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Methane Hydrate Formation under Different Surfactants

THESIS

Submitted in partial fulfillment of
the requirement for the degree

Master of Engineering (Chemical Engineering)

at

The City College

of the

City University of New York

by

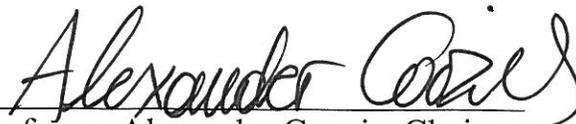
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January 2012

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Abstract

Gas hydrate formation is a stochastic and slow process. However, with the use of surfactants, that process became phenomenally faster. This work investigates the effect of Dowfax surfactants on gas hydrate formation and determines the adsorption isotherms of the surfactants using liquid-liquid titration methods. The isotherms of two noble Dow surfactants show the multi-layer type of adsorption and they promote methane hydrate growth significantly. These surfactants have doubly charged head groups which may influence the formation of hydrates due to the accumulation of negative charges. Both surfactants have almost similar structure but these surfactants shows different behavior in solution. The surfactants adsorption isotherms were determined by liquid-liquid titrations. Also the role of surfactant in methane hydrate formation is investigated in a nonstirred batch reactor. The extension of this work will provide complete sets of adsorption isotherms with optimized amounts of the Dow surfactants for the fast formation of methane hydrates.

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Chapter-1. Introduction

What are Gas Hydrates?

Gas hydrates are unique and most abundant natural forms of chemical compounds which are known as clathrate hydrates. Clathrate hydrates are non-stoichiometric crystalline in which small molecules such as methane, ethane, carbon dioxide, and hydrogen are hosted in hydrogen bonded water molecules. [1] The host water molecules enclose the guest molecules of same size without direct chemical bonding. These unusual associations of two molecules in a solid substance have intrigued scientists since the first discovery of chlorine hydrate almost two centuries ago. [1] However it appeared to pure attention to the scientists and industries after found that hydrate plugged the natural gas transmission lines in the 1930s. [1]



Figure 1: Burning methane hydrates [2].

The most common form of gas hydrate available in nature is methane hydrate which was observed first in the 1960s in Siberian gas reservoirs. [1] The specific combination of hydrogen-bonded structure of water molecule only exists because guest molecules stabilize the structure. Methane hydrate is a host lattice of water-ice encloses guest molecules of methane. Methane, made one carbon atom and four hydrogen atoms, is the primary component of natural gas. [1, 3]

In methane hydrate, the gas molecules are not chemical bound to the water molecules but instead they are trapped within their crystalline lattice. The resulting substance looks like white ice, but it does not behave like ice. When methane hydrates dissociate, the solid crystalline lattice turns to liquid water and methane molecules are release as gas. [4]

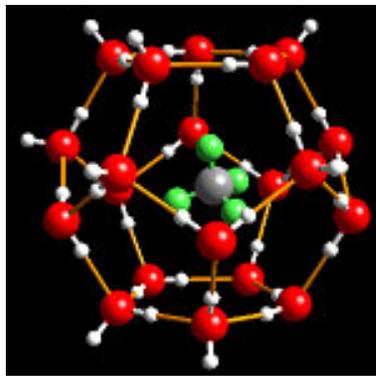


Figure 2: The schematic drawing of a type of gas-hydrate structure in which methane molecules are caged in hydrogen-bonded water molecules. [5]

Methane hydrate is a material very much tied to its environment and requires very specific conditions to form and remain stable. Pressure, temperature, and availability of sufficient quantities of water and methane are the primary factors controlling the methane

hydrate formation stability. If the temperature and pressure are just right, free methane gas and water may form solid methane hydrate. [1, 4-7]

Motivations for gas hydrate studies:

Today's time the rapidly increasing energy demand, natural gas is rapidly becoming premium fuel for this century for two reasons.

- Natural gas gives clean burning. It also makes less pollution than coal and less carbon dioxide emission too.
- Natural gas is also a better feed stock for petrochemical production.

The continuous increase in demand of Natural Gas generates the need to find out new resources for natural gas. Hence, gas hydrate is emerged as a prominent source of natural gas because one volume of methane hydrate contains ~170 volumes of methane gas and largely available at ocean coasts.

Table: 1 Estimated Quantity of Gas Hydrate [1]

| | Estimated Quantity (trillion cubic meters) |
|--------------------------------|--|
| Gas Hydrate in Permafrost Area | 14-34000 |
| Gas Hydrate in Ocean Sediments | 3100-76,00,000 |
| US coastal areas | 3200-19000 |

From above we can reach the following estimation

- Available Natural Gas from Gas Hydrates can serve the demand of human kind for 600 yrs.

- The methane stored in form of Gas Hydrate is two orders of magnitude larger than it is conventionally available.

Gas Hydrate is recently active field for research not only because of potential source of natural gas but also with its unique quality of storage of high volume of gas.

Storage of gas in form of hydrate is important due to following factors:

- Flammable gases are entrapped in crystalline structure. Until dissociation of hydrate they are not harmful to our natural environment.
- High capacity of storage, reducing handling and transportation cost.

The major hindrance here is the rate of formation of Gas Hydrates, because of low solubility of non-polar gases in water, the process becomes slow and not become commercially feasible. Even the higher rate of formation would be necessary to make the process continuous one and efficiently converting gas to the hydrate for storage and transportation. [6-8]

Gas Hydrate can spontaneously form in petroleum production equipment and pipelines associated with deep-water petroleum production and arctic on-shore petroleum production. These unwanted hydrates can clog equipment, preventing the continuous production of hydrocarbons. [9]

Historical Background of Gas Hydrates:

Gas Hydrates have a lot of attention because they are not only a potential cause of pipeline blockage in oil and gas industries but also a promising storage medium for natural gas. These attentions or works can be divided into five parts or phases which are phase I- phase V. [1-9]

Phase I: hydrate as laboratory curiosity

Clathrate hydrates were first observed in the early 1800s by two scientists Humphrey Davy and Michael Faraday [9]. They found the solid material formation when they experimenting with chlorine water mixtures. As a mixtures cooled, the scientists noticed a solid material forming at temperature above the normal freezing point of water. Throughout the remainder of the century, many other scientists were trying to study these strange materials; most of them found that they were typically unstable open frameworks of water molecules of smaller guest into cavities within the structures. [1, 9]

Phase II: Hydrate as an industrial nuisance

In the 1930s, E.G. Hammerschmidt revealed that the hydrate was responsible for plugging natural gas pipelines, particularly those located in cold environments. [9] In the same time another researchers of Dr. Dendy Sloan, at the Colorado school of mines group try to investigate the physics of various catharsis, including the construction of the first predictive models of their formation. [1-9]

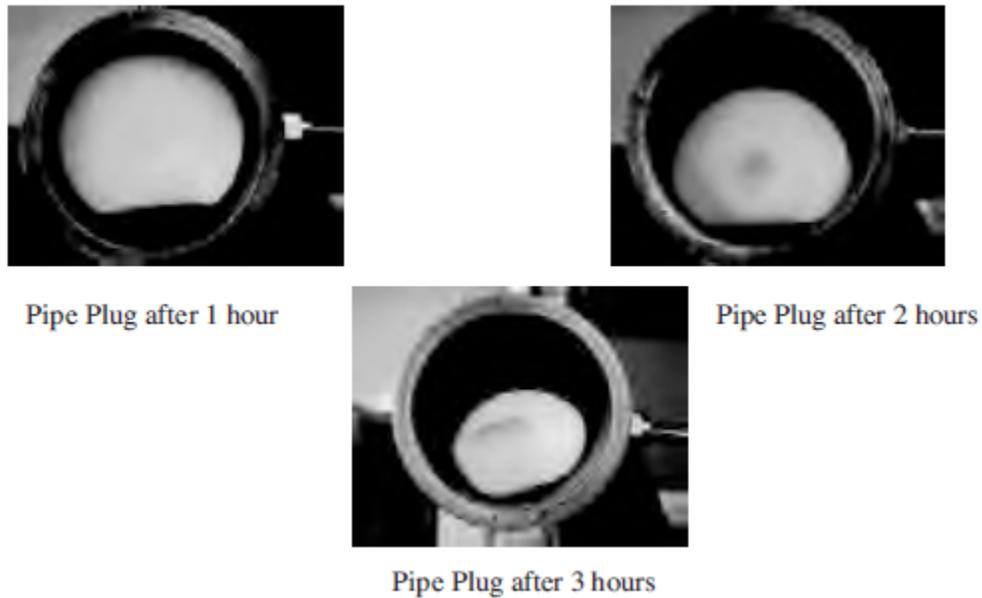


Figure 3: Gas hydrates production from pipe plugging. [10]

Phase III: Hydrate as a naturally occurring substance

In the late 1960s, the western Siberia Basin gas field has found out solid natural gas or methane hydrate as naturally occurring substance under subsurface sediments which changed the global view of clathrate science dramatically. But in mid 1970, the former Soviet Union scientists began to speculate that high pressure and low temperature required for hydrate formation and it should extensively exist in the ocean. They also found hydrate nodules under black sea in 1074. The research vessel Glomer challenger traveled the globe to collect cores of ocean bottom sediment confirms many sediments as evidence of hydrate. [1, 9]

Phase IV: International R&D efforts to test the production potential of natural methane hydrate

In this phase, Japan and India start aggressively well funded hydrate programs for commercial production of methane. Also this time, two wells were drilled into hydrate bearing strata by Canada and Japanese government agencies respectively. Both wells showed the presence of highly concentrated methane hydrate. But production testing was not performed in this phase on either well. Also in this phase, it was well clear that ignorance of study and preparation of commercial methane hydrate, the United States was behind than others. [1, 9]

Phase V: Current Research and Development Trends

In this phase, US congress offered legislation that culminated in the signing into law of the “Methane Hydrate research and development act of 2000”.

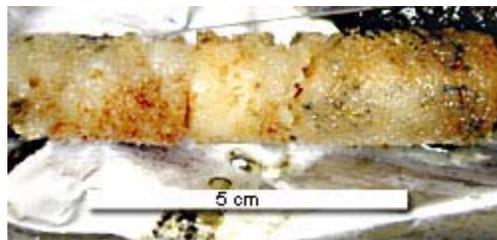


Figure 4: Core recovered from Johnson Sealink cruise in the golf of Mexico in July 2001. [9]

Currently by realizing the importance of gas hydrate, there is a great emphasis on gas hydrate research to make a commercial process of recovering gas hydrate from deep ocean bottoms. The geological survey already figured out the location and depth of the gas hydrate sites available around the globe. [1, 9]



Figure 5: methane bubbles escaping from sea floor. [11]

In 2002, a series of experiments tested by Mallik consortium to both thermal simulation and depressurization. Both methods resulted in hydrate dissociation and the release of gas, which is confirmed the technical feasibility of methane production. [1, 9]

A survey of the accuracy of hydrate phase equilibrium prediction programs was recently made by Ballard and Sloan. [10] Five different prediction programs were tested against all of the published hydrate data (1685 points) [10] in the following six categories:

- Single guest (simple) hydrates (632 points)
- Binary guest hydrates (747 points)
- Ternary guest hydrates (89 points)

- Natural gas mixed hydrates (72 points)
- Black oil and gas condensate hydrates (10 points)
- Structure H hydrate formers (135 points)

Most recent area of research is to use gas hydrate to separate close boiling compound and to break azeotropes. Another area of great research is to separate methane with help of carbon dioxide because phase equilibrium lines close enough to make this process feasible. This will help to reduce the problem of global warming by eliminating carbon dioxide from the atmosphere.

Structure of Gas Hydrate

Gas hydrate shows highly organized structure like zeolites. The main difference between them is guest molecules move freely inside zeolites whereas host molecules are stationary in hydrates. Gas hydrates generally have three different crystal types. They are type I, type II and type H. Each type of hydrate has a different number and size of the cavities in the unit cell. [1, 9]

Type I:

- This structure predominates in earth's environment; it contains small molecules (0.4-0.55 nm) as guests.
- The common molecules that form Type I hydrates are: methane, ethane, carbon dioxide, and hydrogen sulfide.
- Type I hydrates are made up of 8 polyhedral cages -- 6 large ones ($5^{12}6^2$) and 2 small (5^{12}). They are made up of 46 water molecules and thus have a theoretical composition of $8X \cdot 46 \text{H}_2\text{O}$ or $X \cdot 5 \frac{3}{4} \text{H}_2\text{O}$, where X is the guest molecule.
- To form small cavities 5^{12} , molecules are joined from their vertices and for the large cavities $5^{12}6^2$, the large 5^{12} is filled with other 6^2 cavities to relieve the strain induced due to large size.



Figure 6: Type I cavities containing gas molecule in the structure with 14 faces in which 12 pentagonal and 2 hexagonal faces. [12]

Type II

- This structure generally occurs with comparatively larger (0.6-0.7nm) guest molecules in mostly man-made environment
- The Type II hydrate former includes: propane, iso-butane, though nitrogen is comparatively smaller still it forms Type II hydrates.
- Type II hydrates are made up of 24 polyhedral cages -- 8 large ones ($5^{12} 6^4$) and 16 small (5^{12}). They are made up of 136 water molecules and thus have a theoretical composition of $24 X \cdot 136 H_2O$ or $X \cdot 5 \frac{2}{3} H_2O$. If only the large cages are occupied, which is typical, then the theoretical composition is $8 X \cdot 136 H_2O$ or $X \cdot 17 H_2O$.



Figure 7: Structures of Type II Hydrates containing 8 large and 16 small faces. [12]

Type H

- Type H hydrates are formed by larger molecules but only in the presence of a smaller molecule, such as methane. Type H hydrates only form in the presence of both the large and small molecules.
- Type H hydrates are made up of six polyhedral cages - 1 large, 3 medium and 2 small. The large molecule occupies the large cage and the small molecule occupies the small and medium cages. They are made up of 34 water molecules and have a theoretical composition of $X \cdot 5 Y \cdot 34 H_2O$ where X is the large molecule and Y is the small.
- Type H formers include: 2-methylbutane, methylcyclopentane, methylcyclohexane, and cyclooctane. It bears repeating, Type H hydrates only form if another, small molecule (such as methane) is present.

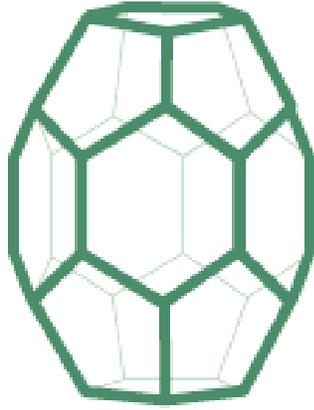


Figure 8: Structures of Type H Hydrates containing 8 large and 16 small faces. [12]

Chapter-2. The Gemini surfactant effect on gas hydrate formation

Hydrate formation is a stochastic and slow process. In this work, we try to improve hydrate formation by using doubly charged surfactants. We choose two noble Dow surfactants for promoting hydrate growth and their adsorption isotherms on cyclopentane hydrates. The structure of Dowfax surfactants are shown below:

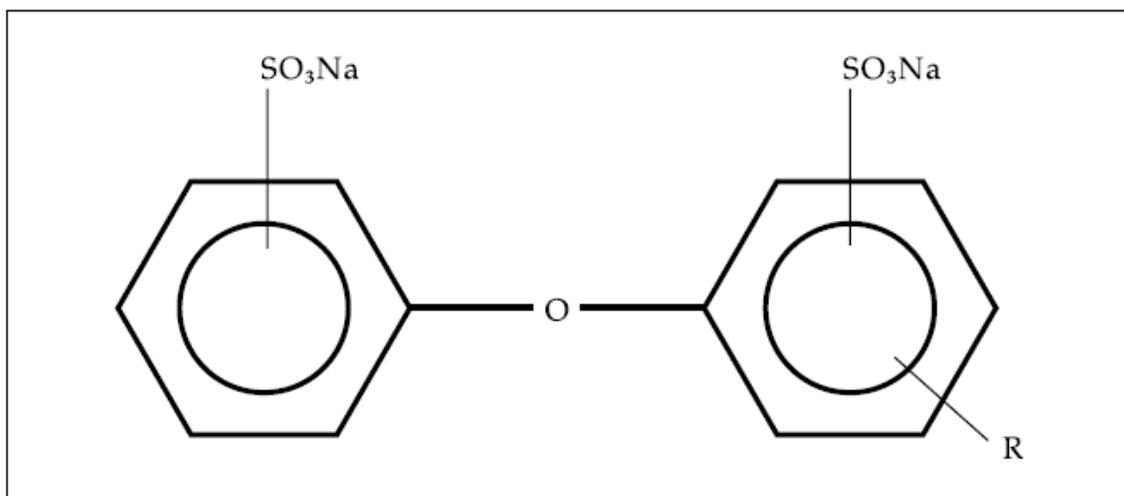


Figure 9: structure of Dowfax surfactants. [13]

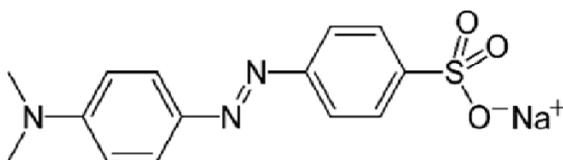
R=Carbon Hydrophobe

DOWFAX C6L: Linear 6- Carbon Hydrophobe.

DOWFAX 2A1: Branched 12 Carbon Hydrophobe

DOWFAX 3B2: Linear 10 Carbon Hydrophobe

DOWFAX 8390: Linear 16 Carbon Hydrophobe



Methyl Orange

Figure 10: Structure of Methyl Orange used as an indicator for titration [14]

Two different surfactants are dowfax8390 and dowfax3B2. These dowfax surfactants have doubly charged head groups which may promote hydrate formation because Zhang et al. [6] proposed that the higher negative charges they have, the higher hydrate formation rate they cause. The adsorption behavior between these two surfactants will determine the active roles of these dowfax surfactants.

Dowfax surfactants are doubly charged with two anionic sulfate heads. Along with the idea of more negative charges being the contributing factor for promotion [6], having two heads may lead to increased hydrate promotion due to electrostatic repulsion of hydrate particles.

By titrating noble doubly charged surfactants, adsorption isotherms are observed. These titrations are called back titration. This method utilizes methyl orange, which is an anionic indicator. Methyl orange is able to attract only positively charged molecules. The adsorption isotherms can reveal the mechanisms of the surfactant adsorption on hydrate.

Experimental Section

Materials:

Cyclopentane (CP) and dodecyl trimethylammonium bromide (DTAB) were purchased from Sigma-Aldrich with a purity of + 99%. Methyl Orange was also purchased from Sigma-Aldrich with indicator purity. Sulfuric acid 96% and sodium sulfate 99% were supplied by Sigma-Aldrich. Dowfax8390 and Dowfax3B2 samples were generously supplied by Dow Chemical. The ultra high purity of methane (99.997) was purchased from Praxair for high-pressure methane hydrate formation experiments. All chemicals were used as received without further purification. Deionized (D.I.) water was produced in our lab with a resistivity of $18 \text{ M}\Omega \text{ cm}^{-1}$.

Calibration Experiments:

To make our reference solutions, we need molecular weight of the surfactants. Problem is that the molecular weights of them are unknown. But their weight percentages of surfactants are given. So we try to find a relation between wt% and mM of each surfactant. For that we use a titration method by using known concentrations of DTAB. First, we found the molar amount of DTAB which we used for the titration of known wt% of surfactant. The half of the molar amount of DTAB will be the molar amount of the Dow surfactants having two negatively charged heads. Then we plot the recorded data

which were obtained from titration. And finally we got our equation of relation between the wt% and mM of the surfactants. The equations are shown below.

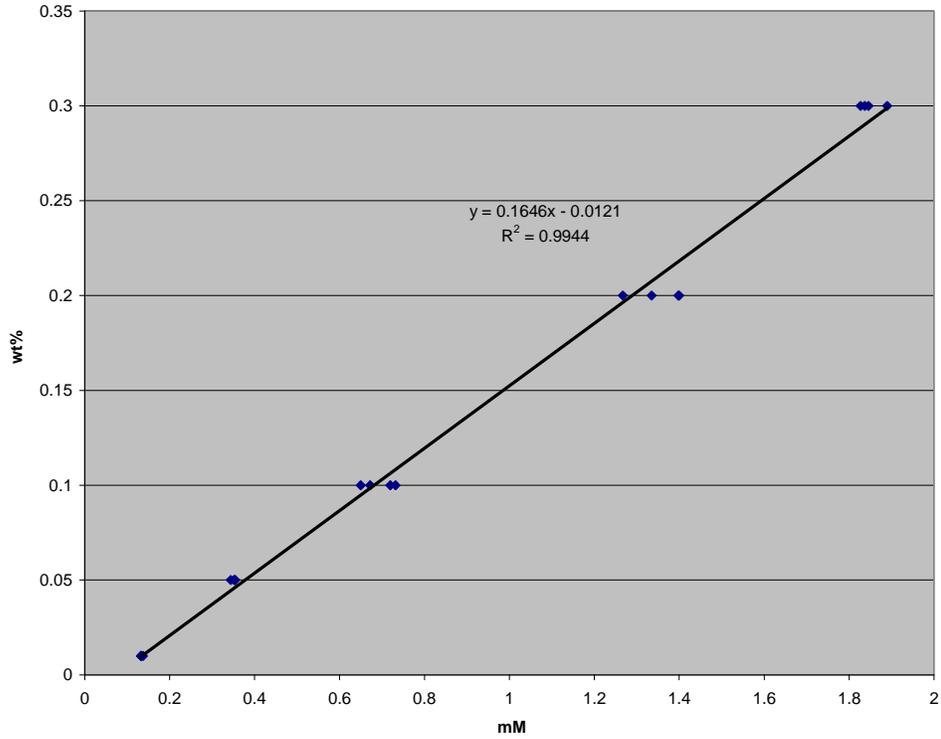


Figure 11: the calibration equation of Dowfax3B2 surfactant.

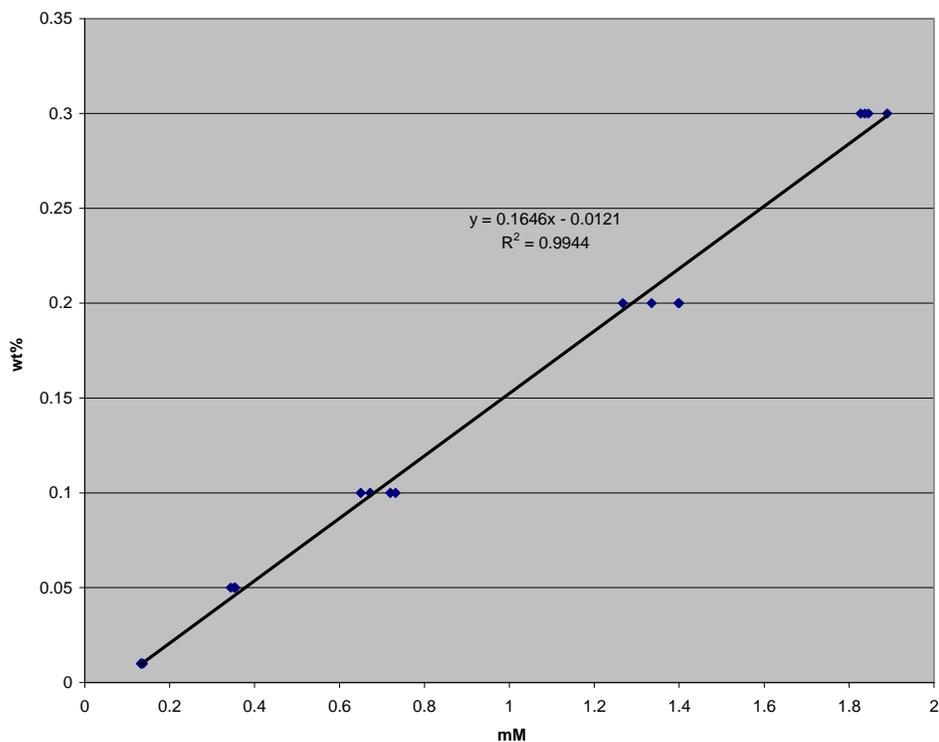


Figure 12: the calibration equation of Dowfax8390 surfactant.

Isotherm experiment:

Preparations of CP hydrate slurries: A 10 wt% of CP-water mixture was charged to a 500 mL polypropylene bottle and hermetically sealed. Then it was placed in a freezer at a temperature of 263 K. After ice formation, the bottle was vigorously shaken at ambient conditions. When ice melts, CP is enclathrated at the same time. The formation of CP hydrates was confirmed by the appearance of white particles. The bottle was put in a chiller at 277 K for one week and shaken daily to accelerate the enclathration. The concentration of CP hydrates in slurries was found to be 51 wt % by calorimetric measurements. The reason we started with CP hydrate slurries instead of solid CP hydrates in adsorption measurements is to avoid the variation of vapor condensation on

hydrate particles and to avoid variation of total hydrate surface area when adding hydrate former in surfactant solutions. Preparing CP hydrates from surfactant solutions first could result in different particle sizes due to the effect of surfactants on the enclathration

Preparation of the mixture of hydrate slurry and surfactant solution:

First ten grams of surfactant solutions were charged to a 25 mL vial. Then we placed it in a chiller at 277 K overnight. Next day, ten grams of CP hydrate slurries were quickly added to the solutions (both the slurries and solutions were put in an ice bath). Then, the vial was sealed by Para film and kept in a chiller at 277 K for ten days to allow the adsorption to reach equilibrium. The vial was shaken daily to accelerate surfactant adsorption on hydrates. Because of the density difference between hydrates and solutions, all of CP hydrates were located at the upper portion of vials. Finally, after ten days we withdrew several milliliters of solution from the lower portion of the vial by using a 10 mL plastic syringe. And we assumed that there will be no more hydrates in that withdrawn solution.

Titration:

0.5 gram of the unknown surfactant solution is place into a 20 mL test tube. Then for Dowfax 8390, 2.5 g of orange indicator solution containing 0.003 wt % Methylene orange, 1.20 wt % sulfuric acid, and 5.00 wt % sodium sulfate were added, and also 2.5 g of Chloroform was charged to the test tube. In the same way, for Dowfax 3B2, 2.5 g of orange indicator solution containing 0.003 wt % Methyl Orange, 1.20 wt % sulfuric acid, and 5.00 wt % sodium sulfate was added, and then 2.5 g of Chloroform was charged to

the test tube. These were then shaken to promote mass transfer and titrated with a known DTAB solution. We collect the end point of titration. The start and end points of these experiments are shown in following figure.

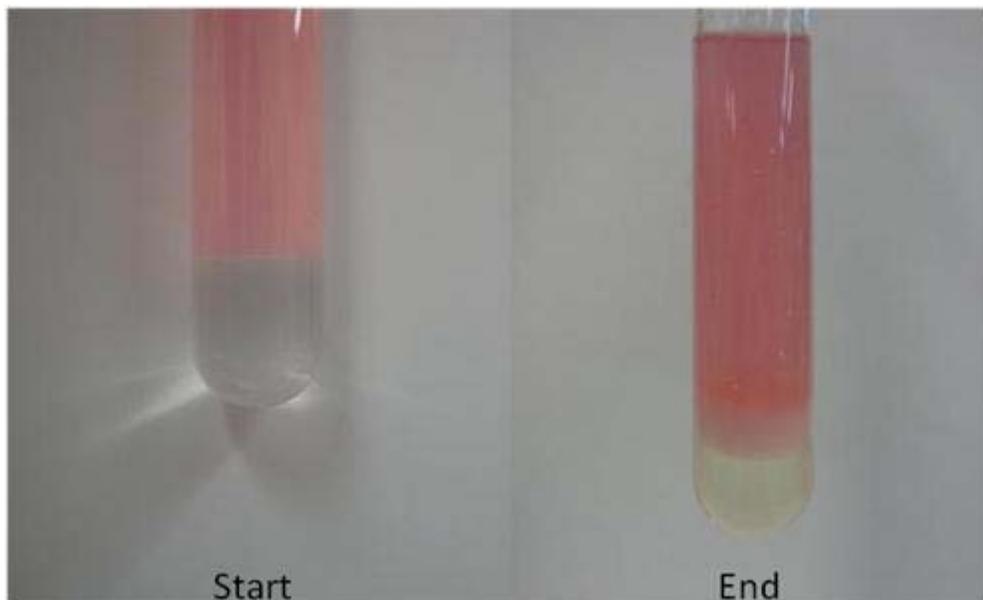


Figure 13: The start and end point of titration.

The liquid-liquid back titration method is used for Dowfax8390 and dowfax3B2. Methyl Orange is able to attract only positively charged molecules like DTAB, which we use to titrate. Once the formation of DTAB-Dowfax8390 and dowfax3B2 complexes is completed, DTAB-Methyl Orange can form complexes with each other. The result is a yellow color in the chloroform layer.

High pressure methane hydrate formation experiments

To relate the surfactant isotherm results to high-pressure hydrate forming systems, methane hydrates are made in an acquiescent system. We will maintain the pressure and temperature of the formation of methane hydrates using a high pressure reactor. This will

be the essential proof that will determine whether the hypothesis of increased hydrophobicity at the hydrate/water interface will increase fast formation.

High-pressure reactor system: Figure 14 shows the schematic diagram of the experimental setup to analyze the nucleation and growth of methane hydrate in the presence of surfactants. For this experiment we used a 450 mL high pressure reactor that was purchased from Parr Instruments with two view windows. However, the actual volume of the reactor with void space of fitting is 474 mL. The reactor temperature was controlled by using Isotemp 3006P thermostat with circulating coolant with a stability of 0.01 K inside the jacket around the cell. The temperature of the reactor was monitored with two type-T thermocouples (Omega Engineering), where one was immersed in the liquid and the other was placed in the headspace. The accuracy of the temperature measurement is ± 0.5 K. The pressure of the reactor is measured by using a 9001PDM pressure transducer (Ashcroft) with an accuracy of ± 0.03 MPa. This pressure transducer can measure 0-34.47 MPa. The temperatures of the liquid and gas phases as well as the pressure were sampled every 20 s by the Labview interface and recorded in a computer.

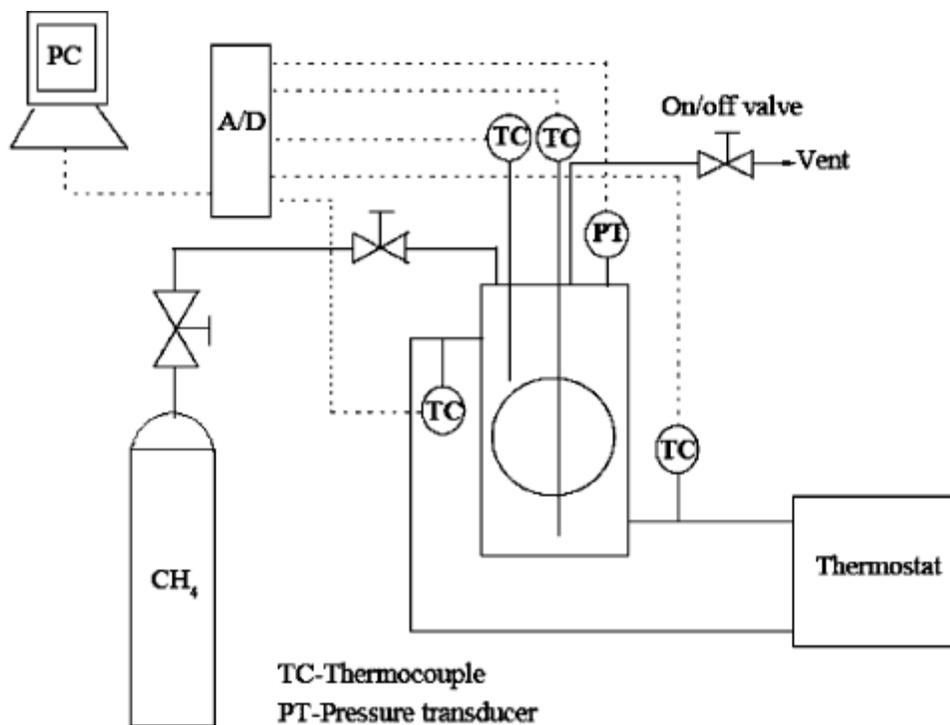


Figure 14: The schematic diagram of experimental setup. [6]

Procedure: We charged 150 mL of surfactant solution to the reactor followed by setting the reactor temperature to 12°C. Then we purged the reactor twice with methane up to 200psi pressure. After that, methane introduced to the reactor up to 7.1 MPa. We injected 1 mL of CP to the reactor at 1mL/min after methane charge was completed for 15 min. After 5 min of CP injection, the reactor was cooled to 1°C and the reactor was maintained at that temperature rest of the run.

Results and discussion

Adsorption Isotherms:

Adsorption isotherms were used in this study to quantify the adsorption of dowfax surfactants on CP hydrate-water interface at different aqueous surfactant concentrations. From the adsorption isotherm, we can better understand the effect of surfactants on CP adsorption and the role of surfactants in enclathration. We do not have any previous data for the equilibrium adsorption. Lo et al. [5, 15] determined the adsorption isotherm of SDS onto the CP hydrate-water interface and they identified the type of isotherm as L-S type with the amount of SDS adsorbed at the first step of the Langmuir isotherm reported as 0.01 mM SDS/g of CP Hydrate.

The adsorption of Dowfax 3B2 and 8390 are shown in figure 15 and 16. They both exhibit favorable affinity to hydrate interface. But the adsorption isotherms are slightly different. Dowfax 3B2 adsorption isotherm shows an L-S type isotherm. The first step (0.2 to 0.7 mM) has a leveling off about 0.02 mM/g hydrate, which is approximately linear shape. The second step is starting above 0.7 mM. This adsorption isotherm is similar to SDS in respect to its low adsorption amount. [14] From Figure 15, it shows that monolayer coverage at the CP hydrate-water interface at a lower concentration. The monolayer forms at an equilibrium concentration ranging from 0.2 to 0.7 mM of 3B2 equilibrium concentration. The graph also shows bi-layer coverage at the hydrate-water interface. The dense and highly charged layer would act to reduce the adhesion of hydrates to each other and provide a barrier for hydrate growth.

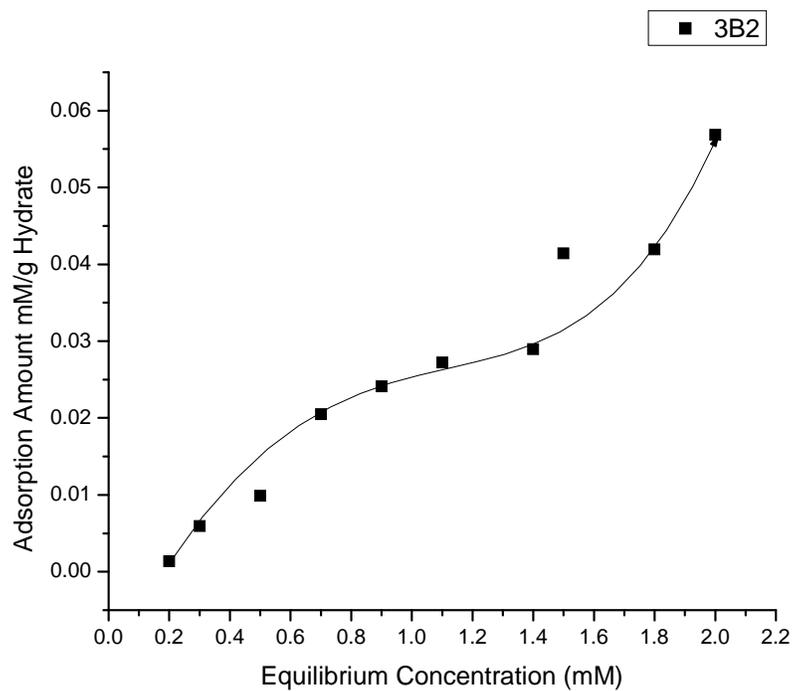


Figure 15: An adsorption isotherm of Dowfax 3B2 on CP hydrates

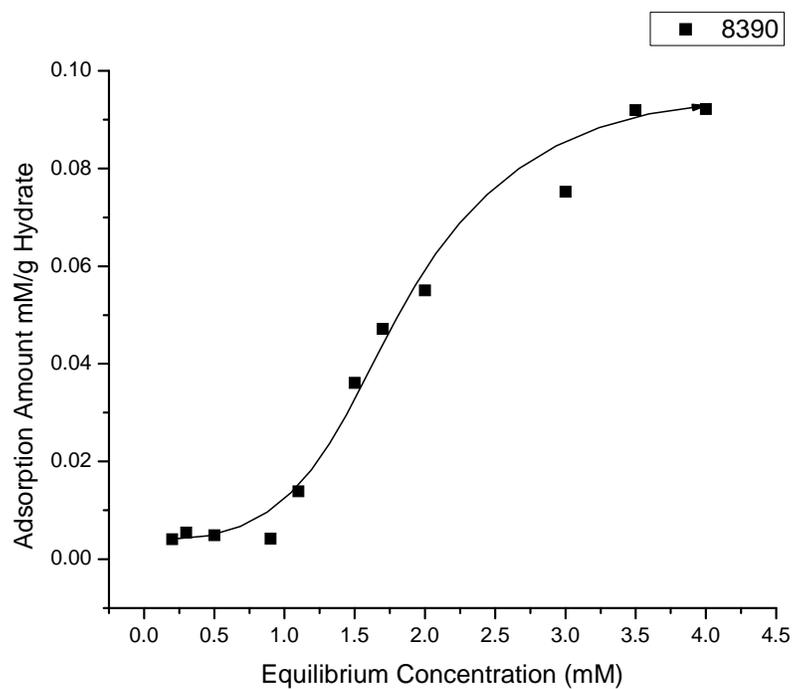


Figure 16: An adsorption isotherm of Dowfax 8390 on CP hydrates.

In Figure 16, the adsorption isotherm of Dowfax 8390 appears to be S type curve, which means that it is bi-layer coverage at the hydrate-water interface.

High-pressure methane hydrates formation:

Figure 17 and 18 shows profiles of temperature and pressure during the enclathration with 600ppm of the Dow surfactants. Here the surfactants concentration is the one at the start of cooling and the time is also set to be zero at this point. As shown in Figure 17, the temperature spike is observed at 0.277h surfactant 8390, at 1.0h surfactant C6L, at 9.0h surfactant 2A1 and at 13.0h surfactant 3B2 with 600ppm.

Dowfax 8390 shows the fastest hydrate formation from all of four surfactants. It also happens at around 10°C compared to the cases of other surfactants, because it needs less energy to cool down the system. Also the first hydrate formation pressure (72.82 bar) is lower than the equilibrium pressure (75.19 bar) of methane hydrate formation at the peak temperature (9.89°C). Figure 18 also shows that the pressure decreases from 74.18 to 36.42 bar within 2.5h after the onset of enclathration. But the other three surfactants decreases to around 33 bars which is lower than 8390 surfactant. The induction time also is lowest for 8390 surfactant and highest for 3B2. The induction time for 2A1 and 3B2 is longer than 8390 and C6L surfactants.

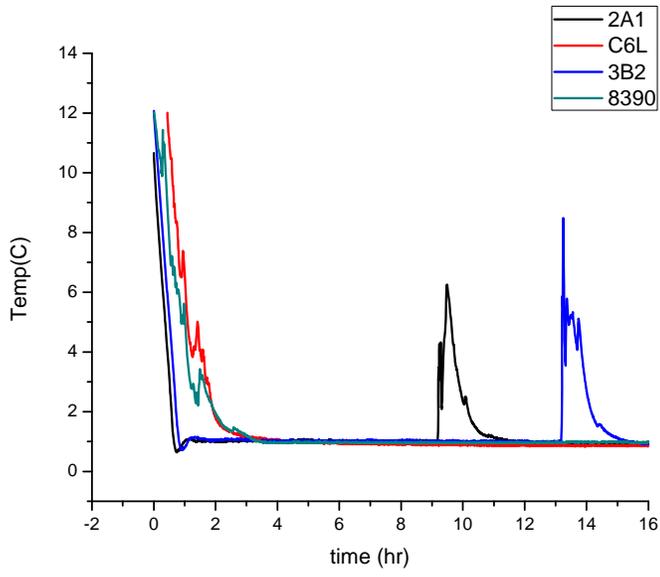


Figure 17: Profile of temperature during the enclathration with 600ppm of surfactants.

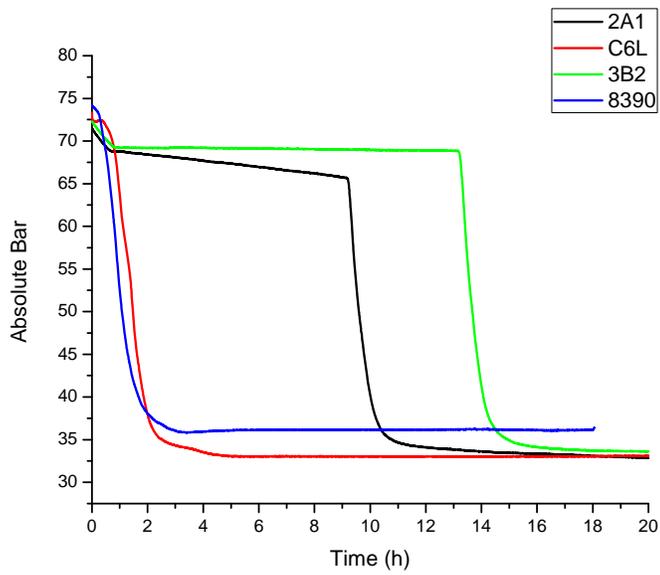


Figure 18: Profiles of pressure during the enclathration with 600ppm of surfactants.

Conclusions

In this work, the effect of Dowfax surfactants at the CP hydrate-water interface was investigated and analyzed using adsorption isotherms. Also we try to proof our concept by using high pressure reactor to form methane hydrate with those surfactants. We have determined the roles of these similar surfactants and how they can be used on hydrate formation processes. Though the main structure and the head groups are similar, but each of them can act differently and have a different purpose on hydrate formations. The isotherm of Dowfax 8390 is similar to the most effective surfactant promoter molecule, SDS. This indicates that Dowfax 8390 may be act a promoter molecule as like as SDS. The affinity of Dowfax surfactant chains to hydrates is proportional to the number of hydrogen bonds formed between head groups and pendant hydrogen on the hydrate surface. Hydrophobic microdomains, into which hydrocarbon molecules could solubilize, occur on the hydrate surface at high surfactant concentrations. These are the reasons may be the factor for fast hydrate formations.

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