The only quantity which is so far unknown is water activity coefficient, α_w. To calculate this quantity, Nasrifar offered a simple equation below for "aqueous electrolyte solution with dissolved gas" (Nasrifar et al, 1998).

$$\ln \alpha w = \ln \alpha w.elec + \ln \alpha w.gas \qquad \text{Eq. 13}$$

If the gas which forms the hydrate is a solution gas, the value of water activity coefficient changes with the amount of dissolved gas. In equation 13, $\alpha_{w\,gas}$ is water activity coefficient in the presence of dissolved gas in solution, which can be regarded as the mole fraction of dissolved gas in water due to the low solubility of methane gas in water, and therefore can be determined by Henry low (Klauda& Sandler, 2000).

$$\ln\left(\frac{f_{gas}}{x_{gas}}\right) = \ln(H_{gas,w}) + \frac{\bar{v}_{gas}^{\infty}(P - P_w^S)}{RT} \qquad \text{Eq. 14}$$

In which, $\alpha_{w\,elec}$ is activity coefficient of water in a solution containing electrolyte compound, and we use state equation (GV-SAFT-MSA) to determine it:

$$\ln(a_{w,elec}) = \frac{vmM_{H2O}\varphi^m}{1000} \qquad \text{Eq. 15}$$

$$\varphi^{(m)} = 1 + \frac{1}{m}\int_0^m m \frac{\partial \ln\gamma_{\pm}^{(m)}}{\partial m}_{T,P} dm \qquad \text{Eq. 16}$$

In which M_{H_2O} is molecular weight of water, ϕ is osmotic coefficient, m is the molality of the electrolyte, v is ionic stoichiometric coefficient in aqueous solution, and $\gamma_{\pm}$ is the average ionic activity coefficient of the solution. Average ionic activity coefficients for NaCl and Na2SO4 electrolyte solutions can be seen in figures 1 and 2. The activity coefficient of water molecules is calculated by Golburg (1981) for Na2SO4 which can be seen in figure 2.

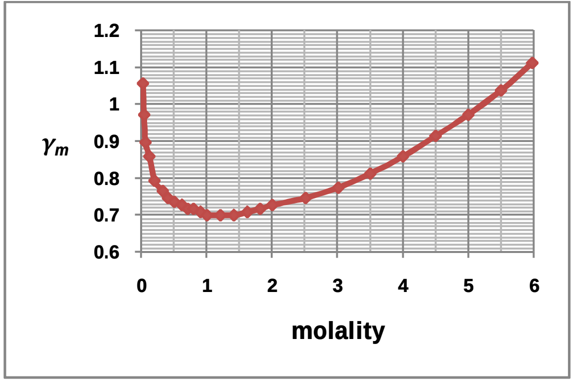
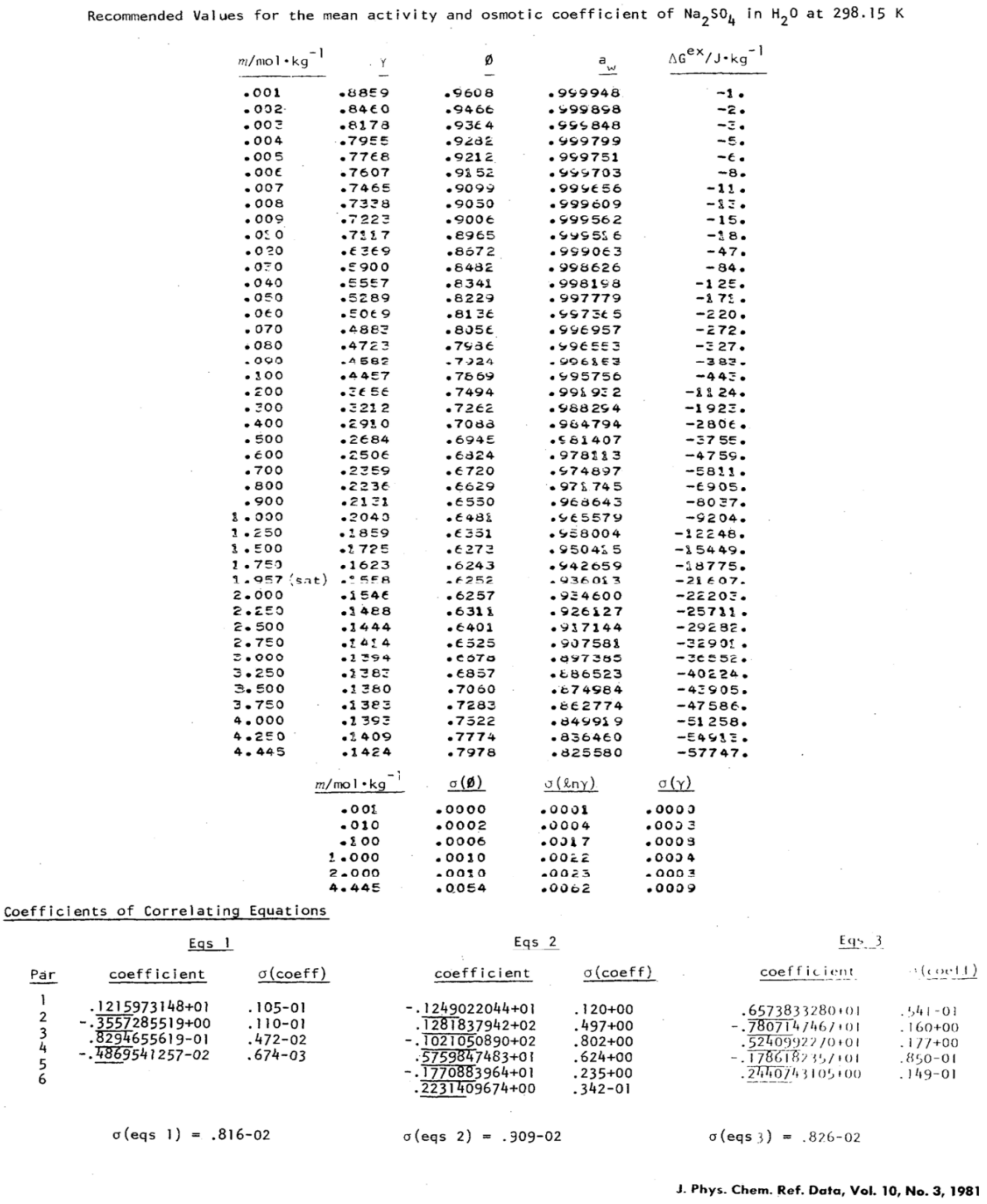


Fig. 1. Average ionic activity coefficients for NaCl electrolyte solution (Guendouzi, Dinane, 2000).

γ_m	molality
1.05644	0.02826
0.97166	0.04710
0.89631	0.06593
0.85863	0.12245
0.79270	0.20722
0.76444	0.32967
0.74560	0.40502
0.73619	0.50863
0.72735	0.62166
0.71714	0.71586
0.71735	0.80063
0.70735	0.90424
0.69851	1.00785
0.69851	1.21507
0.69893	1.41287
0.70793	1.62009
0.71735	1.81790
0.72677	2.00628
0.74560	2.51491
0.77386	3.01413
0.81154	3.50392
0.85863	4.00314
0.91515	4.50235
0.97166	5.00157
1.03760	5.50078
1.11295	5.98116

Fig. 2. Average ionic activity coefficients for Na2SO4 electrolyte solution (Guendouzi, Dinane, 2000).



Recommended Values for the mean activity and osmotic coefficient of Na_2SO_4 in H_2O at 298.15 K

m/mol·kg^{-1}	γ	∅	a_w	ΔG^{ex}/J·kg^{-1}
.001	.8859	.9608	.999948	-1.
.002	.8460	.9466	.999898	-2.
.003	.8178	.9364	.999848	-3.
.004	.7955	.9282	.999799	-5.
.005	.7768	.9212	.999751	-6.
.006	.7607	.9152	.999703	-8.
.007	.7465	.9099	.999656	-11.
.008	.7338	.9050	.999609	-13.
.009	.7223	.9006	.999562	-15.
.010	.7117	.8965	.999516	-18.
.020	.6369	.8672	.999063	-47.
.030	.5900	.8482	.998626	-84.
.040	.5557	.8341	.998198	-125.
.050	.5289	.8229	.997779	-171.
.060	.5069	.8136	.997365	-220.
.070	.4883	.8056	.996957	-272.
.080	.4723	.7986	.996553	-327.
.090	.4582	.7924	.996153	-383.
.100	.4457	.7869	.995756	-443.
.200	.3656	.7494	.991932	-1124.
.300	.3212	.7262	.988294	-1923.
.400	.2910	.7088	.984794	-2806.
.500	.2684	.6945	.981407	-3755.
.600	.2506	.6824	.978113	-4759.
.700	.2359	.6720	.974897	-5811.
.800	.2236	.6629	.971745	-6905.
.900	.2131	.6550	.968643	-8037.
1.000	.2040	.6481	.965579	-9204.
1.250	.1859	.6351	.958004	-12248.
1.500	.1725	.6273	.950415	-15449.
1.750	.1623	.6243	.942659	-18775.
1.957 (sat)	.1558	.6252	.936013	-21607.
2.000	.1546	.6257	.934600	-22203.
2.250	.1488	.6311	.926127	-25711.
2.500	.1444	.6401	.917144	-29282.
2.750	.1414	.6525	.907581	-32901.
3.000	.1394	.6678	.897385	-36552.
3.250	.1383	.6857	.886523	-40224.
3.500	.1380	.7060	.874984	-43905.
3.750	.1383	.7283	.862774	-47586.
4.000	.1393	.7522	.849919	-51258.
4.250	.1409	.7774	.836460	-54913.
4.445	.1424	.7978	.825580	-57747.

m/mol·kg^{-1}	σ(∅)	σ(ℓnγ)	σ(γ)
.001	.0000	.0001	.0000
.010	.0002	.0004	.0003
.100	.0006	.0017	.0008
1.000	.0010	.0022	.0004
2.000	.0010	.0023	.0003
4.445	.0054	.0062	.0009

Coefficients of Correlating Equations

	Eqs 1		Eqs 2		Eqs 3	
Par	coefficient	σ(coeff)	coefficient	σ(coeff)	coefficient	σ(coeff)
1	.1215973148+01	.105-01	-.1249022044+01	.120+00	.6573833280+01	.541-01
2	-.3557285519+00	.110-01	.1281837942+02	.497+00	-.7807147467+01	.160+00
3	.8294655619-01	.472-02	-.1021050890+02	.802+00	.5240992270+01	.177+00
4	-.4869541257-02	.674-03	.5759847483+01	.624+00	-.1786182357+01	.850-01
5			-.1770883964+01	.235+00	.2440743105+00	.149-01
6			.2231409674+00	.342-01		

σ(eqs 1) = .816-02

σ(eqs 2) = .909-02

σ(eqs 3) = .826-02

J. Phys. Chem. Ref. Data, Vol. 10, No. 3, 1981

The method which was used in this study, is modeling and experimental method. First of all, for studying thermodynamic conditions on the mentioned laboratory unit, we investigated sodium chloride and sodium sulfate. Therefore, at first different concentrations (0.5, 2.5, 3.5, 4.5, 5 molal) sodium chloride was tested for finding hydrate formation equilibrium conditions, and then repeated the same experiment for sodium sulfate, and equilibrium pressure and temperatures were recorded. In next step mathematical programing in visual basic and regression method was used for modeling to offer a mathematical model for thermodynamic equilibrium of hydrate formation, and finally to predict the equilibrium temperature.

Results and discussions

1- The effect of sodium chloride electrolyte on hydrate formation of methane

In this step of the study, sodium chloride in five different concentrations (0.5, 2.5, 3.5, 4.5, 5 molal) was injected to the system and the conditions of hydrate formation for methane was recorded on monitor according to the pressure changes. The following figure shows the experimental results.

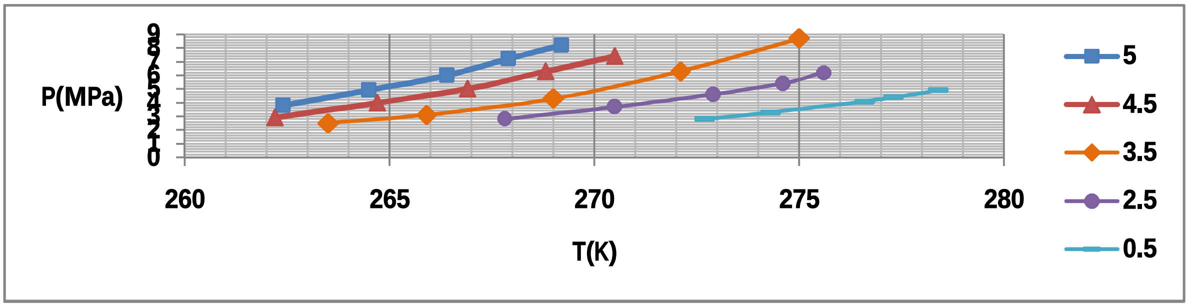


Fig. 3. Equilibrium pressure and temperature data for hydrate formation of methane in the presence of sodium chloride in different molalities.

As can be seen in figure 3, equilibrium pressure and temperature is increased with sodium chloride concentration is increased.

2- The effect of sodium sulfate electrolyte on thermodynamics of hydrate formation of methane

Like that for sodium chloride, sodium sulfate was however studied, and for a better comparison, we used the same concentrations for this step as was seen in previous step. For this part of study, equilibrium pressure and temperature for hydrate formation in the presence of sodium sulfate can be seen in figure 4.

As can be seen in figure 4, equilibrium pressure and temperature is increased with sodium sulfate concentration is increased.

3- Comparing the thermodynamic effect of sodium chloride and sulfate electrolytes on hydrate formation.

. For this purpose, we study five diagrams in five different concentrations, in each of them equilibrium data for hydrate formation of is given in the absence of sodium chloride or sulfate electrolytes. Figure 5 shows the diagrams.

As can be seen in figure 5, at low concentrations (0.5 molal) no appreciable difference can be observed between the two electrolytes, but in higher concentrations (5 molal) the difference between them will be significant, so that both of them possess inhibition effect on hydrate formation, but sodium chloride shows larger effect than sodium sulfate and increasing the concentration will increase the inhibition effect and however, the difference between both electrolyte's will become more significant in higher concentrations.

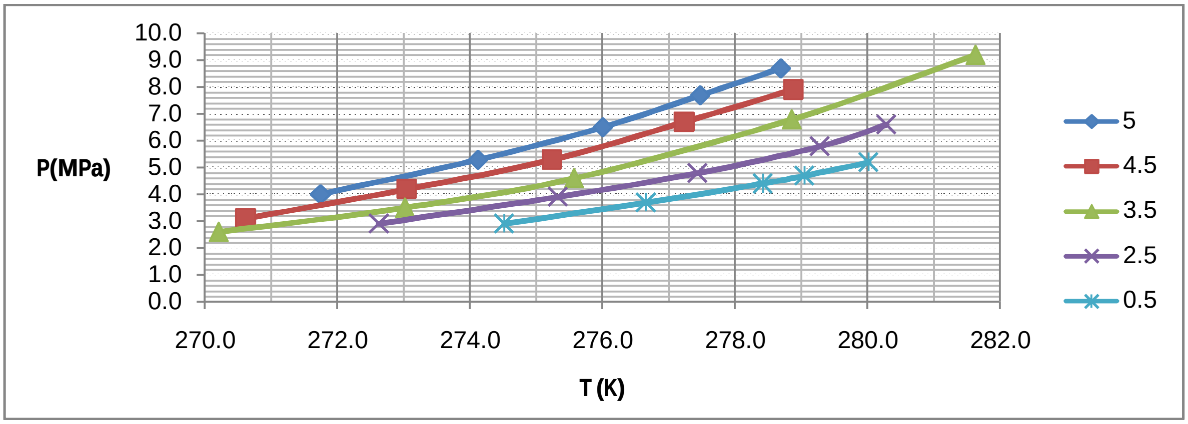


Fig. 4. Equilibrium pressure and temperature data for hydrate formation of methane in the presence of sodium sulfate in different molalities.

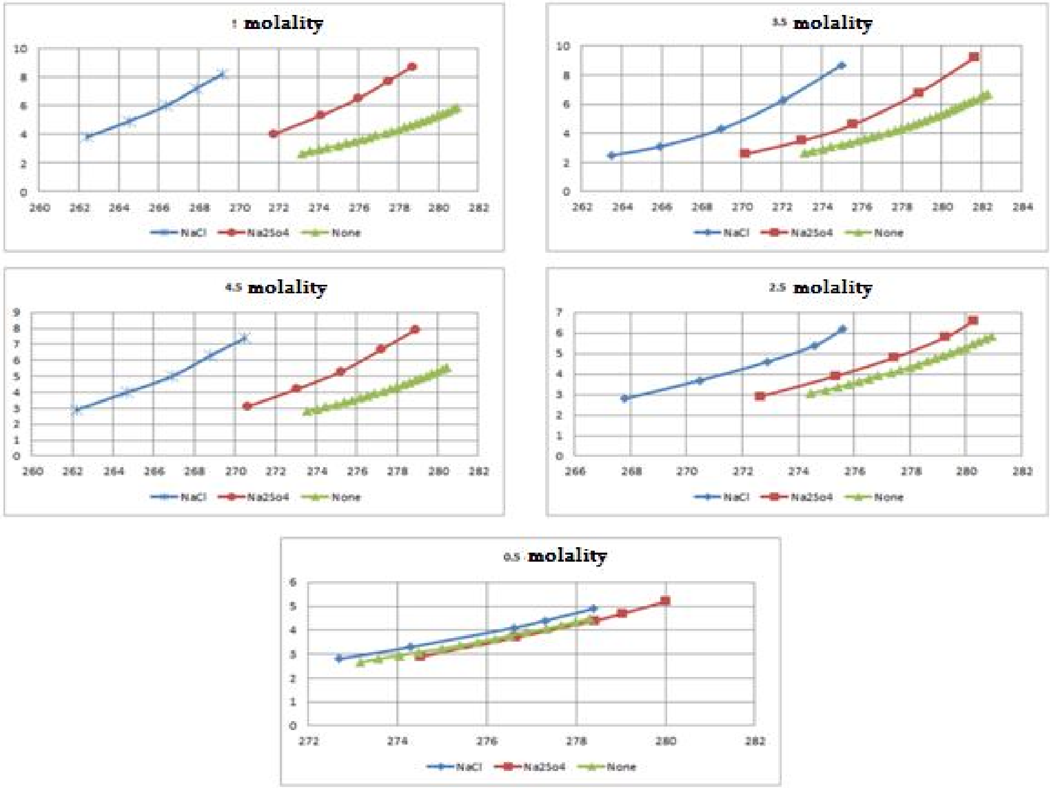


Fig. 5. Comparing the thermodynamic effect of sodium chloride and sulfate electrolytes on hydrate formation of methane

4- Thermodynamic model for hydrate formation in the presence of electrolyte inhibitor.

So far, several models are offered for hydrate formation of methane in the presence of electrolytes, which have acceptable ability to predict the equilibrium conditions of hydrate formation. Nevertheless, most of these models are based on phase equilibrium of gas and hydrate, and suffer their need to complicated calculations for obtaining equilibrium temperature in a given concentration and pressure. In this work, we used regression model which does not need complicated calculations and with having only pressure and electrolyte concentrations, we can predict equilibrium temperature for hydrate formation.

The regression model we used can be demonstrated as following:

$$\begin{aligned}\ln(Tpr) = {} & b_o + b_1(\ln p)^2 + b_2\frac{C_{nacl}}{\gamma} + b_3\gamma^2 + b_4\frac{(1 - C_{nacl})}{\gamma^3} \\ & + b_5\frac{\ln\gamma}{\ln p} + b_6\frac{\ln\gamma}{(\ln p)^4} + b_7\frac{\ln p}{\gamma} \\ & + b_8\frac{(\ln p)^2}{\gamma} + b_9\frac{(\ln p)^3}{\gamma} + b_{10}\frac{(\ln p)^4}{\gamma} \\ & + b_{11}\ln(pr) + b_{12}(\ln pr)^2\end{aligned}$$

This model is assumed for above thermodynamic equilibrium data and $\{b_0 - b_{12}\}$ coefficients were estimated by regression.

5- Description of the neural network model

To build this model, there are various methods and networks, Each of which their own unique abilities and advantages. In this study, a training algorithm has been used to build the model.

Terms of the type topology is feedforward. In this method after the calculating prediction error For the first input synaptic weights of the last layer to the first layer gradually changed so that the prediction error is less. After reading enough of the input network, called network is converging and its error rate is minimized. Learning rule in this model has been (trainlm).

The model is made consists of three layers: the input layer is containing 10 neurons, hidden layer are containing 50 neurons, finally output layer consists of a neuron that will be represents a output network. Selection the number of layers and number of neurons in each layer is completely optional and after the a lot of testing and to test several models with different number of neurons eventually lowest rate of error is obtained by the described model. The overall structure of the network that made can be seen in Figure 6.

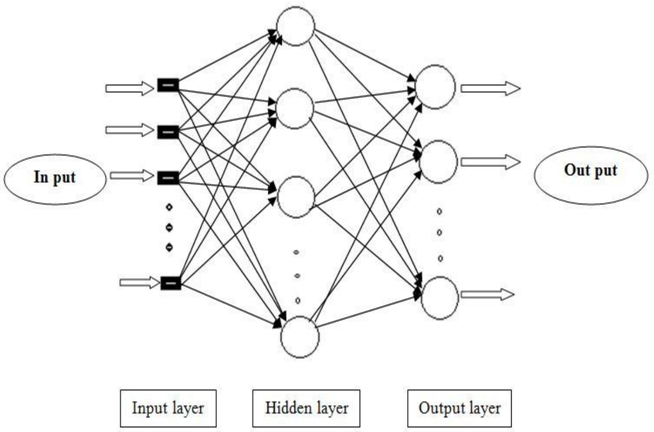


Fig. 6. Structure of the network

One of the problems that may be the network encountered by it during converging this is a system instead of data analysis protect their and Called with (overfitting). the obtained model can be predict the same data that is used in the process of learning , but if the new data to be presented, performance of system will be very bad and the forecast error is high. in order to prevent this phenomenon Cross-validation method is used. In this method primary collection of data are classified into three categories: training, validation and testing. network reliability is measured simultaneously with the training in all round and when the data validation error starts to increase network training is stopped. In the construction of desired network twenty-five percent of the data as the validation data, twenty-five percent as the test data and the rest of the data as the training data are selected at random from among all. Network after thirty epoch submits the best performance in the eleventh epoch.

Using the power of neural networks tools in forecasting and optimization for complex relationships between the various parameters, model in order to Predicting The thermodynamics effect of sodium chloride and sodium sulfate on the prevention of methane hydrate formation was presented. Network built by data obtained from the experimental data was performed. Correlation coefficient was obtained from the model is more than 0.99 and the mean-square error is less than 0.002. Therefore, we can conclude from the values of the model that this model is a suitable model for predicting the thermodynamics effect of sodium chloride and sodium sulfate on the prevention of methane hydrate formation and can he ensure the accuracy of laboratory results. It can reduced a lot of cost during the thermodynamics and industrial projects.

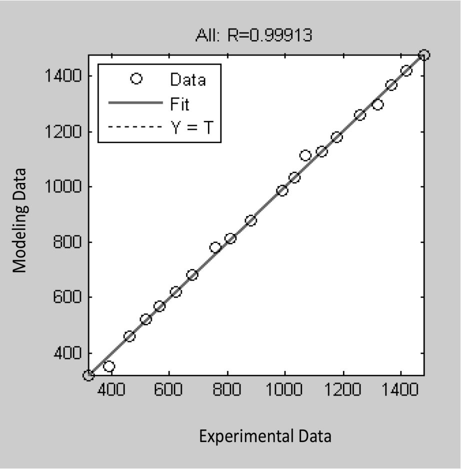


Fig. 7. Correlation between experimental and modeling data for sodium chloride

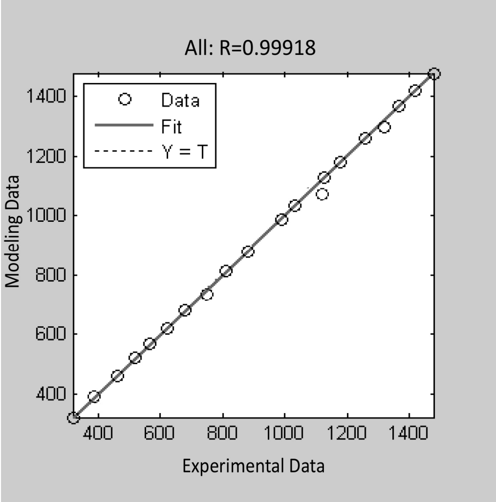


Fig. 8. Correlation between experimental and modeling data for sodium sulfate

Conclusion

Sodium chloride possess a greater effect on thermodynamic equilibrium of hydrate formation. It was found that increasing the concentration of sodium chloride raises this effect. At low concentrations (0.5 molal) no appreciable difference can be observed between the two electrolytes, but in higher concentrations (5 molal) the difference between them will be significant, so that both of them possess inhibition effect on hydrate formation, but sodium chloride shows larger effect than sodium sulfate and increasing the concentration will increase the inhibition effect and however, the difference between both electrolyte's will become more significant in higher concentrations.

A 10 variable linear regression model was offered for thermodynamic model of hydrate formation of methane in the presence of electrolytes, and the obtained data was compared with the model calculations numerical results. The study's estimation model was greatly capable in explaining pressure and temperature equilibrium date for hydrate formation in the presence of sodium chloride and sulfate.

The results showed that regarding the cost of sodium chloride in Iran and the world, and its nontoxic nature, it can be consumed as an ideal inhibitor for hydrate formation in gas industries. The results, however, showed that this compound can inhibit hydrate formation and therefore can be used in oil and gas transport systems to prevent cost impositions of pipe damages, repair and reconstructions.

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