Experimental Measurement and Kinetic Modeling of Ethane Gas Hydrate in the Presence of Sodium Dodecyl Sulfate Surfactant

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Abstract: In this work, the kinetics of ethane hydrate formation has been studied experimentally and a kinetic model based on chemical affinity has been described for predicting the hydrate growth process in the stirred batch reactor at a constant volume. The experiments were done with both pure water and aqueous solution of sodium dodecyl sulfate (SDS). The effect of SDS on formation kinetics has been investigated in concentrations: 300, 500 and 1000 PPM at different temperatures: 273.15, 274.15, 275.15 and 276.15 K. Experimental results showed the use of SDS decreases surface tension between the liquid and gas, then the ethane hydrate formation rate is increased, especially in SDS concentration of 500 PPM. The parameters of the model, A_r/RT and t_K, were optimized for each experiment. The parameter A_r/RT was obtained a constant value for ethane gas. Acceptable agreement between the experimental and predicted data was generally found, and this model can sufficiently predict the formation pressure.

Keywords: Gas Hydrate, Kinetics of Formation, Ethane Hydrate, SDS Aqueous Solution, Chemical Affinity

1. Introduction

Clathrate hydrates are crystalline solid compounds. These crystals are composed of hydrogen-bonded water molecules (host molecules), and some other gas species (guest molecules). Water molecules form a cage-like structure at high pressure and low temperature conditions; then guest molecules such as methane and ethane and other hydrocarbons are trapped in the lattice and stabilize the structure (Ballard & Sloan Jr, 2001; Li, Liang, Guo, Wang, & Fan, 2006; Sloan Jr & Koh, 2007). Gas hydrates can store 180 volumes of natural gas per volume of hydrate at standard temperature and pressure, so hydrates crystals have unrivaled gas storage properties. The

hydrate structures (sI, sII and sH) are determined by the shape and size of guest molecules (Erfan-Niya, Modarress, & Zaminpayma, 2011; Sloan Jr & Koh, 2007). To solve the problem related to natural gas pipelines by hydrate formation, the study of hydrate-related scientific and technical problems is urgent. These subjects contain the kinetics of hydrate formation, the thermodynamics of hydrate formation systems, mass and heat transfer during hydrate formation and dissociation, and the using of clathrate hydrate in gas transportation, energy storage and water desalination. Therefore in recent years, the prediction of hydrate formation rate has been investigated. Also, the study of gas hydrates because of their large

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potential as a future energy source is important (Erfan-Niya et al., 2011; Sloan Jr & Koh, 2007).

A lot of studies have been performed on effects of various surfactants on rate of gas hydrate formation and dissociation by researchers. During the hydrate formation, the resistance of mass transfer between gas and liquid phases can be declined by using an appropriate quantity of the promoter, therefore the rate of gas hydrate formation increases efficiently. The promoters have the both of kinetic or thermodynamic effects in hydrate formation process and are divided into surfactants (surface active agent) and hydrotropes. The surfactants contain three classes: anionic, cationic and non-ionic substance.

Zhong and Rogers investigated the formation rate of gas hydrate in a static system with solution containing sodium dodecyl sulfate (SDS) surfactant (as anionic surfactant) and found the critical micellar concentration (CMC) at ethane and natural gas hydrate at SDS solution (Zhong & Rogers, 2000).

It is determined that the maximum of natural gas hydrate formation in presence of a promoter occurred at a concentration of 300 PPM of SDS solution by Han et al. (Han, Wang, Chen, & Liu, 2002). Link et al. investigated, for promoting methane hydrate formation, SDS is the best surfactant (Link, Ladner, Elsen, & Taylor, 2003). Also Mandal and Laik studied the effects of SDS as an anionic surfactant on ethane hydrate formation, dissociation and storage capacity in a static system(Mandal & Laik, 2008).

Gayet et al. found that using SDS is a constraint that prevents hydrate particles from agglomerating and forming a rigid hydrate film at the liquid-gas interface (Gayet et al., 2005). Zhang et al. studied the hydrate formation at SDS concentration from 260 to 10000 PPM and showed that SDS addition reduces the induction time; however, a systematic trend was not observed between induction time and SDS concentration (Zhang, Lee, & Lee, 2007). The effect of various concentrations of SDS as an anionic surfactant on methane hydrate formation rate, stability and induction time was investigated by Keshavarz and Sadeghi (Moraveji, Sadeghi, Fazlali, & Davarnejad, 2010).

Manteghian and co-workers investigated the effects of sodium dodecyl sulfate (SDS) and linear alkyl benzene sulfonate (LABS) as anionic surfactants, cetyl trimethyl ammonium bromide (CTAB) as cationic surfactant and ethoxylated nonylphenol (ENP) as non-ionic surfactant on the formation, dissociation and storage capacity of methane hydrate at three temperatures of 268.2, 270.2 and 272.2 K with three concentrations of 300, 500 and 1000 PPM of promoters (Ganji, Manteghian, Omidkhah, & Rahimi Mofrad, 2007). They found SDS surfactant has the maximum promotion among the studied surfactants for methane hydrate. Experimentally the effect of surfactant SDS on the formation and dissociation kinetic behaviors of methane hydrate and the storage capacity have been studied below ice point by Chen and Yang (Lin et al., 2004). They found the formation rate of methane hydrate could be speeded up by adding SDS, and a critical SDS concentration of 650 PPM was determined for a maximum storage capacity of 170 standard volume of methane per volume of hydrate (Lin et al., 2004).

Englezos and Yoslim studied the formation and dissociation of hydrate from a gas mixture of 90.5% of methane and 9.5% of propane mixture by anionic surfactant at three different degrees of undercooling and two surfactant concentrations, and showed the mole consumption for hydrate formation was increased by 4.4 times by the addition of 2200 PPM of SDS (Yoslim & Englezos, 2008). Beak and Cho found the influence of gas storage capability and the formation rate of hydrate with anionic surfactants among ionic surfactants with a low concentration are greater than those of hydrate using cationic one (Cho, & Beak, 2005).

Most of performed researches studying promoters are related to methane hydrate formation while the scarce studies have been found on ethane hydrate in surfactant solution in the literatures. Therefore in this work, the aim is to study the effect of the anionic surfactant sodium dodecyl sulfate at different concentrations on the rate of ethane hydrate formation.

The hydrate formation has also been introduced as nucleation and growth processes. Different models were studied by many researchers based on mass and heat transfer problem (Clarke & Bishnoi, 2005; Varaminian, 2002; ZareNezhad & Varaminian, 2012) in isothermal and isobaric conditions, however, because of complex nature involve (ZareNezhad & Mottahedin, 2012), the model needed uses initial and final conditions of the process to predict the formation rate. A macroscopic kinetic model based on the reaction chemical potential is used by so many researchers (Mottahedin, Varaminian, & Mafakheri, 2011; ZareNezhad & Varaminian, 2012) for describing gas hydrate formation processes in isothermal systems that the effect of different driving forces on the model accuracy is validated (ZareNezhad & Varaminian, 2012).

The main purpose of this work is to investigate ethane hydrate formation kinetics in

distilled water and aqueous solutionsh with various concentrations of the anionic surfactant sodium dodecyl sulfate (SDS) and at different stirred speeds (400, 650 and 900 rpm) experimentally and correlation. Modeling the kinetics based on chemical affinity is used for the prediction of the moles of ethane gas consumed (or ethane pressure) versus reaction time during the hydrate crystal formation and growth processes.

The different parameters, the stirrer speed, experimental temperature and SDS solution concentration affect the kinetics modeling parameters (t_k and A_r/RT) in hydrate formation process. The effective parameters on t_k value are ranked by importance as stirrer speed, SDS solution concentration and experimental temperature. The effective parameters on A_r/RT value are ranked by importance as SDS solution concentration, experimental temperature and stirrer speed.

In this work, the different sets of experiments have also validated the new correlation for systems containing SDS surfactant. Acceptable agreement between the experimental and the predicted data is generally found.

2. Experimental Section

2.1. Apparatus and Materials

The experiments were performed in a system that consisted of a reactor, a jacket for heat transfer and a data acquisition system. The apparatus is shown in Figure 1.

Hydrate decomposition was performed in a stirred batch reactor, that was capable of operating at pressures between 0-90 bar, and the volume of the reactor was 990 cc. A jacket was used to heat and cool the system, and the temperature of reactor was controlled by the flow of ethanol in the jacket and an external circulating temperature bath. The cell pressure was measured by a Druck PTX1400 pressure transmitter (0-200 bar, ±0.1 bar). The temperature was measured using PT100 thermometers (±0.1 K). The signals of pressure and temperature were acquired by a data acquisition system driven by a personal computer. For mixing, the experimental cell included a magnetically coupled stirrer shaft and stirring motor speed controller. The experiments reported in this paper were obtained with stirrer speeds of 400, 650 and 900 rpm. Ethane (crystal I hydrate former) with a normal purity of 99.5% was supplied by Technical gas service, and de-ionized-distilled water was used. SDS surfactant ($C_{12}H_{25}O_4SNa$) with purity of 98% was purchased from Merck Company.
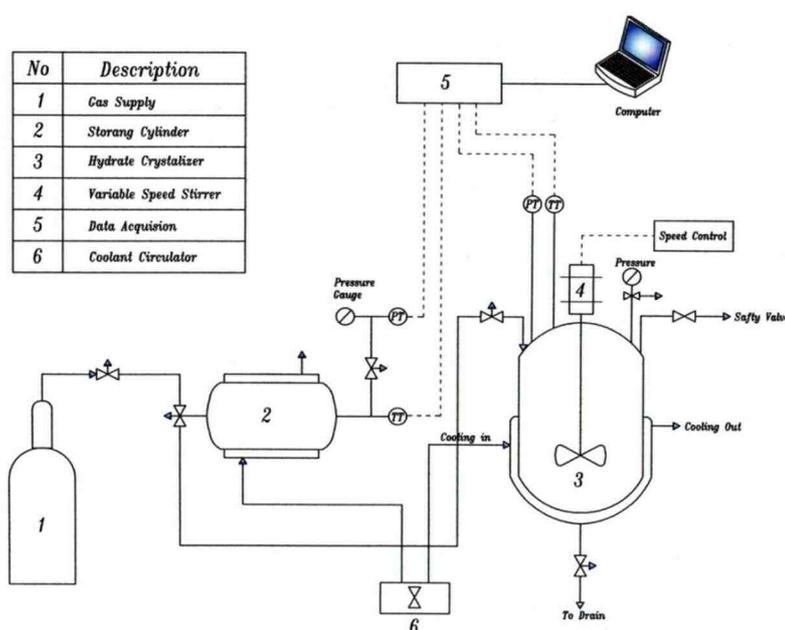
No	Description
1	Gas Supply
2	Storang Cylinder
3	Hydrate Crystalizer
4	Variable Speed Stirrer
5	Data Acquision
6	Coolant Circulator

Figure 1. Experimental setup, hydrate formation apparatus

2.2. Experimental Procedures – Hydrate Formation

First, the hydrate formation reactor was evacuated, and the cell was rinsed with de-ionized water. Then, 750 cc of distilled water (or an aqueous solution of SDS) was charged to the reactor. The required amount of SDS was weighed on an electronic balance and was dissolved in 750 cc of de-ionized water. The reactor was pressurized to approximately 0.05 MPa below the equilibrium pressure for hydrate formation at the specified experimental temperature. The constant temperature bath was turned on, and the reactor was allowed to reach the constant experimental temperature. When the solution attained thermal equilibrium, the reactor was pressurized to the experimental pressure by supplying gas from a cylinder. Ethane gas was injected into the cell with driving force of approximately 12 bar, mixing started and data collection began. The pressure was recorded as a function of time during hydrate formation. When the pressure of the reactor reaches a constant value, it means that the process of gas hydrate formation is complete.

3. Kinetic Modeling – Chemical Affinity

To model and predict the kinetic experimental data for hydrate formation, the property of chemical affinity was used in the modeling of the hydrate formation rate in a constant volume process. In this model, a macroscopic driving force was defined requiring only the initial (experimental temperature, and pressure) and final conditions (equilibrium conditions); thus, this model does not have the limitations of microscopic models, such as the need for heat and mass transfer coefficients or the population of particles, which may differ in each experiment.

The driving force for the reaction is the chemical potential difference between the products and the reactants, and this difference is reduced as the reaction proceeds. At first, the chemical affinity that is shown by A**,** was defined as a thermodynamic function.

All chemical reactions follow the direction that decreases the chemical affinity. Prigogine and Defay defined the chemical affinity as a generalized driving force for a chemical reaction and explained it as follows (Prigogine, Defay, & Everett, 1962):

$$A = -\sum \upsilon_i \mu_i \qquad (1)$$

where μ_i is chemical potential and υ_i is the stoichiometric coefficient of its compounds. At equilibrium, A=0, and in the other state, (A>0), the reaction is advancing toward equilibrium.

Chemical affinity can be expressed by an equation of the form:

$$A = A^0 - RT \sum_i \ln(a_i)^{\upsilon_i} \qquad (2)$$

where $A0$ is the affinity of the reacting system if the components are in their standard state and A is only a function of temperature.

By defining $A^{\bullet}_{T,V} = A_r(\frac{1}{t} - \frac{1}{t_k})$ as affinity decay rate, it was apparent that $A^{\bullet}_{T,V}$ was inversely proportional to the elapsed time (Garfinkle, 1999) and by integration, the following equation has been obtained:

$$A_i = A_r \ln(\zeta_{t_i} \exp(1 - \zeta_{t_i})) \qquad (3)$$

In equation (3), A_r is a constant of proportionality, and denotes the affinity rate constant, and $\zeta_{t_i} = \frac{t_i}{t_k}$. The extent of reaction ζ_{t_i} is limited to the range 0 to 1. However, the value of ζ_{t_i} must be known to correlate empirical data by Eq (3) to determine the value of t_K, but ζ_{t_i} itself depends on t_K. This problem can be solved by generating values of t_K by an iterative method.

3.1. Modeling of Hydrate Formation

The experimental conditions for hydrate formation must be far away from the 3-phase equilibrium curve. In constant volume – constant temperature experiments, after the formation of hydrate crystals; the pressure decreases gradually because of gas production, and the final pressure must be equal to P_{eq}. When P_{eq} is reached, the hydrate formation stops, and the system reaches equilibrium (B point).

For calculating the affinity in different conditions, we must measure the extent of the reaction with time with the pressure of gas. The amount of total gas generated during hydrate formation is equal to (n_A-n_B), and with the equation of state, the extent of the reaction can be obtained from equation (4). A and B subscripts indicate initial condition and finial condition for hydrate formation respectively.

$$\zeta_{Qi} = \frac{n_A - n_i}{n_A - n_B} = \frac{(P_A/Z_A) - (P_i/Z)}{(P_A/Z_A) - (P_B/Z_B)} \qquad (4)$$

The affinity for each time was obtained by the following formula: $A_i = -RT \ln(\zeta_{Qi})$ (5)

By plotting A_i versus $\ln(\zeta_{t_i} \exp(1 - \zeta_{t_i}))$, A_r and t_K were obtained.

4. Results and Discussion

4.1. Experimental Results

The experiments were performed at temperatures of 273.15, 274.15, 275.15 and 276.15 K and SDS concentrations of 300, 500 and 1000 PPM with different stirrer speeds. Experimental kinetics curves for ethane hydrate formation are given for the two cases of pure water and an SDS aqueous solution at 273.15 and 274.15 K in Figures 2 and 3 respectively. The other kinetic results were given in our previous experimental work (Karamoddin, Varaminian, & Daraee, 2011), and the modeling in this study has been performed based on the obtained data.

Also, to determine the optimal concentration of SDS for ethane hydrate formation, experiments were performed at 300, 500 and 1000 PPM concentrations and at the temperature of 273.15 K. The results show that the rate of ethane hydrate formation is the highest for an SDS aqueous solution with a concentration of 500 PPM (Karamoddin, Varaminian, & Daraee, 2011). The surface tension of the aqueous phase can be reduced at SDS solution concentrations of 500 PPM.

The obtained results by Manteghian and Ganji related to the effect of SDS on *methane* hydrate at concentrations of 300, 500 and 1000 PPM show that the maximum promotion effect of SDS was also observed at the concentration of 500 PPM (Ganji et al., 2007).

Additionally in this work, experiments were performed with different stirrer speeds of 400, 650 and 900 rpm at 273.15 K. The influence of the stirrer speeds in pure water and in the ethane system on the ethane hydrate formation rate is given in Figure 4 which shows that the rate of hydrate formation at 400 rpm is low.
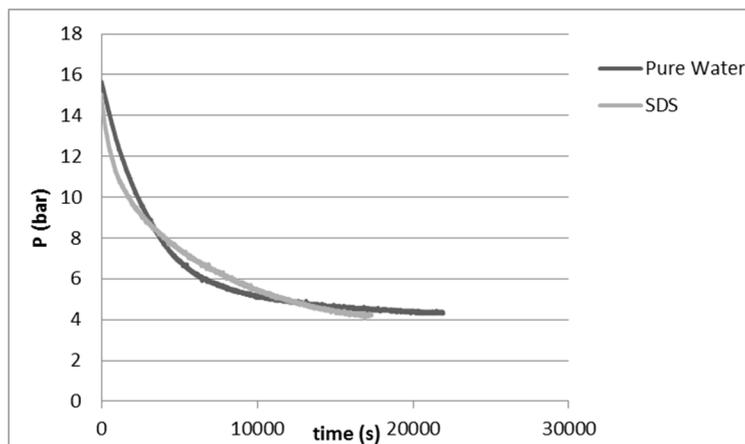

Figure 2. Experimental kinetic curve for ethane hydrate formation in pure water and in an SDS aqueous solution (500 PPM) at 273.15 K and stirrer speed of 900 rpm
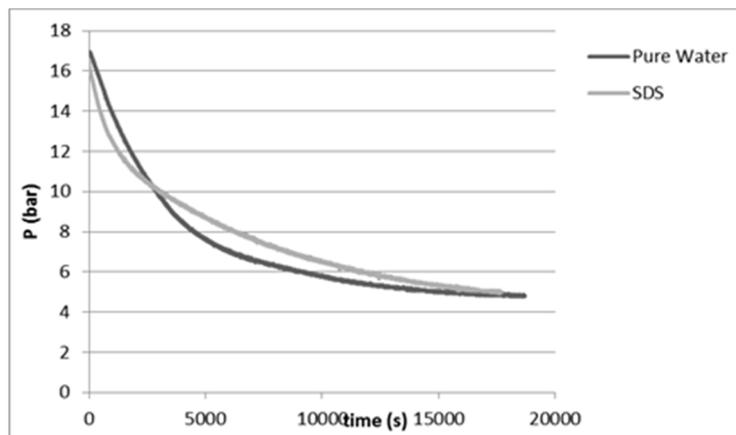

Figure 3. Experimental kinetic curve for ethane hydrate formation in pure water and in an SDS aqueous solution (500 PPM) at 274.15 K and stirrer speed of 900 rpm
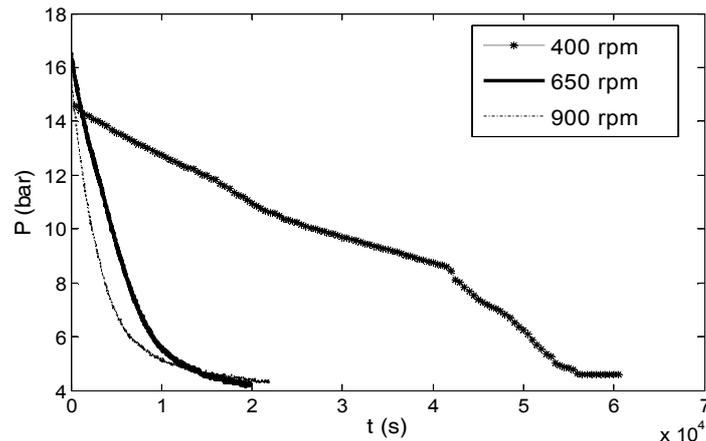
Figure 4. Effect of different stirrer speeds of on ethane hydrate formation

4.2. Modeling Results

The A_r/RT and t_K parameters were obtained for different temperatures, concentrations of SDS aqueous solution and stirrer speeds with the chemical affinity and the obtained experimental results for pressure versus hydrate formation time. These values are presented in Tables 1 to 4. The results in Tables 1 and 2 are related to the pure water – ethane hydrate system, and Tables 3 and 4 are related to the SDS aqueous solution – ethane system.

Table 1. Results of modeling for the (pure water – ethane) system at different temperatures and a stirrer speed of 900 rpm

T (K)	Δp (bar)	t_k (sec)	A_r/RT	Average relative deviation (%)
273.15	11.21	11454	-0.9212	0.18
274.15	12.22	11455	-0.9698	0.21
275.15	10.58	12354	-0.8842	0.21
276.15	10.56	10722	-1.056	0.26

Table 2. Results of modeling for the (pure water – ethane) system at 273.15 K and different stirrer speeds

Stirrer speed (rpm)	Δp (bar)	t_k (sec)	A_r/RT	Average relative deviation (%)
400	11.31	124425	-0.9399	62.27
650	12.71	17572	-0.9577	0.20
900	11.21	11454	-0.9212	0.18

Table 3. Results of modeling for the (SDS aqueous solution – ethane) system at different temperatures, an SDS solution concentration of 500 PPM and a stirrer speed of 900 rpm

T (K)	Δp (bar)	t_k (sec)	A_r/RT	Average relative deviation (%)
273.15	10.78	17573	-0.4993	0.18
274.15	11.55	17914	-0.5867	0.21
275.15	9.37	13792	-0.7816	0.23
276.15	10.30	14814	-0.7057	0.24

Table 4. Results of modeling for the (SDS aqueous solution – ethane) system at 273.15 K, different SDS solution concentrations and a stirrer speed of 900 rpm

Concentration (PPM)	Δp (bar)	t_k (sec)	A_r/RT	Average relative deviation (%)
300	10.01	14687	-0.6550	0.23
500	10.78	17573	-0.4993	0.18
1000	10.24	15073	-0.5914	0.15

The results presented in the Tables indicate that the A_r/RT parameter has a value near -0.9 for systems with pure water (Tables 1 and 2), while this value approaches -0.6 for systems containing SDS solution (Tables 3 and 4). Therefore, these values can be used in other similar situations. We use these modeling parameters for predicting experimental data, and the variation of pressure with time is shown in Figures 5 to 8 for a stirrer speed of 900 rpm and at 273.15 K. Kinetic curves for ethane hydrate was calculated at other temperatures in the pure water and SDS aqueous solution systems. These results are given in Figures 9 and 10 for a temperature of 275.15 K. When comparing the calculated and experimental data, it is clear that this model can predict the experimental data with high accuracy.

Based on described theory of researchers (Daimaru, Yamasaki, & Yanagisawa, 2007), the surface tension of the aqueous phase can be declined with adding the surfactant to aqueous solution. At the lower surface tension, interaction among interfacial host molecules (water) is weakened and the guest molecules (such as ethane) can be placed into the aqueous phase more easily than the cases without surfactants (Karamoddin, Varaminian, & Daraee, 2011). Then the mass transfer between gas and liquid phases at the gas water interface and the rate of hydrate formation can be increased efficiently.

In the affinity model, the A_r/RT parameter can be expressed as scale of mass transfer resistance between the host and guest molecules. It means that at the higher A_r/RT value, the resistance of mass transfer is further and thereupon, the rate of hydrate formation is reduced. The presented idea was corroborated by the results of modeling in this work; the A_r/RT value for systems containing SDS surfactant (-0.6) is less than the A_r/RT value for systems with pure water (-0.9).
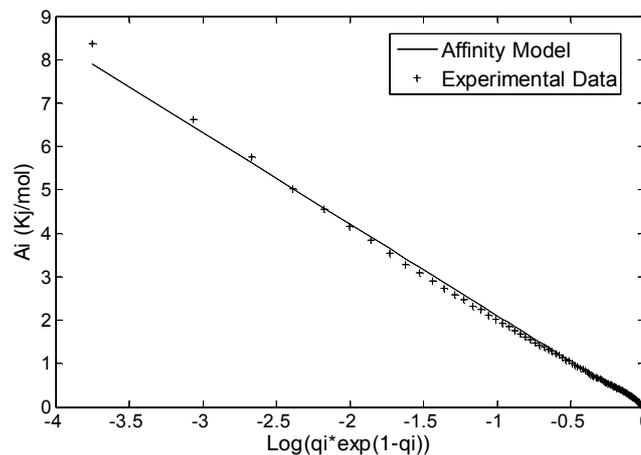

Figure 5. Chemical affinity curve for the (pure water- ethane) system, T=273.15 K, $P_{initial}$=16.86 bar, stirrer speed=900 rpm
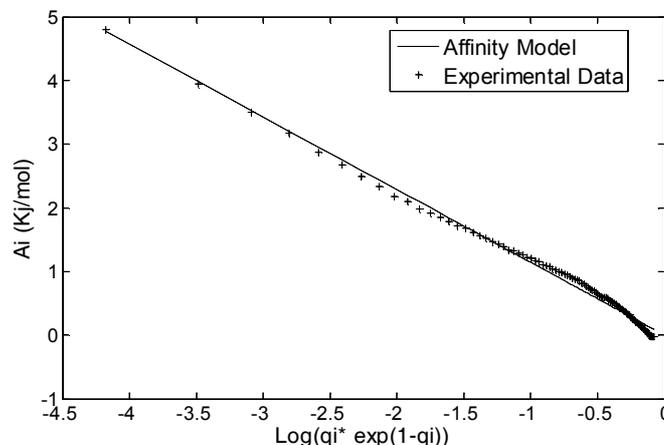

Figure 6. Chemical affinity curve for the (SDS solution of 500 PPM- ethane) system, T=273.15 K, $P_{initial}$=16.86 bar, stirrer speed=900 rpm

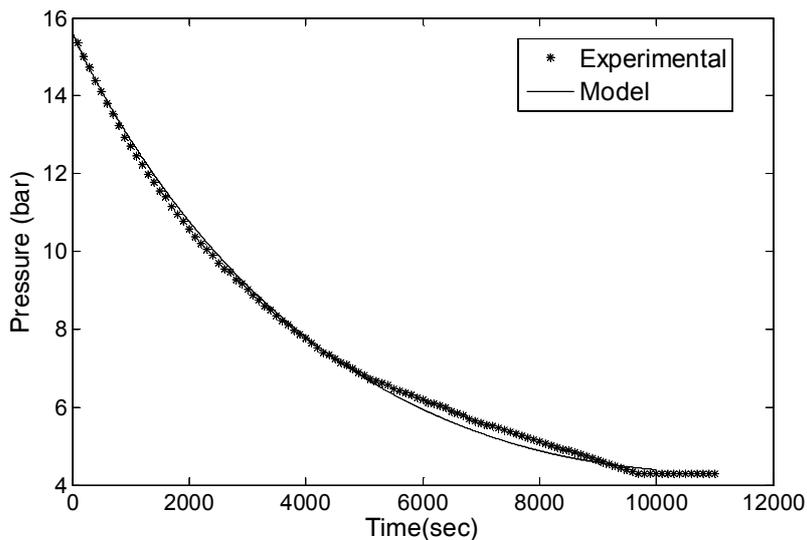**Figure 7.** Experimental and calculated kinetic curves for the (pure water- ethane) system, T=273.15 K, $P_{initial}$=16.86 bar, stirrer speed=900 rpm
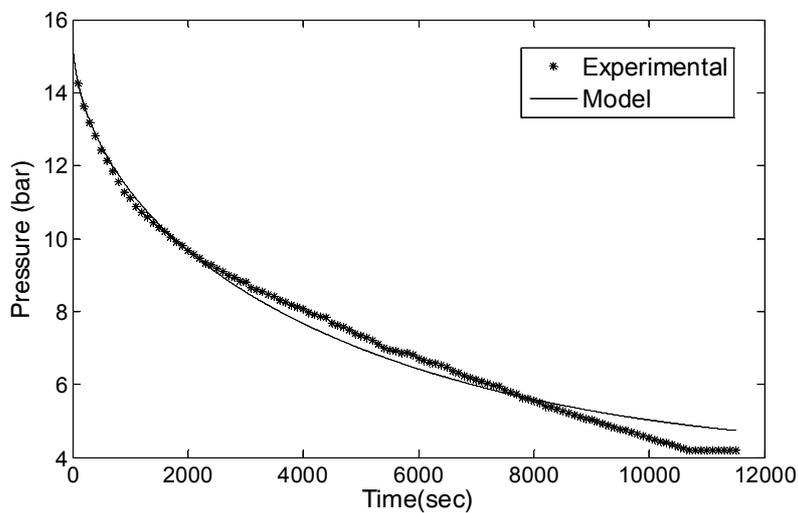

Figure 8. Experimental and calculated kinetic curves for the (SDS solution of 500 PPM- ethane) system, T=273.15 K, $P_{initial}$=16.86 bar, stirrer speed=900 rpm

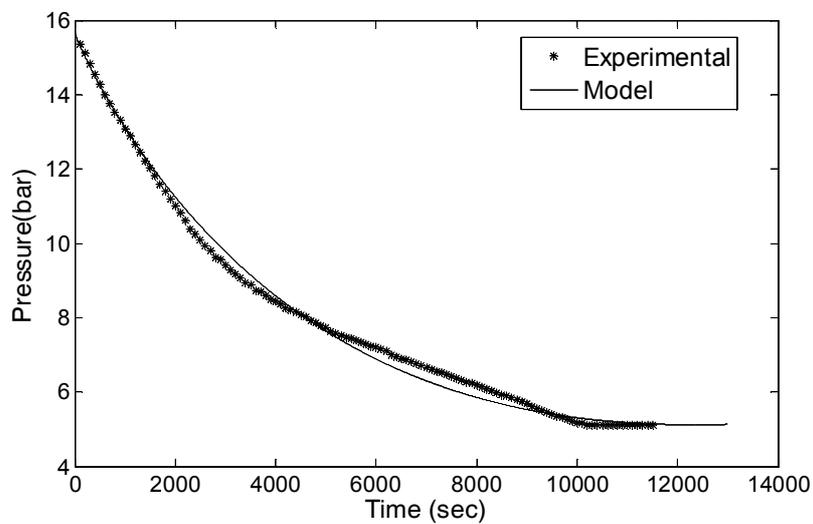**Figure 9**. Experimental and calculated kinetic curves for the (pure water- ethane) system, T=275.15 K, $P_{initial}$=18.26 bar, stirrer speed=900 rpm
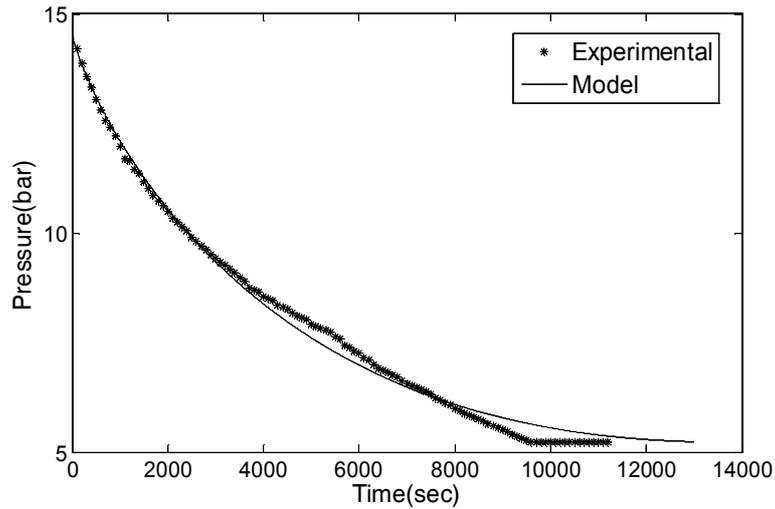
Figure 10. Experimental and calculated kinetic curves for the (SDS solution of 500 PPM- ethane) system, T=275.15 K, $P_{initial}$=18.26 bar, stirrer speed=900 rpm

At other stirrer speeds, the chemical affinity curves and the variation of pressure with time were obtained, and the results are shown in Figures 11-12 and 13-14 for stirrer speeds of 650 rpm and 400 rpm, respectively. When comparing results for the model and the experimental data at different stirrer speeds

(Figures 5-14), it is clear that this model can predict the experimental data with high accuracy at the high stirrer speeds, but the model exhibits a large error (close to 60%) at the low stirrer speed (400 rpm). So the modeling results were improved at the low stirrer speed by changing the chemical affinity model.
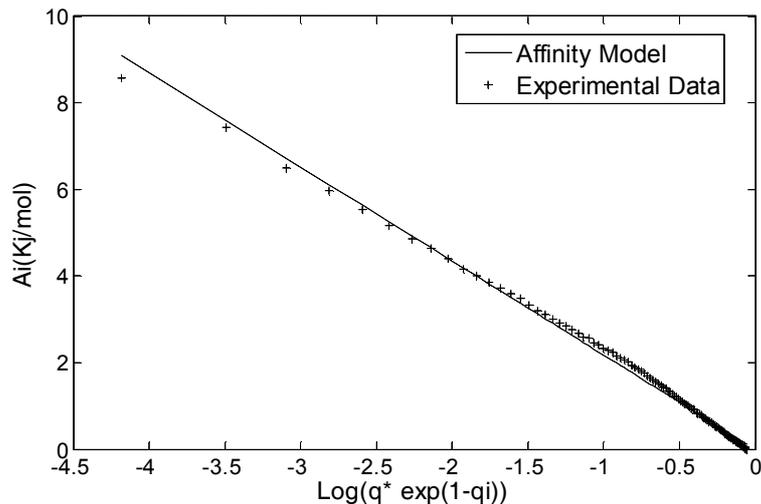

Figure 11. Chemical affinity curve for the (pure water- ethane) system, T=273.15 K, $P_{initial}$=16.86 bar, stirrer speed=650 rpm
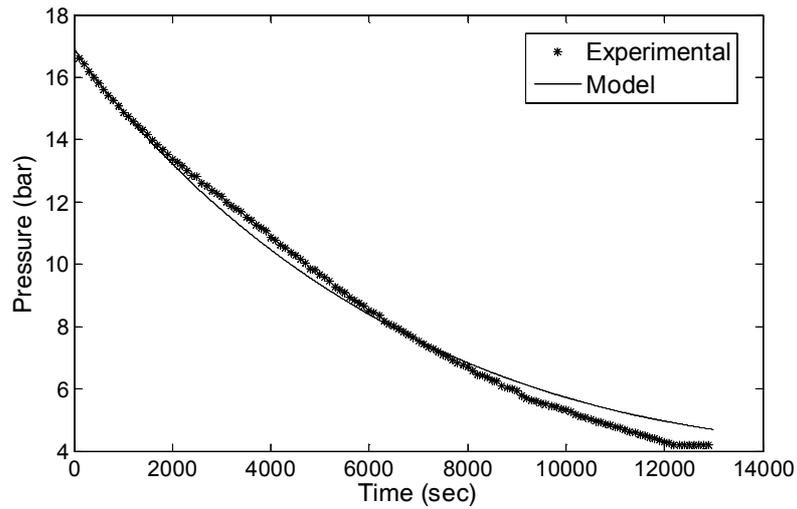
Figure 12. Experimental and calculated kinetic curves for the (pure water- ethane) system, T=273.15 K, $P_{initial}$=16.86 bar, stirrer speed=650 rpm
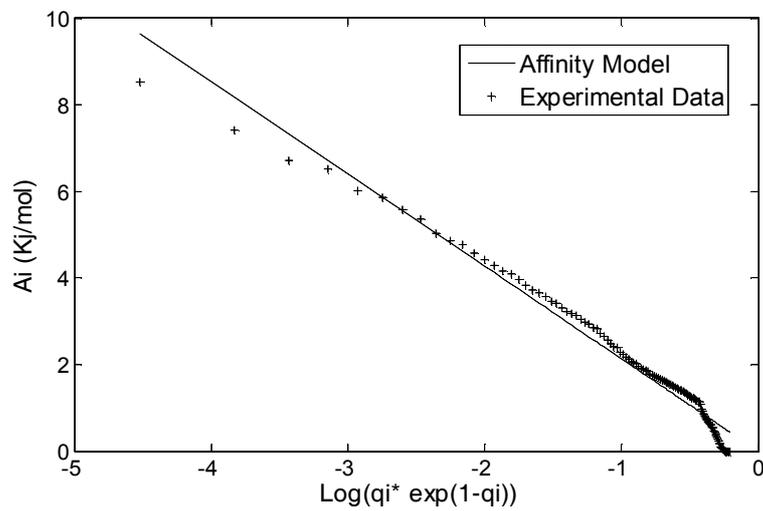

Figure 13. Chemical affinity curve for the (pure water- ethane) system, T=273.15 K, $P_{initial}$=16.86 bar, stirrer speed=400 rpm
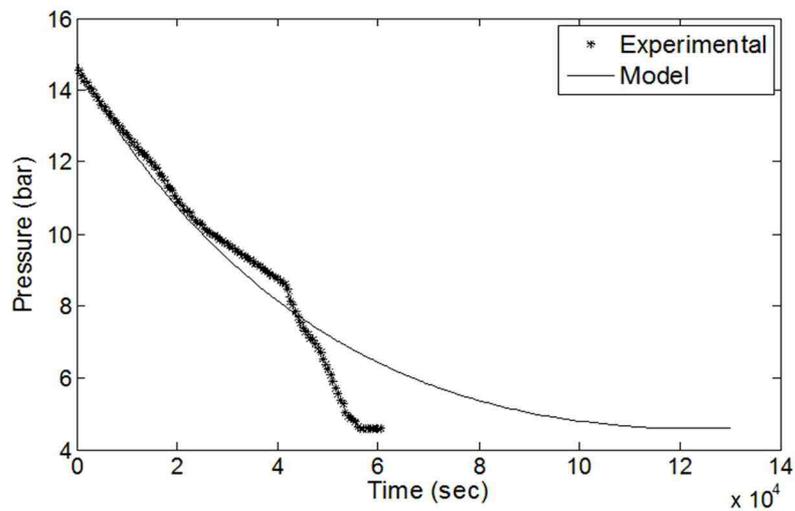

Figure 14. Experimental and calculated kinetic curves for the (pure water- ethane) system, T=273.15 K, $P_{initial}$=16.86 bar, stirrer speed=400 rpm

5. Conclusion

In this paper, experimental and theoretical investigations of two systems containing pure water and an SDS aqueous solution of ethane gas hydrate have been performed. The affinity model can be applied for studying the energy conversion processes in gas hydrate formation in systems with and without surfactant. The following are conclusions abstracted from the results of the present work with regarded to experiences and result of modeling:

1) The experimental results show that the use of SDS increases the hydrate formation rate. SDS serves as an active substance and increases the rate of hydrate formation but does not affect the equilibrium pressure. Additionally, the impact of SDS on ethane hydrate formation was larger at lower temperatures.

2) Experiments were performed at SDS concentrations of 300, 500 and 1000 PPM at 273.15 K, and the results show that the rate of hydrate formation is highest at SDS aqueous solution concentrations of 500 PPM. The optimum concentration of SDS solution is 500 PPM for the ethane hydrate system.

3) The results show that there is a linear relationship between the data, and all correlation coefficients (r^2) are higher than 0.99. The presented modeling results indicate that the parameter A_r/RT has a value near -0.9 for the systems with pure water, while this value approaches -0.6 for the systems containing SDS. The A_r/RT parameter can be expressed as scale of mass transfer resistance between the phases. It means that at the higher A_r/RT value, the resistance of mass transfer is further.

4) Generally, the chemical affinity model can predict experimental data with high accuracy, but the error of the model increased with increasing temperature. The maximum model error occurred at a temperature of 276.15 K (with a stirrer speed of 900 rpm and an SDS concentration of 500 PPM).

5) Results show that the error of the affinity model is highest at low stirrer speeds (particular 400 rpm). The correlation coefficient (r^2) is close to 1 for high stirrer speeds, while this value is equal to 0.97 for the 400 rpm stirrer speed.

Nomenclature

a	Chemical activity
A_r	Constant of Proportionality [Kj.mol^{-1}]
n	Number of moles of gas that occupied the cavities [mol]
P	Pressure [bar]
R	Universal gas constant [bar.m^3]. [mol.K]$^{-1}$
t	Time [Second]
t_k	Time required to obtain equilibrium conditions [Second]
T	Temperature [K]
V	Volume [m^3]
Z	Compressibility Factor

Greek letters:

μ	Chemical Potential [J.mol^{-1}]
ν	Stoichiometric Coefficient of Reaction
ζ_{ti}	Extent of reaction based on time

Subscripts

A	Initial condition for hydrate formation
B	Final condition for hydrate formation
i	Arbitrary component

References

Ballard, A., & Sloan Jr, E. (2001). Hydrate phase diagrams for methane+ ethane+ propane mixtures. *Chemical engineering science, 56*(24), 6883-6895.

Cho, B.H., & Beak, Y.S. (2005). The Influence of Ionic and Nonionic Type Surfactants for Natural Gas Hydrate Formation. *LNG Technology Research Center*, *Korea Gas Corporation.*

Clarke, M. A., & Bishnoi, P. (2005). Determination of the intrinsic kinetics of CO2 gas hydrate formation using in situ particle size analysis. *Chemical engineering science, 60*(3), 695-709.

Daimaru, T., Yamasaki, A., & Yanagisawa, Y. (2007). Effect of surfactant carbon chain length on hydrate formation kinetics. *Journal of Petroleum Science and Engineering, 56*(1), 89-96.

Erfan-Niya, H., Modarress, H., & Zaminpayma, E. (2011). Molecular dynamics study on the structure I clathrate-hydrate of methane+ ethane mixture. *Energy Conversion and Management, 52*(1), 523-531.

Ganji, H., Manteghian, M., Omidkhah, M., & Rahimi Mofrad, H. (2007). Effect of different surfactants on methane hydrate formation rate, stability and storage capacity. *Fuel, 86*(3), 434-441.

Garfinkle, M. (1999). The thermodynamic natural path in chemical reaction kinetics. *Discrete Dynamics in Nature and Society, 4*, 145-164.

Gayet, P., Dicharry, C., Marion, G., Graciaa, A., Lachaise, J., & Nesterov, A. (2005). Experimental determination of methane hydrate dissociation curve up to 55MPa by using a small amount of surfactant as hydrate promoter. *Chemical engineering science, 60*(21), 5751-5758.

Han, X., Wang, S., Chen, X., & Liu, F. (2002). *Surfactant accelerates gas hydrate formation.* Paper presented at the 4th International Conference on Gas Hydrates, Yokohama, Japan.

Karamoddin, M., Varaminian, F., & Daraee, M. (2011). Effect of experimental SDS surfactant on ethane hydrate formation kinetics. *First National Iranian Conference on Gas Hydrate*. Sharif University, Tehran, Iran.

Li, J., Liang, D., Guo, K., Wang, R., & Fan, S. (2006). Formation and dissociation of HFC134a gas hydrate in nano-copper suspension. *Energy Conversion and Management, 47*(2), 201-210.

Lin, W., Chen, G.-J., Sun, C.-Y., Guo, X.-Q., Wu, Z.-K., Liang, M.-Y., . . . Yang, L.-Y. (2004). Effect of surfactant on the formation and dissociation kinetic behavior of methane hydrate. *Chemical engineering science, 59*(21), 4449-4455.

Link, D. D., Ladner, E. P., Elsen, H. A., & Taylor, C. E. (2003). Formation and dissociation studies for optimizing the uptake of methane by methane hydrates. *Fluid Phase Equilibria, 211*(1), 1-10.

Mandal, A., & Laik, S. (2008). Effect of the promoter on gas hydrate formation and dissociation. *Energy & Fuels, 22*(4), 2527-2532.

Moraveji, M. K., Sadeghi, A., Fazlali, A., & Davarnejad, R. (2010). Effect of an Anionic Surfactant on the Methane Hydrate Formation: Induction Time and Stability. *World Applied Sciences Journal, 9*(10), 1121-1128.

Mottahedin, M., Varaminian, F., & Mafakheri, K. (2011). Modeling of methane and ethane hydrate formation kinetics based on non-equilibrium thermodynamics. *Journal of Non-Equilibrium Thermodynamics, 36*(1), 3-22.

Prigogine, I., Defay, R., & Everett, D. H. (1962). *Chemical thermodynamics*: Longmans New York.

Sloan Jr, E. D., & Koh, C. (2007). *Clathrate hydrates of natural gases*: CRC press.

Varaminian, F. (2002). *The role of heat transfer in kinetics of hydrate formation.* Paper presented at the Proceedings of the fourth international conference on gas hydrate, Yokohama.

Yoslim, J., & Englezos, P. (2008). The effect of surfactant on the morphology of methane/propane clathrate hydrate crystals.//paper presented at Sixth International Conference on Gas Hydrate. *British Columbia, Canada.*

ZareNezhad, B., & Mottahedin, M. (2012). A rigorous mechanistic model for predicting gas hydrate formation kinetics: The case of CO_2 recovery and sequestration. *Energy Conversion and Management, 53*(1), 332-336.

ZareNezhad, B., & Varaminian, F. (2012). A generalized macroscopic kinetic model for description of gas hydrate formation processes in isothermal–isochoric systems. *Energy Conversion and Management, 57*, 125-130.

Zhang, J., Lee, S., & Lee, J. W. (2007). Kinetics of methane hydrate formation from SDS solution. *Industrial & Engineering Chemistry Research, 46*(19), 6353-6359.

Zhong, Y., & Rogers, R. (2000). Surfactant effects on gas hydrate formation. *Chemical engineering science, 55*(19), 4175-4187.