Effect of the surfactants on hydrate formation during methane storage process

Panfeng Zhang\(^{1,2,*}\), Yuqian Diao\(^{3}\), Zhao Dong\(^{4}\), Shufeng Pei\(^{1}\), Qiaobo Wang\(^{1}\), Shaoran Ren\(^{1,2,*}\), and Liang Zhang\(^{1,2}\)

1. Key Laboratory of Unconventional Oil & Gas Development (China University of Petroleum (East China)), Ministry of Education, Qingdao 266580, P. R. China
2. School of Petroleum Engineering, China University of Petroleum (East China), Qingdao 266580, P. R. China
3. CNOOC Research Institute Co., Ltd., Beijing 100028, P. R. China
4. CNOOC China Limited, Zhanjiang Branch, Zhanjiang, Zhanjiang 524000, P. R. China

*Corresponding author: rensr@upc.edu.cn (S. Ren); panfengzhang@126.com (P. Zhang)

Abstract: Enhanced hydrate formation rate by adding surfactant for achieving hydrate-based methane storage and transportation has drawn much attention in recent years. In this study, the effect of cocamidopropyl dimethylamine (CPDA), Sodium dodecyl sulfate (SDS), dodecyl trimethyl ammonium bromide (DTAB), and hexadecyl trimethyl ammonium bromide (HTAB) on induction time, the formation rate, water conversion ratio, and dissociation rate of methane hydrate have been investigated. And all the results have been compared with the water system without any additives. After adding surfactant into the aqueous solution, the hydrate formation is promoted, which lead to higher the hydrate formation rate and more water converted to be hydrate. 69.96wt% water was converted to be hydrate and its formation rate is 31.58mmol/min in 1.0wt%CPDA aqueous solution, in water without any additives system, it is 29.44wt%, 11.45mmol/min, respectively. Besides, the highest dissociation rate is also found in CPDA aqueous solution system, it is 42.2mmol/min and is 2.16 times than that of the pure water system.

1. Introduction

Gas hydrates, also known as clathrate hydrate, ice-like crystalline solid, can be formed by host water molecules around small guest gas molecules (e.g. CH\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_8\), CO\(_2\), H\(_2\)S) at relatively low temperature and high pressure (hydrate formation region)[1, 2]. After the formation of hydrate, it shows excellent stability and high storage capacity of natural gas, so natural gas hydrate has great potential for natural gas storage and transportation. Besides, hydrate technologies also can be used for gas separation, seawater desalination, and solute purification[3-5].

The natural gas hydrate can achieve storage of about 180 volume natural gas per volume of hydrate (v/v), and the hydrate can be stably stored at atmospheric and low temperature, so hydrate-based natural gas storage has certain priority over compressed natural (CNG) and liquefied natural gas (LNG) as they requires extreme pressure and temperature[2, 6].

However, industrial application of hydrate-based natural gas storage has been hindered by the slow
hydrate formation rate and low conversion ratio of gas to hydrate[7]. As the hydrate formation is the methane and water molecules reacting on gas-water contact interface, increasing the area of gas-water phase interface is crucial for efficient hydration. Mechanical perturbation, such as liquid stirring and gas bubbling, can increase the gas-water phase interface and enhance hydrate formation rate[8]. Besides, adding some surfactants into the water phase also can enhance hydrate formation rate. Sodium dodecyl sulfate (SDS), linear alkyl benzene sulfonate (LABS), cationic cetyl trimethyl ammonium bromide (CTAB), and nonionic ethoxylated nonylphenol (ENP) all have function of hydrate promoter[9, 10].

In this study, the hydrate formation rate, water conversion ratio, and hydrate dissociation rate in presence of four kinds of surfactant have been studied. All results also compares with the water without any additives. The aim of this study is to find the effect of surfactant on the hydrate formation for methane storage.

2.Experimental

2.1.Materials
Sodium Dodecyl Sulfate (SDS, Chemical pure), Dodecyl Trimethyl Ammonium Bromide (DTAB, Chemical pure), and Hexadecyl Trimethyl Ammonium Bromide (HTAB, Chemical pure) were all purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Cocamidopropyl Dimethylamine (CPDA, AA) was supplied by Shanghai Chuxing Chemical Co., Ltd. CH4 (99.999 mol%) was supplied by Tianyuan Gas Ltd. (Qingdao, China). All the reagents were used without further treatment. The additive aqueous solution was prepared by freshwater.

2.2.Methods
A high pressure and low temperature stirring hydrate reactor was used as shown in Fig. 1. In the experiment, normally 500 cm<sup>3</sup> of aqueous solution of the surfactant was loaded into the reactor (with the chamber volume of 1150 cm<sup>3</sup>), and the reactor was then vacuumized and pressurized with methane gas to 30 MPa at 30 °C. After loading, the cooling bath was set to 0 °C and then the reactor was cooled down with stirring rate at 200 rpm. The pressure (P) and the temperature (T) with time data in the reactor were collected and recorded during the process. Formation of hydrate can be detected by measuring the pressure decline in the system, in which the gas consumption can be calculated as the following equations[11]:

\[ \Delta n_v = \frac{P_v V_s}{Z R T_s} - \frac{P_T V_s}{Z R T} \]  

where \( \Delta n_v \) is the amount of methane gas consumed at time t (mol). \( P_v, V_s, T_s \) and \( P_T, V_s, T \) are the gas pressure, volume, and temperature in the reactor at initial time and time t, respectively. \( Z \) is the compressibility factor obtained from Soave-Redlich-Kwong (SRK) equation of state. R is the universal gas constant.

Water conversion ratio is also calculated to evaluate the extent of the water conversion in the system. It can be calculated by equation[12]:

\[ \text{Water conversion ratio (\%) = } \frac{\Delta n_v \times 5.75}{n_w} \times 100\% \]  

Where, \( n_w \) are total moles of water in the system.
3. Results and discussion

3.1. Induction time of the hydrate formation

The hydrate equilibrium line of methane-pure water (the black line) and the P-T line (the blue line) of the aqueous solution in the reactor during the hydrate formation process are shown in Fig. 2. With the temperature in the reactor decreasing, its P-T condition gradually changes from the starting condition (point A) to equilibrium condition (point B) and hydrate onset condition (point C). Theoretically, the P-T condition between B and C is in the hydrate stable zone, the methane hydrate can form at any point between B and C. However, the surfactant in the aqueous solution can affect on hydrate formation process, so the time of BC (Induction time) varies with the different surfactants.

The hydrate formation process were investigated at the starting condition (around 30 MPa and 30 °C) with cooling bath temperature of 0 °C. Induction time of the systems with and without additives (pure water, 1.0wt% CPDA, 1.0wt% SDS, 1.0wt% HTAB, and 1.0wt% CTAB) have been calculated and shown in Fig. 3. For H2O system (pure water without any additives), Induction time is 45 minutes. For an aqueous solution system with the additive, Induction time is shorter as the surfactant accelerating the hydrate formation. The Induction time ranking can be concluded as 1.0wt% CTAB > 1.0wt% SDS > 1.0wt% HTAB > 1.0wt% CPDA. It means that CPDA have best promoter performance than the other surfactants.

![Fig. 1- High-pressure and low-temperature hydrate experimental apparatus.](image1)

![Fig. 2 P-T curve during hydrate formation process](image2)
3.2 Hydrate formation rate and water conversion ratio

During the hydrate formation process, the hydrate formation rate is the highest at the initial stage beginning with point C. The average hydrate formation rate in 100 min from point C can be calculated by total methane consumed dividing with reaction time (100min). Fig.4 (red bar) compares the average hydrate formation rate in presence of four kinds of additives and pure water. At additives concentration of 1.0wt%, these additives all can increases the hydrate formation rate effectively. As shown in Fig. 4, the hydrate formation rate of CPDA is 31.6mmol/min, which is 1.4 times than that of SDS and 2.76 times than that of pure water.

With the hydrate formation in the reactor, more and free water was consumed. At the end of the experiment, the amount of water converted into methane hydrate reached the maximum. The maximum water conversion ratio was calculated by equation (2) and is shown in Fig. 4 (blue hollow column). In CPDA aqueous solution system, 69.96 wt% water was converted to be methane hydrate, which is far more than 29.44wt% in pure water without any additives.

The changes of water conversion ratio with experimental time in the different systems are plotted in Fig.5. As it can be seen that CPDA effectively enhance hydrate formation rate and promote water converting to be hydrate. In other words, CPDA can enhance the efficiency of methane storage during the hydrate formation.

Fig. 4 Hydrate formation rate and the maximum of water conversion ratio with different additives.
3.3. Hydrate dissociation rate

The hydrate formation experiments with and without additives can reveal their effect on the methane storage process. The hydrate dissociation rate can be used to characterize the ability of releasing methane gas from the hydrate. The hydrate dissociation rate is by the mole of methane released dividing by dissociation time (from the time of heating start to the time of all hydrate dissociation). The results of hydrate dissociation rate with different additives is shown in Fig. 6. The system with 1.0 wt% CPDA has the biggest hydrate dissociation rate among the different additives. The finding may be interpreted by the hydrate morphology after the formation of hydrate. The powder-like hydrate particles can be formed at the presence of CPDA, which has the biggest surface area of hydrate[13, 14]. The larger surface area of hydrate particles, the more hydrate can dissociate at the same time, and the bigger dissociation rate.

4. Conclusion

Four kinds of surfactant, including cocamidopropyl dimethylamine (CPDA), Sodium dodecyl sulfate (SDS), dodecyl trimethyl ammonium bromide (DTAB), and hexadecyl trimethyl ammonium bromide (HTAB) were investigated, and their effect on induction time, the formation rate, water conversion ratio, and dissociation rate of methane hydrate have been evaluated. The results show that adding the surfactant in the aqueous phase has signification potential to increase the hydrate formation rate, facilitate more water conversion to hydrate, and even accelerate hydrate dissociation. Especially in the presence of the CDPA, the formation rate, water conversion ratio, and dissociation rate were 31.6 mmol/min, 69.96wt%, and 42.2 mmol/min, respectively, which are 2.76 times, 2.37 times, and 2.16 times than that of the pure water system, respectively.

Acknowledgments

Financial supports from the Major Research Project of China National Offshore Oil Corporation (CNOOC) during the “13th Five-Year Plan” (No. CCL2018ZJFN0461) is greatly acknowledged.
Reference

[1] W. Fu, Z. Wang, B. Sun, L. Chen, Int. J. Heat Mass Tran, 127, 611-621 (2018).
[2] E.D. Sloan Jr, C. Koh, Clathrate hydrates of natural gases, CRC press, (2008).
[3] K.C. Kang, P. Linga, K.-n. Park, S.-J. Choi, J.D. Lee, Desalination, 353, 84-90 (2014).
[4] M. Yang, H. Zhou, P. Wang, Y. Song, Appl. Energ., 221, 374-385 (2018).
[5] Y. Song, H. Dong, L. Yang, M. Yang, Y. Li, Z. Ling, J. Zhao, Sci. Rep-UK., 6, 21389 (2016).
[6] Y. He, M.-T. Sun, C. Chen, G.-D. Zhang, K. Chao, Y. Lin, F. Wang, J. Mater. Chem. A, 7, 21634-21661 (2019).
[7] S. Fan, L. Yang, Y. Wang, X. Lang, Y. Wen, X. Lou, Chem. Eng. Sci., 106, 53-59 (2014).
[8] L. Yang, G. Cui, D. Liu, S. Fan, Y. Xie, J. Chen, Chem. Eng. Sci., 146, 10-18 (2016).
[9] J. Yoslim, P. Linga, P. Englezos, J. Cryst. Growth, 313, 68-80 (2010).
[10] H. Ganji, M. Manteghian, K. Sadaghian zadeh, M.R. Omidkhah, H. Rahimi Mofrad, Fuel, 86, 434-441 (2007).
[11] A. Mohammadi, M. Manteghian, A.H. Mohammadi, A. Jahangiri, Chem. Eng. Commun., 204, 1420-1427 (2017).
[12] E. Chaturvedi, N. Prasad, A. Mandal, J. Nat. Gas Sci. Eng., 56, 246-257 (2018).
[13] H. Zhao, M. Sun, A. Firoozabadi, Fuel, 180, 187-193 (2016).
[14] M. Sun, A. Firoozabadi, Energ. Fuel, 28, 1890-1895 (2014).