Role of Chain Length and Type on the Adsorption Behavior of Cationic Surfactants and the Silica Floatability

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In this study, we investigated the adsorption isotherms of cationic surfactants (i.e., distearyl dimethyl ammonium chloride (DDAC), behenyl trimethyl ammonium chloride (BTAC), and stearyl trimethyl ammonium chloride (STAC)) onto silica surface and the corresponding silica floatability according to chain type and length of cationic surfactants. The results for the adsorption isotherms of cationic surfactants showed that the adsorptive amounts increased with increasing surfactant concentration, but differences in the position of the adsorption isotherms existed between DDAC, BTAC, and STAC. Specifically, in the high range of initial surfactant concentrations (i.e., 10^{-3}–10^{-1} M), the adsorptive amounts increased with increasing hydrocarbon chain length. In addition, in the presence of DDAC, the adsorptive amounts were much greater than those in the presence of BTAC and STAC. The results were attributed to the fact that the increase in the hydrocarbon chain group of surfactants decreased the Gibbs free energy of the system, resulting in a shift of hemimicelle concentration toward lower concentration. Meanwhile, in the low range of initial surfactant concentrations (i.e., 5 \times 10^{-7}–5 \times 10^{-4} M), the adsorptive amounts were comparable regardless of surfactant type, which was due to the fact that the interaction between the cationic surfactants and the silica surface was mainly governed by electrostatic attractive force. The results from silica flotation and hydrophobicity tests showed that silica floatability increased with increasing hydrocarbon chain group of surfactants (i.e., floatability was in the order of DDAC > BTAC > STAC) under the conditions where the adsorptive amounts of the surfactants were comparable and that floatability results were consistent with those for the hydrophobicity of silica surface. Overall, the findings from the present study suggested that the hydrocarbon chain length and type of cationic surfactants play a significant role in both the adsorption behavior of surfactants and the silica floatability.

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1. Introduction

The plot of the amount of surfactant adsorbed at the solid–liquid interface per unit mass or unit area of a solid versus the equilibrium concentration is called the adsorption isotherm.\(^1\) The study of the adsorption isotherm is important for determining the maximum amount of surfactant adsorbed per unit mass or area of the adsorbent, and for understanding the adsorption mechanism of surfactant on a solid surface.\(^1,5\)

There have been many adsorption isotherm studies of ionic surfactants on oppositely charged solid surfaces, such as mica,\(^3\) alumina,\(^4,5\) silica,\(^2,6–8\) hematite,\(^9\) diaspore,\(^10\) and kaolinite.\(^10\) According to previous studies, in the low range of ionic surfactant concentration, the adsorption is thought to be driven by electrostatic attractive forces between the ionic surfactant head group and the oppositely charged surface (Region I in Fig. 1).\(^3,5,10,11\) As surfactant concentration increases, hemimicelle and micelle start to form onto a solid surface (Region II and III in Fig. 1) and eventually no change is observed in adsorption amount of surfactant (Region IV in Fig. 1). Meanwhile, the chain length of surfactants has been also considered to be an important factor in determining the adsorption behavior of surfactants. Surfactants with increasing hydrocarbon chain length have a much greater driving force for the aggregation, and thus dramatically reduce the solution hemimicelle concentration (HMC) and critical micelle concentration (CMC). The shifting of the isotherm to lower concentrations for longer chained surfactants is a result of increased hydrophobicity imparted by longer tail groups.\(^1,2,6,8,12\)

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Fig. 1 A schematic illustration showing adsorption isotherm of ionic surfactants and the corresponding adsorption mechanism. Images were redrawn based upon the information discussed in Ref. 7).

In addition, research on the relationship between surfactant adsorption and flotation behavior of a solid has been reported.\(^2,3,9,10,13\) It has been known that the flotation behavior highly depends on the adsorption of ionic surfactants on a solid surface according to the carbon chain length of ionic surfactants because the carbon chain groups of a surfactant

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can modify their hydrophobicity. Hence, in the field of flotation, it is very important to understand the ionic surfactant adsorption on a solid surface according to the chain group of the ionic surfactants. Nevertheless, to the best of our knowledge, there has been no attempt to investigate the influence of chain type (e.g., single versus double) of ionic surfactants on their adsorption behavior and the corresponding particle floatability. In addition, until recently, although the adsorption isotherm of ionic surfactants according to chain length \(( \leq C_{16} )\) has been thoroughly investigated,\(^{14-20}\) few studies exist for the case of the longer chain length \(( \geq C_{18} )\) of ionic surfactants. Therefore, in this study, to better advance the understanding of cationic surfactant adsorption onto a solid surface according to the type and length of surfactants, we determined the adsorption isotherm of cationic surfactants, such as stearyl trimethyl ammonium chloride (STAC, \(C_{18}NCl\)), behenyl trimethyl ammonium chloride (BTAC, \(C_{22}NCl\)), and distearyl dimethyl ammonium chloride (DDAC, \(C_{18}C_{18}NCl\)) (Fig. 2) onto a silica surface using a potentiometric titration method. In addition, to understand the relationship between the adsorptive amounts of cationic surfactants and the flotation behavior of silica, we also conducted micro-flotation tests using a well-controlled Hallimond tube.

2. Materials and Methods

2.1 Silica sieving and cleaning

Silica (purity of \(SiO_2 > 99\%\)) used in the present study was obtained from SAC Co., South Korea. The silica was sieved (Testing screen sieve, Tokyo Screen Co. Ltd., Japan), and the 100–150 \(\mu\)m-sized silica was first washed thoroughly with deionized (DI) water (Milli-Q Plus 185 purification, Millipore Ltd., U.K.), followed by immersion in sulfuric acid (95\%, \(H_2SO_4\)) solution at 40\% (\(v/v\)) for about 10 h to remove surface metallic components.\(^{21}\) The silica was then rinsed thoroughly with deionized (DI) water until the pH of the wash water showed the value of pure water (\(~6.5–7.0\)). The cleaned silica was then dried in an oven at 60°C for 24 h.

2.2 Silica characterization

In order to determine the zeta potential of silica, the samples whose size was smaller than 5 \(\mu\)m were prepared in distilled water and the samples were used to measure electrophoretic mobility at different pH conditions by a zeta-potential analyzer (ELS-Z, Otaka Eletronics Co., Japan). The measured mobility values were converted to zeta potentials based on Smoluchowski equation.\(^{22,23}\) The solution pH was adjusted using 1N HCl (Fisher Scientific) and 1N NaOH (Fisher Scientific). The specific surface area of the silica was determined via gas physisorption at \(-196°C\) using a Micromeritics ASAP 2020M analyzer and from nitrogen adsorption data in the partial relative pressure from 0.05 to 0.25 using the Brunauer–Emmett–Teller (BET) method.\(^{24,25}\) The specific surface area of silica was determined to be 4.08 \(m^2/g\). The characterization of surface OH group content was performed via a thermogravimetric analysis (TGA, S-1000, SCINCO) analysis operated at atmospheric pressure. The following procedure was used\(^{26}\) under nitrogen, silica was heated from 25 to 100°C at a rate of 10°C min\(^{-1}\) (step 1). The heating was continued from 100 to 800°C at a rate 10°C min\(^{-1}\) with keeping at 120°C for 30 min to remove the physically adsorbed water (step 2) and with keeping at 800°C for 30 min (step 3). The step 3 represents the weight loss associated to the removal of chemically adsorbed water. The surface hydroxy group density (\(D_{OH}\)) \((OH\ nm^{-2})\) was calculated based on weight loss (\(g\)) between 120 and 800°C using eq. (1).

\[
D_{OH} = \alpha (\frac{wt_{T_f} - wt_{T_1}}{wt_{T_1}}) \\
\times \left\{ \frac{N_A}{SA_{BET} \times MW_{H_2O}} \right\}
\]

(1)

where, \(\alpha\) is calibration factor, \(T_1 = 120°C\) and \(T_2 = 800°C\), \(N_A\) is Avogadro’s number and \(SA_{BET}\) \((nm^2 g^{-1})\) is the BET surface area and \(MW_{H_2O}\) is the molecular weight of water \((g mol^{-1})\). And, OH content was determined as:

\[
OH\ g^{-1} = D_{OH} \times SA_{BET}
\]

(2)

The OH density and content of silica determined by the aforementioned method were about 1.02 \(nm^{-2}\) and 4.18 \times 10\(^{18}\) \(g^{-1}\), respectively.

2.3 Reagents

In order to examine the adsorption behavior of cationic surfactants onto a silica surface and the flotation behavior of silica, three types of cationic surfactants with different chain structures (i.e., STAC \((C_{18}NCl)\), BTAC \((C_{22}NCl)\), and DDAC \((C_{18}C_{18}NCl)\)) were employed, and they were provided by KCI Ltd., South Korea. Sodium dodecyl sulfate (SDS, \(CH_3(CH_2)_{11}SO_3Na\)) from Sigma-Aldrich, U.S.A., was used as a titrant, and analytical grade of HCl and NaOH (Fisher Scientific) were used as pH modifiers.

2.4 Determination of adsorption isotherms

Adsorption experiments were carried out at pH 6 where electrostatically favorable interaction between cationic surfactants and silica is expected since the isoelectric point of silica is less than 2 (Fig. 3). Adsorption tests were conducted in a 50 mL plastic bottle (Polypropylene conical tube, BD Falcon, U.S.A.) using a mechanical shaker at 25°C. 1 g of silica was mixed with BTAC, STAC, and DDAC solutions with the concentration range of 5 \times 10^{-7} to 10^{-3} M, and the mixture was stirred for 1 h at room temperature. Then, surfactant-adsorbed silica was filtered through a membrane filter using a syringe filter (Disposable syringe, SIR Medical.
The surfactant concentration in the filtrate was then determined using a potentiometric titrator (905 titrando, Metrohm Co., Switzerland) equipped with polyvinyl chloride (PVC) liquid membrane surfactant-sensing electrodes (656 electrochemical detector, Metrohm Co., Switzerland). The titrator was programmed to work in dynamic equivalence point titration (DET) mode with a signal drift of 1 mV/min. The waiting time before the start of titration was 1 min. The amount of adsorbed cationic surfactant onto the silica surface was calculated as:

$$\Gamma = \left( C_0 - C \right) \times \frac{V}{m}$$

Where, $\Gamma$ is the amount of cationic surfactant adsorbed on the silica, $C_0$ and $C$ are the initial and equilibrium concentrations of surfactant in bulk phase, $V$ is the solution volume, and $m$ is the mass of silica.

Here, it should be noted that previous studies reported that the solubility of surfactants in water is sensitive to temperature change and the solubility substantially increases above Krafft point (temperature). In addition, the Krafft point is reported to increase with increasing chain length of surfactant and the point to be higher than 58°C when hydrocarbon chain length is larger than 15, indicating that the adsorption tests in the present study were carried out below Krafft point with negligible effect of temperature. Meanwhile, the Krafft point is considered to be also important especially at the concentration level of surfactant that is supersaturated since liquid crystals and micelles would form when the surrounding temperature is lower and higher than Krafft point, respectively.

Hence, to verify that the concentration of ionic surfactants in bulk phase at the condition where the adsorption tests were carried out did not reach the concentration with negligible effect of temperature. Meanwhile, the Krafft point is considered to be also important especially at the concentration level of surfactant that is supersaturated since liquid crystals and micelles would form when the surrounding temperature is lower and higher than Krafft point, respectively.

2.6 Contact angle measurements

In order to investigate the hydrophobicity of silica surfaces treated with different cationic surfactants, a horizontal silica plate provided by Hanjin quartz Ltd., South Korea (purity of SiO$_2 > 99\%$) was employed. Briefly, the horizontal silica plate was mixed with $10^{-6}$ M BTAC, STAC, and DDAC solution and stirred for 1 h at 25°C. Then, the contact angles of the plate treated with different cationic surfactants were measured by a goniometer (Phoenix150, SEO, South Korea) via a sessile drop method. The drop shape was recorded with a camera, and the images were processed by a computer and stored. The drop shape was then automatically evaluated in terms of contact angle, as represented by the angle between the horizontal silica plate surface and a tangent from the edge to the contour of the drop.

3. Results and Discussion

3.1 Effect of chain length and type on adsorption behavior of cationic surfactants

The measured adsorption isotherms for different cationic surfactants onto silica at pH 6 are shown in Fig. 5. In the log-log plot, overall the adsorptive amounts onto silica increased with increasing initial and equilibrium concentration of cationic surfactants. In addition, the shapes of the adsorption isotherms of DDAC, BTAC, and STAC onto silica were nearly the same, but there were differences in the position of the adsorption isotherms. Specifically, in the high range of cationic surfactant concentrations, i.e., adsorptive amounts $> 1.6 \times 10^{-7}$ moles/g (dotted line A in Figs. 5(a))
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and STAC, may have a much greater driving force for the aggregation and thus dramatically reduce the solution HMC compared to those in the presence of BTAC and STAC.3,10,12,18,19 This explains the observation that the adsorptive amounts were in the order of DDAC > BTAC > STAC in the high range of cationic surfactant concentrations, i.e., adsorptive amounts $> 1.6 \times 10^{-7}$ moles/g (dotted line A in Figs. 5(a) and 5(b)).

Meanwhile, in the low range of cationic surfactants, i.e., adsorptive amounts $< 1.6 \times 10^{-7}$ moles/g (dotted line A in Figs. 5(a) and 5(b)), the adsorptive amounts of cationic surfactants onto silica according to initial and equilibrium concentration were interestingly identical regardless of chain type and length. Previous studies reported that the adsorption of ionic surfactants occurs mainly due to the electrostatic interaction between the charged solid surface and the ionic surfactant in the low range of surfactant concentrations (Region I in Fig. 1).1,31 In fact, several studies observed that the adsorptive amounts of cationic surfactant onto silica particularly increase with increasing pH at low surfactant concentrations, which was explained by the enhancement of the electrostatic attractive force between the cationic surfactant and silica surface at higher pH because the surface charge of silica became more negative with increasing pH.1,31-35 These results suggested that the interactions induced by hydrophobic tails of ionic surfactants are not important in the low range of surfactant concentration. Considering the results in the aforementioned studies,1,31,34,35 we also proposed that the electrostatic attractive interaction between the negatively charged silica surface and the cationic surfactants was a dominant mechanism (Region I in Fig. 1) controlling the adsorptive amounts of different cationic surfactants in the low range of surfactant concentration, i.e., adsorptive amounts $< 1.6 \times 10^{-7}$ moles/g (dotted line A in Figs. 5(a) and 5(b)) in the present study. Accordingly, the adsorptive amounts of cationic surfactant onto silica in the low range of cationic surfactants were observed to be nearly the same due to the constant surface charge of silica and the identical structure of charged head groups of cationic surfactants.

### 3.2 Effect of chain length and type of cationic surfactants on silica floatability

Since the main purpose of this study was to investigate the relationship between the adsorption behavior of cationic surfactants and the silica floatability according to chain length and type, we further conducted micro-floatation tests in the presence of DDAC, BTAC, and STAC using a well-controlled Hallimond tube. The initial surfactant concentrations investigated in flotation tests were $5 \times 10^{-7}$, $10^{-6}$, and $5 \times 10^{-6}$ M where the adsorptive amounts of cationic surfactants onto silica were comparable regardless of surfactant type (Fig. 5(a)) and the adsorption of the surfactants was governed by electrostatic force as described in section 3.1. Here, it should be noted that no difference in silica floatability according to surfactant type was observed at the conditions where initial surfactant concentration was greater than $5 \times 10^{-6}$ M (silica floatability $\approx 100\%$). Overall, the floatability results showed that silica floatability is largely affected by the chain length and type in the surfactant...
concentration range investigated (Fig. 6). More specifically, the silica floatability with BTAC was determined to be about 49.05, 65.33, and 98.79% at the initial concentration of 5 × 10⁻⁷, 10⁻⁶, and 5 × 10⁻⁵ M, respectively. Additionally, in the presence of STAC, the silica floatability was determined to be approximately 32.30, 52.56, and 90.21% at the initial concentration of 5 × 10⁻⁷, 10⁻⁶, and 5 × 10⁻⁵ M, respectively. The results clearly showed that the silica floatability increased with increasing chain length while the adsorptive amounts of both BTAC and STAC onto silica were comparable. Meanwhile, in the presence of DDAC the silica floatability was determined to be about 60.10, 76.27, and 99.4% at the initial concentration of 5 × 10⁻⁷, 10⁻⁶, and 5 × 10⁻⁵ M, respectively, showing greater silica floatability than other two types of surfactants (i.e., the silica floatability was in the order of DDAC > BTAC > STAC) while the adsorptive amounts of three types of surfactants were comparable. These results indicate that increasing the number of hydrocarbon in the tail of cationic surfactants enhances the silica floatability.

3.3 Effect of hydrophobicity on silica floatability

In order to fully understand the underlying mechanism driving to the difference in the silica floatability according to the chain length (i.e., BTAC versus STAC) and type (i.e., DDAC versus STAC) observed in Fig. 6, we determined the contact angles of silica plates treated with three types of surfactants at the representative initial surfactant concentration (i.e., 10⁻⁵ M), and the results are presented in Fig. 7. The contact angles of silica plates were determined to be about 68.61, 55.01, and 46.68° for the samples treated with DDAC, BTAC, and STAC, respectively, indicating that the hydrophobicity of the silica plate treated with different cationic surfactants was in the order of DDAC > BTAC > STAC. The trend for the hydrophobicity was consistent with that for the silica floatability, suggesting that varying the hydrocarbon chain type and length of cationic surfactants plays a significant role in silica floatability while the adsorptive amounts of surfactants onto silica were comparable.

4. Conclusions

To advance our knowledge on the relationship between the adsorption behavior of ionic surfactants onto a solid surface and the particle floatability according to the chain type and length, the adsorption isotherms of three types of cationic surfactants (i.e., DDAC, BTAC, and STAC) onto a silica surface and the corresponding silica floatability were investigated. The specific findings from this study are summarized as follows:

1) In the high range of cationic surfactants concentration, the adsorptive amounts of the surfactant onto silica tended to increase with increasing hydrocarbon chain group of the cationic surfactants. An increase in the hydrocarbon chain group was considered to decrease the Gibbs free energies of the system to form hemimicelle, resulting in a shift of HMC toward lower concentration.

2) In the low range of cationic surfactants concentration, the values of adsorptive amounts of surfactants onto silica were comparable regardless of the chain length and type of cationic surfactants. The insensitivity in the adsorption isotherms of three types of cationic surfactants was due to the electrostatic interaction between the charged head groups of cationic surfactants and the negatively charged silica surface.

3) The silica floatability increased with increasing hydrocarbon tail groups of cationic surfactants under the conditions where the adsorptive amounts of the surfactants were comparable. The trend was attributed to the increase in the hydrophobicity of the silica surface with increasing hydrocarbon chain groups.

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REFERENCES