

# Experimental Study of Methane Hydrate Formation in the Presence and Absence of Tetra n-butylammonium Chloride and Sodium Dodecyl Sulfate

**Mohammadi, Abolfazl\***<sup>+</sup>

*Department of Chemical Engineering, University of Bojnord, Bojnord, I.R. IRAN*

**Alqasi, Akram**

*Department of Chemical Engineering, Omidiyeh Branch, Islamic Azad University, Omidiyeh, I.R. IRAN*

**Abachi, Mohammad**

*Department of Chemical Engineering, University of Bojnord, Bojnord, I.R. IRAN*

**Abedi Farizhendi, Saeid**

*Department of Chemical Engineering, Tarbiat Modares University, Tehran, I.R. IRAN*

**ABSTRACT:** *The kinetics of methane hydrate formation in the presence of tetra n-butylammonium chloride (TBAC) and sodium dodecyl sulfate (SDS) is investigated in this research. The hydrate formation reactions are carried out in the isothermal condition of 278.15 K in a 169 cm<sup>3</sup> stirred batch reactor. The amount of gas uptake and the storage capacity of methane hydrate formation are calculated. Results indicate that utilization of TBAC with a concentration of (3 and 5) wt% and SDS with a concentration of 400 ppm increases the amount of gas consumption and the storage capacity of methane hydrate formation. Utilization of TBAC along with SDS decreases the amount of gas consumption and storage capacity, compared to aqueous the solution of SDS. Investigation of the impact of pressure on the gas hydrate formation indicates that by increasing the initial pressure of the cell from 6 MPa to 8 MPa, the amount of gas consumption and the storage capacity of methane hydrate formation increases, considerably.*

**KEYWORDS:** *Semiclathrate hydrate; Energy; Surfactant; Kinetics; Methane; TBAC.*

## INTRODUCTION

Methane is the major component of natural gas and natural gas is one of the main and clean energy sources. Because of the significant growth in worldwide energy demand, natural gas has an important role in meeting this need. On the other hand, the consumption of natural gas

is rapidly increasing. Thus, finding a safe and cost-efficient method to store a high volume of natural gas seems to be very necessary.

Gas Hydrates are non-stoichiometric crystalline compounds composed of a "guest" molecule of a certain

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\* To whom correspondence should be addressed.

+ E-mail: mohammadi.a@ub.ac.ir

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size clathrate by a hydrogen-bonded host water cage of hydrate crystal lattice [1]. Recently, many researchers have focused on the positive applications of gas hydrates due to the high storage capacity of these compounds [2-15]. Natural gas storage and transportation by hydrate technology are safer than other technologies such as LNG. However, the slow kinetics of the hydrate formation process and the need for high operating pressure and low operating temperature, increase the cost of this technology [1, 16, 17]. Therefore, researchers devoted more energy to promoting the kinetics [16, 18-35] and moderating the thermodynamics [36-50] of gas hydrate formation.

Slehfekr and coworkers studied the thermodynamic conditions of propane and normal butane mixture. Their results showed that by increasing the concentration of propane in the mixture, the equilibrium pressure of hydrate formation decreases [51]. Tetra n-butylammonium salts are environmentally friendly compounds that moderate the gas hydrate formation conditions, noticeably. These compounds form a new structure of hydrates, called semi-clathrate hydrates. In this type of hydrate, the large cavities occupied by tetra n-butyl ammonium ions and the small cavities could be occupied by small gas molecules [47, 52, 53]. In 2007, Arjmandi and coworkers measured the semi-clathrate hydrate dissociation data of natural gas, methane, carbon dioxide, and nitrogen in presence of TBAB. They found that by increasing the concentration of TBAB the stability and promotion effect of hydrate formation increases [37]. Mohammadi and coworkers studied the effect of various concentrations of TBAC and TBAF on methane, carbon dioxide, and nitrogen phase diagram. They concluded that these additives, considerably, moderate the thermodynamics of hydrate formation [42, 47]. Makino et al. in 2010 widely investigated the thermodynamic stabilities of TBAC semi-clathrate hydrate formation in presence of hydrogen, nitrogen, methane, carbon dioxide, and ethane. Their studies showed that the presence of these gas along with TBAC, moderate the hydrate formation conditions compared to the simple TBAC semi-clathrate hydrate [54].

The thermodynamics of semi-clathrate hydrates is widely studied in recent years but the kinetics of these compounds need more investigation. In 2018, Bavoh and coworkers investigated the effect of two amino acids on the kinetics and thermodynamics of methane hydrate formation. They showed that arginine and valine inhibit the methane

thermodynamics hydrate formation and promote the kinetics of this process [55]. Chen and coworkers suggested the oleic acid potassium as a strong kinetic additive that considerably promotes the kinetics of methane hydrate formation. They showed that the addition of 500 ppm of this component presents a similar effect with SDS [56]. The effect of SDS on the kinetics of methane-THF hydrate formation investigated by Kumar et al., in 2019. They showed that the addition of SDS as a strong kinetic promoter in this mixture causes the co-existence of pure methane hydrate with structure SI and double methane-THF hydrate with structure SII [57].

In 2018, Mohammadi et al. studied the kinetics of carbon dioxide hydrate formation in the presence and absence of TBAF and SDS [16]. Their results indicate that utilization of 0-5 wt% TBAF and 400 ppm SDS increases the storage capacity and the amount of gas consumed during the hydrate formation process and decrease the induction time of carbon dioxide hydrate formation. The Kinetics of hydrogen + TBAB semi-clathrate hydrate formation is investigated by Trueba et al., in 2012 [58]. They experimentally showed that using TBAB promotes the kinetics of hydrogen hydrate formation. They also investigated the effect of pressure on the kinetics of hydrate formation. They showed that kinetics is favored at higher pressures [58]. In another work, Mech and coworkers investigated the methane hydrate formation in presence of TBAB, THF, and SDS [59]. Their study showed that simultaneous utilization of TBAB and THF increases the amount of gas consumption and storage capacity of methane at low pressures [59]. Roosta et al. [60], investigated the effect of TBAB and THF on the rate of methane hydrate formation. They showed that utilization of low concentrations of TBAB increases the rate of methane hydrate formation [60].

An economic study of using additives in the process of hydrate formation should be noticed before the process design. TBAC is an environmentally friendly compound that is not toxic, volatile, or flammable. This salt is an expensive additive but the experimental investigations showed that utilization of low concentrations of this additive promotes the thermodynamic conditions of methane hydrate formation, significantly [41, 42, 61]. The use of low concentrations of TBAC reduces the costs of the hydrate formation process. On the other hand, SDS is one of the best-tested kinetic additives that strongly promotes

the kinetics of methane hydrate formation and therefore reduce the costs of this process [62-65].

In recent years, many researchers have focused on the kinetics of methane hydrate formation in presence of kinetic promoters (such as surfactants and nanoparticles). TBAC is one of the most promising thermodynamic additives for methane hydrate formation that by changing the structure of gas hydrate formation, moderates the phase equilibrium of methane hydrate formation, considerably. Investigating the kinetics of methane hydrate formation in presence of thermodynamic additives such as TBAC needs more attention. In this work, the effect of low concentrations of an environmentally friendly thermodynamic additive, TBAC with the concentration of (3 and 5) wt%, and an anionic surfactant, SDS with a concentration of 400 ppm being investigated on the amount of gas uptake and storage capacity of methane hydrate. We, also, study the effect of initial pressure on the kinetics of methane hydrate formation in the presence and absence of TBAC and SDS.

## EXPERIMENTAL SECTION

### Materials and apparatus

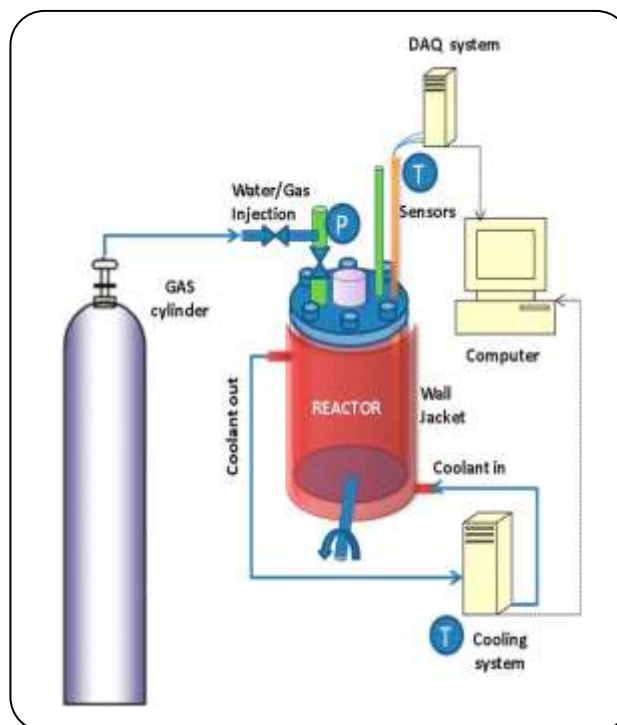
Table 1 shows the names, purities, and suppliers of chemicals used in this research. The experimental apparatus used for the kinetic investigation of methane + TBAC semi-clathrate hydrate formation is depicted in Fig. 1. The main part of the setup is a high-pressure cell with an inner volume of 169 cm<sup>3</sup> and maximum working pressure of 20 MPa. The contents of the cell are agitated using a rocking cell stirrer with a speed of 10 rpm. The temperature of the cell is controlled by a cooling medium circulatory system having a mixture of 50% ethylene glycol and water as a coolant. A 0.01 MPa scale pressure transducer and a 0.1 K scale thermocouple (PT100) were used to measure the pressures and temperatures.

### Procedure

At first, the various aqueous solutions of TBAC and SDS were prepared. And then a certain amount of the prepared solution was introduced into the batch crystallizer. After adjusting the crystallizer temperature to the temperature of 278.15 K by the circulator, the gas was injected into the crystallizer to reach the desired pressures. Then, the rocking cell stirrer was turned on with the speed of 10 rpm to agitate the solution inside the crystallizer.

**Table 1: Purities and suppliers of materials used in this work.**

Chemical	Supplier	Purity
SDS	Daejung	98 wt%
Methane	Varian Gas	99.995 mole%
TBAC	Merck	95 mole%



**Fig. 1: Schematic illustration of the experimental apparatus.**

The temperature and pressure of the crystallizer were recorded on a computer with an electronic measuring device.

## RESULTS AND DISCUSSION

The kinetic promotion effect of TBAC and SDS on the storage capacity, amount of gas uptake, and apparent rate constant of methane hydrate formation is assessed in this work.

### Amount of gas uptake

To evaluate the impact of pressure, SDS, and various concentrations of TBAC on the kinetics of methane hydrate formation, samples of (a) 3, and 5 wt% TBAC (b) 400 ppm SDS and (c) a mixture of TBAC + SDS were prepared. The experimental temperature of methane hydrates has been fixed at 278.15 K with operating pressures of 6 and 8 MPa.

Peng-Robinson equation [66] of state was employed to evaluate the amount of gas uptake in the process of gas hydrate formation [67].

$$\Delta n_{\text{CH}_4} = \frac{P_0 V_0}{Z_0 R T_0} - \frac{P_t V_t}{Z_t R T_t} \quad (1)$$

Figs. 2 and 3 depict the impact of TBAC with concentrations of 3 and 5 wt% on the quantity of methane uptake. As shown in these figures, utilization of low concentrations of TBAC increases the quantity of methane uptake at both initial pressures of 6 and 8 MPa. At initial pressure of 6 MPa, the amount of methane uptake per mole of water in presence of 0, 3, and 5 wt% TBAC are 40.2, 49.4, and 47.8 mmol/mol, respectively. The solution of TBAC with the concentration of 3 wt% shows the best result of gas uptake in the gas hydrate formation process. investigation of the effect of various concentrations of TBAC on the quantity of methane uptake at the initial pressure of 8 MPa shows similar results. Utilization of 3 and 5 wt% TBAC by shifting the phase diagram of methane hydrate formation to the stabilized regions [42], increases the driving force of methane hydrate formation and therefore increases the amount of methane uptake.

In fact, the presence of TBAC plays a dual role in the hydrate formation process. This compound by increasing the driving force of gas hydrate formation promotes the kinetics of methane hydrate formation and changing the structure of gas hydrates to semi-clathrates and occupying the large cages by TBA<sup>+</sup> ions inhibit the kinetics of gas hydrate formation. As shown in Figs. 2 and 3, at low concentrations of TBAC, the positive effect of this compound dominates its negative effect.

Figs. 4 and 5 show the quantity of methane uptake per mole of water in presence of SDS with a concentration of 400 ppm and TBAC with concentrations of 3 and 5 wt%. At initial pressure of 6 MPa, the amount of methane uptake during the hydrate formation process in presence of 400 ppm SDS and TBAC with concentrations of 0, 3, and 5 wt%, are 63.7, 41.3, and 31.3 mmol/mole of water, respectively. The experiments conducted at 400 ppm SDS in the absence of TBAC show higher moles of methane uptake per mole of water as compared with SDS (400 ppm) + TBAC (3 and 5 wt%) aqueous solutions.

The presence of SDS, decreases the interfacial tension of water molecules and therefore increases the amount of gas uptake during the hydrate formation process.

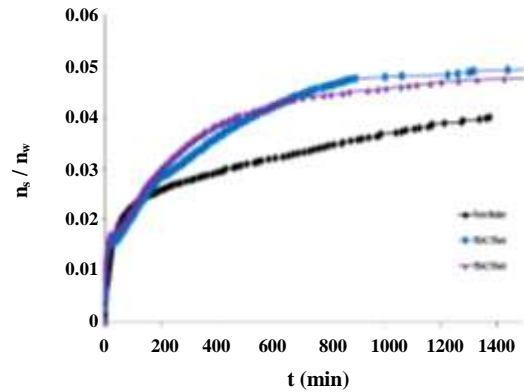


Fig. 2: The effect of TBAC on the amount of methane uptake during hydrate formation at an initial pressure of 6 MPa and temperature of 278.15 K.

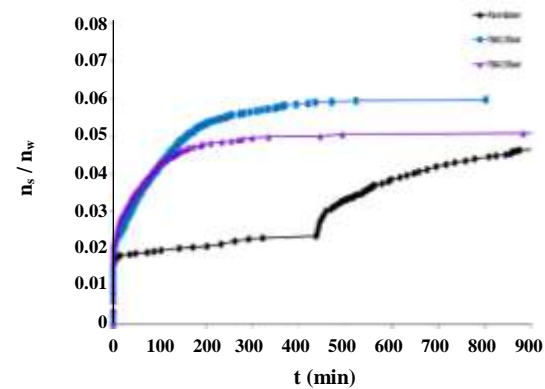


Fig. 3: The effect of TBAC on the amount of methane uptake during hydrate formation at an initial pressure of 8 MPa and temperature of 278.15 K.

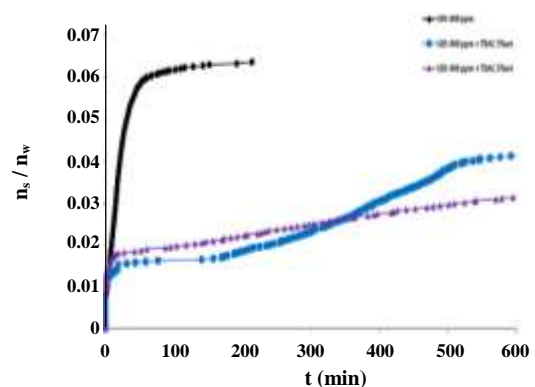


Fig. 4: The effect of TBAC on the amount of methane uptake during hydrate formation in presence of SDS with a concentration of 400 ppm at an initial pressure of 6 MPa and temperature of 278.15 K.

As shown in Figs. 4 and 5, simultaneous utilization of SDS (400 ppm) and TBAC ((0.03 and 0.05) mass fraction) decreases the quantity of gas uptake, compared to the system of  $\text{CO}_2 + \text{SDS}$  (400 ppm) + water. In other words, adding TBAC (with concentrations of (0.03 and 0.05) mass fraction) to an aqueous solution of SDS (with a concentration of 400 ppm) results in a negative effect on the quantity of gas uptake during hydrate formation. A likely reason for this phenomenon is as follows: The strong interaction between the ions of  $\text{Na}^+$  (released from SDS) and  $\text{Cl}^-$  (in the lattice structure of semi-clathrate hydrates) results in a negative effect on the stability of the semi-clathrate lattice structure and consequently, the number of trapped gases will be decreased. The interaction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions (released from SDS and TBAC) reduces the stability of semi-clathrate lattice structure and consequently decreases the quantity of methane uptake.

Figs. 6 and 7 depict the amount of gas consumed during the hydrate formation process in the presence and absence of 400 ppm SDS at initial pressures of 6 and 8 MPa. At initial pressure of 6 MPa, the amount of methane uptake per mole of water in the presence and absence of 400 ppm are 26.4 and 63.7 mmol/mol, respectively; and at an initial pressure of 8 MPa, the amount of methane uptake per mole of water in presence and absence of 400 ppm are 48.1 and 118 mmol/mol, respectively. This means that using SDS with a concentration of 400 ppm at initial pressures of 6 and 8 MPa, respectively, increases the amount of gas uptake 141.3% and 145.8%. SDS is one of the best surfactants in the hydrate formation process that by decreasing the interfacial tension of water molecules, promotes the kinetics of this process, noticeably.

The initial pressure of the cell is another effective parameter in the process of hydrate formation. The effect of this parameter on the amount of methane uptake is illustrated in Figs. 8-13. It has been observed that by increasing the initial pressure of the cell from 6 MPa to 8 MPa, the number of gas uptake increases, considerably, for all samples.

As shown in Fig. 8, the amount of methane uptake in pure water at initial pressures of 6 and 8 MPa, respectively, are 40.2 and 53.8 mmol/mole. Increasing the cell initial pressure from 6 MPa to 8 MPa in presence of SDS with a concentration of 400 ppm increases the amount of gas uptake, 82.7%, as observed in Fig. 9.

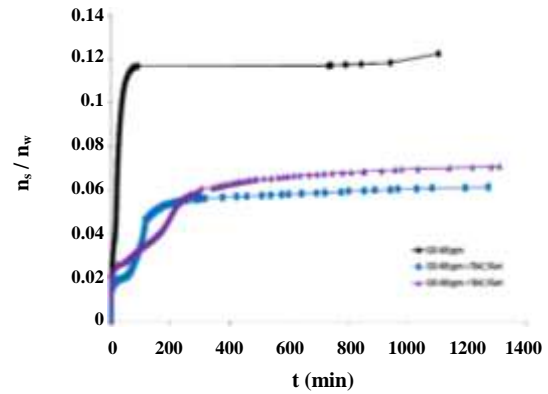


Fig. 5: The effect of TBAC on the amount of methane uptake during hydrate formation in presence of SDS with a concentration of 400 ppm at an initial pressure of 8 MPa and temperature of 278.15 K.

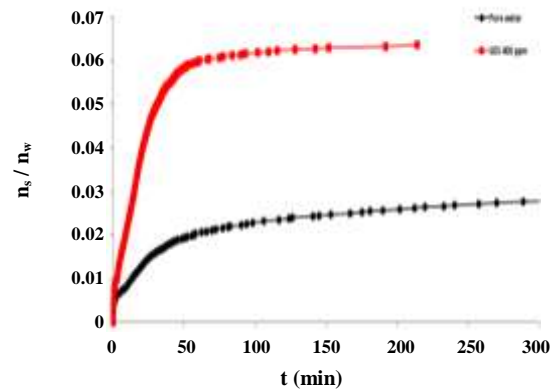


Fig. 6: The effect of SDS on the amount of methane uptake during hydrate formation at an initial pressure of 6 MPa and temperature of 278.15 K.

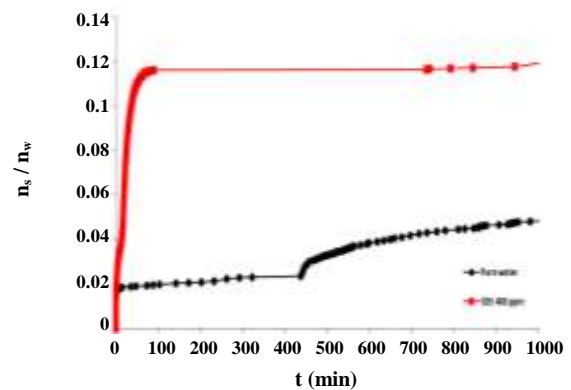


Fig. 7: The effect of SDS on the amount of methane uptake during hydrate formation at an initial pressure of 8 MPa and temperature of 278.15 K.

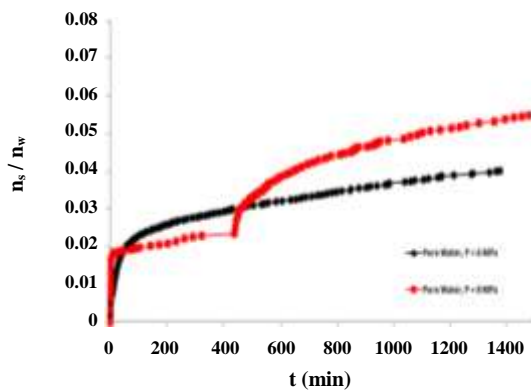


Fig. 8: The effect of initial pressure of the cell on the amount of methane uptake during hydrate formation for the system of methane + water at a temperature of 278.15 K.

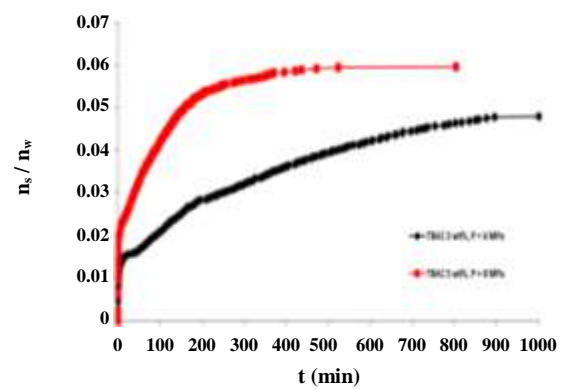


Fig. 10: The effect of initial pressure of the cell on the amount of methane uptake during hydrate formation for the system of methane + water + TBAC (3 wt%) at a temperature of 278.15 K.

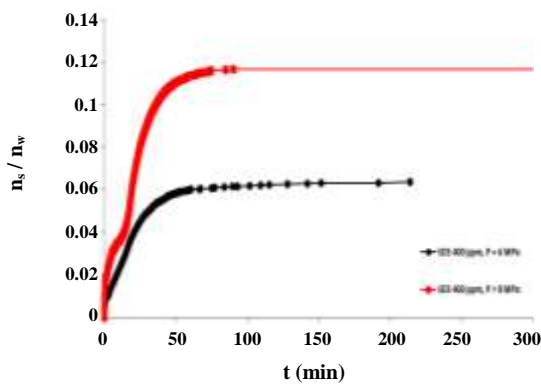


Fig. 9: The effect of the initial pressure of the cell on the amount of methane uptake during hydrate formation for the system of methane + water + SDS (400 ppm) at a temperature of 278.15 K.

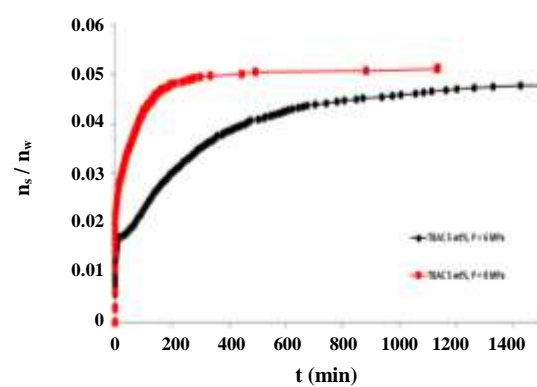


Fig. 11: The effect of the initial pressure of the cell on the amount of methane uptake during hydrate formation for the system of methane + water + TBAC (5 wt%) at a temperature of 278.15 K.

Increasing the initial pressure of the cell increases the driving force of gas hydrate formation. The equilibrium pressure of methane hydrate formation at 278.15 K is about 4.3 MPa. this means that the driving force of methane hydrate formation at the feed pressures of 6 and 8 MPa are 1.7 and 3.7 MPa, respectively. The driving force of methane hydrate formation at 8 MPa is more than twice the driving force of methane hydrate formation at 6 MPa. The higher driving force of methane hydrate formation at 8 MPa, promotes the kinetics of the methane hydrate formation process.

As can be found in Figs. 10 and 11, the positive effect of initial pressure on the kinetics of methane hydrate formation in presence of TBAC is less than in other samples. So, increasing the initial pressure of the cell from 6 MPa

to 8 MPa in presence of 3 and 5 wt% TBAC, respectively, increases the amount of gas uptake, 24.4% and 8.9%, while this amount is 33.8% in pure water. In the presence of TBAC, some cages are occupied by  $TBA^+$  ions and therefore, the ability of generated driving force in promoting the kinetics of methane hydrate formation decreases.

The effect of initial pressure on the kinetics of methane hydrate formation in the simultaneous presence of TBAC and SDS is illustrated in Figs. 12 and 13. As observed in these two figures, increasing the initial pressure of the cell, by increasing the driving force of the hydrate formation process, increases the amount of methane uptake.

The following equation is employed to evaluate the storage capacity of methane hydrate [67].

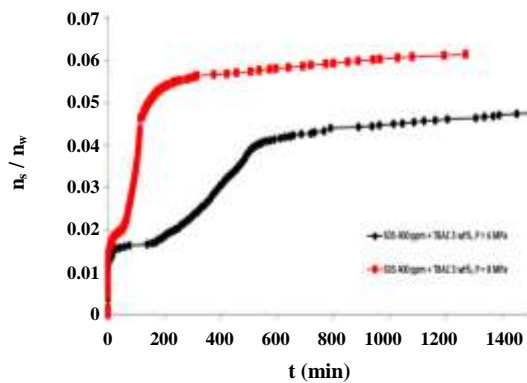


Fig. 12: The effect of the initial pressure of the cell on the amount of methane uptake during hydrate formation for the system of methane + water + TBAC (3 wt%) + SDS (400 ppm) at a temperature of 278.15 K.

$$SC = \frac{V_{STP}}{V_H} = \frac{\Delta n_{CH_4} RT_{STP} / P_{STP}}{V_H} \quad (2)$$

The calculated amount of storage capacity of methane hydrate formation in the presence and absence of SDS and TBAC is given in Table 2 and plotted in Fig. 14. As presented in Fig. 14 and Table 2, using low concentrations of TBAC (3 and 5 wt%) increases the amount of storage capacity, compared to pure water, in both initial pressures of 6 and 8 MPa. In fact, TBAC by moderating the thermodynamic conditions of methane hydrate formation increases the driving force of methane hydrate formation and consequently increases the storage capacity of methane hydrate. As presented in this figure and Table, hydrate formed from an aqueous solution of SDS shows higher storage capacities. SDS by decreasing the interfacial tension of water molecules, noticeably, promoted the kinetics of methane hydrate formation. The presence of SDS, decreases the interfacial tension of water molecules and therefore increases the amount of gas uptake during the hydrate formation process. In the presence of TBAC, some cages are occupied by TBA<sup>+</sup> ions and therefore, the ability of generated driving force in promoting the kinetics of methane hydrate formation decreases. The interaction between Na<sup>+</sup> and Cl<sup>-</sup> ions (released from SDS and TBAC) reduces the stability of the semi-clathrate lattice structure and consequently decreases the quantity of methane uptake.

The apparent rate constant of hydrate formation ( $k_{app}$ ) is another kinetic parameter in the hydrate formation

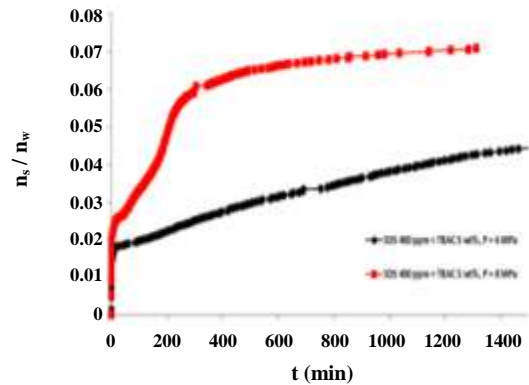


Fig. 13: The effect of the initial pressure of the cell on the amount of methane uptake during hydrate formation for the system of methane + water + TBAC (5 wt%) + SDS (400 ppm) at a temperature of 278.15 K.

process that shows the growth rate constant of methane hydrate at the induction time of hydrate formation. This parameter is calculated from the following equation [62]:

$$k_{app} = - \frac{dn_{CH_4} / dt}{f_g - f_{eq}} \quad (3)$$

Fig. 15 depicts the amount of initial apparent rate constant of methane hydrate formation in the presence and absence of TBAC and SDS. The numerical data are given in Table 2. As shown in Fig. 15 and Table 2, The amount of initial apparent rate constant in presence of 400 ppm SDS, is noticeable, higher than other samples at both initial pressures of 6 and 8 MPa. The lower amount of apparent rate constant in presence of TBAC is due to the fact that TBA<sup>+</sup> ions (released from TBAC) occupy the large cavities of formed semi-clathrate at the induction time of hydrate formation and only small cavities are left to occupy by methane molecules. Therefore, the apparent rate constant of methane hydrate formation in the systems containing TBAC is lower than in other samples.

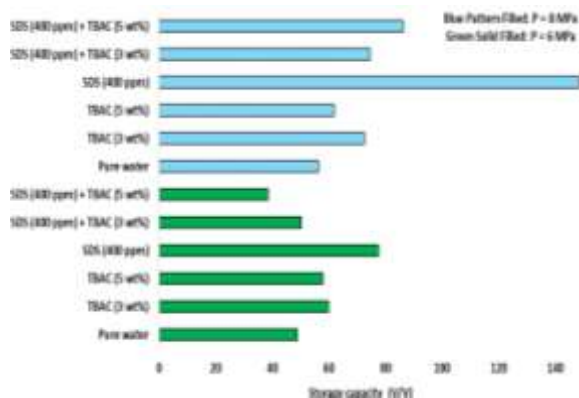
## CONCLUSIONS

Kinetics of methane hydrate formation in the presence and absence of an environmentally friendly thermodynamic additive, TBAC, and an effective kinetic promoter, SDS, is investigated in this paper, at initial cell pressures of 6 MPa and 8 MPa and the temperature of 278.15 K.

**Table 2: Storage capacity and initial apparent rate constant of methane hydrate formation in presence and absence of TBAC and SDS at a temperature of 278.15 K**

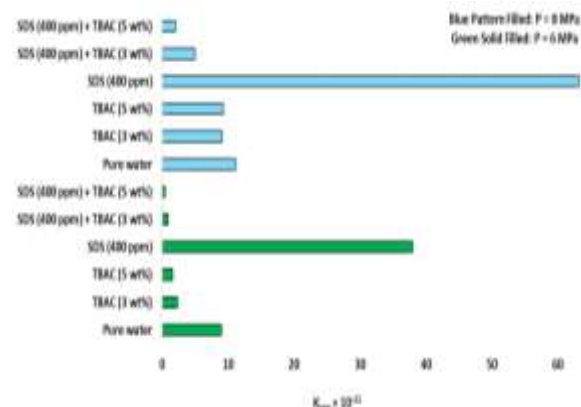
additive	P / MPa	Storage capacity <sup>a</sup> (V/V)	$K_{app} \times 10^{11}$
Pure water	6	48.87	9.00
TBAC (3 wt%)	6	59.82	2.30
TBAC (5 wt%)	6	57.82	1.58
SDS (400 ppm)	6	77.46	37.94
SDS (400 ppm) + TBAC (3 wt%)	6	50.20	0.88
SDS (400 ppm) + TBAC (5 wt%)	6	38.42	0.43
Pure water	8	56.35	11.10
TBAC (3 wt%)	8	72.58	9.07
TBAC (5 wt%)	8	61.80	9.25
SDS (400 ppm)	8	148.77	63.14
SDS (400 ppm) + TBAC (3 wt%)	8	74.49	4.99

<sup>a</sup> The maximum uncertainty in the measured storage capacity is expected to be 4 v/v.



**Fig. 14: Storage capacity of methane hydrate formation in the presence and absence of TBAC and SDS at a temperature of 278.15 K. Blue pattern filled: P = 8 MPa, and green solid filled: P = 6 MPa.**

Utilization of 3 and 5 wt% TBAC, at both initial pressure of 6 and 8 MPa, by increasing the driving force of methane hydrate formation, increases the amount of methane uptake, compared to pure water. An aqueous solution of SDS with a concentration of 400 ppm at 8 MPa has shown higher methane uptake, compared to other samples. Investigation of the effect of pressure on the amount of gas consumed per mole of water showed that increasing the initial pressure of the cell from 6 MPa to 8 MPa, by increasing the driving force of methane hydrate



**Fig. 15: Initial apparent rate constant of methane hydrate formation in the presence and absence of TBAC and SDS at a temperature of 278.15 K. Blue pattern filled: P = 8 MPa, and green solid filled: P = 6 MPa.**

formation, increases the amount of gas uptake per mole of water for all samples.

The storage capacity of methane hydrate formation is evaluated in the presence and absence of TBAC and SDS. Low concentrations of TBAC by moderating the thermodynamic conditions of methane hydrate formation and SDS by decreasing the surface tension of water molecules, increase the storage capacity of methane hydrate formation.

The initial apparent rate constant of methane hydrate formation is calculated. The presence of TBAC, due to



occupying the large cages *via* TBA<sup>+</sup> decreases the initial apparent rate constant of methane hydrate formation.

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### REFERENCES

- [1] Sloan J.E.D., Koh K.A., "Clathrate Hydrates of Natural Gases". 3rd ed.: CRC Press, Taylor & Francis Group; (2008).
- [2] Kanda H., "Economic Study on Natural Gas Transportation with Natural Gas Hydrate (NGH) Pellets". *23rd World Gas Conference*, Amsterdam (2006).
- [3] Javanmardi J., Nasrifar K., Najibi S., Moshfeghian M., *Economic Evaluation of Natural Gas Hydrate as an Alternative for Natural Gas Transportation*, *Applied Thermal Engineering*, **25**: 1708-1723 (2005).
- [4] Hao W., Wang J., Fan S., Hao W., *Evaluation and Analysis Method for Natural Gas Hydrate Storage and Transportation Processes*, *Energy Conversion and Management*, **49**: 2546-2553 (2008).
- [5] Nogami T., Oya N., Ishida H., Matsumoto H., *Development of Natural Gas Ocean Transportation Chain by Means of Natural Gas Hydrate (NGH)* (2008).
- [6] Taylor M, Dawe RA, Thomas S. "Fire and Ice: Gas Hydrate Transportation-A Possibility for the Caribbean Region", *SPE Latin American and Caribbean Petroleum Engineering Conference*: Society of Petroleum Engineers; (2003).
- [7] Mori Y.H., *Recent Advances in Hydrate-Based Technologies for Natural Gas Storage-A Review*, *J. Chem. Ind. & Eng. China*, **54**: 195 - 307 (2003).
- [8] Park K-n, Hong SY, Lee JW, Kang KC, Lee YC, Ha M-G, Lee J.D., *A New Apparatus for Seawater Desalination by Gas Hydrate Process and Removal Characteristics of Dissolved Minerals (Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, B<sup>3+</sup>)*, *Desalination*, **274**: 91-96 (2011).
- [9] Kang K.C., Linga P., Park K.-n, Choi S.-J., Lee J.D., *Seawater Desalination by Gas Hydrate Process and Removal Characteristics of Dissolved Ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, B<sup>3+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>)*, *Desalination*, **353**: 84-90 (2014).
- [10] Choi W., Lee Y., Mok J., Lee S., Lee J.D., Seo Y., *Thermodynamic and Kinetic Influences of NaCl on HFC-125a Hydrates and Their Significance in Gas Hydrate-Based Desalination*, *Chemical Engineering Journal*, **358**: 598-605 (2019).
- [11] Babu P., Nambiar A., He T., Karimi I.A., Lee J.D., Englezos P., Linga P., *A Review of Clathrate Hydrate Based Desalination to Strengthen Energy-Water Nexus*, *ACS Sustainable Chemistry & Engineering*, **6**: 8093-8107 (2018).
- [12] Linga P., Babu P., Nambiar A., "Effect of NaCl on Clathrate Hydrate Based Desalination Hydesal Process with Fixed Bed Approach. Qatar Foundation Annual Research Conference Proceedings", HBKU Press Qatar; EEPP1035 (2018).
- [13] Delahaye A., Fournaison L., Dalmazzone D., "Use of Hydrates for Cold Storage and Distribution in Refrigeration and Air- Conditioning Applications", *Gas Hydrates 2: Geoscience Issues and Potential Industrial Applications*, 315-358 (2018).
- [14] Arai Y., Yamauchi Y., Tokutomi H., Endo F., Hotta A., Alavi S., Ohmura R., *Thermophysical Property Measurements of Tetrabutylphosphonium Acetate (TBPAce) Ionic Semiclathrate Hydrate as Thermal Energy Storage Medium for General Air Conditioning Systems*, *International Journal of Refrigeration*, **88**: 102-107 (2018).
- [15] Mahmoudi B., Naeiji P., Varaminian F., *Study of Tetra-N-Butylammonium Bromide and Tetrahydrofuran Hydrate Formation Kinetics as a Cold Storage Material for Air Conditioning System*, *Journal of Molecular Liquids*, **214**: 96-100 (2016).
- [16] Mohammadi A., Pakzad M., Mohammadi A.H., Jahangiri A., *Kinetics of (TBAF + CO<sub>2</sub>) Semiclathrate Hydrate Formation in the Presence and Absence of SDS*, *Petroleum Science*, **15**: 375-384 (2018).
- [17] Englezos P., Kalogerakis N., Dholabhai P.D., Bishnoi P.R., *Kinetics of Formation of Methane and Ethane Gas Hydrates*, *Chemical Engineering Science*, **42**: 2647-2658 (1987).
- [18] Veluswamy H.P., Kumar S., Kumar R., Rangsunvigit P., Linga P., *Enhanced Clathrate Hydrate Formation Kinetics at Near Ambient Temperatures and Moderate Pressures: Application to Natural Gas Storage*, *Fuel*, **182**: 907-919 (2016).

- [19] Kumar A., Bhattacharjee G., Kulkarni B., Kumar R., [Role of Surfactants in Promoting Gas Hydrate Formation](#), *Industrial & Engineering Chemistry Research*, **54**: 12217-12232 (2015).
- [20] Mohammadi M., Haghtalab A., Fakhroueian Z., [Experimental Study and Thermodynamic Modeling of CO<sub>2</sub> Gas Hydrate Formation in Presence of Zinc Oxide Nanoparticles](#), *The Journal of Chemical Thermodynamics*, **96**: 24-33 (2016).
- [21] Bhattacharjee G., Kumar A., Sakpal T., Kumar R., [Carbon Dioxide Sequestration: Influence of Porous Media on Hydrate Formation Kinetics](#), *ACS Sustainable Chemistry & Engineering*, **3**: 1205-1214 (2015).
- [22] Pahlavanzadeh H., Rezaei S., Khanlarkhani M., Manteghian M., Mohammadi A.H., [Kinetic Study of Methane Hydrate Formation in the Presence of Copper Nanoparticles and CTAB](#), *Journal of Natural Gas Science and Engineering*, **34**: 803-810 (2016).
- [23] Linga P., Clarke M., [A review of Reactor Designs and Materials Employed for Increasing the Rate of Gas Hydrate Formation](#), *Energy & Fuels*, **31**: 1-13 (2016).
- [24] Park T., Kwon T-H., [Effect of Electric Field on Gas Hydrate Nucleation Kinetics: Evidence for the Enhanced Kinetics of Hydrate Nucleation by Negatively Charged Clay Surfaces](#), *Environmental Science & technology*, **52**: 3267-3274 (2018).
- [25] Arjang S., Manteghian M., Mohammadi A., [Effect of Synthesized Silver Nanoparticles in Promoting Methane Hydrate Formation at 4.7 MPa and 5.7 MPa](#), *Chemical Engineering Research and Design*, **91**: 1050-1054 (2013).
- [26] Zhang C, Fan S, Liang D, Guo K. [Effect of Additives on Formation of Natural Gas Hydrate](#), *Fuel*, **83**: 2115-2121 (2004).
- [27] Ganji H., Manteghian M., Sadaghiani Zadeh K., Omidkhah M.R., Rahimi Mofrad H., [Effect of Different Surfactants on Methane Hydrate Formation Rate, Stability and Storage Capacity](#), *Fuel*, **86**: 434-441 (2007).
- [28] Mohammadi A., Babakhanpour N., Javidani A.M., Ahmadi G., [Corn's Dextrin, a Novel Environmentally Friendly Promoter of Methane Hydrate Formation](#), *Journal of Molecular Liquids*, **336**: 116855 (2021).
- [29] Mohammadi A., Kamran-Pirzaman A., Rahmati N., [The Effect Tetra Butyl Ammonium Hydroxide and Tween on the Kinetics of Carbon Dioxide Hydrate Formation](#), *Petroleum Science and Technology*, **39**: 647-665 (2021).
- [30] Mohammadi A., Fazli R.H., Asil A.G., [Influence of Tetra n-Butylammonium Chloride and Polysorbate 80 on the Kinetics of Methane Hydrate Formation](#), *Journal of the Japan Petroleum Institute*, **64**: 22-28 (2021).
- [31] Mohammadi A., [The roles TBAF and SDS on the Kinetics of Methane Hydrate Formation as a Cold Storage Material](#), *Journal of Molecular Liquids*, **309**: 113175 (2020).
- [32] Yan K., Lv C., Wang Q., Hu X., [Effect of Different Kinds of Hydrate Promoters on the Kinetics of Methane Hydrate Formation in Methane-Water-Oil System](#), *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **41(1)**: 232-241 (2020).
- [33] Bozorgian A., Arab Aboosadi Z., Mohammadi A., Honarvar B., Azimi A., [Statistical Analysis of the Effects of Aluminum Oxide \(Al<sub>2</sub>O<sub>3</sub>\) Nanoparticle, TBAC and APG on Storage Capacity of CO<sub>2</sub> Hydrate Formation](#), *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **41(1)**: 220-231 (2022).
- [34] Askari Agh Masjed N., Pahlavan Zadeh H., [Experimental Investigation toward the Kinetic Study of Methane Hydrate Formation in the Presence of THF+ SDS](#), *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **40 (1)**: 261-273 (2021).
- [35] Mohammadi A., [Effect of SDS, Silver Nanoparticles, and SDS+ Silver Nanoparticles on Methane Hydrate Semicompletion Time](#), *Petroleum Science and Technology*, **35**: 1542-1548 (2017).
- [36] Hashimoto S., Sugahara T., Moritoki M., Sato H., Ohgaki K., [Thermodynamic Stability of Hydrogen+ Tetra-n-butyl Ammonium Bromide Mixed Gas Hydrate in Nonstoichiometric Aqueous Solutions](#), *Chemical Engineering Science*, **63**: 1092-1097 (2008).
- [37] Arjmandi M, Chapoy A, Tohidi B. [Equilibrium Data of Hydrogen, Methane, Nitrogen, Carbon Dioxide, and Natural Gas in Semi-clathrate Hydrates of Tetrabutyl Ammonium Bromide](#), *Journal of Chemical & Engineering Data*, **52**: 2153-2158 (2007).

- [38] Deschamps J., Dalmazzone D., Dissociation Enthalpies and Phase Equilibrium for TBAB Semiclathrate Hydrates of  $N_2$ ,  $CO_2$ ,  $N_2+CO_2$  and  $CH_4+CO_2$ , *Journal of Thermal Analysis and Calorimetry*, **98**: 113-118 (2009).
- [39] Lin W., Delahaye A., Fournaison L., Phase Equilibrium and Dissociation Enthalpy for Semiclathrate Hydrate of  $CO_2+TBAB$ , *Fluid Phase Equilibria*, **264**: 220-227 (2008).
- [40] Makino T., Yamamoto T., Nagata K., Sakamoto H., Hashimoto S., Sugahara T., Ohgaki K., Thermodynamic Stabilities of Tetra-n-butyl Ammonium Chloride+  $H_2$ ,  $N_2$ ,  $CH_4$ ,  $CO_2$ , or  $C_2H_6$  Semiclathrate Hydrate Systems, *Journal of Chemical & Engineering Data*, **55**: 839-841 (2009).
- [41] Kim S., Baek I.-H., You J.-K., Seo Y., Guest Gas Enclathration in Tetra-n-butyl Ammonium Chloride (TBAC) Semiclathrates: Potential Application to Natural Gas Storage and  $CO_2$  Capture, *Applied Energy*, **140**: 107-112 (2015).
- [42] Mohammadi A., Manteghian M., Mohammadi A.H., Phase Equilibria of Semiclathrate Hydrates for Methane+ Tetra n-butylammonium Chloride (TBAC), Carbon dioxide+ TBAC, and Nitrogen+ TBAC Aqueous Solution Systems, *Fluid Phase Equilibria*, **381**: 102-107 (2014).
- [43] Kamran-Pirzaman A., Pahlavanzadeh H., Mohammadi A.H., Hydrate Phase Equilibria of Furan, Acetone, 1, 4-dioxane, TBAC and TBAF, *The Journal of Chemical Thermodynamics*, **64**: 151-158 (2013).
- [44] Sun Z.-G., Liu C.-G. Equilibrium Conditions of Methane in Semiclathrate Hydrates of Tetra-n-Butylammonium Chloride, *Journal of Chemical & Engineering Data*, **57**: 978-981 (2012).
- [45] Linga P., Kumar R., Lee J.D., Ripmeester J., Englezos P., A New Apparatus to Enhance the Rate of Gas Hydrate Formation: Application to Capture of Carbon Dioxide, *International Journal of Greenhouse Gas Control*, **4**: 630-637 (2010).
- [46] Sfaxi I.B.A., Durand I., Lugo R., Mohammadi A.H., Richon D., Hydrate Phase Equilibria of  $CO_2+ N_2+ Aqueous$  Solution of THF, TBAB or TBAF System, *International Journal of Greenhouse Gas Control*, **26**: 185-192 (2014).
- [47] Mohammadi A., Manteghian M., Mohammadi A.H., Dissociation Data of Semiclathrate Hydrates for the Systems of Tetra-n-butylammonium Fluoride (TBAF)+ Methane+ Water, TBAF+ Carbon Dioxide+ Water, and TBAF+ Nitrogen+ Water, *Journal of Chemical & Engineering Data*, **58**: 3545-3550 (2013).
- [48] Mohammadi A.H., Eslamimanesh A., Belandria V., Richon D., Phase Equilibria of Semiclathrate Hydrates of  $CO_2$ ,  $N_2$ ,  $CH_4$ , or  $H_2 + Tetra-n-butylammonium Bromide Aqueous Solution$ , *Journal of Chemical & Engineering Data*, **56**: 3855-3865 (2011).
- [49] Shi L., Liang D., Semiclathrate Hydrate Phase Behaviour and Structure for  $CH_4$  in the Presence of Tetrabutylammonium Fluoride (TBAF), *The Journal of Chemical Thermodynamics*, **135**: 252-259 (2019).
- [50] Parhizgar H., Javanmardi J., Mohammadi A.H., Moshfeghian M., Parvasi P., A Thermodynamic Framework for Modeling Semiclathrate Hydrate Phase Stability Conditions in Gas+ Tetra- n- butyl Ammonium Halide Aqueous Solution System, *Asia-Pacific Journal of Chemical Engineering*, **13**: e2199 (2018).
- [51] Salehfekr S., Porgar S., Rahmanian N., Investigation of Propane and N-Butane Hydrate Formation Condition and Determination of Equilibrium Pressure, (2019).
- [52] Fowler D.L., Loebenstein W.V., Pall D.B., Kraus C.A., Some Unusual Hydrates of Quaternary Ammonium Salts, *Journal of the American Chemical Society*, **62**: 1140-1142 (1940).
- [53] Lee S., Lee Y., Park S., Kim Y., Lee J.D., Seo Y., Thermodynamic and Spectroscopic Identification of Guest Gas Enclathration in the Double Tetra-n-butylammonium Fluoride Semiclathrates, *The Journal of Physical Chemistry B*, **116**: 9075-9081 (2012).
- [54] Makino T., Yamamoto T., Nagata K., Sakamoto H., Hashimoto S., Sugahara T., Ohgaki K., Thermodynamic Stabilities of Tetra-n-butyl Ammonium Chloride +  $H_2$ ,  $N_2$ ,  $CH_4$ ,  $CO_2$ , or  $C_2H_6$  Semiclathrate Hydrate Systems, *Journal of Chemical & Engineering Data*, **55**: 839-841 (2010).
- [55] Bavoh C.B., Nashed O., Khan M.S., Partoon B., Lal B., Sharif A.M., The impact of Amino Acids on Methane Hydrate Phase Boundary and Formation Kinetics, *The Journal of Chemical Thermodynamics*, **117**: 48-53 (2018).

- [56] Chen J., Wang T., Zeng Z., Jiang J.-H., Deng B., Chen C.-Z., Li J.-Y., Li C.-H., Tao L.-M., Li X., Xiao S.-X., [Oleic Acid Potassium Soap: A New Potential Kinetic Promoter for Methane Hydrate Formation](#), *Chemical Engineering Journal*, **363**: 349-355 (2019).
- [57] Kumar A., Kumar R., Linga P., [Sodium Dodecyl Sulfate Preferentially Promotes Enclathration of Methane in Mixed Methane-Tetrahydrofuran Hydrates](#), *Science*, **14**: 136-146 (2019).
- [58] Trueba A.T., Radović I.R., Zevenbergen J.F., Kroon M.C., Peters C.J., [Kinetics Measurements and in Situ Raman Spectroscopy of Formation of Hydrogen-Tetrabutylammonium Bromide Semi-Hydrates](#), *International Journal of Hydrogen Energy*, **37**: 5790-5797 (2012).
- [59] Mech D., Gupta P., Sangwai J.S., [Kinetics of Methane Hydrate Formation in an Aqueous Solution of Thermodynamic Promoters \(THF and TBAB\) with and Without Kinetic Promoter \(SDS\)](#), *Journal of Natural Gas Science and Engineering*, **35**: 1519-1534 (2016).
- [60] Roosta H., Khosharay S., Varaminian F., [Experimental Study of Methane Hydrate Formation Kinetics with or Without Additives and Modeling Based on Chemical Affinity](#), *Energy Conversion and Management*, **76**: 499-505 (2013).
- [61] Kamran-Pirzaman A., Pahlavanzadeh H., Mohammadi A.H., [Hydrate Phase Equilibria of Furan, Acetone, 1,4-Dioxane, TBAC and TBAF](#), *The Journal of Chemical Thermodynamics*, **64**: 151-158 (2013).
- [62] Mohammadi A., Manteghian M., Haghtalab A., Mohammadi A.H., Rahmati-Abkenar M., [Kinetic Study of Carbon Dioxide Hydrate Formation in Presence of Silver Nanoparticles and SDS](#), *Chemical Engineering Journal*, **237**: 387-395 (2014).
- [63] Najibi H., Mirzaee Shayegan M., Heidary H., [Experimental Investigation of Methane Hydrate Formation in the Presence of Copper Oxide Nanoparticles and SDS](#), *Journal of Natural Gas Science and Engineering*, **23**: 315-323 (2015).
- [64] Yang M., Song Y., Liu W., Zhao J., Ruan X., Jiang L., Li Q., [Effects of Additive Mixtures \(THF/SDS\) on Carbon Dioxide Hydrate Formation and Dissociation in Porous Media](#), *Chemical Engineering Science*, **90**: 69-76 (2013).
- [65] Zhang J.S., Lee S., Lee J.W., [Kinetics of Methane Hydrate Formation from SDS Solution](#), *Industrial & Engineering Chemistry Research*, **46**: 6353-6359 (2007).
- [66] Peng D.Y., Robinson D.B., [A New two Constant Equation of State](#), *Ind. Eng. Chem. Fundam.*, **15**: 59-64 (1976).
- [67] Mohammadi A., Manteghian M., Mohammadi A.H., Jahangiri A., [Induction Time, Storage Capacity, and Rate of Methane Hydrate Formation in the Presence of SDS and Silver Nanoparticles](#), *Chemical Engineering Communications*, **204**: 1420-1427 (2017).