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COMMUNICATION

Cloud Point Foaming Technique for Separation of Nonionic Surfactant from Solution

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ABSTRACT

We explored a novel cloud point foaming technique to separate nonionic surfactant from aqueous solutions with a wide range of surfactant concentrations. The phase transformation of nonionic surfactant micelles at the cloud point changes the foaming behavior of surfactant solutions during foaming and results in excellent separation efficiency in terms of the volume reduction ratio compared to foaming at room temperature.

INTRODUCTION

The foaming abilities of surfactants have been widely used in foam separation techniques. The basic principle of foam separation is that surface-active materials tend to concentrate on a gas–liquid interface. When air bubbles are generated in solution, surface-active materials attach to the rising bubbles which then separate into a foam layer. Increasing attention has been given in recent years to the application of the foaming technique for the separation and purification from aqueous solution of various environmental pollutants and byproducts such as heavy metal ions (1, 2), dyes (3, 4), cells (5), and proteins (6). Surfactants molecules adsorb readily on a gas–liquid interface owing to their amphiphilic characteristics. It therefore seems reasonable to assume that separation of surfactants from aqueous solutions by foaming is feasible. The foaming technique possesses several distinct advantages over membrane methods (7, 8) to recover surfactants from water: small requirements for energy, small requirements for space, and moderate cost (9). Several studies on the separation of surfactants by foaming from wastewater with dilute surfactant concentrations have been reported (10–13). However, separation of surfactant from concentrated solutions with a surfactant concentration above its critical micelle concentration (cmc) has not yet been reported. Somasundaran (14) noted that the adsorption density of surfactants on bubble surfaces would not increase by any significant amount on increasing the surfactant concentration above its cmc, and separation efficiency is expected to be low in concentrated surfactant solutions.

In this study we explored a novel strategy to separate nonionic surfactant from aqueous solutions with a wide range of surfactant concentrations. This strategy, which is called the cloud point foaming technique, relies on the phase transformation of nonionic surfactant micelles above their cloud point temperature. Aqueous solutions of nonionic surfactants become turbid on being heated to a temperature known as the cloud point. This phenomenon is due to the decreased hydration of the oxyethylene oxygen in the polyoxyethylene hydrophilic group with increasing temperature. As the temperature increases, micelle growth and increased intermicellar attraction cause the formation of particles that are so large that the solution becomes visibly turbid. We hypothesize that this phase transformation of micelles at the cloud point may change the foaming behavior of surfactant solutions and may be advantageous when foam separating nonionic surfactants from solutions. In addition to its use for surfactant recovery, this technique is favorable for the novel cloud point extraction process proposed by Watanabe (15), Hinze (16), and Armstrong's (17) group. We here attempt to illustrate the separation efficiency of this new foaming strategy. Hence, the results are focused on the separation of a representative nonionic surfactant, polyethylene glyco mono-*p*-nonylphenyl ether.

EXPERIMENTAL

Batch foam separation tests were performed using an apparatus adopted from Huang's (18, 19) group. The Pyrex glass column was 3.5 cm in diameter by 90 cm in length with a water jacket for temperature control. The bottom of the column was closed with a silicone rubber stopper with holes for a fine pore fritted glass sparger and a stopcock to take samples and to drain the column. A lipped side arm near the top of the column served as a foam outlet. Nitrogen gas was supplied by a nitrogen cylinder with a pressure regulator. The gas flow rate was adjusted using a single tube flowmeter with a needle valve. The gas was passed through distilled water for controlled rehumidification.

Reagent-grade polyethylene glyco mono-*p*-nonylphenyl ether (PGE, Tokyo Kasei Organic Chemicals, Japan), a nonionic surfactant, was used as received. The chemical formula of PGE is $C_{15}H_{23}(CH_2CH_2O)_{10}OH$ and its cmc, determined by the surface tension method, is 6.9×10^{-5} M. Also, the cloud point of PGE was determined to be 62°C in this study.

For the foam separation runs, PGE was added to distilled water to form surfactant solutions; the pH of the solution was maintained at 6.5 ± 0.2 throughout this study. A 250 mL volume of the solution was poured into the separation column and the timer was started. The gas flow rate was adjusted before the surfactant solution was poured into the column. The end of a foam separation run was signified by the collapse of a stable foam layer. The concentration of PGE in sample solutions was determined by a UV/Vis spectrophotometer (Shimazdu UV160A). The absorbance of the solution was measured at 275 nm and compared with the calibration curve. The efficiency of foam separation in this study was evaluated through three parameters: surfactant recovery, volume reduction ratio, and flotation time. Surfactant recovery was defined as the weight percentage of surfactant collected in the foamate. Volume reduction ratio was defined as the ratio of the original solution volume (250 mL) to the final foamate volume. The volume reduction ratio generally increases with the efficiency of foam separation. Finally, flotation time was counted from the pouring of surfactant solution into the separation column to the end of the separation run. Three different surfactant concentrations, 5×10^{-5} M, 5×10^{-4} M, and 5×10^{-3} M, were used in separation tests which corresponded to a surfactant concentration range from sub-cmc to a concentration almost 2 orders of magnitude higher than cmc.

RESULTS AND DISCUSSION

Figure 1 demonstrates the effect of the cloud point temperature on the separation efficiency under a low gas flow rate (40 mL/min). The surfactant recovery was high for all cases, probably because the foam separation tests were allowed to continue until the foam layer collapsed, which indicated a very low residual surfactant concentration in solution. Moreover, the slightly lower surfactant recovery above the cloud point temperature (70°C) is explained by the fact that the foaming potential of PGE decreased at the cloud point. This decrease in the foaming potential of PGE turns out to be an advantage for separation in terms of the volume reduction ratio. Figure 1(b) shows that the volume reduction ratio for tests at the cloud point temperature was almost an order of magnitude higher than that for tests at room temperature. For example, the volume reduction ratios for 5×10^{-3} M PGE solution at 25 and 70°C were 1.56 and 9.25,

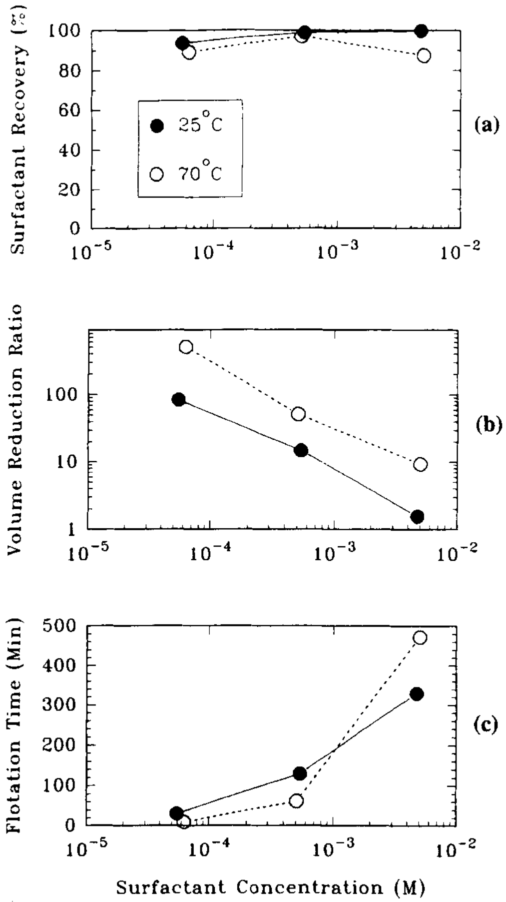

FIG. 1 Efficiency of foam separation under low gas flow rate conditions (40 mL/min).

respectively. In other words, 1000 mL of 5 × 10^{-3} M PGE solution will be concentrated to final volumes of 641 and 108 mL at 25 and 70°C, respectively. This is a significant difference in terms of separation efficiency. The lower volume reduction ratio for PGE solution at 25°C than 70°C is presumably due to phase transformation of PGE micelles at 70°C. At 25°C, micelles act as reservoirs of surfactant which can readily supply molecules to any new surface available. In this way, a large number of bubbles are produced promptly, and that results in fast rising foam in the column. This, in turn, causes a very short foam retention time in the column and

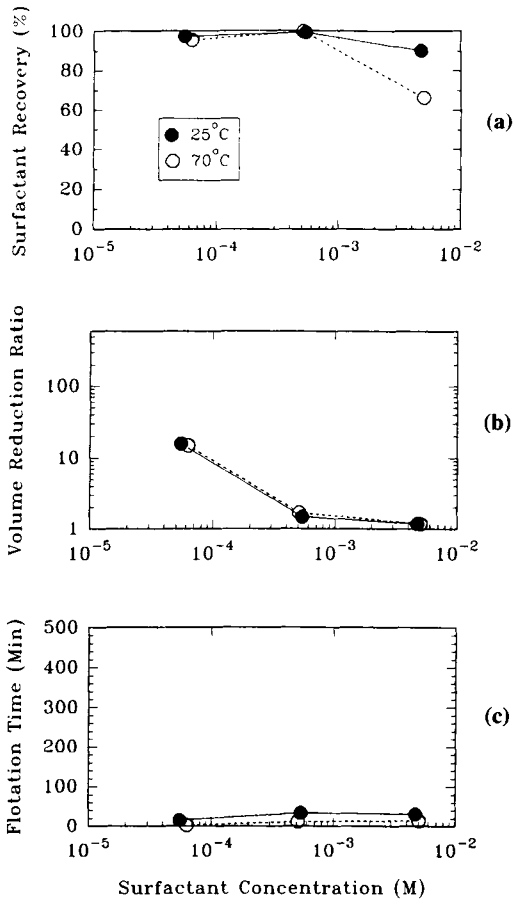

FIG. 2 Efficiency of foam separation under high gas flow rate conditions (100 mL/min).

very poor foam drainage. On the other hand, the micelles were actually being "heating out" from solution at 70°C, and there were no longer plenty of surfactant monomers available for foaming. In this case a stable foam with a slow rising speed was observed in the column and excellent foam drainage was achieved. In addition, dehydration of the outer hydrophilic portion of PGE micelles at 70°C made their surfaces more hydrophobic, so that the precipitated micelles (the cloud) could easily attach to air bubbles and be carried out of the separation column by the foam. This explains the excellent volume reduction ratio for foam separation of a nonionic surfactant at 70°C. Figure 1(c) shows that the flotation time for tests at 70°C is slightly shorter for the two low surfactant concentration tests (5×10^{-5} M and 5×10^{-4} M) than these at room temperature. However, for the high surfactant concentration tests (5×10^{-3} M), flotation time was longer for the 70°C test than for the 25°C test. This is presumably due to the very poor foam drainage phenomenon at 25°C. In this case a large volume of solution was transferred to concentrate rapidly, which caused a short flotation time.

Figure 2 demonstrates the effect of cloud point temperature on the separation efficiency under a high gas flow rate condition (100 mL/min). It is clearly seen that the advantage of cloud point separation disappears at high gas flow. The volume reduction ratios were very poor for all cases. This observation indicates that separation of a nonionic surfactant from solution by foaming at the surfactant's cloud point is effective only at a proper gas flow rate. A high gas flow rate causes a large number of fast rising bubbles and very poor foam drainage, which results in the very poor volume reduction ratios and the very short flotation times that were observed.

This preliminary study regarding the concentration of nonionic surfactant solutions by a foam separation technique has demonstrated the feasibility of flotation at cloud point of nonionic surfactant solutions. To the best of our knowledge, this communication is the first such reported surfactant concentrating technique in the literature. Generally speaking, foam separation of a nonionic surfactant at the cloud point results in excellent volume reduction ratios compared to that at room temperature, presumably due to the different physical states of surfactant micelles which can exist in solution. However, this advantage will be effective only at proper gas flow rate conditions. This technique, which may be useful for surfactant recovery and coalescence extraction, deserves further study.

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