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Hydrate Formation Using Dowfax Gemini Surfactants

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Hydrate Formation Using Dowfax Gemini Surfactants

THESIS

Submitted in partial fulfillment of
the requirement for the degree

Master of Engineering (Chemical Engineering)

at

The City College

of the
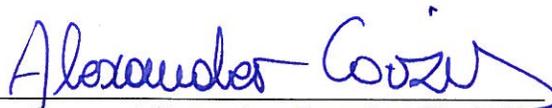
City University of New York

by

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Abstract:

Gas hydrate formation is a stochastic and slow process. However, the use of a small amount of surfactant can speed up the rate of hydrate formation. This work investigates the effect of two Dow surfactants, Dowfax 2A1 and Dowfax C6L, on gas hydrate formation, first by determining the adsorption isotherms via liquid-liquid titration methods, and then investigating the role in methane hydrate formation in a non-stirred batch reactor. Both surfactants have almost similar structure, sharing doubly charged headgroups, but these surfactants express different effects on hydrate formation. 2A1 and C6L both show monolayer formation at around concentration of 1.0 mM; however the isotherm of Dowfax 2A1 shows multi-layer type of adsorption whereas that of Dowfax C6L shows monolayer adsorption only. High pressure experiment results reveal that 2A1 has a faster induction and growth than C6L. Thus, 2AI is a more suitable hydrate promoter than C6L.

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Acknowledgements:

I'd like to take this opportunity to give thanks to those who have supported me throughout the time I was doing research, this thesis would not have been possible to accomplish without them.

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I would also like to thank my classmates who worked alongside me in the hydrate lab. You have all been such a great help to me, taking some time out to help me better understand an experimental procedure, or help me out with a problem when I didn't understand. I will not forget.

Lastly I would like to thank all my friends and family who, during times I thought I would lose my sanity, helped me to somehow stay sane during the good times and bad. Thank you, everyone.

1. Introduction

Gas hydrates are nonstoichiometric crystalline compounds in which a network of hydrogen-bonded molecules surrounds a guest molecule (usually one of low molecular weight).[1] Hydrate structures can be classified by cavity sizes as sI, sII, and sH, with sI structures having the smallest cavity size and sH having the largest cavity size, respectively. sI type hydrates have a hydration number of 5.75 H_2O; examples of guest molecules of sI hydrates include carbon dioxide, methane, and ethane.[2] sII hydrates have a hydration number of 17 H_2O; guest molecules of sII hydrates have a moderate size range, examples of such guest molecules include propane, isobutene, and cyclopentane.[2] sH hydrates are more unique in that they can encapsulate large guest molecules ($\leq$ 9 Å) with the help of smaller ones.[3]

Gas hydrates were discovered in the early 1800's by Sir Humphrey Davy[4]; the discovery of gas hydrates spurred on greater interest in hydrate molecules. In the 1930's, Hammerschmidt's discovery of gas hydrate formation above the ice point in oil pipes[5] led to the application-oriented study of gas hydrates.

There are many motivations for studying gas hydrates. One such motivation is its potential as a form of energy storage. One volume of gas hydrates can store up to 170 volumes of gas at STP conditions, this under the assumption that all of the cavities are occupied by a guest molecule.[1] This could be used in an advantageous way, wherein gas hydrates can serve as a promising storage medium for energy forms such as natural gases and hydrogen.[6]

The capabilities of gas hydrates as a form of storage has also led some to consider gas hydrates as a means to reduce greenhouse gases. The need to reduce the amount of carbon dioxide in the

atmosphere, and fears of the "clathrate gun" hypothesis had led some to look into the possibility of using hydrates as a means of carbon sequestration and methane sequestration.[7]

In the petroleum industry, gas hydrates serve more as a nuisance than something desirable since they can clog up equipment and prevent further production of hydrocarbons[8] – in this case, the motivation behind hydrate study is to instead find ways to prevent hydrate formation.

One of the major issues to address when considering the application of hydrates is the slow and stochastic rate of hydrate formation. Mixing and agitation can be employed to induce the formation process. Conversion, however, is usually incomplete due to the diffusion limitation of guest molecules.[9] Previous studies, however, have found that surfactants, such as sodium dodecyl sulfate (SDS), can greatly enhance the hydrate formation rate with greater amounts of conversion.[6,10,11]

Although it is known that surfactants can be used to speed up hydrate formation, one might want to look into the structure of the surfactant itself to see if it has any significant effect on hydrate formation. In this case, Gemini surfactants are of interest given its unusual structure. Whereas the typical surfactant molecule consists of a single hydrophilic head and a hydrophobic tail, Gemini surfactants can be described as two surfactant molecules joined by a spacer.[12] They're considered to be more superior than conventional surfactants in terms of surface activity.[8] For the case of the study of hydrate formation, the use of doubly charged surfactants might prove better for hydrate formation on account that Gemini surfactants contain two hydrophilic heads instead of one. Previous initial studies by Lo et al.[11] investigated the use of two surfactants, Dowfax surfactants, 2A1 and C6L, both of which are Gemini surfactants that contain two anionic heads instead of one. Lo's initial studies on the structure of these two Dowfax surfactants

suggested that 2A1 might be better for hydrate formation than C6L. This paper further investigates the effects of the above mentioned Dowfax surfactants on hydrate formation.

1.1. Effect of Surfactants on Gas Hydrate Formation

There have been previous studies of the effects of surfactants on hydrate formation. Looking into these studies gives insight into the adsorption mechanism of hydrate formation and what role these surfactants have played on them. In consideration that the Dowfax Gemini surfactants being studied in this paper are anionic surfactants, one can look into previous studies regarding other anionic surfactants and their effects on hydrate formation; previous studies by Lo et al.[6,10,11] proposed the mechanism of how hydrates interact with the hydrate surface, which can provide some clues as to how an anionic surfactant improves the rate of hydrate formation.

At relatively low concentrations, it was found that surfactant molecules take up adsorption sites on the surface of the cyclopentane (CP) hydrate, in which the surfactant chains lay down low on the hydrate surface, with both headgroups and tails touching the surface; the hydrogen bonding between the hydrate surface and the head of the surfactant molecules, as well as the slightly hydrophobic surface of the hydrate surface that attracts the hydrophobic tails of surfactants, causes the surfactant molecules to configure in this manner.[10]

However, the hydrophobic nature of the surfactant tails is weaker than the hydrogen bonding between the surfactant head and the hydrate surface;[6] as the concentration of surfactant in the aqueous phase increases, hydrophobic force causes the tails of the chain to align parallel to each other as opposed to bonding with the hydrate surface; this results in the surfactant heads staying close to the hydrate surface while the surfactant tails become oriented towards the aqueous phase

forms, resulting in the formation of a surfactant monolayer on top of the hydrate surface.[10] At even higher concentration, surrounding surfactants molecules can also occupy this monolayer, in which the tails of the surrounding free surfactants molecules interact with the tails of the surfactants found in the monolayer, thus resulting in a bilayer of surfactant molecules on top of the hydrate surface.[10]
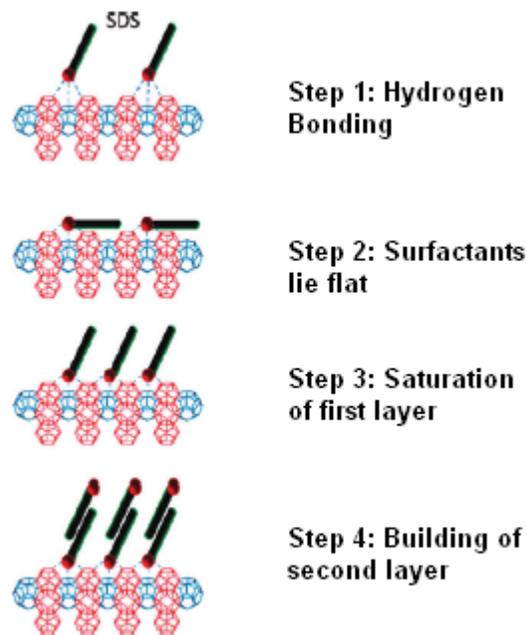
Figure 1.1. Schematic of surfactant (SDS is shown) adsorption on hydrate surface.[11]

Isotherms of surfactant adsorption can be used to quantitatively show the effects of different surfactant concentrations can affect hydrate formation. Lo et al.'s study[11] showed that the isotherm of SDS on hydrate formation was that of an L-S (two-plateau) type; the plateaus in the isotherm are indicators of a formation of a surfactant monolayer and later a bilayer around the hydrates as surfactants concentration increased.

The effectiveness of surfactants on hydrate formation depends on the surfactant concentration. Studies suggest that rapid formation occurs when the surfactant concentration is enough to form

a monolayer. A previous study by Zhong and Rogers[13] looked into the effectiveness of SDS on ethane enclathration, of which it was found that around 1.0 mM of SDS was the effective concentration of ethane enclathration, which suggests that a surfactant monolayer starts forming at around this concentration.

The reason as to why monolayer formation encourages hydrate growth is still unknown. One possible explanation is that the surfactants on the surface of the hydrate molecules change the net surface charge of the hydrate; a study by Beecraft and Richmond[14] of the CaF_2-water interface found that enclathration was favorable as the net surface charge increased; perhaps the same behavior could also be applied to the hydrate-water interface where the surfactant charge contributes to the overall net surface charge. At the monolayer when hydrate tails are parallel to each other, hydrophobic microdomains form around hydrate particles, forming an area into which hydrate formers could solubize.[11] Another possible explanation for the fast formation of hydrates in the presence of surfactants is reduced adhesion force between hydrate particles[15], (also caused by increasing the net charge), or the surfactants forming an adsorbed layer around the hydrate particles[11], or perhaps even both occurring, resulting in the lowered possibility of agglomeration, and thus increasing the total surface area at which hydrate growth can proceed and increasing the length of time of contact between water molecules and the guest molecules.[11]

Another aspect of surfactants that could also play a role in the rate of hydrate formation is the surfactant carbon chain length. A study by Daimaru et al.[16] studied the rate of hydrate formation using various anionic surfactants that contained similar structures differing only in the length of the carbon chains (which were C4, C12, and C18, respectively); it was discovered that the rate of hydrate formation improved best using the surfactant with the shortest carbon chain.

1.2. Gemini Surfactant Effect on Gas Hydrate Formation

In the previous section, it was suggested that an increased net surface charge can play a role in the rate of hydrate formation; Lo suggested that perhaps the presence of two anionic heads in Gemini surfactants promotes better hydrate growth because of the increased negative charge.[11]

Very few studies have been done on how Gemini surfactants can affect the rate of hydrate formation. Mishal's study[17] of the effects of Gemini surfactant on the rate of methane hydrate formation notes that the formation rate of gas hydrates increased linearly in the and plateau at some maximum; Mishal attributes this increase in formation rate due to an increase in the solubility and mass transfer conductance of the surfactant.

A previous study by Kwon et al.[18] did examine the effects of Gemini surfactants on hydrate formation; however, the surfactants used in Kwon's study were anionic multi-chain surfactants that varied in length (an experiment very much similar to Daimaru's study of single-chain surfactants[17]); the surfactants used in Kwon's study may not be applicable to all Gemini surfactants given that not all Gemini surfactants have multiple carbon chains and can take on various structures.[12] It is important to note this difference in structure since reasons for applications and usage of a specific type of surfactants depend largely on the surfactant's overall structure and interfacial properties.[11]

Previous preliminary work by Lo[11] studied the effects of two Gemini surfactants, Dowfax 2A1 and Dowfax C6L, both of which are produced by the Dow Company, respectively. These two surfactants are similar in chemical structure, and they contain two anionic sulfate heads.
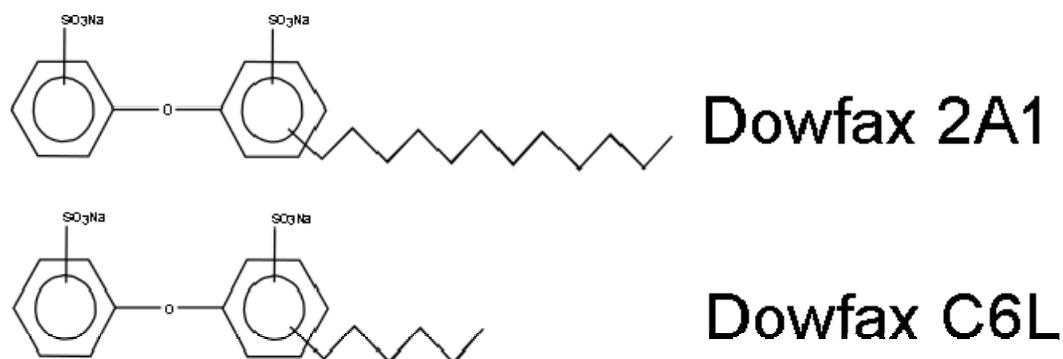
Figure 1.2. Chemical structures of Dowfax 2A1 and C6L.[11]

The main differences between 2A1 and C6L are in the length of their hydrophobic tails and in the bending of the C-O-C movement. C6L having the shorter hydrophobic tail, containing only six carbon molecules, as opposed to 2A1, which has a longer tail containing twelve carbon molecules. ATR measurements seen on Figure 1.3 reveal that 2A1 has C-O-C bending movements, whereas C6L does not have this bending movement such that its structure is more rigid.

Lo's preliminary work suggests that, although the two Gemini surfactants have the same head and similar structures, they may have different effects in terms of hydrate formation.[11] RAMAN spectroscopy experiments have revealed that 2A1 has a blue shift in the ring breathing of cyclopentane, whereas this blue shift is not expressed in C6L, as seen in Figure 1.4

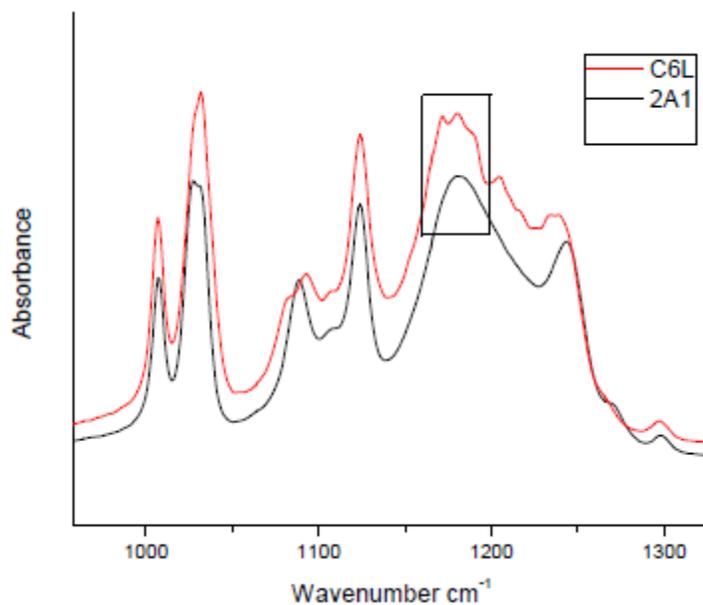**Figure 1.3.** ATR-IR spectra graph for Dowfax 2A1 and C6L. C-O-C stretch region is encircled in image.[11]
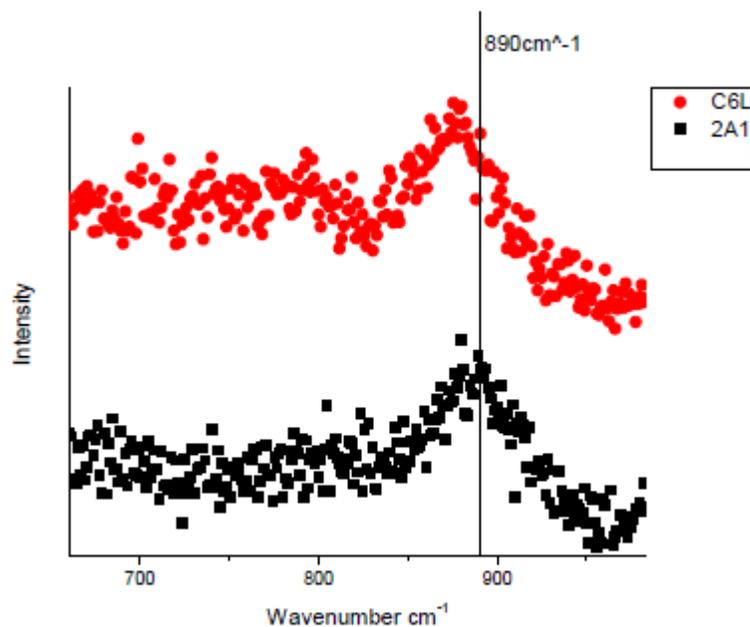
Figure 1.4. Raman Spectra of the CP ring breathing for 1 wt% CP in two 1wt% Dowfax surfactants.[11]

The presence of the blue shift in 2A1 suggests that it contains a hydrate-like environment, whereas the lack of the blue shift for C6L indicates otherwise. This suggests that C6L might

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serve better as an anti-agglomerate agent whereas 2A1 might serve better in promoting hydrate formation.[11]

Lo's study also contains some initial titration work in producing adsorption isotherm graphs for 2A1 and C6L to help quantify the effects of 2A1 and C6L on hydrate formation.[11]. His initial work suggested that 2A1 has the shape of an L-S isotherm as described by Zhu et al.[18], whereas C6L seems to have the shape of a Langmuir isotherm.[11]
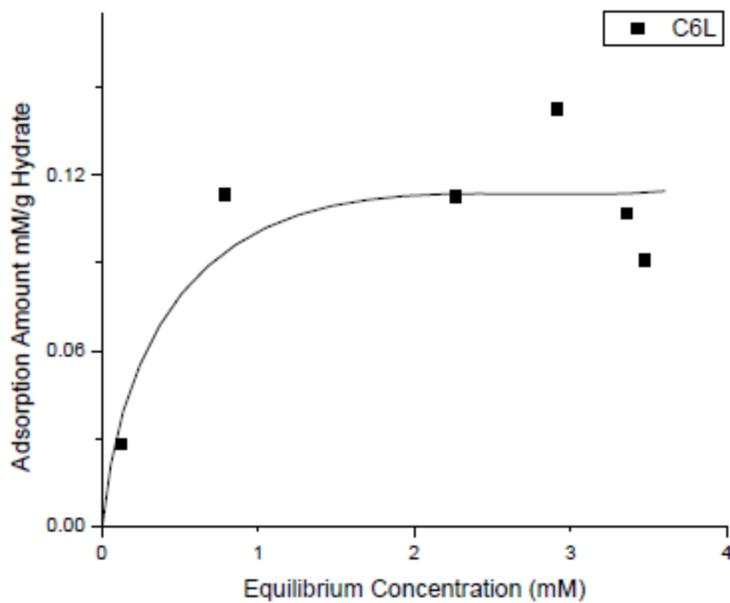
Figure 1.5. Lo's initial adsorption isotherm diagram for Dowfax 2A1.[11]
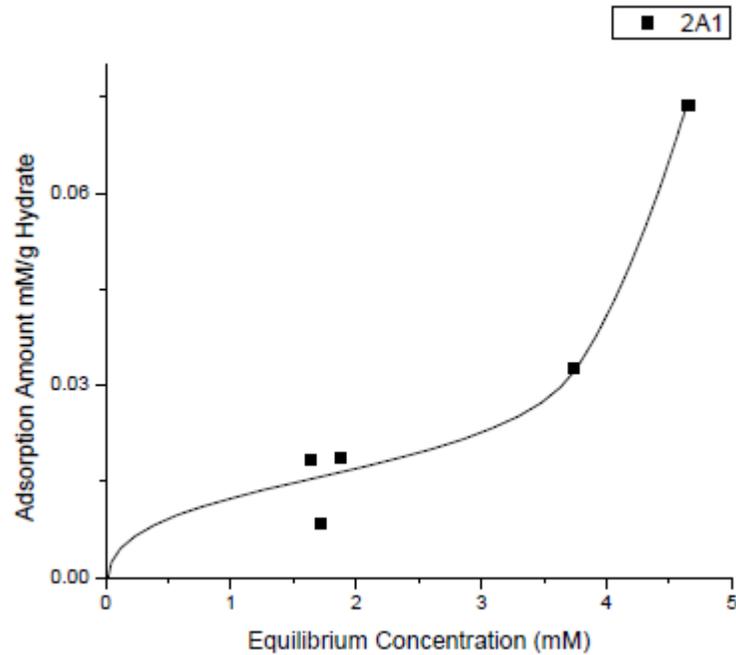
Figure 1.6. Lo's initial adsorption isotherm diagram for Dowfax 2A1.[11]

The work, however, was preliminary and needed to be finalized with more data points; kinetic data was also needed to compare the promotion effects of 2A1 and C6L to that of SDS.

Although there has been previous work studying the effects of some Gemini surfactants on hydrate formation, in general, more study still needs to be done to better understand how some surfactant structure can affect the rate of hydrate growth.

Thus, this thesis mainly focuses on the adsorption study of two Dow surfactants, Dowfax 2A1 and Dowfax C6L, onto the cyclopentane (CP) hydrate-water interface and their effects on gas hydrate formation.

The next chapter describes the experimental procedures designed to further study 2A1 and C6L, this is followed by another chapter discussing the results of the experiments.

The final chapter goes into possible further studies of 2AI and C6L, namely improvements in

modeling the hydrate formation mechanism of these two surfactants and further investigating the

effect of surfactants on hydrate formation, in order to have more information for application in

the industry.

2. Experimental Section

The further study of the Dowfax surfactants 2A1 and C6L comes as a continuation of Lo's preliminary work on the mentioned surfactants.[11] Lo constructed with preliminary isotherm diagrams for 2A1 and C6L; the same titration method used to obtain data for the isotherm was used here. Zeta potential experiments were conducted and compared with the isotherms determined from titration experiments.

High pressure experiments were conducted as a means to relate the hydrate kinetics to the isotherms.

2.1. Materials

Cyclopentane (CP) and dodecyl trimethylammonium bromide (DTAB) were purchased from Sigma-Aldrich with a purity of +99%. Methylene blue and methyl orange were obtained from Sigma-Aldrich with an indicator purity. Sulfuric acid (96%) and sodium sulfate (99%) were also purchased from Sigma-Aldrich. The Dowfax surfactants 2A1 and C6L (both at 46 wt%) were supplied by Dow Chemical. For high-pressure methane hydrate formation, ultra high purity (Grade 3.7) compressed methane gas was purchased from Praxair. All chemicals were used as received without further purification. Deionized water was produced in the lab with a resistivity of 18 MΩ cm^{-1}.

2.2. Preparation of CP Hydrate Slurries

For this experiment use of CP slurries were used as opposed to CP hydrates. The use of CP slurries was to prevent vapor condensation on hydrate particles and to avoid variation of the total hydrate surface area.

To prepare the CP slurry mixtures, a 1:9 CP-water mixture was charged to a 1000 mL propylene bottle and hermetically sealed.

2.3. Adsorption Isotherms

Adsorption isotherms were determined by the same procedure as Lo et al.[10] Ten grams of the Dowfax surfactant solution were charged to a 25 mL vial and placed in a chiller (at 277 K) overnight. Ten grams of the CP hydrate slurry were then quickly added to the solutions (the slurries and solutions were kept in an ice bath to help keep the surrounding temperature cool). The vials were kept in the chiller for a week, and were shaken daily to accelerate surfactant adsorption on the hydrates.

Because the density of the CP hydrates is lower than that of water, all the CP hydrates were located in the upper portion of the vials; several millimeters of solution were extracted from the lower portion of the vials via 10 mL plastic syringe.

The concentration of Dowfax C6L surfactants was determined via Methylene Blue titration as similarly described by Epton.[10] Because of steric hindrances, the concentration of Dowfax 2A1 surfactant was determined by Methyl Orange liquid-liquid back titration. A more detailed explanation of the titration methods is explained later on.

The adsorption amount is the depletion of surfactants in the aqueous phase.

2.4. Titrations

A measured aliquot of the unknown surfactants solution is placed into a 20 mL test tube.

For the titration of Dowfax C6L, the indicator solution was a methylene blue solution, containing 0.003 wt% methylene blue, 1.20 wt% sulfuric acid, and 5.00 wt% sodium sulfate; 2.5 mL of the methylene blue solution was charged to the test tube, followed by 2.5 mL of chloroform. For the titration of Dowfax 2A1, the indicator solution was a methyl orange solution, containing 0.003 wt% methyl orange, 1.20 wt% sulfuric acid, and 5.00 wt% sodium sulfate; 2.5 mL of the methyl orange solution was charged to the test tube, followed by 2.5 mL of chloroform. The tubes were shaken to promote mass transfer.

A known solution of Dodecyltrimethyl ammonium bromide (DTAB) was used for titration. For the titration of C6L, the DTAB displaces the methylene blue from the methylene blue-anionic surfactant complex, pushing the blue color from the lower anionic layer to the upper hydrophilic layer. For the titration of 2A1, the methyl orange attracts the positively charged DTAB molecules, however, it is believed that the positively charged DTAB has a greater affinity for the 2A1 surfactant molecules in the solution; thus, DTAB-methyl orange complexes form when all the DTAB-Dowfax 2A1 surfactants are fulfilled, resulting in the a yellow color forming in the lower hydrophobic chloroform layer. The endpoints for C6L and 2A1 are as shown below.
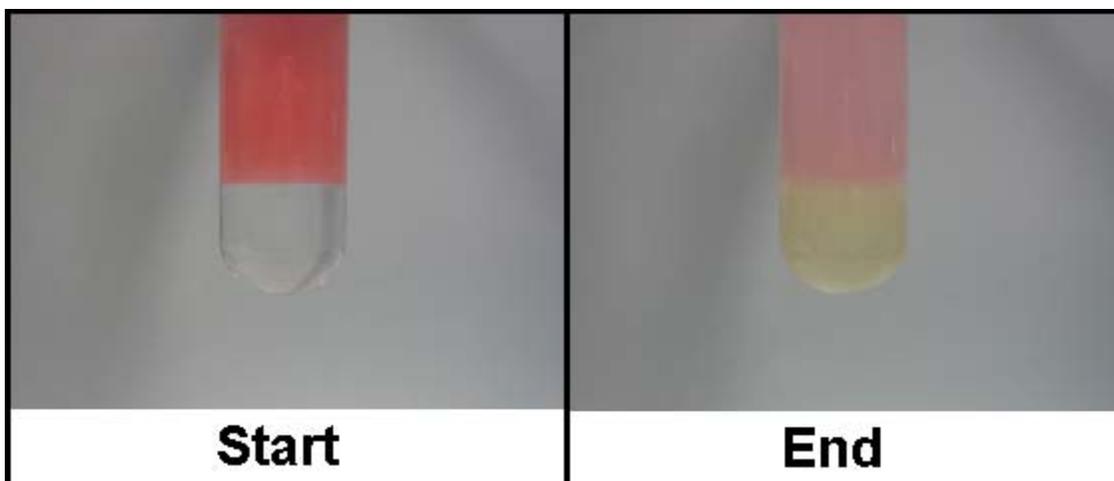
Figure 2.1. Start and endpoint for Dowfax 2AI titration. Solution is initially pink/clear and shifts to pink/yellow.
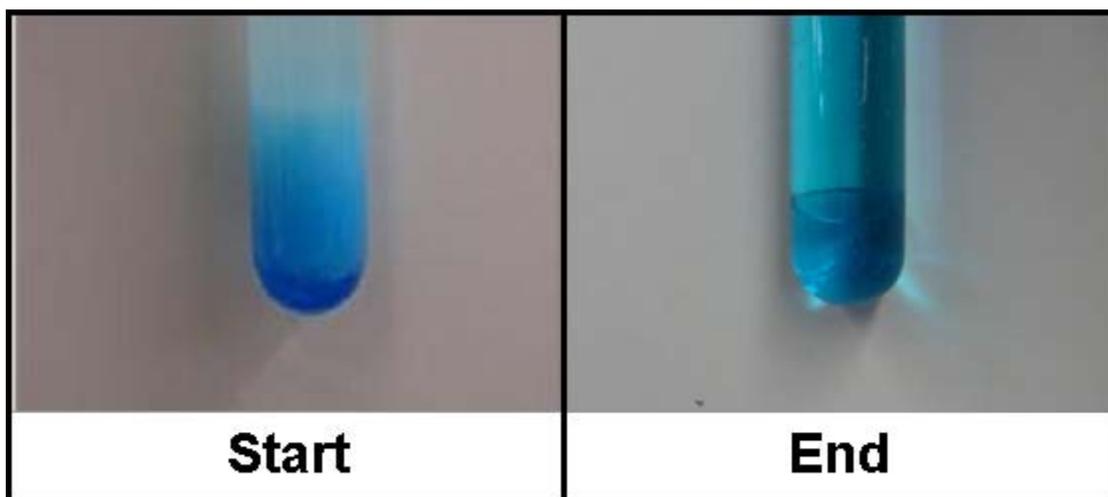

Figure 2.2. Start and endpoint for Dowfax C6L Titration. Solution is initially white/blue[11] and shifts to blue/blue.

2.5 Zeta Potential Experiment

The procedure used for measuring zeta potential follows a similar procedure described in a previous paper by Lo et al.[6] Solutions containing a known concentration of Dowfax 2A1 and C6L surfactant and 1gm of CP hydrate slurry were created. The solutions were placed in the freezer at around 269 K for 1 day. 1-mL of the solutions were quickly placed in a Folded Capillary zeta cell (DTS1060, Malvern Instruments), and then inserted into a Zetasizer Nano ZS

(Malvern Instruments) set to 277 K. Zeta potential experiments were measured after the cell was maintained at 277 K for around 10 minutes.

2.6 High pressure system setup and formations procedure

A 450 mL pressure reactor with two view windows from Parr Instruments was used (the actual volume of the reactor is around 474 mL if one was to consider void fitting space).

Reactor temperature was controlled via a Fisher Scientific Isotemp 30006P thermostat with a circulating coolant having a stability of 0.01K inside the jacket around the cell, and the temperature was monitored via two type-T thermocouples from Omega Engineering (one thermocouple was placed in the liquid, the other was placed in the headspace); the accuracy of these measurements is ±0.5 K. The temperature of the liquid and gas interface was measured every 20 seconds by the Labview interface software and recorded on a computer. Pressure was measured via 9001 PDM pressure transducer from Ashcroft, and the readings have an accuracy of ±0.03 mPa. The setup is shown in Figure 2.3 below.
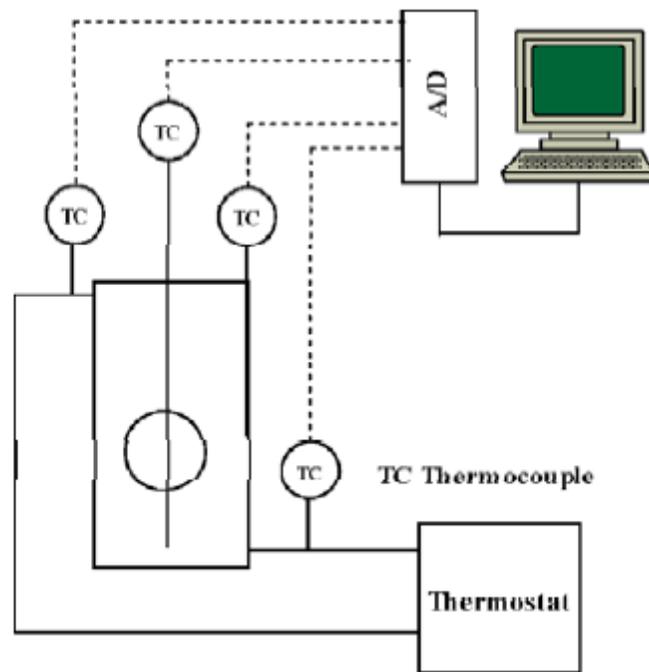
Figure 2.3. Experimental setup for induction time measurements.[11]

150 mL of a known surfactant solution was charged to the reactor, and the temperature of the reactor was set to 12.0°C. The reactor was then twice purged with 200 psi of methane gas, followed by filling the reactor with up to around 1000 psi of methane gas. 1 mL of CP hydrates was then injected into the reactor, and then the temperature set to 1°C, which was maintained for the rest of the run.

3. Results and Discussion

3.1. Isotherm experiment

Adsorption isotherms are used to quantitatively study the adsorption of surfactants on the hydrate surface at different concentrations. Monolayer formation is determined at the first point where the isotherm plateaus; subsequent plateaus in the isotherm indicate extra layers of formation.

Preliminary work done by Chi Lo suggested that the shape of the 2A1 isotherm is that of an L-S type of isotherm, similar to that of SDS;[11] whereas the shape of the C6L isotherm is of a Langmuir type. Building upon Lo's work, one can see a more complete isotherm for these two surfactants.

As seen in Figure 3.1, the shape of the isotherm for 2A1 is an L-S type of isotherm, similar to that of the shape of the SDS surfactant isotherm; however, the high adsorption range at higher concentrations may indicate multilayer formation.
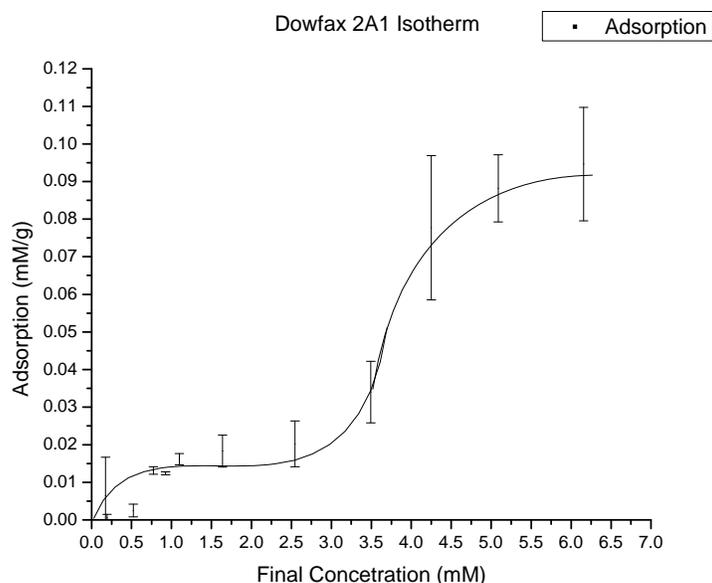

Figure 3.1. Adsorption isotherm of Dowfax 2A1 surfactant

Figure 3.2 shows a different shape for the adsorption isotherms from C6L. The shape of the isotherm for C6L is unclear; it is possible that the adsorption isotherm for C6L exhibits the shape of a Type 1 isotherm (marked out in red), or exhibits a different shape much like that of an L-S type of isotherm instead (marked out in blue).
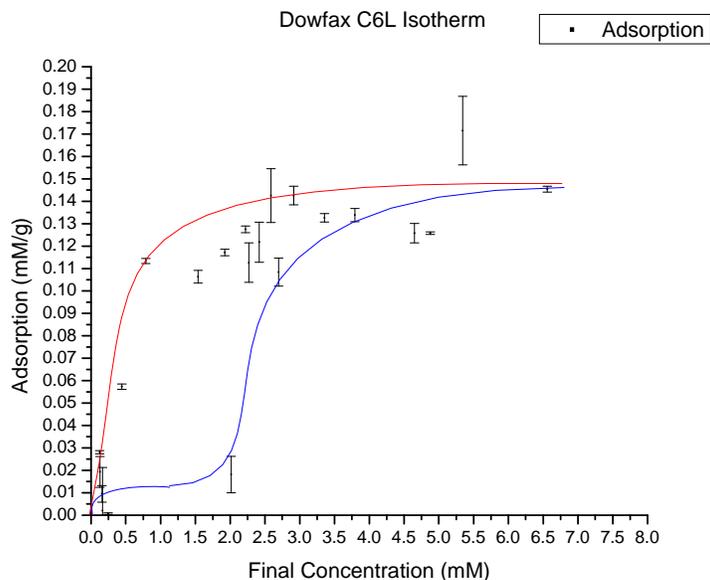

Figure 3.2. Adsorption Isotherm for Dowfax C6L surfactant, with two suggested isotherm shapes.

The isotherm for 2A1 suggests that monolayer formation occurs at around a concentration of 1.0 mM 2A1. If one were to assume that the shape of the isotherm for C6L was that of a Type 1 isotherm, then one could also assume that monolayer formation occurs for concentrations of 1.0 mM C6L as well; however, it is possible that monolayer formation occurs early at low concentrations, with multilayer formation occurring past concentrations of 2.0 mM C6L.

2A1 shows an adsorption of 0.017 mM/g at the monolayer, with 0.09 mM/g being the highest adsorption amount shown at higher concentrations. If one postulates that the C6L isotherms shape is that of a Type 1 isotherm, then it appears that C6L shows much higher adsorption, the

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maximum adsorption amount being about 0.12 mM/g; otherwise, if an L-S type of isotherm is assumed, then C6L shows an adsorption amount of 0.01 mM/g at the start of monolayer formation, with 0.12 mM/g being the maximum adsorption amount at higher concentrations.

The isotherm of the 2A1 surfactant is comparable to that of SDS, which also forms a monolayer around hydrates at also 1.0 mM.[10]

One point of concern with regards to the C6L titration experiment is the endpoint is not very clear; it is possible the resulting isotherm might be skewed as a result. Previous titration experiments for SDS performed by Lo et al.[6] followed a methodology outline by Epton[19] for titration of anionic surfactants, which utilizes methylene blue as the color indicator and hyamine as the titrant; here, the end point using is more established, with the bottom layer being colorless when titration is complete. The presence of blue color in the bottom layer when titrating with DTAB might indicate that the end point was never reached, so perhaps the adsorbed amount of C6L on the hydrate surface might be lower. One might want to look into improving the titration, and ultimately the isotherm, with C6L.

3.2 Zeta Potential Experiment

The isotherm data from the titration experiments suggests that there is monolayer formation at a concentration of around 1.0 mM for both 2A1 and C6L. The isotherm data for 2A1 suggests formation of multilayer as surfactant concentration increases, whereas the isotherm data for C6L suggests that C6L only forms a monolayer over the surface of the hydrate. Thus it is expected that the zeta potential readings using 2A1 would increase as the surfactant concentration increases, and that the zeta potential readings using C6L would eventually remain consistent regardless of how much the surfactant concentration increased.

Figure 3.3 represents the variation of the particle charge on CP hydrates with increasing 2A1 concentration. It is seen that the overall charge on the particles decreases from -23mV to -35 mV as the 2A1 concentration increases from 0mM to 0.75mM. Afterwards the surface charge remains steady as the concentration is increased up to 4mM, which suggest monolayer formation starting around 0.75mM. The overall charge is seen to decrease at concentrations past 4mM, which suggests multilayer formation at concentrations past 4mM.
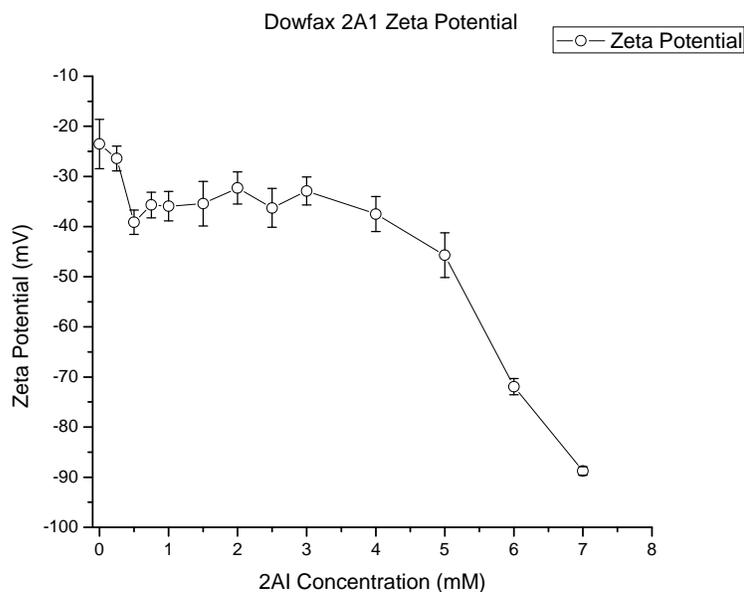

Figure 3.3. Zeta potential of CP hydrates using Dowfax 2A1

Figure 3.4 represents the variation of the particle charge on CP hydrates with increasing C6L concentration. It is seen that the overall charge on the particles decreases from -23 mV to -33 mV as the C6L concentration increases from 0.0 mM to 1.0 mM. Afterwards, the surface charge remains fairly steady despite increasing the C6L concentration, suggesting monolayer formation despite higher concentrations.
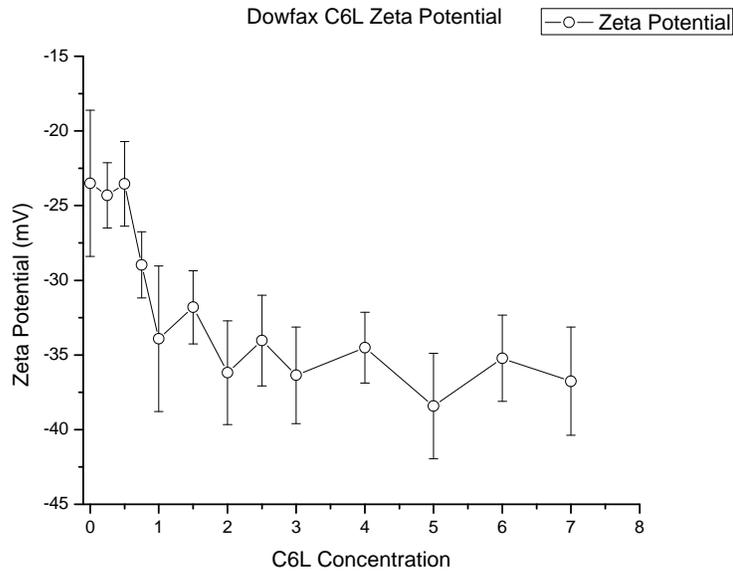
Figure 3.4. Zeta potential of CP hydrates using Dowfax C6L

Another graph of zeta potential C6L data (Figure 3.5) with different results shows an alternative view for adsorption of C6L on the hydrate surface. Here, the overall particle charge decreases from -23 mV to -33 mV as the C6L concentration increases from 0.0 mM to 1.0 mM. Afterwards, the surface charge remains fairly steady until 4.0 mM, where the surface charge starts to decrease.

It's interesting to note that, despite the fact that both 2A1 and C6L are negatively doubly charged, the zeta potential reading are initially relatively low. This is an especially unexpected result for C6L, whose isotherm suggests that a very high amount of adsorption takes. However, given the issues of the isotherm for C6L mentioned earlier, it could be that the zeta potential reflects the real nature of adsorption on the hydrate surface, one that might be more accurate than what is implied in the C6L isotherm.

Low adsorption could be possibly due to the structure of the surfactants themselves. Both 2A1 and C6L are doubly charged surfactants, their anionic heads lined together with an –O– bond; both the anionic sulfate heads and the oxygen molecule can form hydrogen bonds with the sulfate surface, thus taking up many possible adsorption site on the surface of the hydrates. As a result, not many surfactant molecules can be adsorbed onto the surface.

In the case of 2A1, the surfactant tail is large; thus it is possible that the surfactant tail can stand up and eventually from multiple surfactant layers. However, in the case of C6L, the surfactant tail is rather short; it is hard to say determine the exact mechanism of the C6L surfactant on the hydrate surface that results in monolayer formation only, especially given the shaky nature of the isotherm and zeta potential data. Some possibilities include the hydrophobic force not being strong enough to repel the tail off the hydrate surface, resulting in only surfactants lying flat on the hydrate surface when the C6L hydrate molecule tails overlap and bind together while still lying flat on the hydrate surface.

3.3 High pressure experiment

Given the isotherm data and zeta potential data, it can be suggested that for 2A1 and C6L monolayer forms at concentrations of around 1.0 mM. For the case of 2A1, 1.0 mM is equivalent to 576 ppm; for the case of C6L, 1.0 mM is equivalent to 459 ppm.[20]

The concentrations that were tested in the high pressure experiment were 50 ppm, 100 ppm, and 600 ppm, respectively. One would expect the rate of formation to increase as the concentration of the surfactant used also increased.

Experiments conducted at 50 ppm showed very slow formation was slow for both 2A1 and C6L. This was expected as the concentration was well under the determined monolayer concentration as given by the isotherms.

When using 50 ppm 2A1, it was found that the induction time could take as long as around 17 to 18 hours, as seen in Figure 3.5. Other times hydrate formation would remain incomplete even after 20 hours, as seen in Figure 3.6; one can see the pressure dropping very slowly and never reaching completion. One notable exception can be seen in Figure 3.7, where the induction time seems to be fall under 5 hours instead; however, it was difficult to replicate such a result using 50 ppm of Dowfax 2A1.
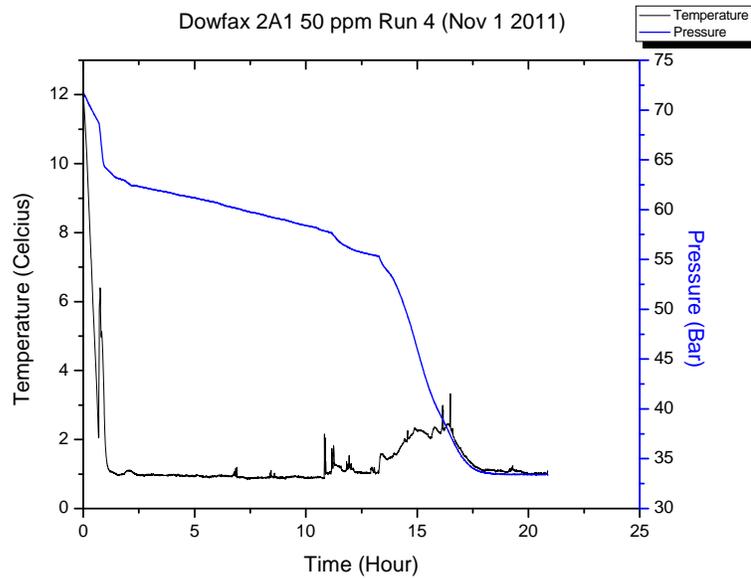

Figure 3.5. High pressure experiment for formation of hydrates using Dowfax 2A1 (50 ppm), Run 4. The induction time for this run is about 17 to 18 hours.
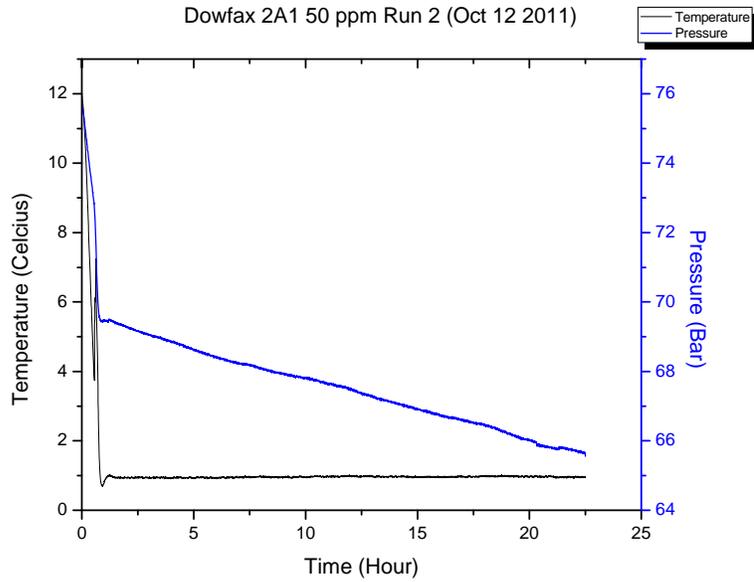
Figure 3.6. High pressure experiment for formation of hydrates using Dowfax 2A1 (50 ppm), Run 2. Hydrate formation is incomplete in this run.
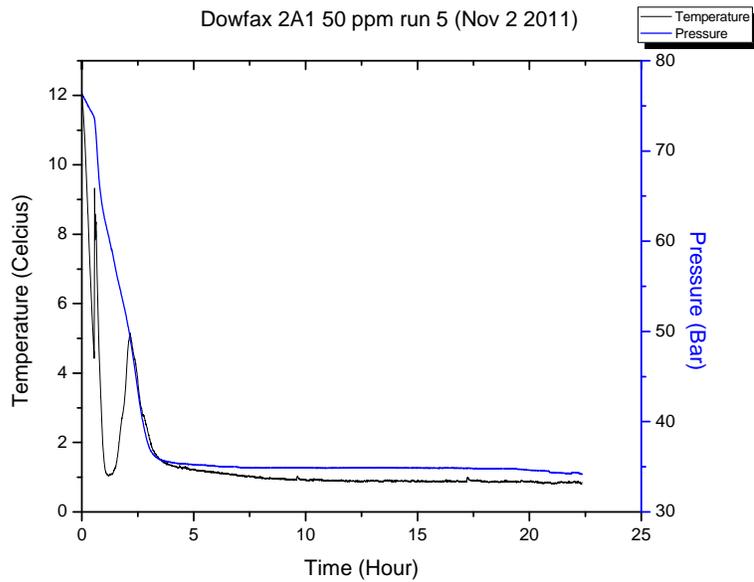

Figure 3.7. High pressure experiment for formation of hydrates using Dowfax 2A1 (50 ppm), Run 5. The induction time for this run is under 5 hours.

Similar behavior could be seen with the high pressure experiments conducted with C6L at 50 ppm, which showed an induction time of around 9.5 hours in one case (Figure 3.8), and showing incomplete hydrate formation in another (Figure 3.9).
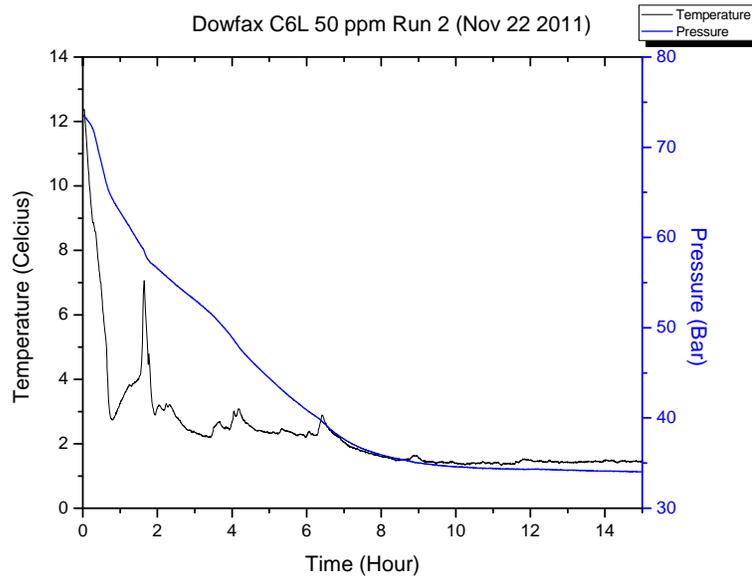

Figure 3.8. High pressure experiment for formation of hydrates using Dowfax C6L (50 ppm), Run 2. The induction time for this run is about 9.5 hours.
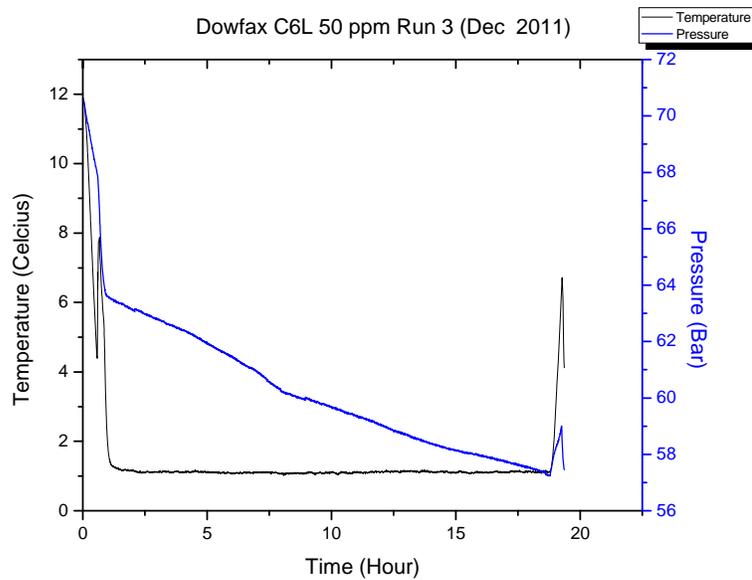

Figure 3.9. High pressure experiment for formation of hydrates using Dowfax 2A1 (50 ppm), Run 3. Hydrtae formation is incomplete in this run.

Experiments conducted at 100 ppm showed a faster formation rate as expected, with 2A1 showing an induction time of around 5 to 7 hours (Figures 3.10 and 3.11); in one instance, the induction time was very short, having a span of around 2 hours only (Figure 3.12).
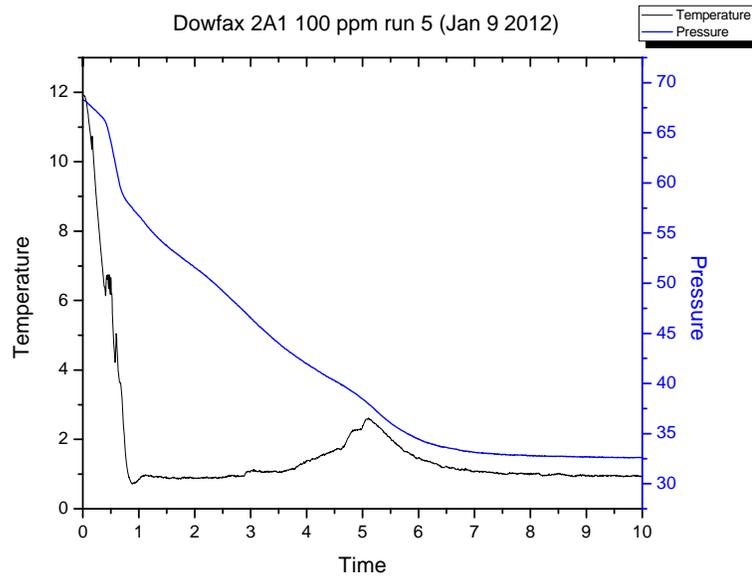

Figure 3.10. High pressure experiment for formation of hydrates using Dowfax 2A1 (100 ppm), Run 5. The induction time for this run is about 7 hours
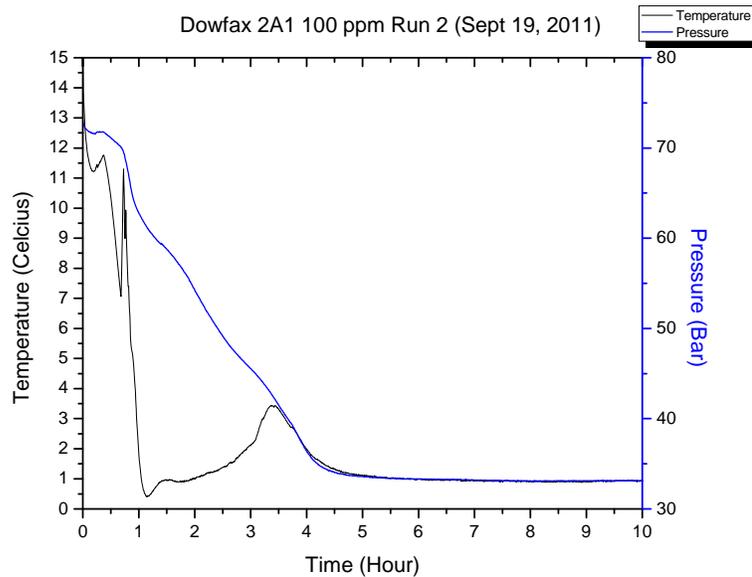

Figure 3.11. High pressure experiment for formation of hydrates using Dowfax 2A1 (100 ppm), Run 2. The induction time for this run is about 5 hours.

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Figure 3.12. High pressure experiment for formation of hydrates using Dowfax 2A1 (100 ppm), Run 4. The induction time for this run is about 2 hours.

Using 100 ppm C6L revealed an induction time of about 3.5 to 8 hours (Figures 3.13 and 3.14); although in one event the induction time was around 4.5 hours (Figure 3.15).

Figure 3.13. High pressure experiment for formation of hydrates using Dowfax C6L (100 ppm), Run 3. The induction time for this run is about 3.5 hours.

Figure 3.14. High pressure experiment for formation of hydrates using Dowfax C6L (100 ppm), Run 2. The induction time for this run is about 8 hours.
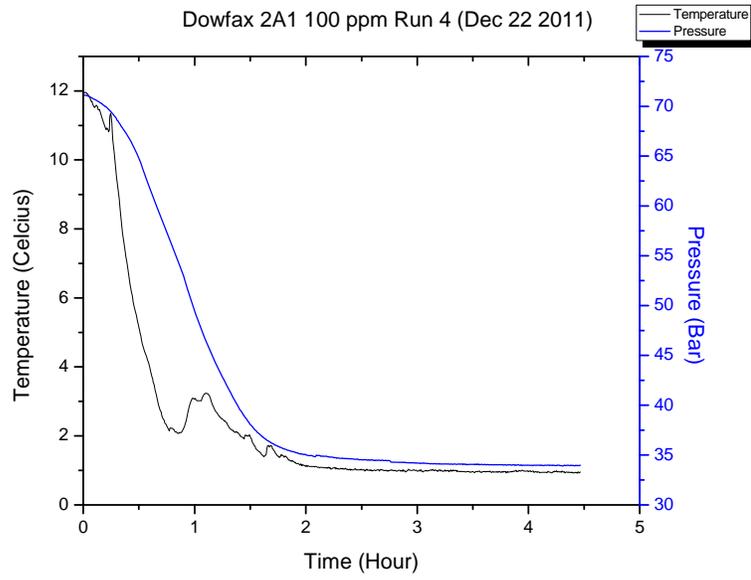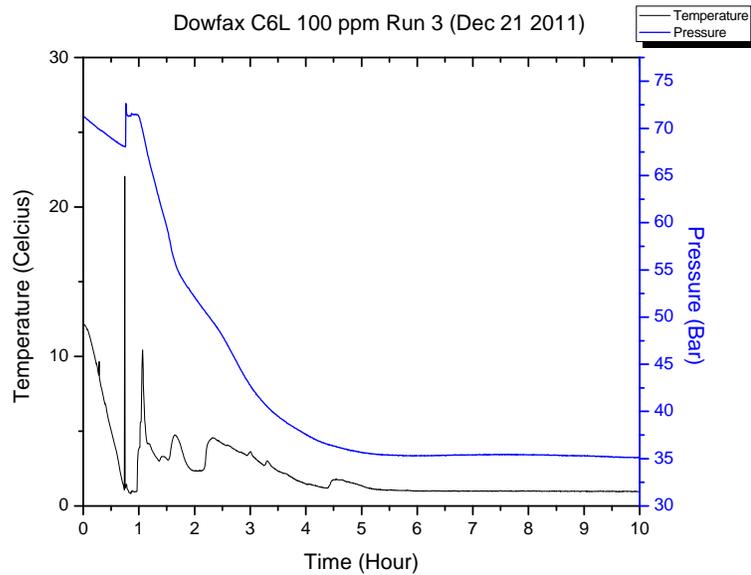

Figure 3.15. High pressure experiment for formation of hydrates using Dowfax C6L (100 ppm), Run 1. The induction time for this run is about 4.5 hours.

The experiments conducted at 600 ppm showed the fastest formation rates, as expected since they were clearly above the concentration for monolayer formation. The induction time when using 600 ppm 2A1 was around 2 hours (Figures 3.16 and 3.17).

Figure 3.16. High pressure experiment for formation of hydrates using Dowfax 2A1 (600 ppm), Run 1. The induction time for this run is about 2 hours.
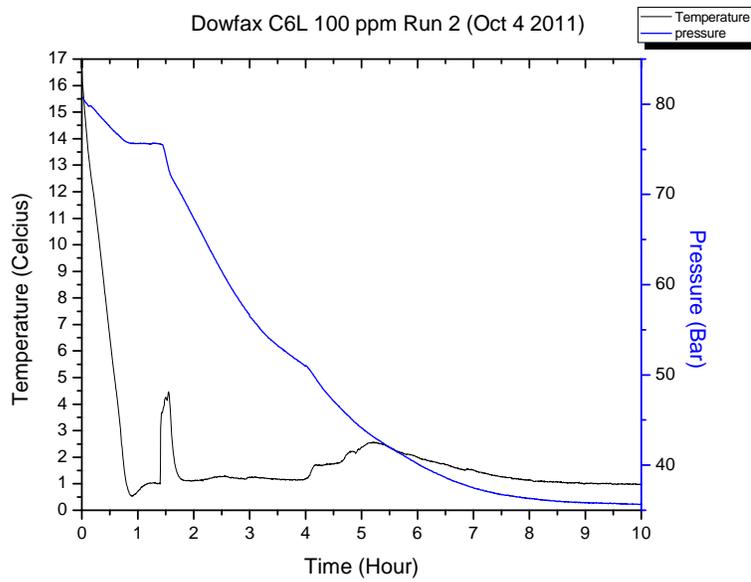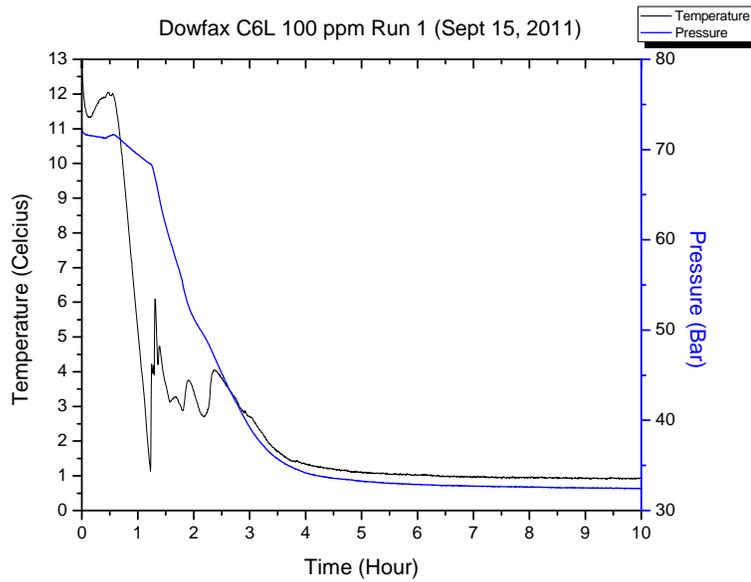

Figure 3.17. High pressure experiment for formation of hydrates using Dowfax 2A1 (600 ppm), Run 2. The induction time for this run is about 2 hours.

The induction time when using 600 ppm C6L was just slightly longer than when using 600 ppm

2A1, taking about 2.5 hours for complete hydrate formation (Figures 3.18 and 3.19).
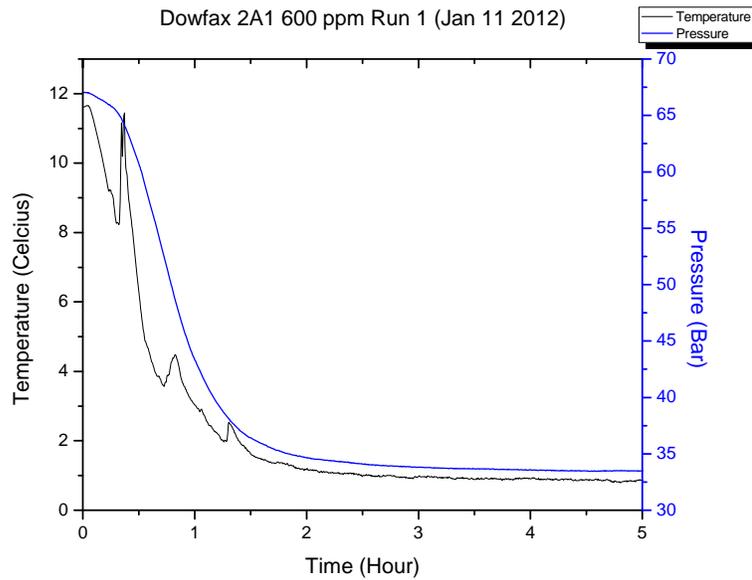

Figure 3.18. High pressure experiment for formation of hydrates using Dowfax C6L (600 ppm), Run 1. The induction time for this run is about 2.5 hours.
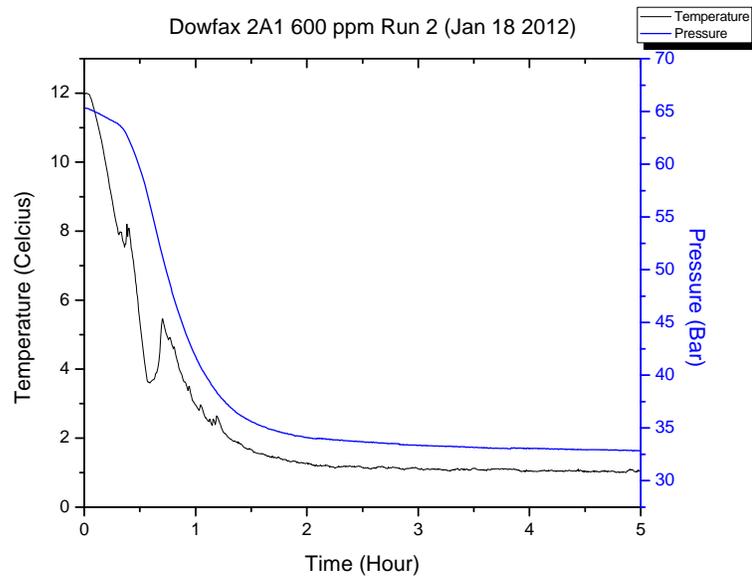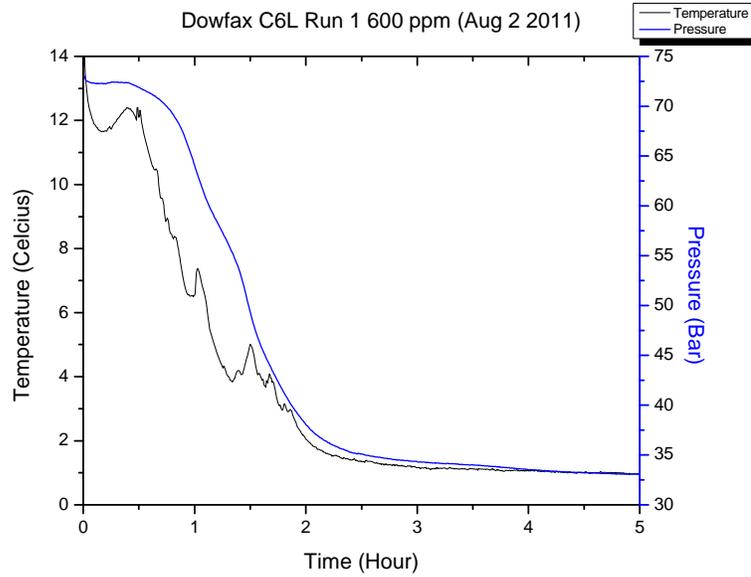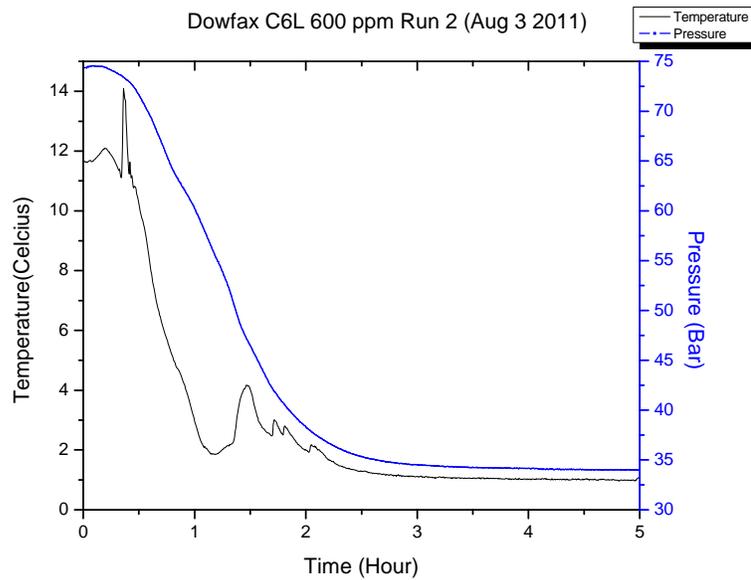

Figure 3.19. High pressure experiment for formation of hydrates using Dowfax C6L (600 ppm), Run 2. The induction time for this run is about 2.5 hours.

The difference in induction times at 600 ppm is rather interesting. For both 2A1 and C6L, 600 ppm is above the monolayer concentration point; so fast formation is expected. However, 600 ppm of C6L is a higher concentration of surfactant than 600 ppm of 2A1 and has a shorter tail,[17,18] yet the induction time for C6L is slightly longer than that of 2A1. This likely relates back to the structure of the two surfactants as noted in Chapter 3, where Lo had observed earlier that the structure for 2A1 contains a hydrate-like environment, making it more ideal for hydrate formation.[11]

4. Conclusion and Future Direction

Isotherm data and zeta potential data for Dowfax 2A1 and Dowfax C6L suggest that both 2A1 and C6L encounter monolayer formation at around a concentration of 1.0 mM. 2AI encounters multilayer formation at higher concentrations whereas higher concentrations of C6L result in monolayer formation only. The rate of hydrate formation increases when using either surfactant, but 2A1 has a shorter induction time than C6L.

The study of Dowfax 2A1 and Dowfax C6L showed that two different surfactants with very similar structures can have different effect on hydrate growth. 2A1 has proven to be more of a hydrate promoter like SDS, forming hydrates at a faster rate than C6L. One would probably choose 2AI for hydrate formation-related applications for that reason.

More work still needs to be done to further finalize and confirm the shape of the isotherm data for C6L to gain a better initial insight into how C6Lis adsorbed onto the hydrate surface.

Future work needs to be done to form a better understanding of the surfactant mechanism behind the two Dowfax surfactants. While isotherm and zeta potential data provide information when monolayer formation (and thus suitable hydrate formation) is formed, this is not enough information for its application in the industry today. One must better understand the mechanism by which the surfactants interact with the hydrate surface. Use of a surfactant-alcohol mixture can be used to better determine the mechanism by which the Gemini surfactants adsorb onto the hydrate surface.

Given the possibility of using sea floor hydrates as an energy resource, it is of great interest to pursue the effects of Dowfax surfactants even further. Study of the adsorption of salt and surfactant on hydrate surfaces allows for one to develop a more realistic model of sea floor

hydrates. Additionally, the adsorption isotherm can be better resolved via titration and surfactant selective ion electrode, which can determine whether or not the surfactant can improve the hydrate environment.

Surface-enhanced Raman can then be used to determine if the system described above is suitable to form hydrates, and further hydrate pressure experiments can be used to confirm these results.

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