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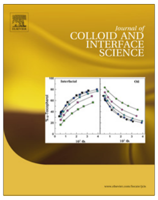

Adsorption of Gemini surfactants onto clathrate hydrates

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ABSTRACT

This work addresses the adsorption of two Gemini surfactants at the cyclopentane (CP) hydrate–water interface. The Gemini surfactants investigated here are Dowfax C6L and Dowfax 2A1 that have two anionic head groups and one hydrophobic tail group. The adsorption of these surfactants was quantified using adsorption isotherms and the adsorption isotherms were determined using liquid–liquid titrations. Even if the Gemini surfactant adsorption isotherms show multi-layer adsorption, they possess the first Langmuir layer with the second adsorption layer only evident in the 2A1 adsorption isotherm. Zeta potentials of CP hydrate particles in the surfactant solution of various concentrations of Dowfax C6L and Dowfax 2A1 were measured to further explain their adsorption behavior at the CP hydrate–water interface. Zeta potentials of alumina particles as a model particle system in different concentrations of sodium dodecyl sulfate (SDS), Dowfax C6L and Dowfax 2A1 were also measured to confirm the configuration of all the surfactants at the interface. The determination of the isotherms and zeta-potentials provides an understanding framework for the adsorption behavior of the two Gemini surfactants at the hydrate–water interface.

1. Introduction

Clathrate hydrates are a non-stoichiometric, ice-like crystalline compound. They are formed when host water molecules provide three-dimensional cages for trapping guest low molecular weight molecules such as methane, ethane, carbon dioxide, and cyclopentane (CP) [1]. Since the discovery of large deposits of natural gas hydrates in oceans and permafrost areas, there has been a spike in studies of clathrate hydrate [1]. It has been estimated that the amount of natural gas trapped in the natural gas hydrate deposits is approximately 1.5×10^{16} m^3 [2]. This amount makes natural gas hydrates a potentially viable energy resource if properly recovered. Clathrate hydrates can be also used a gas storage medium because natural gas can be stored in the clathrate hydrate form; up to 170 volumes of natural gas per volume of hydrates [1,3]. Other potential applications of clathrate hydrates are for CO_2 separation from flue gases and desalination of seawater [4]. There are negative aspects to clathrate hydrates as they can form inside oil and gas pipelines, which cause the nuisance of continuous oil/gas production.

Understanding the kinetics of clathrate hydrate formation is essential for both the utilization of the positive aspects of clathrate hydrate technology and the risk management of its negative aspect of hydrate blockage in the pipeline. One major obstacle to applying hydrate technology for gas storage is that clathrate hydrate formation is very slow because of the formation of a thin layer of hydrate at the gas/water interface which effectively blocks the diffusion of the guest molecule into the water phase; hence, ending the process of hydrate formation [5]. The kinetics of hydrate formation can be accelerated through mechanical agitation or addition of surfactants to the reaction system [3,6–8]. The high energy cost of stirring in a large reactor system makes the method of agitation less economically favorable when compared to addition of surfactants that is very effective for promoting hydrate formation even at low surfactant concentrations. Several studies [2] have shown that sodium dodecyl sulfate (SDS) is a very effective promoter of the kinetics of hydrate formation.

Adsorption of surfactants at the hydrate–water interface was proposed by Zhang et al. [9] to be the reason for surfactant's ability to accelerate hydrate formation. In a previous work, Lo et al. [10] studied the adsorption of SDS on cyclopentane (CP) hydrate–water interface and proposed a two-step adsorption mechanism of SDS at the CP hydrate–water interface. Salako et al. [11] investigated the effect of salt on the adsorption of SDS on the CP hydrate–water interface and proposed a pseudo-monolayer adsorption mechanism at the Langmuir adsorption range. It was shown that Gemini

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surfactants could also be good promoters of hydrate formation kinetics [12–16]. However, the adsorption of Gemini surfactants has never been investigated at hydrate–water interface and understanding their adsorption behaviors at the interface is very important to accelerate the formation kinetics.

Gemini surfactant, also known as dimeric surfactants [17,18], are a relatively new class of surfactants. Gemini surfactants are composed of two identical conventional surfactants joined at the head groups or very close to the head groups by a spacer group [19–22]. Gemini surfactants have attracted lots of attention because their critical micelle concentrations (CMC) are much lower than the CMC of conventional single head, single-tail surfactant [18,23]. Also, Gemini surfactants are more efficient in reducing surface tension than their corresponding conventional surfactants [24,25].

In this work, we will study the adsorption of two Dowfax Gemini surfactants at the CP hydrate–water interface by determining adsorption isotherms and zeta-potentials. The two Gemini surfactants studied in this work are Dowfax 2A1 and Dowfax C6L. These surfactants are asymmetric Gemini surfactants [22] because they have two head groups and one hydrophobic tail. The isotherms will be determined by liquid–liquid titrations. We will also investigate the change in the surface charge of CP hydrate particles in different Gemini surfactant concentrations in order to have a better understanding of the adsorption isotherms and the configuration of the surfactants at the CP hydrate–water interface. Since very little is known about the surface properties of clathrate hydrate in the literature, we will use alumina particles as a model system to understand the orientation of Dowfax 2A1 and Dowfax C6L at the CP hydrate–water interface.

2. Experimental section

2.1. Materials and methods

Anionic Gemini surfactants of Dowfax 2A1 (>98% surfactant solution) and Dowfax C6L (>97% surfactant solution) were obtained from Dow Chemicals. Sodium dodecyl sulfate (SDS) and cyclopentane (CP) of 99% purity were purchased from Sigma–Aldrich. Methylene blue with indicator purity was purchased from Sigma–Aldrich. The deionized (D.I.) water used for the experiment has a resistivity of 18 $\text{M}\Omega\,\text{cm}^{-1}$. The sodium sulfate and sulfuric acid, with purity of 99% and 96% respectively, were purchased from Sigma–Aldrich. 100 nm AG alumina powder was purchased from Ocean State Abrasive.

2.2. Preparation of CP slurry

A 300 mL of CP and water mixture (10 wt.% CP) was charged into a 1 l bottle; after which the bottle was tightly sealed, vigorously shaken and then transferred into a freezer set at 263 K. After the ice formation is noticed at the interface of CP and water, the bottle was shaken at ambient conditions to melt the ice. As the ice begins to melt, CP is quickly enclathrated. The appearance of whitish particles confirms the beginning of CP hydrate formation. The bottle was quickly transferred into the chiller for at least a week, during which the bottle was shaken at least five times per day to accelerate enclathration and ensure complete formation. Calorimetric measurements showed that the concentration of CP hydrate in the CP hydrate slurry is 51 wt.%. We used the CP hydrate slurry for this experiment in order to minimize variations in CP hydrate particle surface area during adsorption isotherm and zeta potential experiments and to avoid moisture condensation on hydrates.

2.3. Adsorption isotherms

A 10 g of Gemini surfactant solutions were charged into 25 mL vials after which the vials were quickly transferred into a chiller at 275 K for about 12 h. 10 g of CP hydrate slurry was quickly transferred into the vial, tightly sealed and then returned into the chiller one after the other. The vials were left in the chiller for a week to allow surfactant adsorption to reach equilibrium. The vials were periodically shaken to accelerate the adsorption of surfactants. At the end of 1 week, several milliliters of the Gemini surfactant solution were extracted from the lower part of the vials with a syringe. The sample extraction usually lasts for less than 1 min and it is done inside the chiller to avoid CP hydrate melting. The Gemini surfactant solutions were analyzed by taking the difference between the concentration of the surfactant solution before and after the addition of CP hydrate particles. This difference gives the amount of Gemini surfactant adsorbed per gram of CP hydrate particles.

2.4. Liquid–liquid titrations

One milliliter of both initial Gemini surfactant solution and extract was pipetted into different 20 mL test-tubes followed by the addition of 2.5 mL methylene blue solution (0.003 wt.% Methylene Blue, 1.2 wt.% H_2SO_4 and 5 wt.% Na_2SO_4) and 2.5 mL chloroform. The test-tube was vigorously shaken till the contents of the test-tube split into two phases. The upper part of the content in the test-tube is clear and the lower part of the test-tube is blue. Hyamine solution (titrant) was added to the test-tube in drops till both the top and the bottom phase have the same shade of blue color. This signifies the endpoint. The triplicate measurements done with this procedure have an error within 2%.

2.5. Zeta potential measurements

A 10 g of surfactant solutions were added to 25 mL vials and the vials were transferred into a chiller at 275 ± 0.2 K for about 12 h after which 1 g of CP hydrate was quickly added to the vial. The vials was then tightly sealed and quickly transferred into the chiller for 1 week to allow surfactant adsorption to reach equilibrium. For the zeta potential reading, the CP hydrate particles from the chilled vials were quickly transferred into a chilled folded capillary cell with a chilled pipette. The capillary cell was then loaded into the zeta potential machine (Zetasizer Nano ZS, Malvern Instrument) that was preset to a temperature of 277 K; after which the zeta potential measurements were recorded.

For the zeta potential of alumina particles, 0.05 g of alumina particles was added to vials containing 10 g of surfactant solution. Each vial was well shaken and stored under ambient conditions for a day to allow adsorption to completely reach equilibrium. The zeta potential measurements for alumina particles were taken at 298 K.

3. Results and discussion

Gemini surfactants used for this study are Dowfax C6L and Dowfax 2A1 whose two head groups are negatively charged (Fig. 1) with one hydrophobic tail. They have been shown to increase the rate and amount of hydrate enclathration and some Gemini surfactants could be as good as sodium dodecyl sulfate (SDS) in promoting hydrate enclathration [12]. Zhang et al. [9] proposed that the adsorption of SDS at the hydrate–water interface is the explanation behind SDS's ability to accelerate hydrate enclathration. Therefore, it is important for us to study the adsorption behavior of Gemini surfactants at hydrate–water interface.