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Surfactants as Hydrate Promoters?

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Natural gas hydrates from different types and concentrations of surfactant solutions were produced in a high-pressure cell. An anionic, a cationic, and a nonionic surfactant were used to prepare different concentration of surfactant solutions from deionized water. Although the thermodynamics of hydrate formation from a gas mixture is not affected with the existence of surfactants in the environment, there is an appreciable effect of type and concentration of surfactant on hydrate formation rate. The hydrate formation rate is increased with the use of anionic surfactant for all concentrations tested. Hydrate formation rate is also increased at low concentrations of cationic surfactant. The effect of nonionic surfactant is less pronounced compared to anionic and cationic ones.

Introduction

Although natural gas hydrates are traditionally accepted as a nuisance in the oil industry, their high gas storage capacity can be utilized for several industrial applications. They are considered as a nuisance in the oil industry because they plug pipelines and cause costly operations. On the other hand, there are several possible applications of hydrates such as storage and transportation of natural gas, desalinization of water, or recovery of rare gases. In addition, in-situ hydrates are considered as the commercial energy supply for future.

These two aspects of gas hydrates stimulated the studies on hydrates in two opposite directions. While the studies related to the problematic side of hydrates are those of trying to find ways of hydrate inhibition, there are some studies for finding some means for the promotion of hydrate formation.

The traditional hydrate inhibitors such as methanol and glycols have been in use for several decades, but as production platforms are becoming more remote within deeper and colder water, use of these chemicals will become more and more costly. Replacing these traditional thermodynamic inhibitors with a new generation of kinetic hydrate inhibitors or anti-agglomerators can lead to very substantial cost savings. Kelland et al.¹ discuss the types and properties of these new generation gas hydrate inhibitors.

Surfactants and polymers are the classes of chemicals that affect the hydrate formation process and are considered as new hydrate inhibitors (Kelland et al.²). These chemicals affect the hydrate formation through

one of the two processes as kinetic inhibitor or anti-agglomerator. While polymers are mainly considered as kinetic inhibitors, surfactants exhibit diverse agglomeration characteristics.

Kalogerakis et al.³ investigated experimentally the effect of surfactants on the kinetics of methane hydrate. They reported that surfactants do not influence the thermodynamics, however, they have a strong influence on the kinetics of gas dissolution in the water phase as well as on the overall rate of hydrate formation (an increase). They also observed that the formed hydrate particles in the presence of the various surfactants exhibit diverse agglomeration characteristics.

Urdahl et al.⁴ developed an experimental setup for characterization of gas hydrate inhibitor efficiency with respect to flow properties and deposition. They reported that the chemicals used in their study are surfactants, polymers, and various patented chemicals. The surfactants among those are known to stabilize water in oil emulsions. These chemicals showed some positive effects, but at concentrations above 1 wt % of the aqueous phase. However, they did not prevent deposition of hydrates at the water pipe wall. The isolation of the water phase by formation of a finely dispersed water/oil emulsion is suggested by the authors as a mechanism for suppression of gas hydrate formation.

The main focus of this study is to investigate experimentally the effect of surfactants on the formation kinetics of gas hydrate, particularly to observe their ability as hydrate promoter (i.e., production of hydrates for storage and transport).

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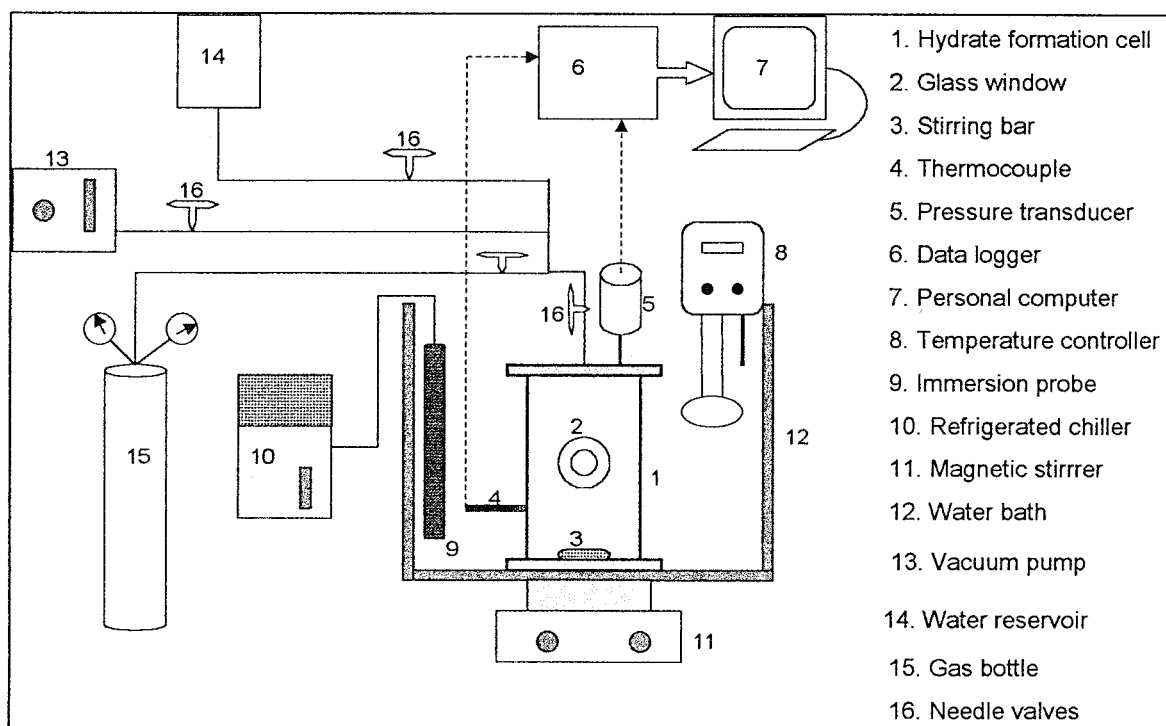


Figure 1. Experimental setup for high-pressure test.

Experimental Set-Up and Procedure

In this study, a high-pressure system was used to produce gas hydrate. A schematic diagram of the experimental setup is given in Figure 1. A cylindrical high-pressure reactor with dimensions of 3.4 cm in inner diameter, 15 cm in length, and total available volume of 142 cm³ including connections is used to produce gas hydrate. It is made of brass and tested up to 1000 psig pressure. Two windows are placed on two opposite faces of the cell to make the visual observation of hydrate formation possible. These windows have a diameter of 2 cm and are located such that it is possible to see the gas–water interface while forming hydrate. The high-pressure cell is placed into a constant-temperature bath made by Plexiglass that allows the observation of the system easily. A temperature controller and a refrigerated chiller are connected to the water bath to provide temperature control of the experiments. Also a thermocouple and a pressure transducer are connected to the high-pressure cell to measure temperature and pressure inside the high-pressure cell. They are connected to a data-logger to record the temperature and pressure in the hydrate formation cell as functions of time. The accuracy of temperature and pressure measurements is better than 0.1 °C and 0.2 psi, respectively. A magnetic stirrer, rotating a stirring bar within the cell, accomplishes the stirring of the system. The magnetic stirrer has a speed range of 0–1200 rpm and it was kept at 500 rpm throughout this study. Tap water, natural gas, and surfactants were used as reagents in experiments. Names of the surfactants and their types are given in Table 1. A natural gas from Değirmenköy Gas Field of Turkish Petroleum Corporation was used to produce hydrate during this study. The composition of natural gas is given in Table 2. Hydrate equilibrium curve for the gas/water system is given in Figure 2. The equilibrium curve was determined experimentally and the experimental results are tabulated in Table 3.

Three different surfactants, namely ETHOXALATE (non-ionic), DAM (cationic), and LABSA (anionic) were used throughout the study to observe the effect of type and concentration

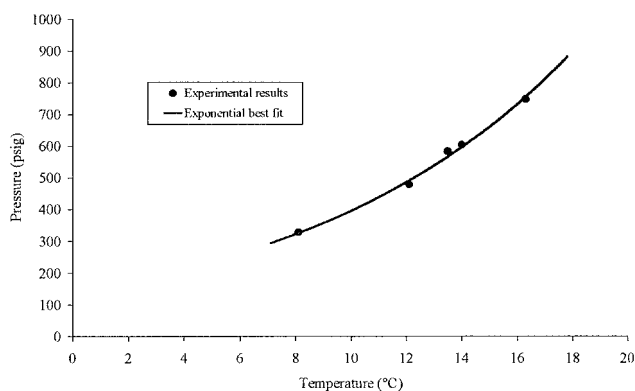


Figure 2. Hydrate equilibrium curve for the gas/water system.

Table 1: Names and Types of Surfactants Used in This Study

commercial name	structure	type
LABSA	linear alkyl benzene sulfonic acid	anionic
Dehyguard Dam (DAM)	quaternary ammonium salt	cationic
ETHOXALATE	nonylphenol ethoxalate	nonionic

of surfactants on the formation of natural gas hydrates. Thirteen experiments (four experiments for each type of surfactant and one experiment without surfactant) were carried out. The experimental conditions of these tests are presented in Table 4. The initial temperature and pressure of each test were tried to be kept the same at 18 ± 1 °C and 576 \pm 2 psi, respectively.

After preparing the system and getting temperature and pressure equilibrium, the system was cooled and the temperature and pressure inside the high-pressure cell were recorded every 10 s. After forming hydrates and getting the cell temperature below 4 °C, the cooler is switched off and the hydrate is left to dissociate with the aid of ambient temperature. Details of the experimental setup and procedure can be found from Karaaslan.⁵

Table 2: Chemical Composition of Gas Used in Experiments

component	CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂	N ₂	CO ₂
mol %	89.47	5.39	1.89	0.40	0.62	0.28	0.19	1.58	0.18

Table 3: Hydrate Equilibrium Conditions for the Gas/Water System

temperature (°C)	16.3	14.0	13.5	12.1	8.1
pressure (psig)	750	605	585	480	328

Table 4: Experimental Conditions of the Tests

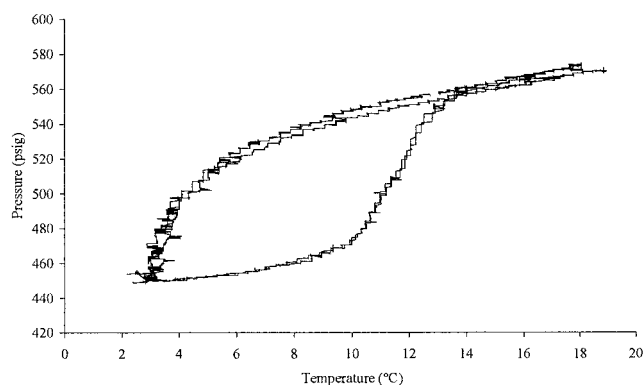
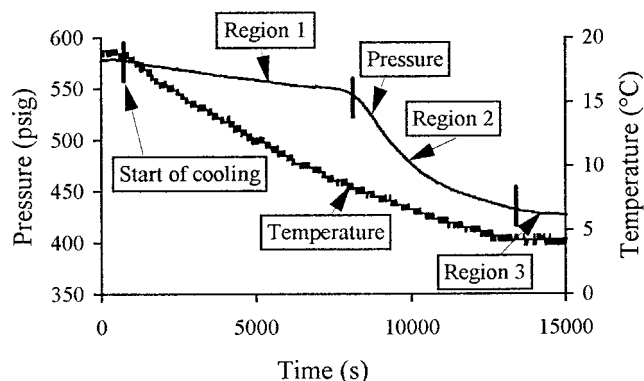
expt. no.	surfactant	concentration (weight %)	initial temperature (°C)	initial pressure (psig)
1	-	-	18.0	576
2	ETHOXALATE	0.005	18.5	576
3	ETHOXALATE	0.01	18.3	576
4	ETHOXALATE	0.1	17.9	574
5	ETHOXALATE	1.0	18.2	576
6	LABSA	0.005	17.6	577
7	LABSA	0.01	18.4	576
8	LABSA	0.1	19.0	575
9	LABSA	1	19.0	575
10	DAM	0.005	18.5	576
11	DAM	0.01	18.6	577
12	DAM	0.1	18.8	576
13	DAM	1	18.5	578

Results and Discussion

Hydrate Formation Thermodynamics. A sample plot of the change in pressure and temperature during hydrate formation and dissociation is shown in Figure 3 from Test 4. This test was carried out twice to check the reproducibility of hydrate formation and dissociation. Since water will have some inherent structure and have a well-known "memory" effect after forming hydrates, these two tests were run with different water/surfactant solutions having the same concentration. The temperature and pressure records of two tests are almost the same, indicating the reproducibility of hydrate formation and dissociation.

Another sample plot is given in Figure 4 showing the change in pressure and temperature of experiments during hydrate formation for Test 11, where the type of surfactant was DAM (cationic) with a concentration of 0.01%. As observed from this figure that there exist three regions of pressure drop with time during hydrate formation after the start of cooling. At the initial stage of experiment, the drop in pressure is due to cooling. The second region starts with a change (an increase) in the rate of pressure drop. This is an indication of the start of gas consumption for hydrate formation. The third region shows itself with a reduction in rate of pressure drop. This is due to the loss of gas–water interaction because of a solid hydrate layer between them. Hydrate particles grow up a certain thickness and make a solid boundary on the water surface. Since hydrate is a less permeable substance it limits gas transportation into the water phase. Another possible reason could also be that some components of hydrate-forming gas is consumed more as compared to others resulting with a new equilibrium.

Pressure–temperature plots of each test during hydrate formation were utilized to observe the effect of

**Figure 3.** Pressure–temperature plot of two different experiments with same solution during hydrate formation and dissociation (Test 4).**Figure 4.** Change in pressure and temperature during hydrate formation (Test 11).

surfactants on hydrate formation thermodynamics (Figure 5). The temperatures at which the system entered into Region 2 as given in Figure 4 (start of gas consumption for hydrate formation) are encircled in these plots. As seen from these plots that the starting temperatures of hydrate formation do not differ significantly with the change in surfactant type and concentration. This observation agrees with the observation made by Kalogerakis et al.³ that the surfactants do not influence the hydrate formation thermodynamics.

Hydrate Formation Kinetics. The consumption rate of natural gas during the hydrate formation process was determined from the pressure–temperature data. The compressibility factor real gas law ($PV = znRT$) was utilized to compute the number of moles of free gas present in the cell at each time step. The compressibility factor was calculated by using Lee and Kesler's⁶ compressibility factor expression and the free gas volume was assumed constant throughout the reaction (i.e., volume changes due to phase transitions were neglected).

A typical change of the gas content in the cell is shown in Figure 6 for Test 11. As observed there is a slight decrease in the gas content at the initial stage of

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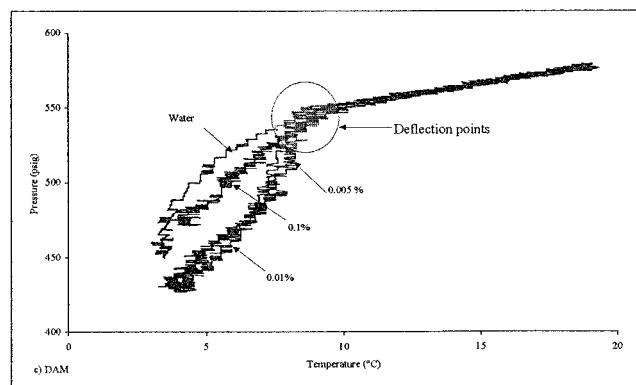
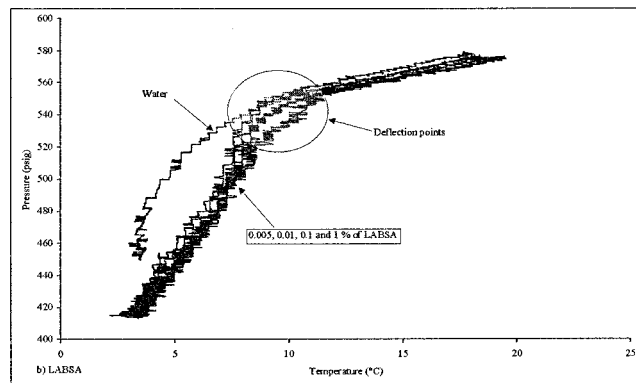
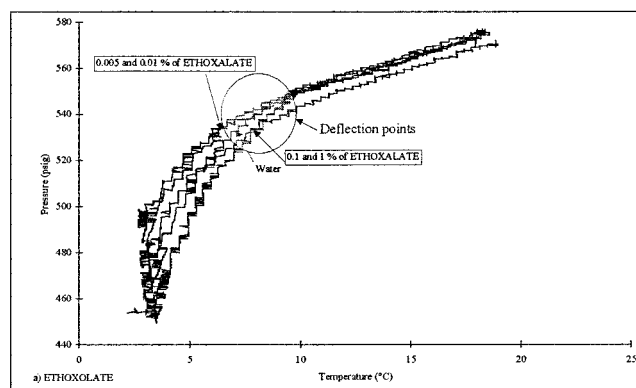


Figure 5. Pressure-temperature plots.

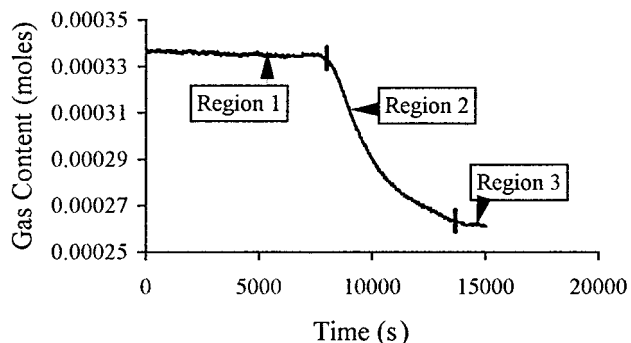


Figure 6. Change in free gas content during Test 11 (0.01 wt % DAM).

experiment (region 1) which can be considered as the dissolution of gas in hydrate-forming solution. After a certain point, the slope changes drastically, which can be taken as the initiation point of hydrate formation. The change in gas content with time shows a linear

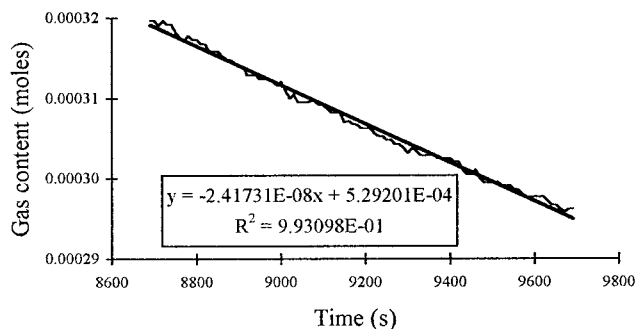


Figure 7. A typical change in gas consumption rate during hydrate formation (Test 11).

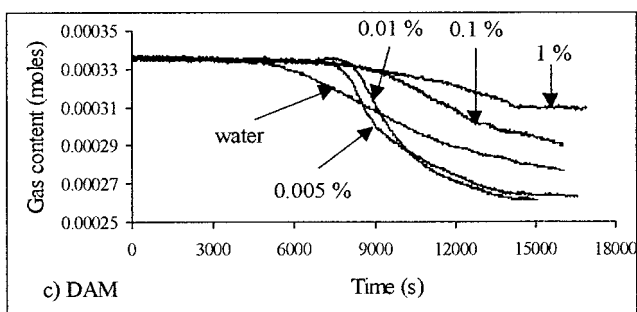
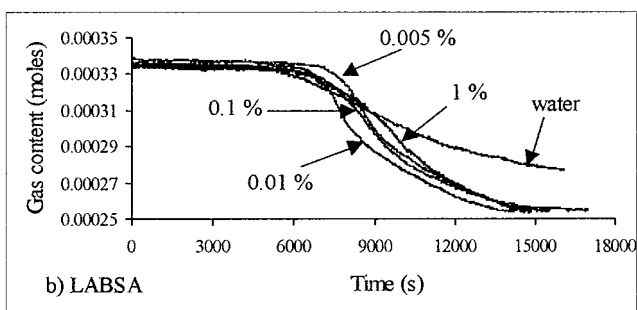
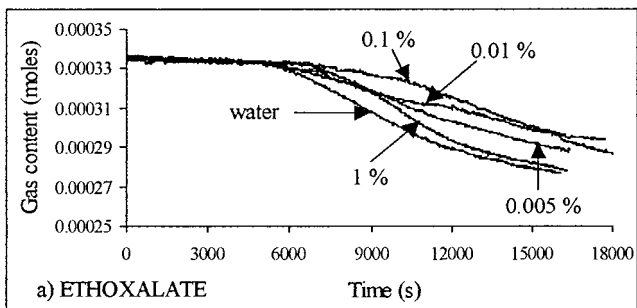


Figure 8. Change in gas content during hydrate formation.

behavior after the commencement of hydrate formation in region 2. But since the gas-water interaction reduces because of the hydrate layer, this linearity disappears gradually. It was assumed that the initial linear part of the data of region 2 give more realistic and deterministic results on surfactant effect on hydrate formation. A plot of these data is shown in Figure 7 with a linear fit and the slope of this straight line is the rate of gas consumption.

The change in gas content for various surfactant concentration of (a) ETHOXALATE, (b) LABSA, and (c) DAM are given, respectively, in Figure 8 as function of time. The estimated initial gas consumption rates for all tests taken from region 2 are presented in Table 5.

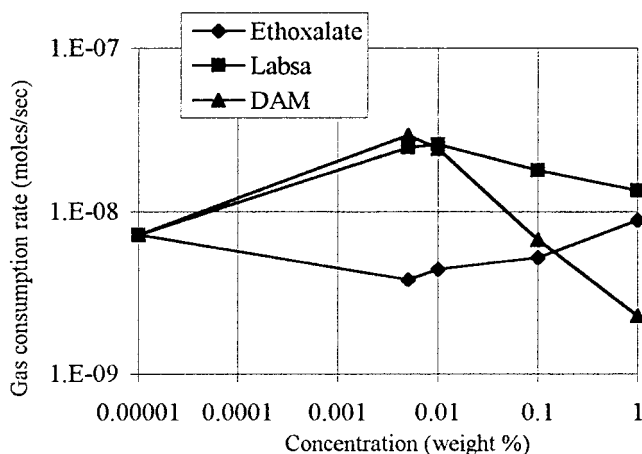


Figure 9. Gas consumption rates of ETHOXALATE, LABSA, and DAM.

Table 5: Gas Consumption Rates during Hydrate Formation (mol/s)

concentration (weight %)	ETHOXALATE (nonionic)	LABSA (anionic)	DAM (cationic)
0.0	7.143×10^{-9}	7.143×10^{-9}	7.143×10^{-9}
0.005	3.799×10^{-9}	2.452×10^{-8}	2.931×10^{-8}
0.01	4.393×10^{-9}	2.553×10^{-8}	2.417×10^{-8}
0.1	5.197×10^{-9}	1.773×10^{-8}	6.687×10^{-9}
1	8.832×10^{-9}	1.343×10^{-8}	2.285×10^{-9}

Change in gas consumption rate as a function of surfactant concentration is given in Figure 9.

Analysis of Figure 8 by visual inspection show that all tests with LABSA and 0.005% and 0.01% concentration tests with DAM have higher slopes compared to water-only test. These observations have been quantitatively verified in Figure 9.

As observed from Figures 8 and 9, ETHOXALATE (nonionic) always has lower gas consumption rates with respect to the water-only case (0.00001% was taken as 0% for logarithmic plot purposes). There is a slight decrease in the global hydrate formation rate. Kalogerakis et al.³ made the same observation for nonionic surfactants that they studied. They had

qualitative observations for the appearance of hydrate particles. The following is quoted from Kalogerakis et al.³ for nonionic surfactant: "the formed hydrate particles appeared to remain separated from each other at all times in the bulk"—an indication of anti-agglomerator effect.

The presence of LABSA (anionic) has a pronounced effect on the global rates of hydrate formation. It shows always higher gas consumption rates (higher hydrate formation rates), compared to the water-only case, for all concentrations studied. This observation also agrees the observation of Kalogerakis et al.³ that they observed a noticeable increase in the hydrate formation rate with anionic surfactant. It is therefore possible to consider this surfactant as a good candidate of being a hydrate promoter.

DAM showed similar behavior with LABSA for the lower concentrations (0.005 and 0.01 wt %) but this behavior is reversed for higher concentrations of DAM.

Conclusions

A series of experiments were conducted to investigate the influence of surfactants on the rate of hydrate formation. There is no appreciable effect of surfactants on the thermodynamics of hydrate formation, for surfactant concentrations studied. The overall hydrate formation rate is increased with the use of anionic surfactant for all concentrations tested. It is therefore possible to use this surfactant as a hydrate promoter. The effect of a nonionic surfactant is less pronounced compared to an anionic one. The cationic surfactant showed two opposite behaviors at low and high concentrations. It is effective as a promoter at low concentrations.

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