Foam Separation of Dyes Using Anionic, Cationic, and Amphoteric Surfactants
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Abstract: Foam separation can selectively remove a target substance from a solution via adsorption of the substance with the surfactant at the surface of the bubble. A cationic dye, methylene blue, and an anionic dye, Fast Green FCF, were prepared as substances to be removed via foam separation. Anionic (sodium dodecyl sulfate, SDS), cationic (dodecyltrimethylammonium chloride, DTAC), and amphoteric (3-(dodecyldimethylammonio)propane-1-sulfonate, SB-12) surfactants were used in the foam separation process. The effectiveness of the surfactants for removing the cationic methylene blue increased as follows: DTAC < SB-12 < SDS. On the other hand, the effectiveness of the surfactants for removing the anionic Fast Green FCF was in the opposite order. The dyes were effectively adsorbed by the foams via electrostatic interactions between the oppositely charged surfactant and the dye molecules. Since amphoteric surfactants have both anionic and cationic charges in a molecule, they could effectively remove both dyes in the foam separation process. Therefore, it was found that the amphoteric surfactant was highly versatile. Analysis of the kinetics of the removal rate showed that the aqueous solutions of monomers could remove the dyes more effectively than micellar solutions in foam separation.

Key words: foam separation, amphoteric surfactant, dye, bubble

1 Introduction

Adsorbents are often used to remove dissolved organic substances from aqueous solutions. For example, zeolite and ion exchange resins are used as adsorbents for removing organic substances from sewage\(^1\)\(^-\)\(^3\). These adsorbents can smoothly remove organic substances in a short time; however, they are generally expensive and are not advantageous in terms of reducing the volume of waste. Recently, new types of dye adsorbents have been developed and studied, such as ion-exchange cellulose monoliths\(^4\), polydopamine-modified fibers\(^5\), and metal organic frameworks (MOFs)\(^6\). These adsorbents can be used continuously, and their adsorption rates are very high. On the other hand, the foam separation method can also remove organic substances\(^7\), alkaline and alkaline earth metals\(^9\),\(^10\), and heavy metals\(^11\),\(^12\) from aqueous solutions. The method uses ion flotation and foam fractionation. Organic compounds are bound to adsorbed surfactant molecules at the large number of bubble interfaces by electrostatic interactions or hydrophobic interactions. The rising bubbles then form foams at the air-liquid surface. The foams rise in the glass tubes due to a pressure difference, and are then concentrated to generate dry foams that carry the organic compounds. The aqueous solution can then be purified as the surfactant molecules are removed in the foams. Furthermore, the only waste is the removed organic material and the surfactant crystals, which are advantageous in terms of reducing the volume of waste that must be processed.

Ionic dyes are convenient to use as organic probes, as they absorb light in the visible region. Previous studies have shown that electrostatic interactions between surfactants and ionic organic dyes are important for their adsorption\(^13\),\(^14\). For example, Shakir et al. reported that an anionic surfactant was effective for removing a cationic dye, whereas, a cationic surfactant was effective for removing an anionic dye in foam separation\(^15\). In addition, Gross et al. reported that the removal rate of anionic dyes increased with the addition of a small amount of a biopolymer to an aqueous cationic surfactant solution\(^16\). The mechanism of removal for ionic organic substances is presumed to be based on electrostatic interactions rather than hydrophobic interactions with the surfactant molecule.

In this study, three types of ionic surfactants (anionic, cationic, and amphoteric) and ionic dyes were combined for foam separation. The amphoteric surfactant was found to be advantageous in removing ionic dyes with both posi-

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Accepted January 27, 2020 (received for review January 6, 2020)
Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online
http://www.jstage.jst.go.jp/browse/jos/ http://mc.manuscriptcentral.com/jocos
tive and negative charges via foam separation, because amphoteric surfactants have both positive and negative charges on the same molecule. The removal mechanism of foam separation is clarified by investigating the removal rate and the kinetics of these combined systems.

2 Experimental and Procedure

2.1 Materials
Sodium dodecyl sulfate (SDS) (>98% purity), dodecyltrimethylammonium chloride (DTAC) (>98% purity), and 3-(dodecyldimethylammonio)propane-1-sulfonate (SB-12) (>98% purity) were obtained from Tokyo Chemical Industry Co., Ltd. Cationic and anionic dyes, such as methylene blue (>98% purity) and Fast Green FCF (>85% purity) were also purchased from Tokyo Chemical Industry Co., Ltd. The molecular structures of surfactants and dyes are shown in Fig. 1, where the surfactants are classified as anionic, cationic, and amphoteric. Water was purified by ion-exchange treatment (PRA-0015, ORGANO).

2.2 Foam separation of dyes
The foam separation method begins with electrostatic adsorption between the surfactant and the counterion (dyes) at the surfaces of the many bubbles in the bulk solution. The bubbles are converted into foams in the gas phase, and the foams rise up the tube due to the changes in the air pressure. Finally, the foams containing the dyes are concentrated by draining away the excess water. Figure 2 shows a schematic illustration of the foam separation apparatus. The air bubbles (~300 μm) are supplied from a general air pump (NISSO CHIKARA, α4000SW) and dispersed through a “wood stone device” (Mame Design). The air flow rate was controlled at 50 mL min⁻¹. The temperature was set at 298 ± 3 K using an air conditioner.

The anionic (SDS), cationic (DTAC), and amphoteric (SB-12) surfactants were used as dye carriers in the foam separation experiments. Their critical micelle concentrations (CMCs) are reported to be 8.21, 21.3, and 3.5 mmol L⁻¹ at 298.2 K, respectively 16-18. The initial concentrations of the surfactants were changed from below the CMC to above the CMC depending on the experimental system. On the other hand, the initial concentrations of the ionic dyes (methylene blue and Fast Green FCF) were 100 μmol L⁻¹ in almost all cases. The volume of the surfactant solution (including dye) was fixed at 250 mL. The total time for the foam separation experiment was 5 h, and the experiments were repeated three or more times.

The concentrations of the ionic dyes during foam separation were determined from samples taken from the bulk solution every 30 min, and measured using ultraviolet-visible spectrophotometry (JASCO, V-630 iRM) apparatus. The molar absorption coefficients for each dye in the different surfactant solutions are shown in Table 1. The aqueous surfactant solutions had absorbances of almost zero in the visible region.

The concentration of the surfactant in the glass tube was measured at 1 h intervals over the 5 h experiment. The initial surfactant concentrations were set as follows: SDS (8 mmol L⁻¹), DTAC (21 mmol L⁻¹), and SB-12 (3 mmol L⁻¹). To determine surfactant concentration, 5 mL was extracted from residual solutions, and the water was slowly vaporized in a desiccator. The approximate molar concentration of the residual surfactant was calculated from the dry mass of the crystals.
Foam Separation of Dyes

3 Results and Discussion

3.1 Removal of ionic dyes by three kinds of ionic surfactants in foam separation

As shown in Fig. 1, methylene blue and Fast Green FCF are classified as cationic and anionic dyes, respectively. On the other hand, SDS, DTAC, and SB-12 are categorized as anionic, cationic, and amphoteric surfactants, respectively. Foam separation was performed on the two differently charged dyes using the three different surfactants. The pH values of the solutions naturally ranged from 4-6 in all foam separation systems. The initial concentrations of the dyes were changed from below the CMC to above the CMC later in the process were studied to clarify the relationship between surfactant concentration and dye removal. The decrease in the surfactant concentration because we later consider the superiority or inferiority of the surfactants for dye removal using kinetics. Figures 4 (a) and (b) show the removal of methylene blue and Fast Green FCF over time using the three surfactants. The positively charged methylene blue was effectively removed by SDS, whereas the DTAC monomer was also positively charged and thus could not remove methylene blue. Regarding the removal of Fast Green FCF, the DTAC monomer with its opposing charge functioned effectively, while the surfactant with the same charge, SDS, could not remove the negatively charged dye from the solution. The amphoteric surfactant, SB-12, was able to remove both cationic and anionic dyes, but its removal efficiency was slightly inferior to the results obtained using the SDS and DTAC systems. The removal rate for the cationic methylene blue in this study increased as follows: DTAC<SB-12<SDS, whereas for the anionic Fast Green FCF removal rate increased as follows: SDS<SB-12<DTAC. The combination of surfactants with dyes of opposing charges for foam separation has been confirmed in other systems, including orange G and cetylpyridinium chloride8, rhodamine B and SDS13, and DB17 (Direct Black 17) and cetyltrimethylammonium bromide10. This research shows that a surfactant with an opposite ionic charge is more effective for removing an ionic organic compound dissolved in an aqueous solution. However, the use of an amphoteric surfactant such as SB-12 was shown to be practical for removing both positively and negatively charged compounds, because the surfactant has two opposite charges in a molecule.

3.2 Dependence of dye removal on surfactant concentration

As shown in Fig. 4, there were certain surfactant concentrations and types that were better for removing dyes when using the foam separation method. The kinetics of the process were studied to clarify the relationship between surfactant concentration and dye removal. The

Table 1 Molar extinction coefficients (ε) of methylene blue and Fast Green FCF in ionic surfactants of solutions.

| Surfactant | Methylene blue | Fast Green FCF |
|------------|----------------|----------------|
|            | ε (L mol⁻¹ cm⁻¹) | λ_MAX (nm) | ε (L mol⁻¹ cm⁻¹) | λ_MAX (nm) |
| SDS        | 35521          | 660      | 106338       | 624        |
| DTAC       | 71707          | 660      | 75272        | 620        |
| SB-12      | 61602          | 664      | 102424       | 625        |

Fig. 3 Change in ionic surfactant concentrations as a function of time in the foam separation experiment. The initial surfactant concentration was fixed as follows; SDS (8 mmol L⁻¹), DTAC (21 mmol L⁻¹), and SB-12 (3 mmol L⁻¹)
dye concentration continuously decreased over time, as shown in Figs. 4(a) and (b). Therefore, the rate constant was estimated by fitting to these curves using first-order kinetics.

The decrease in ionic dye concentration with time was fitted using the first-order model:

$$\ln[C] = -kt + \ln[C_0],$$  

where $[C]$ is the concentration of ionic dye in the solution, $k$ is the first-order rate constant, $t$ is the removal time, and $[C_0]$ is the initial concentration of ionic dye. The results obtained using eq. (1) for methylene blue and Fast Green FCF are plotted in Figs. 5(a) and (b), respectively.

As shown in Figs. 5(a) and (b), the first-order rate constants ($k$) for dye removal rapidly decreased over the CMC for each surfactant system, except when using SB-12 and methylene blue. This means that the presence of micelles in the aqueous solution is disadvantageous for the adsorption of ionic dyes at the gas-liquid interface. The average micelle aggregation numbers of the surfactants are as follows: SDS = 72, DTAC = 43, and SB-12 = 46$^{18,20}$. The relatively large charges on the micellar surfaces are presumed to prevent the adsorption of the ionic dyes at the gas-liquid interface, making it desirable to adjust the surfactant concentration to below the CMC for the foam separation method. While the removal rate constant for methylene blue was almost constant for all three concentrations of SB-12 solutions, as shown in Fig. 5(a), that for Fast Green FCF was clearly different below and above the CMC. This difference originates from the interactions between micelles and ionic dyes. As shown in Fig. 6(a), the peak wavelength for the absorbance of methylene blue in all solutions containing SB-12 was the same as that in pure water (664 nm). On the other hand, that of methylene blue in micellar solution containing SDS was shifted to 660 nm. Therefore, methylene blue is present in water rather than the small micelles of SB-12. This could be due to the relatively high aqueous solubility of methylene blue (0.16 mol L$^{-1}$ at 293.2 K$^{21}$). Figure 6(b) shows that the peak absorption wavelength of Fast Green FCF shifted from 624 to 627 nm as SB-12 changed from a monomer solution to a micellar
solution. This means that the relatively hydrophobic Fast Green FCF was solubilized in the micelles rather than the aqueous phase. In fact, the aqueous solubility of Fast Green FCF was estimated to be 0.078 mol L\(^{-1}\) using the filtration method at 298.2 K; thus, the solubility of Fast Green FCF was lower than that of methylene blue. These results showed that the nature of the dye affected the foam separation results.

The influence of the initial concentration of ionic dye on the removal rate was also studied using typical systems. Figure 7(a) shows the results for the removal of methylene blue from SDS solutions (8 mmol L\(^{-1}\)) when changing the initial concentration of dye (100 and 200 \(\mu\)mol L\(^{-1}\)), while Fig. 7(b) shows the results for the removal of Fast Green FCF from aqueous DTAC solutions (8 mmol L\(^{-1}\)) under the same conditions. These results were analyzed in terms of their rate constants \((k)\) and half-lives \((t_{1/2} = \ln 2/k)\), and the values are summarized in Table 2. The half-lives of the systems were almost constant even as the initial concentrations of the dyes were changed. This means that dye removal can be sufficiently approximated as first-order under the above conditions. It was found that the rate constant and half-life were constant regardless of the initial concentration of the dyes.

These results showed that the foam separation method strongly depends on the electrostatic interaction between the surfactant and the target substance. Therefore, when the foam separation method is used for removing sewage, the selection of an appropriate surfactant is an important point to consider. Amphoteric surfactants are highly versatile and can be expected to act as effective surfactants.

4 Conclusion

This study showed that the foam separation method is effective for removing organic ions from aqueous solutions. It was demonstrated that the removal mechanism was
mainly controlled by electrostatic interactions between surfactant ions and dye ions. The positively charged methylene blue could be removed using SDS and SB-12, while DTAC and SB-12 were effective for removing negatively charged Fast Green FCF. Therefore, amphoteric surfactants having both positive and negative charges are likely to be practical surfactants for wastewater treatment using the foam separation method.

Future research on foam separation will investigate whether organic substances without charges can be separated by hydrophobic interactions. However, judging from the results of the research so far, the possibility of removing dissolved organic substances having no charges using the foam separation method is very low.

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