



Thermodynamic study of CO₂ hydrate formation in the presence of SDS and graphene oxide nanoparticles

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ABSTRACT

Gas consumption rate is an important factor in the kinetic study of gas hydrate formation. In this study, the kinetics of the hydrate formation was examined in water + carbon dioxide + graphene oxide and water + carbon dioxide + graphene oxide + sodium dodecyl sulfate (SDS) systems. The experiments are carried out at 0.05 and 0.1% of graphene oxide nanoparticle weight and 400 mg/l SDS solution at 3.6 MPa and 4 MPa pressures and temperatures of 275.65, 277.65, and 279.65 K. The results show that as the pressure rises, graphene oxide is responsible for the increase in the storage capacity and gas consumption at constant temperature so that using graphene oxide at 0.1% weight increases the storage capacity by 4.2% and molar gas consumption by 3.8% at the pressure of 3.4 MPa compared to the 0.05% weight. When the surfactant, SDS with the concentration of 400 mg/l, is used, storage capacity and gas consumption increase by 38% and 26%, respectively.

1. Introduction

Carbon dioxide is mainly caused by the combustion of fossil fuel at homes and in vehicles and the burning of the flare stack gas in refineries, petrochemicals, and thermal power plants. Then it enters the atmosphere. CO₂ is one of the most effective pollutants in creating greenhouse effect which causes the warming and gradual increase in Earth temperature. Greenhouse gas separation and storage is one of today's important environmental issues [1,2]. The challenges involved designing novel equipment and implementing new methods [3]. The hydrate formation is a method to separate and store CO₂, which has created a great interest among researchers. In this way, CO₂ is hydrated and stored at the depths of the oceans instead of being released in air. In this method, CO₂ is injected at a depth of over 400 meters. CO₂ is trapped in the water as a result of solution. It is hydrated due to the low temperature and high water pressure at 500-900 m below the sea level. Despite numerous studies to improve the thermodynamic conditions of gaseous hydrate formation, the kinetics of gas hydrates has not been, so far, taken into account [4-6]. In this regard, numerous researchers have proposed solutions to eliminate or absorb CO₂, some of

which are as follows: The kinetic effects of N-butyl-N-methyl pyrrolidinium bromide ([Py14]-Br) on the formation of CO₂ gas hydrates were experimentally investigated by Xiao et al. Both of the induction time of CO₂ hydrates formation and the formation rates were investigated in the aqueous solutions of [Py14]-Br at different concentrations. Pressure and temperature changes versus time during the hydrate formation process were measured under the isochoric conditions. [Py14]-Br aqueous solution could delay the induction time compared with pure water system at relatively high sub cooling, while it appeared to have no inhibition effect at low sub cooling, even enhanced the formation of gas hydrates [7]. The separation of CO₂ from the flue gas by the combination of tetra-N-butyl ammonium additive and tetrahydrofuran was investigated by Yang et al. Various combinations of the two additives were used for testing. The experiments were conducted using an isochoric method to study the effects of additive mixtures with different compositions. A mass fraction of 1% THF with the mass fraction of 0.5%, 1%, 2%, 3% and 5% TBAB, and 5% THF with 3%, 5% and 8% TBAB were used. A mass fraction of 1% THF with the mass fraction of 0.5%, 1%, 2%, 3% and 5% TBAB, and 5% THF with 3%, 5% and 8% TBAB were used. The experiments

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were conducted at 276.35–291.05 K and 0.9–4.4 MPa. For all mixtures with the mass fraction of 1% THF, the effect was subtle (with the exception of the 1% THF + 5% TBAB mixture). On the other hand, the hydrate equilibrium pressure decreased dramatically when mixtures containing 5% THF were added. Also a combination of a mass fraction of 5% THF + 5% TBAB greatly reduced the induction time of hydrate formation compared with the other concentrations tested [8]. The effect of synthesized zinc oxide (ZnO) nanoparticles on the kinetic and thermodynamic equilibrium conditions of CO₂ hydrate formation was investigated by Mohammadi et al. The amount of the gas consumption was measured and compared for the four sample fluids: pure water, aqueous solution of sodium dodecyl sulfate (SDS), water-based ZnO-nano fluid and water-based ZnO-nano fluid in the presence of SDS (0.001 mass fraction). The time of hydrate growth decreased and the amount of the storage gas enhanced in the presence of nanoparticles [9]. The effect of silver nanoparticles and SDS on the rate of formation of CO₂ hydrates and its storage capacity was studied by Mohammadi et al. They showed that the use of SDS (500 mg/l) + silver nanoparticles (0.000045 M) has a significant impact on the storage capacity of CO₂ and increases the carbon dioxide consumption by 94% [10]. The thermodynamic conditions for the formation of carbon dioxide in the presence of a salt stabilizer TBAC (tetra-N-butyl ammonium chloride) at high concentrations was investigated by Kang et al. Equilibrium data at pressures of 10 to 30 bar indicates that at high concentrations of TBAC, the initial pressure has a very small effect on equilibrium points. Also, the use of high-weight TBAC brings the temperature of carbon dioxide gas hydrate closer to ambient temperature. The results indicate that the initial temperature of the reactor is not affected by equilibrium points [11]. The present study aims at investigating storage capacity of CO₂ in hydrate in the presence of different concentration of the surfactant SDS and GO nanoparticles. GO nanofluid showed high absorption capacities toward CO₂ due to the high surface area and existence of OH groups on the GO surface and enhancement in mass transfer coefficient [12].

2. Theory and calculations

2.1. Using Peng-Robinson equation of state for calculating number of moles

Eq. (1) is used to calculate the number of gas consumption moles. In this equation, Z is the coefficient of compressibility obtained from the Peng–Robinson equation [13,14].

$$n = \frac{PV}{ZRT} \quad (1)$$

$$P = \frac{a\alpha}{V-b} - \frac{a\alpha}{V^2 + 2br - b^2} \quad (2)$$

$$a = \frac{0.45724R^2T_c^2}{P_c} \quad (3)$$

$$b = \frac{0.0778RT_c}{P_c} \quad (4)$$

In the above equations, T_c and P_c are critical temperature and pressure, respectively. R is the ideal gas constant. Eq. (5) and (6) are used to calculate the initial and equilibrium moles at initial and equilibrium conditions using Z.

$$n_0 = \frac{P_0V_0}{Z_0RT_0} \quad (5)$$

$$n_e = \frac{P_eV_e}{Z_eRT_e} \quad (6)$$

$$\Delta n = n_0 - n_e \quad (7)$$

Eq. (7) can be used to calculate the CO₂ consumption between the initial and final conditions [15]:

T₀ and P₀ are initial temperature and pressure of the experiment and P_e and T_e are the final pressure and temperature, respectively. V₀ and V_e are the initial and final volume of the solution. In this experiment, the solution volume is considered 100 cm³.

2.2. Calculation of the storage capacity

$$SC = \frac{V_{STP}}{V_H} = \frac{\Delta n_{CO_2}RT_{STP}}{P_{STP}V_H} \quad (8)$$

The above equation is used to calculate the storage capacity of CO₂ in the hydrate [16].

In Eq. (8), P_{STP} and T_{STP} are pressure and temperature at standard conditions and R is the ideal gas constant. In this equation, V_H is the volume of hydrate, which is considered 100 cm³.

3. Materials and methods

3.1. Materials

The carbon dioxide gas used to perform the experiments has a purity of 99.99% that was purchased from the company Arvand Industrial Gases Co. The carbon dioxide gas cylinder has a volume of 50 liters and has an initial pressure of 42 MPa. Graphene oxide was purchased from the US Research Nanomaterials, Inc. And Sodium dodecyl sulfate (SDS) was used as the surfactant was purchased from Merck Co.

3.2. Apparatus

For Experiment, a 316 (S-316) stainless steel jacketed reactor with an internal volume of 296 cm³, which has a bearing operating pressure of 200 bars, is used. The internal chamber of the reactor is equipped with four valves that tolerate the pressure of 6000 psi. Of these four valves, two are ball valves and two are needle valves. The former are used for the injection of the solution and drainage of water and gas mixture after the experiment.

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The latter are used for two purposes: one is used to inject gas and the other is used to connect to the gas chromatograph device and gas sampling. Two vents are embedded at the outer wall of the reactor in order to control the reactor temperature by the inlet and outlet of the coolant by the passage of the refrigerant fluid. Ethylene glycol aqueous solution with the weight concentration of 50% is used as the coolant. Hydrate formation reactor and all refrigerant fluid connections and

transfer tubes are well insulated. A Pt-100 temperature sensor is used with a precision of ± 0.1 K in order to reduce the energy loss. The reactor pressure is measured using a BD sensor with the precision of approximately 0.01 MPa. An oscillating mixer is used for the proper mixture in the hydrate formation reactor. A pump is used to create vacuum inside the reactor. A schematic of hydration formation device is shown in Figure 1.

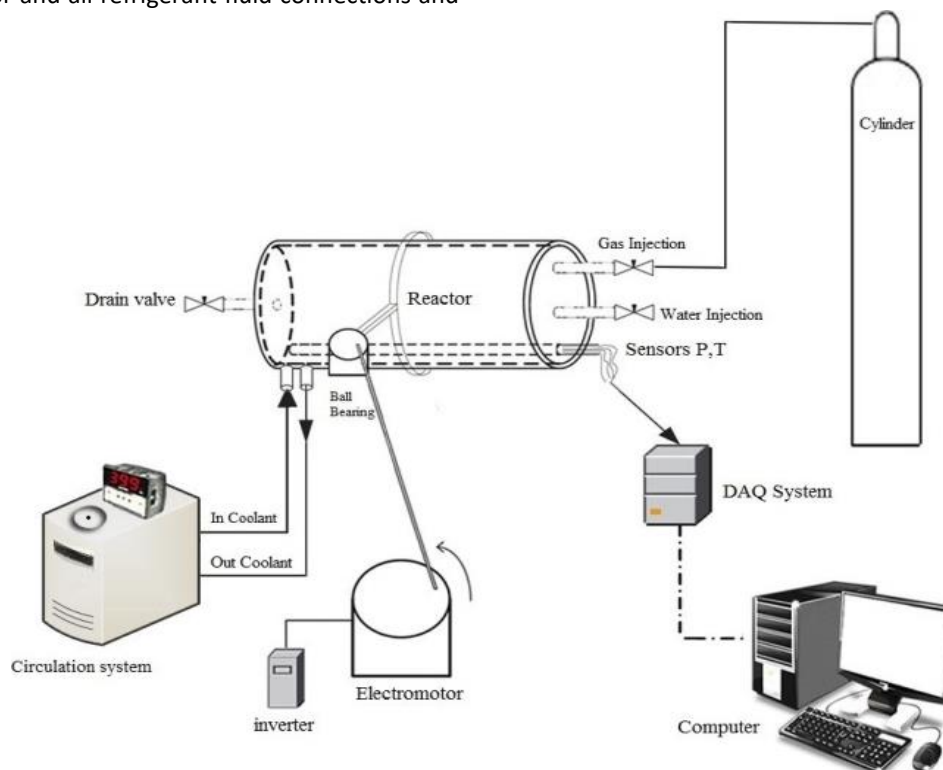


Fig. 1. Schematic of the applicable hydrated device.

Table 1 shows the different conditions of experiment including pressure and temperature changes with/without the presence of graphene oxide nanoparticles and SDS at different concentrations for each experiment, used to calculate the storage capacity and CO₂ molar consumption.

3.3. Procedure

First, the reactor is washed with water by a continuous rotatory system for 10 minutes. Then it is rinsed by the distilled water. Vacuum pump is then used for 5 minutes to ensure the exit of intracellular air and remaining water droplets. 100 cm³ solution with 0.1 and 0.05% of graphene oxide nanoparticle weight concentration is prepared and injected into the cell. After setting the refrigerant temperature and stabilizing the temperature, CO₂ is injected at 40-bar initial pressure and oscillating mixer is turned on at fixed speed at the same time. As soon as the hydration formation process and CO₂ consumption begin, the system pressure declines. Afterwards, pressure and temperature data are recorded on the computer at certain time intervals.

Table 1. The different conditions of experiment

Run	P ₀ (bar)	T ₁ (C)	SDS(mg/l)	GO(mg/l)
1	40	0.2	0	0.1
2	40	2.8	0	0.1
3	40	4	0	0.1
4	36	1.6	0	0.1
5	36	2.8	0	0.1
6	36	3.5	0	0.1
7	40	1.7	0	0.05
8	40	2.8	0	0.05
9	40	3.8	0	0.05
10	36	2.5	0	0.05
11	36	3	0	0.05
12	36	4	0	0.05
13	40	4	400	0.1
14	36	3.8	400	0.1
15	40	5.5	400	0.05
16	36	4	400	0.05

4. Results and discussion

4.1. Calculation of CO₂ consumption

4.1.1. Effect of pressure and temperature on the CO₂ consumption in various concentrations of graphene oxide

Additives, nanoparticles, are responsible for the increase in the cavities that are ready to host the gas molecules. This helps greater gas consumption [17-20]. Figure 2 shows that increased pressure contributes to the increased CO₂ consumption. On the contrary, as mentioned earlier, increased temperature reduces the CO₂ consumption.

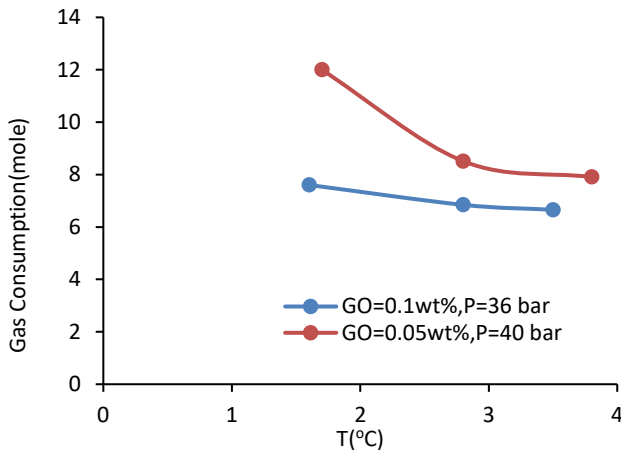


Fig. 2. Effect of pressure and temperature on the number of moles consumed in various concentrations of graphene oxide

4.1.2. Effect of pressure and temperature on the gas consumption in the same concentrations of graphene oxide

As shown in Figure 3, increased temperature has a reverse effect on the CO₂ consumption so that the increased temperature is responsible for reduced CO₂ consumption and increased pressure at similar graphene oxide nanoparticle concentration increased the CO₂ consumption.

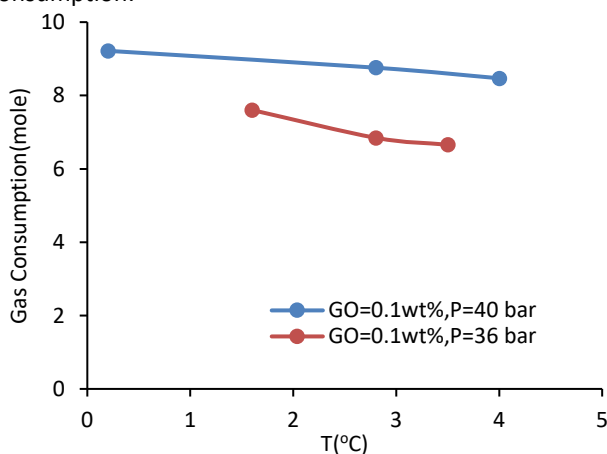


Fig. 3. The effect of pressure and temperature on the number of moles consumed in the same concentrations of graphene oxide.

4.2. Calculation of the storage capacity

As new materials with dimensions of less than 100nm, nanostructures can be effective factors in intensifying the mass and heat transfer in different systems due to preparing the surfaces with special areas and high energy [21]. Hydrate formation is an interdisciplinary phenomenon. Any substance capable of increasing mass and heat transfer at water-gas interface would increase the hydration formation rate and gas dissolution. For instance, the thermal conductivity of copper is 700 times that of water at the room temperature. Metal oxides such as aluminum oxide, considered thermal insulation compared to certain metals such as copper, have thermal conductivity which is 10 times that of water. Graphene oxide solution containing non-suspended solid particles, known as nano-fluid, translates heat far better than its base fluid [22,23].

4.2.1. Effect of pressure and temperature on storage capacity at various concentrations of graphene oxide

As it can be seen in Figure 4, as temperature rises, storage capacity reduces due to the exothermic hydration process; however, increased pressure is more effective in increasing storage capacity due to the increase in the driving force compared to the graphene oxide concentration.

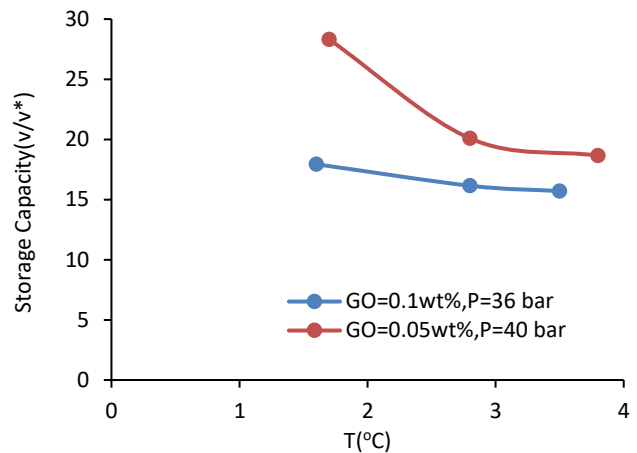


Fig.4. Effect of pressure and temperature on storage capacity at various concentrations of graphene oxide.

4.2.2. Effect of pressure and temperature on storage capacity at the same concentrations of graphene oxide

As it can be seen in Figure 5, when a fixed graphene oxide nanoparticle concentration is taken into account, increasing pressure is responsible for the increase in storage capacity; however, increased temperature leaves a reverse effect.

4.3. Effect of SDS on the gas consumption and storage capacity

Adding surfactant is highly effective in the molar consumption and storage capacity due to the following

reasons: SDS materials have a hydrophilic and a hydrophobic end. During the hydration formation, the best place for these materials is the gas-water interface because the hydrophilic end tends towards the water and the hydrophobic end tends towards the gas. Gas-water surface stretch reduces and the gas penetration into the water becomes faster and, consequently, the hydration formation rate increases as a result of the bond of the hydrophilic and hydrophobic ends with gas and water [24-27]. Since CO₂ has high water solubility, the presence of surfactants and foam caused by them can sometimes increase the gas penetration resistance into the liquid and decrease CO₂ solubility. This assumption is strengthened when the hydration formation rate decreases at a greater pace as the solution concentration rises [27].

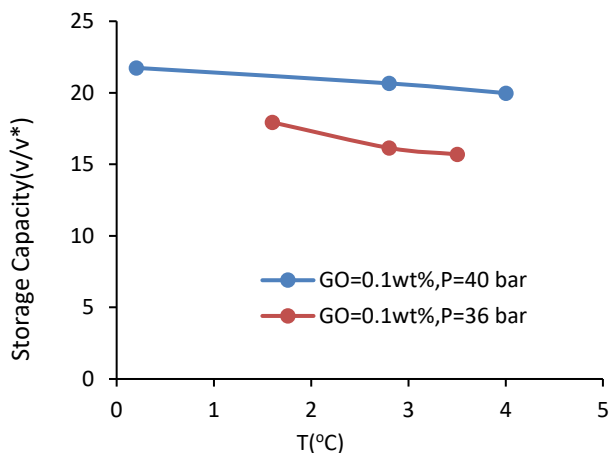


Fig. 5. The effect of pressure and temperature on storage capacity at the same concentrations of graphene oxide.

4.3.1. Effect of SDS and pressure and graphene oxide with different concentrations on storage capacity

As shown in Figure 6 adding surfactant is significantly effective on storage capacity. Increased graphene oxide nanoparticle concentration intensifies such effect. As pressure rises, storage capacity rises, too.

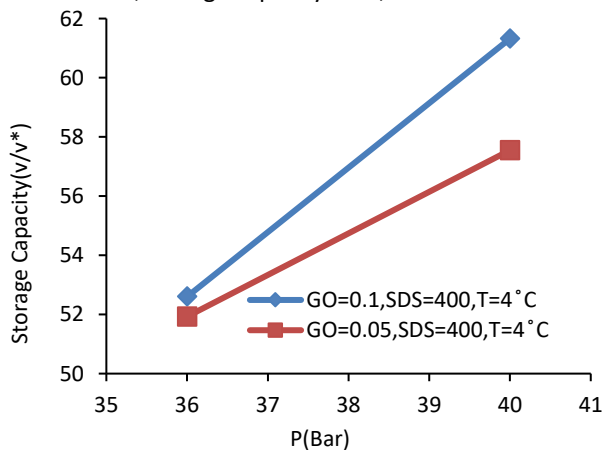


Fig.6. Effect of SDS and pressure and graphene oxide with different concentrations on storage capacity.

4.3.2. Effect of SDS and pressure and graphene oxide with different concentrations on the gas consumption

As in Figure 6, the effect of the surfactant on molar consumption is also seen in Figure 7, simultaneously increasing the concentration of graphene oxide nanoparticles and the pressure increases the consumption of carbon dioxide.

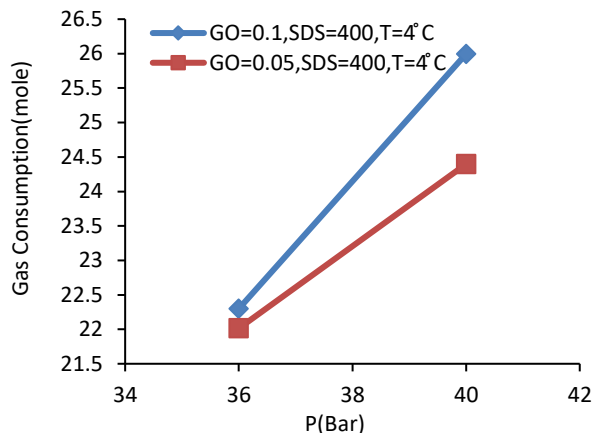


Fig.7. SDS effect and pressure and graphene oxide with different concentrations on the number of moles consumed.

Effect of temperature on the gas consumption and storage capacity is drawn in Figures 8, 9 at pressures of 3.6 and 4 MPa at concentrations of 0.05 and 0.1% weight percent.

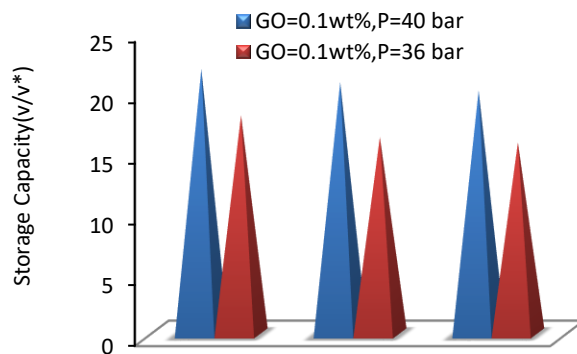


Fig. 8. Effect of temperature on the storage capacity at pressures of 3.6 and 4 MPa at concentrations of 0.05 and 0.1% weight percent.

Figures 10-15 show the effect of adding a surfactant, called SDS, with the concentration of 400 mg/l to the solution at fixed temperature; however, graphene oxide, pressure and concentration vary. In this condition, storage capacity and CO₂ gas consumption are greater and more sensible compared to the previous condition.

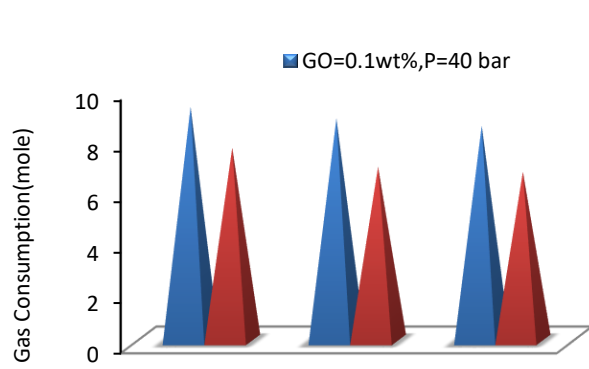


Fig. 9. Effect of temperature on the gas consumption at pressures of 3.6 and 4 MPa at concentrations of 0.05 and 0.1% weight percent.

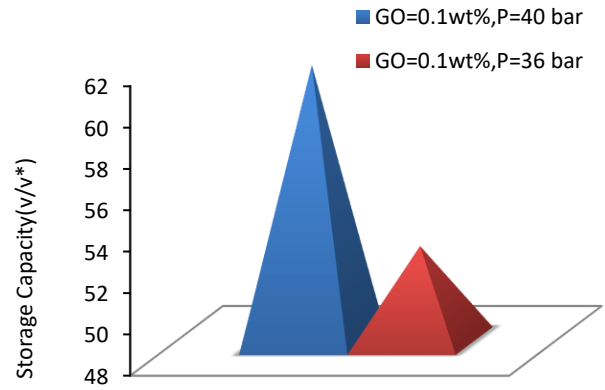


Fig. 12. Effect of SDS and graphene oxide 0.1% on the storage capacity at various pressures.

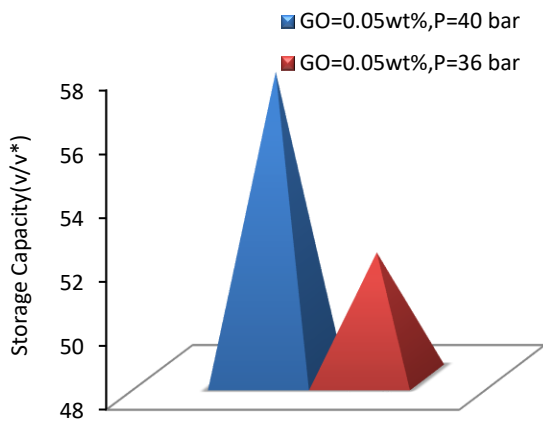


Fig. 10. Effect of SDS and graphene oxide 0.05 % on the storage capacity at various pressures.

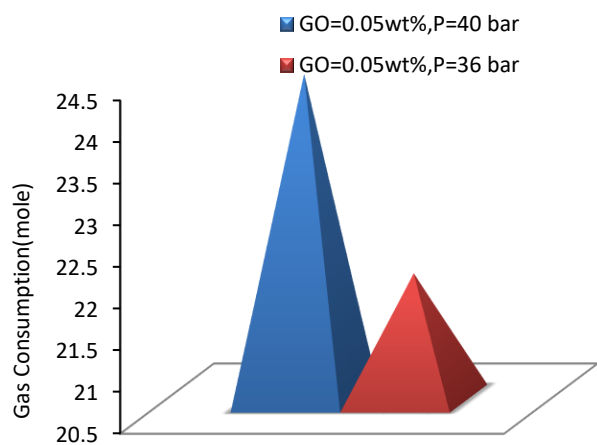


Fig. 13. Effect of SDS and graphene oxide 0.05% on the gas consumption at various pressures.

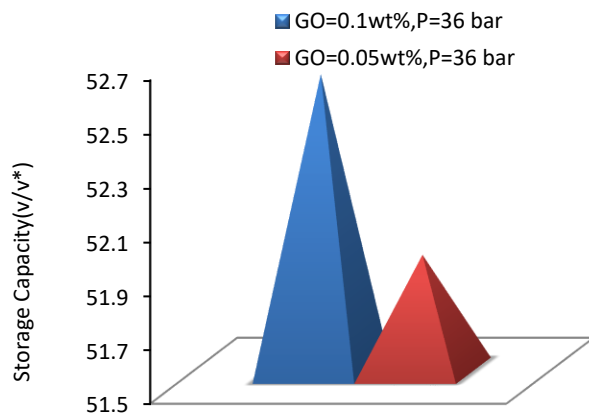


Fig.11. Effect of SDS and graphene oxide on the storage capacity at constant pressures.

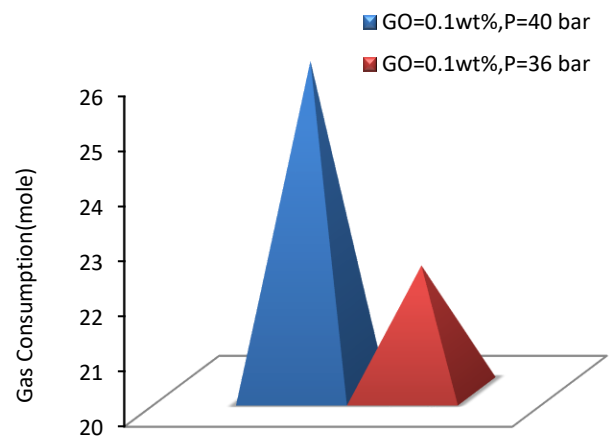


Fig.14. Effect of SDS and graphene oxide 0.1% on the gas consumption at various pressures.

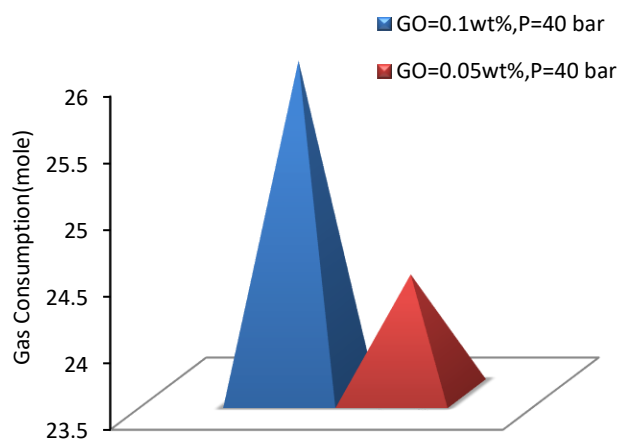


Fig. 15. Effect of SDS and graphene oxide on the gas consumption at constant pressures.

5. Conclusions

In this study, two important parameters, storage capacity and gas consumption, were examined in the CO₂ hydration formation process at the presence of graphene oxide nanoparticles and a surfactant called SDS. In general, increasing graphene oxide nanoparticle concentration is responsible for the increase in the molar consumption by 3.8% and storage capacity by 4.2%. At a fixed graphene oxide concentration, the higher the pressure is, the higher the molar consumption and storage capacity are. At a fixed graphene oxide pressure and concentration, gas consumption and storage capacity decline. If SDS is added to the system, gas consumption and storage capacity rise by 26% and 38%, respectively. Increased pressure is responsible for the increase in gas consumption and storage capacity.

6. Acknowledgment

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References

[1] Xia, Z., Li, Z. Y., Cai, J., Zhang, Y., Wang, Y., Yan, K., Li, X. (2019). Gas Hydrate Formation Process for Simultaneously Capture of CO₂ and H₂S. *Energy procedia*, 158, 5705-5710.

[2] Sloan, E. D., Koh, C. A. (2007). *Clathrate hydrates of natural gases*, 3rd edn. CRC.

[3] Rahimi, M. R., Mosleh, S. (2015). CO₂ removal from air in a countercurrent rotating packed bed, experimental determination of height of transfer unit. *Advances in environmental technology*, 1(1), 25-30.

[4] Sloan Jr, E. D., Koh, C. A. (2007). *Clathrate hydrates of natural gases*. CRC press.

[5] Mohammadi, A. (2017). Semicompletion time of carbon dioxide uptake in the process of gas hydrate formation in presence and absence of SDS and silver nanoparticles. *Petroleum science and technology*, 35(1), 37-44.

[6] Zheng, J., Loganathan, N. K., Linga, P. (2019). Natural gas storage via clathrate hydrate formation: Effect of carbon dioxide and experimental conditions. *Energy procedia*, 158, 5535-5540.

[7] Shen, X. D., Shi, L. L., Long, Z., Zhou, X. B., Liang, D. Q. (2016). Experimental study on the kinetic effect of N-butyl-N-methylpyrrolidinium bromide on CO₂ hydrate. *Journal of molecular liquids*, 223, 672-677.

[8] Yang, M., Jing, W., Wang, P., Jiang, L., Song, Y. (2015). Effects of an additive mixture (THF+ TBAB) on CO₂ hydrate phase equilibrium. *Fluid phase equilibria*, 401, 27-33.

[9] Mohammadi, M., Haghtalab, A., Fakhroueian, Z. (2016). Experimental study and thermodynamic modeling of CO₂ gas hydrate formation in presence of zinc oxide nanoparticles. *The journal of chemical thermodynamics*, 96, 24-33.

[10] Mohammadi, A., Manteghian, M., Haghtalab, A., Mohammadi, A. H., Rahmati-Abkenar, M. (2014). Kinetic study of carbon dioxide hydrate formation in presence of silver nanoparticles and SDS. *Chemical engineering journal*, 237, 387-395.

[11] Kang, S. P., Lee, J. W. (2010). Kinetic behaviors of CO₂ hydrates in porous media and effect of kinetic promoter on the formation kinetics. *Chemical engineering science*, 65(5), 1840-1845.

[12] Irani, V., Maleki, A., Tavasoli, A. (2019). CO₂ absorption enhancement in graphene-oxide/MDEA nanofluid. *Journal of environmental chemical engineering*, 7(1), 102782.

[13] Abolala, M., Varaminian, F. (2015). Thermodynamic model for predicting equilibrium conditions of clathrate hydrates of noble gases+ light hydrocarbons: Combination of Van der Waals-Platteeuw model and sPC-SAFT EoS. *The journal of chemical thermodynamics*, 81, 89-94.

[14] Azimi, A., Mirzaei, M. (2016). Experimental evaluation and thermodynamic modeling of hydrate selectivity in separation of CO₂ and CH₄. *Chemical engineering research and design*, 111, 262-268.

[15] Linga, P., Daraboina, N., Ripmeester, J. A., Englezos, P. (2012). Enhanced rate of gas hydrate formation in a fixed bed column filled with sand compared to a stirred vessel. *Chemical engineering science*, 68(1), 617-623.

[16] Lin, W., Dalmazzone, D., Fürst, W., Delahaye, A., Fournaison, L., Clain, P. (2013). Thermodynamic studies of CO₂+ TBAB+ water system: experimental

- measurements and correlations. *Journal of chemical and engineering data*, 58(8), 2233-2239.
- [17] Haghtalab, A., Mohammadi, M., Fakhroueian, Z. (2015). Absorption and solubility measurement of CO₂ in water-based ZnO and SiO₂ nanofluids. *Fluid phase equilibria*, 392, 33-42.
- [18] Babaee, S., Hashemi, H., Mohammadi, A. H., Naidoo, P., Ramjugernath, D. (2016). Experimental measurement and thermodynamic modelling of hydrate phase equilibrium conditions for krypton+ n-butyl ammonium bromide aqueous solution. *The journal of supercritical fluids*, 107, 676-681.
- [19] Cha, J. H., Ha, C., Kang, S. P., Kang, J. W., Kim, K. S. (2016). Thermodynamic inhibition of CO₂ hydrate in the presence of morpholinium and piperidinium ionic liquids. *Fluid phase equilibria*, 413, 75-79.
- [20] Yu, Y. S., Zhou, S. D., Li, X. S., Wang, S. L. (2016). Effect of graphite nanoparticles on CO₂ hydrate phase equilibrium. *Fluid phase equilibria*, 414, 23-28.
- [21] Sloan, E. D., Koh, C. A. (1998). Hydrates of natural gases.
- [22] Roosta, H., Varaminian, F., Khosharay, S. (2014). Experimental study of CO₂ hydrate formation kinetics with and without kinetic and thermodynamic promoters. *Scientia Iranica. Transaction C, chemistry, Chemical engineering*, 21(3), 753.
- [23] Zhou, S. D., Yu, Y. S., Zhao, M. M., Wang, S. L., Zhang, G. Z. (2014). Effect of graphite nanoparticles on promoting CO₂ hydrate formation. *Energy and fuels*, 28(7), 4694-4698.
- [24] Zhang, Y., Yang, M., Song, Y., Jiang, L., Li, Y., Cheng, C. (2014). Hydrate phase equilibrium measurements for (THF+ SDS+ CO₂+ N₂) aqueous solution systems in porous media. *Fluid phase Equilibria*, 370, 12-18.
- [25] Abedi-Farizhendi, S., Rahmati-Abkenar, M., Manteghian, M., Yekshaveh, J. S., Zahmatkeshan, V. (2019). Kinetic study of propane hydrate in the presence of carbon nanostructures and SDS. *Journal of petroleum science and engineering*, 172, 636-642.
- [26] Mohammadi, A., Pakzad, M., Mohammadi, A. H., Jahangiri, A. (2018). Kinetics of (TBAF+ CO₂) semi-clathrate hydrate formation in the presence and absence of SDS. *Petroleum science*, 15(2), 375-384.
- [27] Mohammadi, A., Manteghian, M., Mohammadi, A. H., Jahangiri, A. (2017). Induction time, storage capacity, and rate of methane hydrate formation in the presence of SDS and silver nanoparticles. *Chemical engineering communications*, 204(12), 1420-1427.