Removal of Zwitterionic Rhodamine B Using Foam Separation

Yusuke Goto, Yuya Nema, and Keisuke Matsuoka *

Faculty of Education, Laboratory of Chemistry, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama City, Saitama 338-8570, JAPAN

Abstract: Foam separation promotes the removal of dissolved materials from solutions by adsorbing the molecules onto a surfactant. The zwitterion of rhodamine B was removed by using both anionic (sodium dodecyl sulfate: SDS) and cationic (dodecyltrimethylammonium chloride: DTAC) surfactants through foam separation. However, rhodamine B could not be removed from a strongly acidic DTAC solution (pH 2), because the molecular form changes from the zwitterion to cation. Moreover, the cationic dye of rhodamine 6G could not be removed from the DTAC solution. Therefore, these results demonstrate that the electrostatic interaction between a surfactant and target ion is an important factor in foam separation.

Key words: foam separation, zwitterion, dye, bubble, rhodamine B, rhodamine 6G

1 Introduction

Foam separation is a useful method to remove solubilized materials from water by using functionalized adsorbents[1-3]. The removal mechanism occurs due to the adsorption of target materials on to a large bubble surface in the surfactant solution. The separation and condensation processes are then proceeded in the surfactant foams. The process of adsorption is attributed to the electrostatic interaction between the target ion and surfactant ion or the hydrophobic interaction between these ions in case of hydrophobic compounds. Foam separation has been reported to remove organic compounds[4-5], metallic ions[6-7], and halide ions[8-9] from a solution. Foam separation is advantageous because the waste consists of only the concentrated surfactant and target substances and that it is a simple process requiring addition of air to the solution for foam formation. Research has also been conducted to improve the removal efficiency of foam separation, and an apparatus has been designed to this end[10, 11].

For foam separation, an appropriate surfactant must be selected depending on the properties of the target substance. For example, anionic surfactants are effective in removing alkali and alkaline earth ions[6-7]. Moreover, some surfactants can selectively target particular compounds, such as sodium dodecyl sulfate (SDS), an anionic surfactant that can selectively remove the positively charged rhodamine-G from mixed dye solutions[10].

In this study, we selected rhodamine 6G, which has the core structure identical to that of rhodamine B. The charge of rhodamine B can change from a zwitterion to cation in response to pH of the materials to be removed[12, 13]. For example, rhodamine B in a pH neutral solution changes to a cationic state in the presence of a carboxylic group due to the decreased pH. Both of these organic dyes are convenient probes to examine the removal of the target material in foam separation, as they exhibit unique absorbance in the visible region.

The purpose of this study is to determine the influence of a zwitterion on the removal rate of foam separation using rhodamine B. We discuss the effect of the difference in the charge of the target ions on foam separation using cationic and anionic surfactants.

2 Experimental

2.1 Materials

Dyes of rhodamine B (>98% purity) and rhodamine 6G (>98% purity) and surfactants of SDS (>98% purity) and dodecyltrimethylammonium chloride (DTAC) (>98% purity) were purchased from Tokyo Chemical Industry Co., Ltd. The reagents were used directly without purification. The molecular structures of dyes are shown in Fig. 1. Water was purified by ion-exchange treatment (PRA-0015,
ORGANO).

2.2 Foam separation of dyes

The apparatus of foam separation for dyes was the same as that for alkali metals, which has been reported previously [6]. The foam separation experiments were performed using anionic (SDS) or cationic (DTAC) surfactants as the dye carrier. The initial concentrations of the ionic dyes (rhodamine B and rhodamine 6G) were 100 μmol L⁻¹. The initial concentration of the surfactants were changed from below the critical micelle concentration (CMC) depending on the experimental system. Their critical micelle concentration (CMC) are reported to 8.2 mmol L⁻¹ (SDS) and 21.3 mmol L⁻¹ (DTAC) at 298.2 K, respectively [14, 16]. The surfactant solution volume with the dye added was 250 mL. The pH of the initial solution was 4–6. The pH of the initial solutions was adjusted by adding appropriate amounts of hydrochloric acid or sodium hydroxide solutions to obtain a pH of 2 and 10, respectively. The total experiment was repeated over three times. The concentrations of the ionic dyes during foam separation were determined by sampling from the bulk solution every 30 min through ultraviolet-visible spectrophotometry (JASCO, V-630 iRM). The molar extinction coefficients (ε) of rhodamine B and rhodamine 6G were 1.08 × 10⁵ L mol⁻¹ cm⁻¹ (558 nm) and 8.94 × 10⁴ L mol⁻¹ cm⁻¹ (533 nm) in SDS and 1.01 × 10⁵ L mol⁻¹ cm⁻¹ (554 nm) and 8.88 × 10⁴ L mol⁻¹ cm⁻¹ (527 nm) in DTAC, respectively.

3 Results and Discussion

As shown in Fig. 1, rhodamine B and rhodamine 6G having similar molecular structures were prepared as removal substances. The dyes have been used as fluorescent dye, biomarker, and staining agent. The rhodamine B is known to exist as zwitterions in aqueous solutions over wide pH range [22]. The acid dissociation constant (pK_a) is estimated to 3.2 [10], and it is known that it exists as a zwitterion over pH 3 (Fig. 1). On the other hand, rhodamine 6G exists as only cation and used as comparison for zwitterion in foam separation measurements.

Fig. 1 Molecular structure of dyes; (a) rhodamine B (zwitterion) and (b) rhodamine 6G (cation).

As shown in Fig. 2(a), rhodamine B was removed by foam separation using both SDS and DTAC. The removal rates are summarized in Table 1. Previous studies have only described the combinations of surfactants and target substances having oppositely charged ions [6, 17]. A substance that can be removed with both anionic and cationic surfactants is very unusual in foam separation. The reason is originated from the rhodamine B is naturally zwitterion in aqueous solution [15, 16].

When compared under the same experimental condition with a surfactant concentration of 8 mmol L⁻¹, SDS was able to remove rhodamine B slightly more efficiently than DTAC (Fig. 2(a)). As shown in Table 1, the removal rate of rhodamine B after 5 h was 100% removal in the SDS system, whereas it was 90% in the DTAC system. This difference is due to the slightly higher foaming properties of SDS than those of DTAC [18] and the difference in the strength of the interaction between rhodamine B and each hydrophilic group. Moreover, Fig. 2(a) indicates that an increase in the surfactant concentration decreases the removal rate of rhodamine B. In particular, rhodamine B gets barely removed from the DTAC solution at 40 mmol L⁻¹.
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which is higher than the CMC of DTAC (21 mmol L⁻¹), because rhodamine B is solubilized in micelles¹⁰, which inhibits adsorption. A similar tendency was also reported for the removal of Cs using SDS through foam separation¹⁰. An aqueous monomer solution is more advantageous than a micelle solution in foam separation.

On the other hand, SDS, an anionic surfactant, could remove the cationic dye of rhodamine 6G, whereas DTAC could not eliminate rhodamine 6G from the solution, as shown in Fig. 2(b). This indicates that the molecules having the charge opposite to that of the surfactant are preferentially adsorbed to the surfactant layer on the gas–liquid surface.

Rhodamine B changed from the zwitterionic to cationic state with decrease in pH. The change in the molecular charge can be identified by comparing the peak wavelength of the absorbance spectrum of rhodamine B (Fig. 3(a))²¹. As shown in Fig. 3(a), the peak was shifted from 557 nm (pH 2) to 553 nm (pH 6) in water, indicating the change from cation to zwitterion with increasing pH. The peaks of the absorbance spectra in both water and DTAC solution (20 mmol L⁻¹) are plotted in Fig. 3(b). As shown in Fig. 3(b), the peak wavelength of rhodamine B became constant over pH 4. This indicates that rhodamine B is present as a zwitterion in the naturally aqueous solution and changes to a cation in the strong acid region by adding HCl to the solution. Thereby, the foam separation measurement was performed by changing the initial pH of the DTAC solution (20 mmol L⁻¹) containing rhodamine B from 2.0 to 4.7 (natural conditions) and 10 (Fig. 3(c)). As shown in Fig. 3(c), the removal rate of rhodamine B in the range of strong acid was extremely low in DTAC solution, because rhodamine B was presented only as a cation at pH 2. On the other hand, the zwitterion of rhodamine B almost decreased in the aqueous solution at pH 4.7 and pH 10. This fact was indicated that the most important factor for removing organic dyes was electrostatic interaction in foam separation.

The removal tendencies for the ionic dyes were evaluated using kinetics for a first-order reaction. The concentrations of dyes continuously decreased with time in Fig. 2 and Fig. 3(c). Therefore, the rate constant was estimated by fitting to these curves through first-order kinetics. The decrease in the 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 dyes in the solution, k is the first-order rate constant, t is the removal time, and [C₀] is the initial concentration of ionic dyes. The results are summarized in Table 1.

As shown in Table 1, the relatively higher k (0.0528 min⁻¹) for removal of rhodamine B at 4 mmol L⁻¹ (SDS) indicates good conditions for foam separation. Similarly, DTAC in an aqueous solution having concentration below the CMC shows the same tendencies as shown in Table 1 and Fig. 2(a). These results suggest that foam separation is a good condition for aqueous monomer solution. On the other hand, the first-order rate constant (k) of rhodamine 6G and typical alkali metals are compared under the same conditions of SDS solutions. For example, the first-order rate constant (k) of rhodamine 6G is 0.0084 min⁻¹, while the k of K⁺ and Cs⁺ ions are 0.0015 and 0.0024 min⁻¹, respectively.²⁰ From this comparison, the cationic dye was more advantageous for removal rather than alkali metal ions in viewpoints of kinetics. The cause of the difference may be originated from size of cation.

4 Conclusion

Foam separation was shown to be a very effective method of removing dissolved substances from aqueous solutions. The zwitterion of rhodamine B could remove by both of anionic and cationic surfactants in the foam separations. However, when the zwitterion change to a cation by lowering pH of the aqueous solution, the rhodamine B was hardly removed from same charge of cationic surfactant. From these results, electrostatic interaction between sur-

| Surfactant | Concentration (mmol L⁻¹) | Removal rate (Rhodamine B) (%) | k (min⁻¹) | Removal rate (Rhodamine 6G) (%) | k (min⁻¹) |
|------------|--------------------------|-------------------------------|-----------|-------------------------------|-----------|
| SDS        | 4                        | 100                           | 0.0528    | –                             | –         |
|            | 8                        | 100                           | 0.0097    | 99                            | 0.0084    |
|            | 16                       | 48                            | 0.0021    | 28                            | 0.0010    |
| DTAC       | 20                       | 90                            | 0.0075    | –                             | –         |
|            | 40                       | 5                             | 0.0002    | –                             | –         |

Table 1  Removal rate and first order rate constant (k) for rhodamine B and rhodamine 6G systems depending on initial concentration of surfactants (SDS and DTAC) after 5 h by foam separation.
factant and target ion is very important factor in foam separation method. Therefore, we have to select appropriate surfactant for removing materials in foam separation.

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