
**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Surfactant Recovery from Water Using Foam Fractionation

Nopparat Tharapiwattananon[a]; John F. Scamehorn[b]; Somchai Osuwan[a]; Jeffrey H. Harwell[b]; Kenneth J. Haller[a]
[a] THE PETROLEUM AND PETROCHEMICAL COLLEGE, CHULALONGKORN UNIVERSITY, BANGKOK, THAILAND [b] INSTITUTE FOR APPLIED SURFACTANT RESEARCH, UNIVERSITY OF OKLAHOMA, NORMAN, OK, USA

**To cite this Article** Tharapiwattananon, Nopparat , Scamehorn, John F. , Osuwan, Somchai , Harwell, Jeffrey H. and Haller, Kenneth J.(1996) 'Surfactant Recovery from Water Using Foam Fractionation', Separation Science and Technology, 31: 9, 1233 — 1258

**To link to this Article: DOI:** 10.1080/01496399608006948

**URL:** http://dx.doi.org/10.1080/01496399608006948

SEPARATION SCIENCE AND TECHNOLOGY, 31(9), pp. 1233–1258, 1996

# Surfactant Recovery from Water Using Foam Fractionation

NOPPARAT THARAPIWATTANANON
THE PETROLEUM AND PETROCHEMICAL COLLEGE
CHULALONGKORN UNIVERSITY
BANGKOK, THAILAND

JOHN F. SCAMEHORN*
INSTITUTE FOR APPLIED SURFACTANT RESEARCH
UNIVERSITY OF OKLAHOMA
NORMAN, OK 73019, USA

SOMCHAI OSUWAN
THE PETROLEUM AND PETROCHEMICAL COLLEGE
CHULALONGKORN UNIVERSITY
BANGKOK, THAILAND

JEFFREY H. HARWELL
INSTITUTE FOR APPLIED SURFACTANT RESEARCH
UNIVERSITY OF OKLAHOMA
NORMAN, OK 73019, USA

KENNETH J. HALLER
THE PETROLEUM AND PETROCHEMICAL COLLEGE
CHULALONGKORN UNIVERSITY
BANGKOK, THAILAND



## ABSTRACT

The purpose of this study was to investigate the use of foam fractionation to recover surfactant from water. A simple continuous mode foam fractionation was used and three surfactants were studied (two anionic and one cationic). The effects of air flow rate, foam height, liquid height, liquid feed surfactant concentration, and sparger porosity were studied. This technique was shown to be effective in

* To whom correspondence should be addressed.

either surfactant recovery or the reduction of surfactant concentration in water to acceptable levels. As an example of the effectiveness of this technique, the cetylpyridinium chloride concentration in water can be reduced by 90% in one stage with a liquid residence time of 375 minutes. The surfactant concentration in the collapsed foam is 21.5 times the feed concentration. This cationic surfactant was easier to remove from water by foam fractionation than the anionic surfactants studied.

## INTRODUCTION

Surfactants are widely used in many industries. As environmental regulations tighten, there is increasing concern about reducing the surfactant concentration in effluent streams. One source of these streams is surfactant-based separations, which are being increasingly used to remove pollutants from wastewater and groundwater (1). In these processes, surfactants are added to a contaminated stream to effect removal of pollutants. Sometimes a stream emitted from one of these processes contains a low surfactant concentration. In addition to satisfying environmental regulations, the value of the surfactant being emitted sometimes make recovery operations economical. The surfactant concentrations of interest are generally around or below the critical micelle concentration (CMC).

One surfactant-based separation of interest is micellar-enhanced ultrafiltration (MEUF) (2). In MEUF, a surfactant is added to an aqueous stream containing dissolved pollutants. The surfactant is at a concentration well above the CMC, so most of the surfactant is present as aggregates called micelles. The micelles solubilize organic contaminants and bind multivalent ions (e.g., heavy metals, chromate) if the surfactant is chosen to have the proper valence. The stream is then treated by ultrafiltration with membrane pore sizes small enough to block the micelles from entering the permeate (stream passing through the membrane). The surfactant concentration in the permeate is at or slightly below the CMC (2). Generally, the surfactant must be recovered from the stream for an economical separation (3).

Foam fractionation has been extensively studied for the purpose of removing pollutants (e.g., heavy metals) from water by adding surfactant on purpose. In this study, the purpose is to recover surfactant itself using foam fractionation. This investigation involves the systematic study of the most important variables on the efficiency of a foam fractionation operation in a pilot-scale fractionator for several different surfactants.

## BACKGROUND

Foam fractionation is a process in which solute species are adsorbed at a gas–liquid interface between a dispersed phase (gas bubble) and a continuous phase (bulk liquid) (4). Foam fractionation processes have been used to concentrate and remove surface-active agents from aqueous solutions (5). Moreover, nonsurface-active materials can be removed by interaction with the surfactant and are carried along into the foam. In the latter case the surfactant is called a collector (6).

In foam fractionation, air is sparged to produce bubbles which rise to the top of a liquid column, producing foam there. As the bubbles travel through the continuous phase, surfactant adsorbs at the air–liquid interface (Fig. 1). When the air bubble emerges from the liquid, it forms a cell in the foam honeycomb. The thin liquid film between air bubbles (foam lamellae) is stabilized by the adsorbed surfactant (7). The liquid drains from the lamellae due to gravity, and plateau border suction effects (8) cause the foam to eventually break or collapse. The collapsed foamate solution is much more concentrated in the surfactant than in the feed solution. In this work, a simple continuous mode of operation was used as shown in Fig. 2.

There have been many studies on foam fractionation including the effect of operating mode (9–15) and foam properties (16–19). Many publications are available on the use of foam fractionation for removing colligends such as metal ions and anionic ions from the aqueous phase by using surfactant as the collector (20–35). The effects of such key variables as temperature,

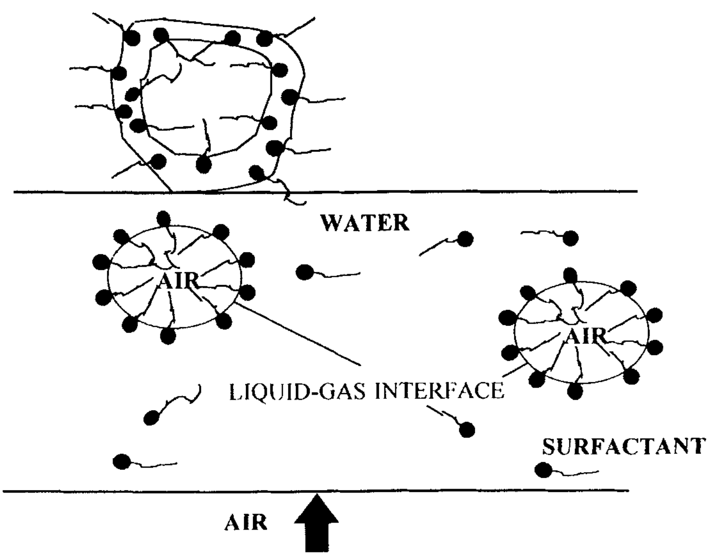


FIG. 1 Foam structure.

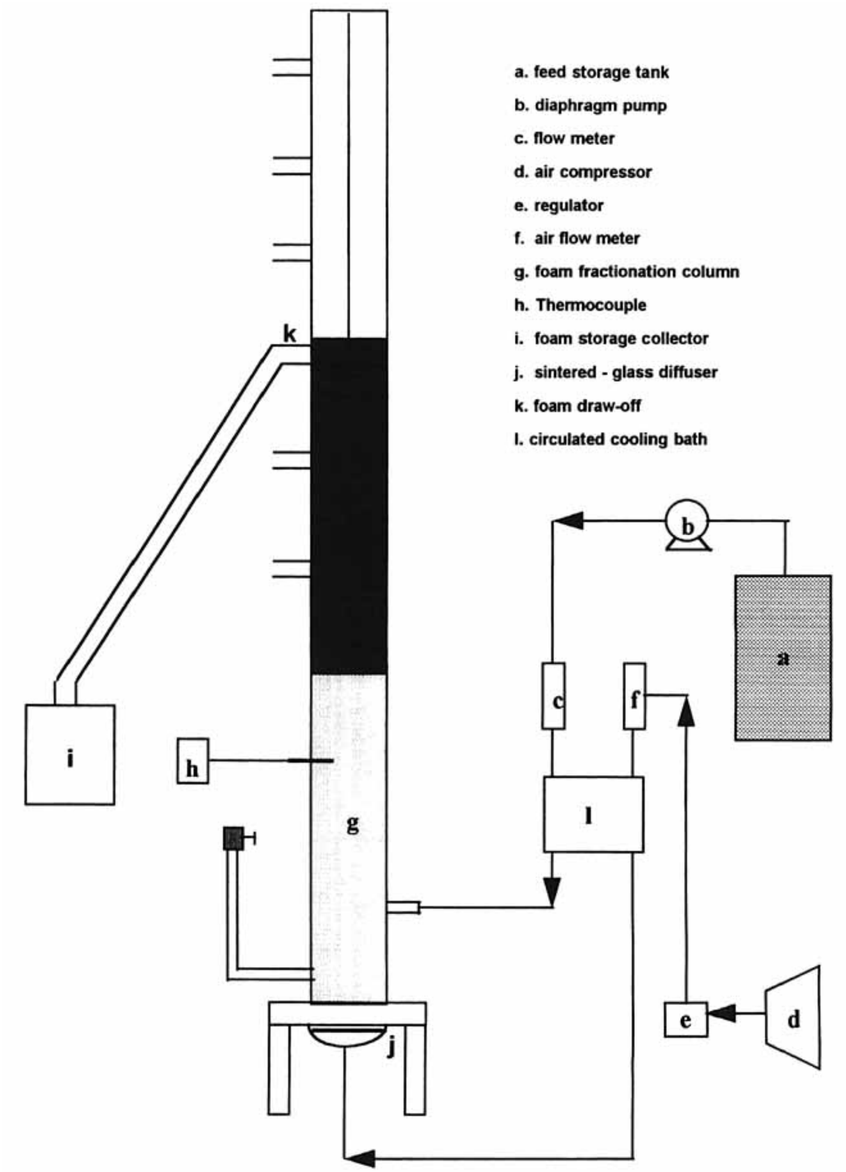


FIG. 2 Schematic diagram of foam fractionation system.

feed rate, pH, gas flow rate, feed concentration, foam height, and bubble diameter on the operation of both batch and continuous fractionation have been studied (10, 14, 36–45). The surface activity in mixed surfactant solutions has been studied (11, 46, 47). Despite this large number of publications, few studies have directly addressed the use of foam fractionation for the purpose of surfactant removal from water.

Three different surfactants were chosen for study: sodium dodecyl sulfate (SDS, a typical anionic surfactant), cetylpyridinium chloride (CPC, a typical cationic surfactant), and sodium *n*-hexadecyl diphenyloxide disulfonate [DADS, an anionic surfactant which shows great promise in several surfactant-based separations (3, 48)].

## EXPERIMENTAL

### Materials



Three surfactants were chosen for study. Sodium dodecyl sulfate (SDS) from Kao Industrial R&D was 96.28% pure. Cetylpyridinium chloride (CPC) from Zealand Chemical was >99% pure. Sodium *n*-hexadecyl diphenyloxide disulfonate (Dowfax 8390 or DADS) from Dow Chemical was 36.5% by weight pure. Distilled water with a conductivity of 2 μmho/cm was used in all experiments. Manufacturer-supplied information about the surfactants used is shown in Table 1.

### Equipment

A schematic flow diagram of the apparatus used is shown in Fig. 2. The fractionator was an acrylic cylindrical column of 12 cm O.D., 3 mm in wall thickness, and 150 cm in height.

TABLE 1
Information on Manufacture-Supplied Surfactant Properties

| Surfactant | Formula weight | Quality | Source |
|---|---|---|---|
| Sodium dodecyl sulfate (SDS) | 288.38 | 96.28% SDS, 1.12% volatile matter, 0.39% *n*-hexane, 2.207% $SO_4$ | Kao Industrial (Emal 10 P) Lot No. 432 |
| Cetylpyridinium chloride (CPC) | 358.01 | >99% pure | Zealand Chemical |
| Sodium *n*-hexadecyl diphenyloxide disulfonate (DADS) | 640 | 36.5% by wt active, 10% NaCl, 0.51% $Na_2SO_4$ | Dow Chemical |

## Methods

The surfactant feed solution was pumped through a flowmeter at 100 mL/min by a diaphragm pump before entering the column at a position 35 cm from the bottom of the column. The liquid level in the column was controlled by adjustment of the bottom stream withdrawal rate. The air pressure from a compressor was maintained by a regulator and was introduced to the column through a sintered-glass diffuser. Sintered-glasses No. 0, 1, 2, and 3 were used to produce bubble sizes of 160–250, 100–160, 40–100, and 16–40 μm, respectively. We will report the median bubble sizes in the work of 28, 70, 130, and 205 μm. Foam was collected in a receiver for a measured time period. The foam was weighed, then frozen, and thawed to get the collapsed foamate volume. The column operating temperature was held at 20°C by using a circulated cooling bath and hose jacket around the column and was measured continuously by a thermocouple.

The foam fractionation was studied under steady-state conditions. The base condition was 150 mL/min (15 L/min·m$^2$) air flow rate, 100 mL/min (10 L/min m$^2$) liquid feed rate, 45 cm foam height, and 45 cm liquid height. The surfactant concentration in the feed solution was held constant at about 80% of the CMC, depending on the surfactant used. Each experiment was carried out for a minimum of 3 hours. Steady-state was insured when all measured parameters were invariant with time.

In each experiment, volumetric foam flow rate production (L/min·m$^2$), flow wetness (g of collapsed foam solution/L of foam), and the surfactant concentration in the collapsed foam solution were measured. SDS concentrations were determined by conductivity while the concentrations of CPC and DADS were determined by UV at wavelengths of 260 and 237 nm, respectively.

The CMC of each surfactant was calculated as the concentration where the specific conductivity of the solution vs surfactant concentration showed an abrupt change in slope.

## RESULTS AND DISCUSSION

The enrichment ratio is defined as the ratio of the concentration of surfactant in the collapsed foam solution to that in the feed solution ($c_f/c_i$). Rate of surfactant recovery is calculated by $Fc_fM_w$ where $F$ is the collapsed foam flow rate and $M_w$ is the molecular weight of that surfactant. The CMC value is 8.2 mM for SDS, 0.9 mM for CPC, and 0.45 mM for DADS.

Table 2 gives results of all the foam fractionation experiments. The effect of air flow rate is shown in Figs. 3–6. The lowest air flow rate shown is close to the lowest possible for the fractionator used; i.e., a lower flow rate would have resulted in such a low production of foam that foam collapse would not allow any foam to reach the overheads draw-off. From Figs. 3 and 4 the enrichment ratio is higher and the foam is dryer when the air flow rate is slower because of the higher residence time of bubbles in the rising foam, resulting in the available drainage time being longer. In this case, more water drainage occurs, leaving a dryer foam with a higher surfactant concentration. This is because a substantial fraction of the surfactant in the foam is adsorbed at the air–water interface rather than in the lamellae liquid which drains off. As the air flow rate increases, a higher volumetric rate of foam (Fig. 5) and a wetter foam (Fig. 4) is collected in the overheads, resulting in a higher collapsed foam flow rate. Even though the foam has a lower surfactant concentration (Fig. 3), the higher flow rate of collapsed foam solution results in a higher rate of surfactant recovery from the liquid feed stream entering the unit as shown in Fig. 6. The effect of air flow rate is in reasonable agreement with other work (10, 11, 14).

The effect of the foam height (distance between top of liquid and foam draw-off) is shown in Figs. 7–10. As expected, as the foam height increased, a greater residence time resulted in a dryer foam (Fig. 8) with a greater enrichment ratio (Fig. 7) for the same reasons as decreasing air flow rate causes these same effects as already discussed. The rate of surfactant recovery decreased with increasing foam height as shown in Fig. 10 because of the increased rate of foam collapse due to foam drainage. The results have the same trends as in previous work (39).

The effect of the liquid height is shown in Figs. 11–14. From Fig. 11, liquid height increases the enrichment ratio for CPC, probably because of an increase in residence time of bubbles in the liquid section. As the bubbles take longer to rise through the solution, adsorption of surfactant at the gas–liquid interface can more closely approach an equilibrium level, increasing the enrichment ratio. Except in the case of CPC, liquid height had little effect on separation over the range studied.

The effect of the surfactant concentration in the liquid feed is shown in Figs. 15–22. A concentration range of 10% of the CMC to the CMC was studied. The wetness of the foam increases with increasing surfactant concentration as shown in Figs. 17 and 18. This may be due to the effect of concentration on air bubble size since the surfactant concentration affects surface tension at the air/water interface and, therefore, the bubble size. Smaller bubbles at a higher surfactant concentration could form a creamier

TABLE 2
Experiment Results for Foam Fractionation Runs[a]

| | $c_f/c_i$ | | | Foam wetness (g/L) | | | Foam flow rate (L/min·m$^2$) | | | Rate of recovery (g/h·m$^2$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SDS | CPC | DADS | SDS | CPC | DADS | SDS | CPC | DADS | SDS | CPC | DADS |
| Air flow rate (L/min·m$^2$): | | | | | | | | | | | | |
| 10.0 | 26.56 | 129.73 | 72.85 | 0.19 | 0.64 | 2.11 | 7.69 | 6.67 | 2.86 | 4.3 | 8.3 | 6.0 |
| 12.5 | 14.14 | 80.55 | 38.22 | 0.37 | 1.57 | 3.08 | 12.50 | 11.11 | 8.33 | 7.3 | 21.1 | 13.6 |
| 15.0 | 11.74 | 27.32 | 16.69 | 0.48 | 3.8 | 6.03 | 16.67 | 16.77 | 14.29 | 10.6 | 26.0 | 16.8 |
| 20.0 | 5.34 | 4.89 | 2.83 | 1.03 | 26.9 | 39.95 | 25.00 | 25.00 | 22.22 | 15.5 | 49.5 | 34.8 |
| 25.0 | 3.66 | 2.21 | 1.69 | 1.62 | 62.38 | 75.71 | 33.33 | 33.33 | 30.00 | 22.2 | 69.2 | 53.4 |
| Foam height (cm): | | | | | | | | | | | | |
| 30 | 5.29 | 8.66 | 6.63 | 0.99 | 17.73 | 12.96 | 18.18 | 20.00 | 16.67 | 10.7 | 46.1 | 19.8 |
| 45 | 11.63 | 27.32 | 16.69 | 0.48 | 3.80 | 6.03 | 16.67 | 16.67 | 14.29 | 10.5 | 20.9 | 19.9 |
| 60 | 22.27 | 53.63 | 35.22 | 0.23 | 1.70 | 1.70 | 14.29 | 14.29 | 10.00 | 8.4 | 15.8 | 8.3 |
| 75 | 37.49 | 106.52 | 68.54 | 0.12 | 0.81 | 1.17 | 12.50 | 11.11 | 5.00 | 6.1 | 11.6 | 5.5 |
| 90 | 51.00 | 272.78 | 82.21 | 0.09 | 0.38 | 1.06 | 10.00 | 6.67 | 1.67 | 5.4 | 8.3 | 2.0 |
| Liquid height (cm): | | | | | | | | | | | | |
| 15 | 9.54 | 14.49 | 13.36 | 0.79 | 8.1 | 7.06 | 16.67 | 16.67 | 14.29 | 14.1 | 29.4 | 18.6 |
| 30 | 10.56 | 21.12 | 14.64 | 0.67 | 5.36 | 6.47 | 16.67 | 16.67 | 14.29 | 13.3 | 28.3 | 18.7 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 45 | 11.82 | 27.32 | 16.69 | 0.47 | 3.8 | 6.03 | 16.67 | 16.67 | 14.29 | 10.4 | 26.0 | 19.9 |
| 60 | 12.80 | 33.22 | 16.91 | 0.41 | 3.62 | 5.98 | 16.67 | 16.67 | 14.29 | 9.8 | 30.1 | 20.0 |
| 75 | 14.32 | 36.56 | 16.91 | 0.37 | 3.56 | 5.94 | 16.67 | 16.67 | 14.29 | 9.9 | 32.6 | 19.8 |
| Feed concentration (% of CMC): | | | | | | | | | | | | |
| 10 | 24.26 | | | 0.14 | | | 6.25 | | | 2.3 | | |
| 20 | | 96.21 | 131.05 | | 2.49 | 1.17 | | 14.29 | 2.50 | | 13.9 | 1.7 |
| 25 | 16.27 | | | 0.25 | | | 12.50 | | | 5.7 | | |
| 40 | 12.44 | 55.60 | 47.97 | 0.37 | 3.26 | 3.14 | 16.67 | 15.39 | 5.00 | 8.6 | 21.5 | 5.3 |
| 55 | 9.92 | | | 0.51 | | | 16.67 | | | 9.5 | | |
| 60 | | 36.54 | 28.93 | | 3.57 | 4.18 | | 16.67 | 10.00 | | 21.5 | 12.2 |
| 70 | 11.90 | | | 0.52 | | | 16.67 | | | 11.5 | | |
| 80 | | 27.32 | 16.69 | | 3.80 | 6.03 | | 16.67 | 14.29 | | 26.0 | 19.9 |
| 85 | 11.25 | | | 0.51 | | | 16.67 | | | 10.8 | | |
| 100 | 11.55 | 21.98 | 12.19 | 0.50 | 3.74 | 5.99 | 16.67 | 16.67 | 14.29 | 10.7 | 26.2 | 17.9 |
| Sintered glass no.: | | | | | | | | | | | | |
| 0 | 10.33 | 71.45 | 73.54 | 0.48 | 0.57 | 1.45 | 14.29 | 5.00 | 5.00 | 8.0 | 3.1 | 14.3 |
| 1 | 9.32 | 66.26 | 49.84 | 0.66 | 0.63 | 2.19 | 15.80 | 8.00 | 6.67 | 10.8 | 5.0 | 19.5 |
| 2 | 6.74 | 28.51 | 4.36 | 1.40 | 0.87 | 8.00 | 16.67 | 12.00 | 14.29 | 17.6 | 9.0 | 13.4 |
| 3 | 1.20 | 2.21 | 0.87 | 39.25 | 62.38 | 75.71 | 16.67 | 33.33 | 30.00 | 88.4 | 69.2 | 53.3 |

[a] Unless otherwise specified, base conditions were: air flow rate = 15 L/min·$m^2$; feed flow rate = 10 L/min·$m^2$; foam height = 45 cm; liquid height = 45 cm; surfactant feed concentration = 80% of CMC; temperature = 20°C.

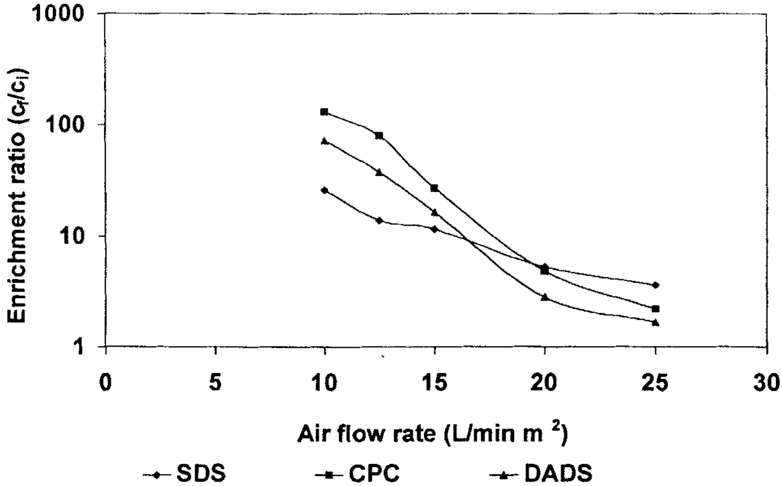


FIG. 3 Effect of air flow rate on enrichment ratio.

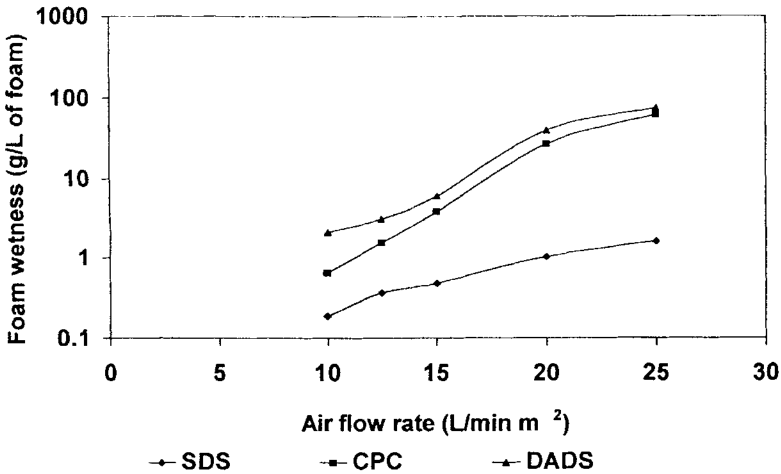


FIG. 4 Effect of air flow rate on foam wetness.

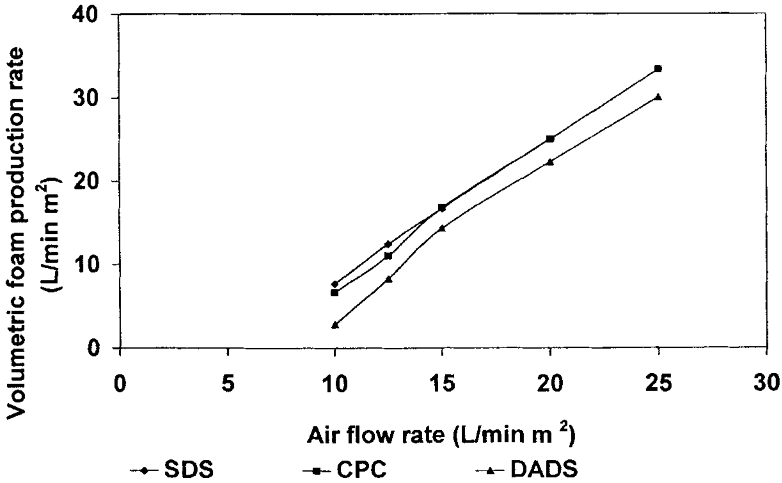


FIG. 5 Effect of air flow rate on volumetric foam production rate.



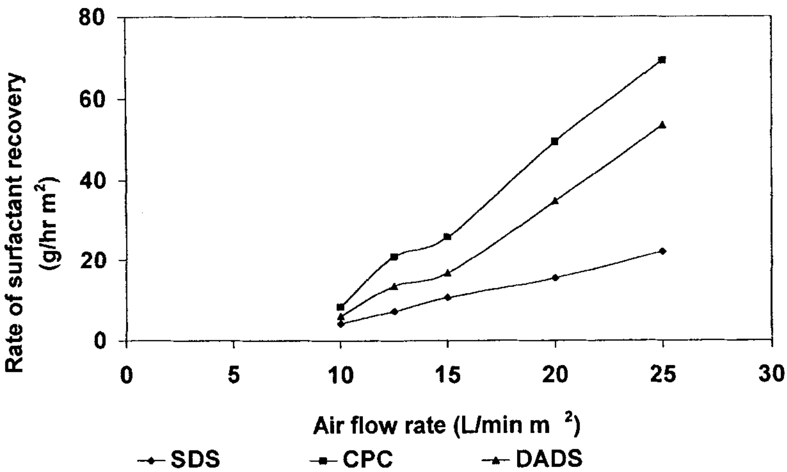


FIG. 6 Effect of air flow rate on rate of surfactant recovery.

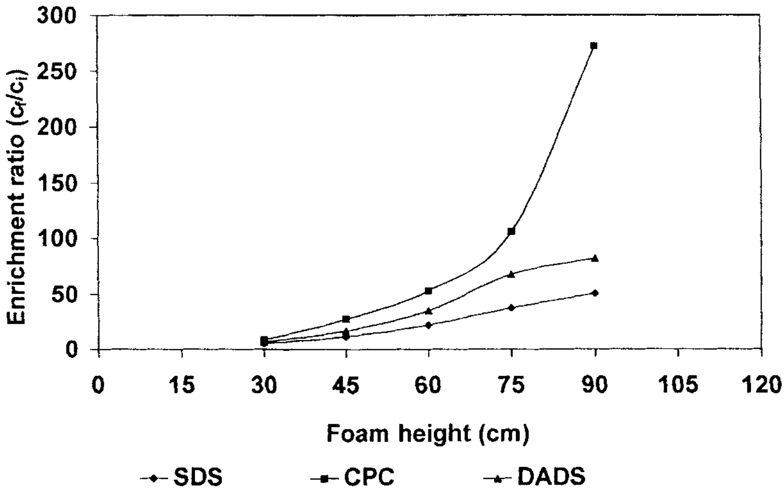


FIG. 7 Effect of foam height on enrichment ratio.



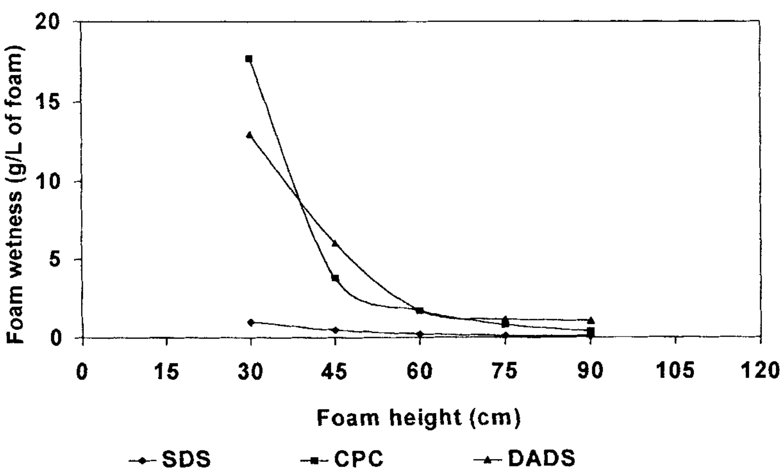


FIG. 8 Effect of foam height on foam wetness.

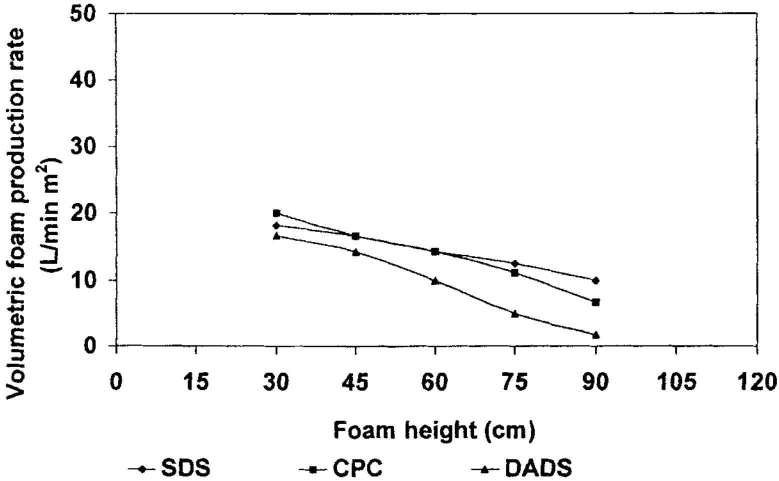


FIG. 9 Effect of foam height on volumetric foam production rate.



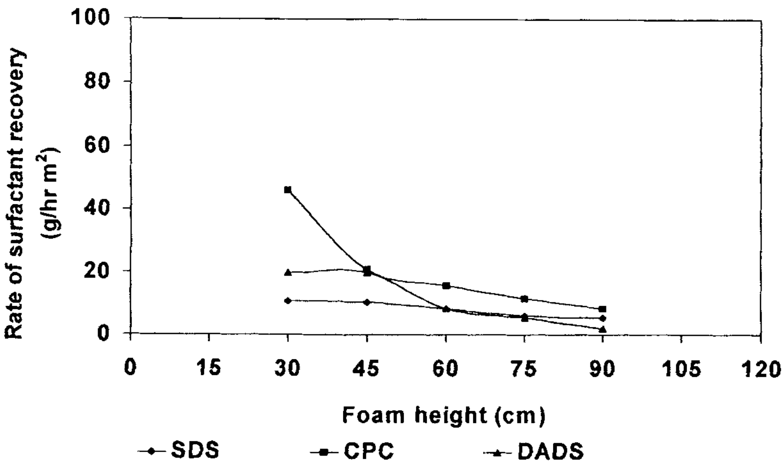


FIG. 10 Effect of foam height on rate of surfactant recovery.

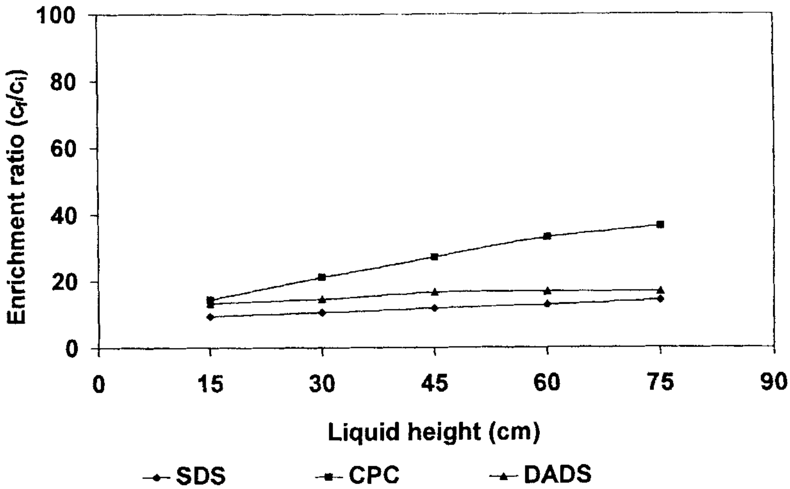


FIG. 11 Effect of liquid height on enrichment ratio.



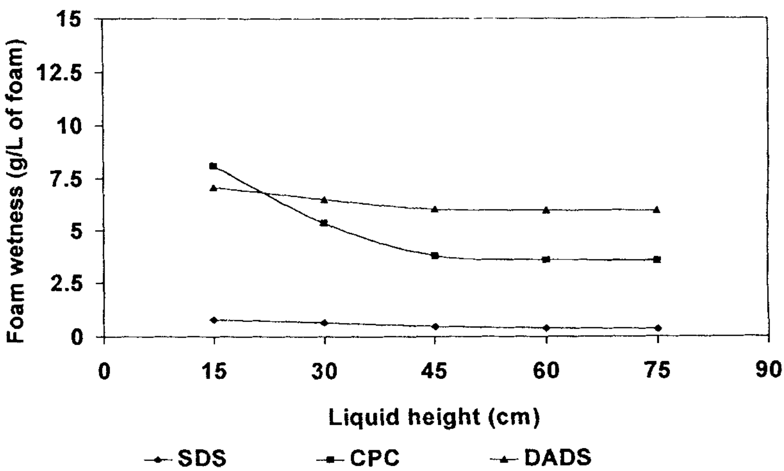


FIG. 12 Effect of liquid height on foam wetness.

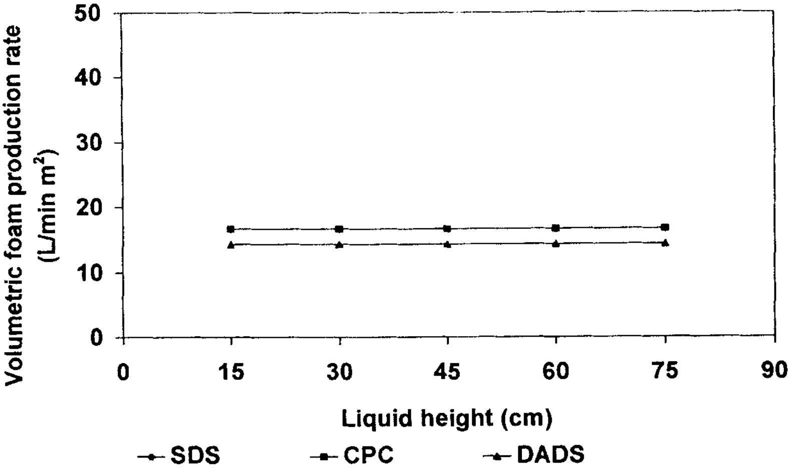


FIG. 13 Effect of liquid height on volumetric foam production rate.



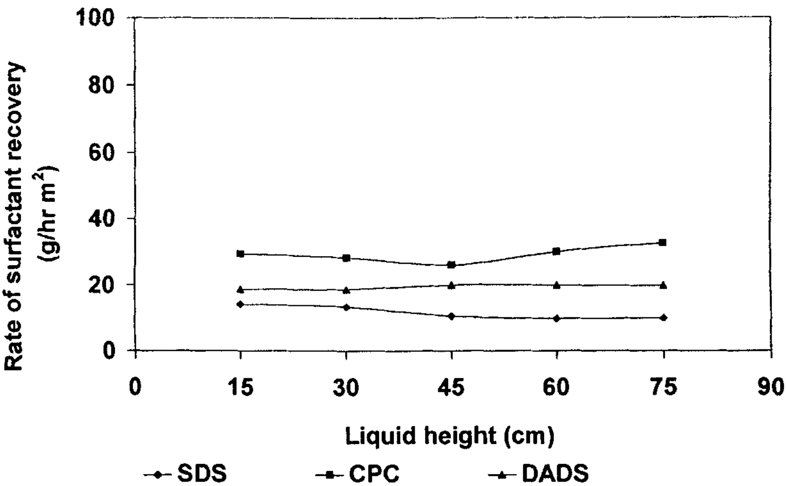


FIG. 14 Effect of liquid height on rate of surfactant recovery.

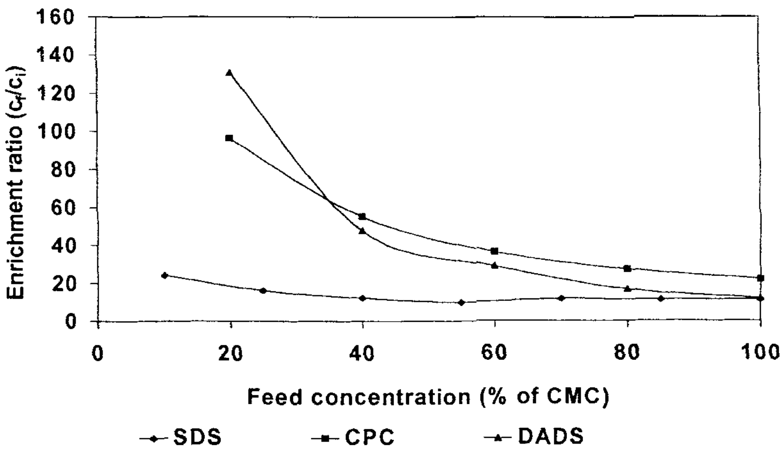


FIG. 15 Effect of surfactant feed concentration (% of CMC) on enrichment ratio.



foam upon emerging from the liquid interface. Another possibility is that higher surfactant concentration in the thin liquid film in the foam lamellae may make this liquid more structured or cause increases in surface viscosity, leading to an decreased rate of film drainage. This could also explain the increasing volumetric foam production with increasing surfactant feed concentration as seen in Figs. 19 and 20. The enrichment ratio increases as feed liquid surfactant concentration decreases (Figs. 15 and 16), presumably due to the increased ratio of bubble surface area to surfactant in the liquid. The rate of surfactant recovered increases with surfactant feed liquid concentration. The results are in agreement with another study (11).

Figures 15–22 are plotted as a function of both actual surfactant concentration and concentration as a fraction of the CMC in order to compare the behavior of different surfactant structures. The SDS has about an order of magnitude higher CMC than the CPC or the DADS. The SDS exhibits a much dryer foam and a lower rate of surfactant recovery than the CPC and the DADS. The DADS exhibits a lower enrichment ratio than the SDS or CPC, and the latter two have about equivalent enrichment ratios (Fig. 16) when plotted on an actual feed concentration basis. When plotted as a function of the CMC (Fig. 15), the SDS has a substantially lower enrichment ratio than the CPC or DADS.

The effect of the porosity of the sintered glass sparger is shown in Figs. 23–26. As the pore size decreases, the smaller bubbles yield a wetter

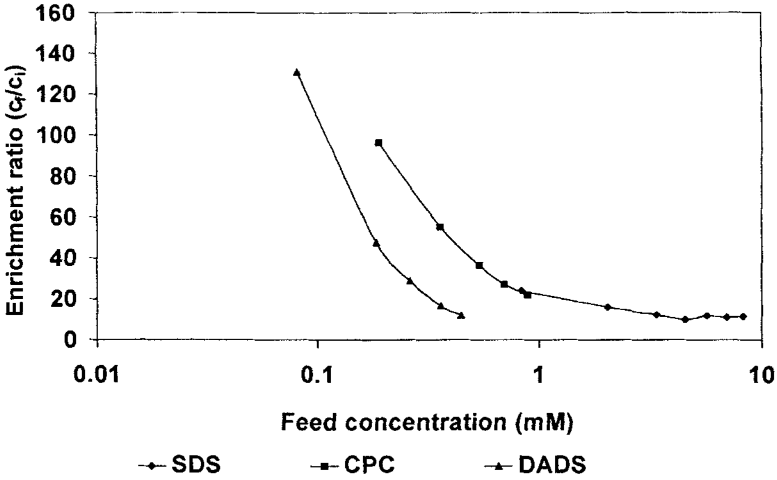


FIG. 16 Effect of surfactant feed concentration on enrichment ratio.



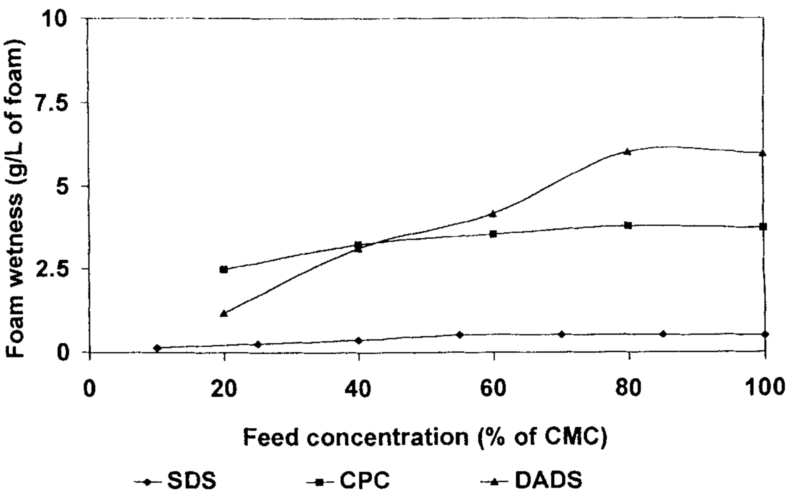


FIG. 17 Effect of surfactant feed concentration (% of CMC) on foam wetness.

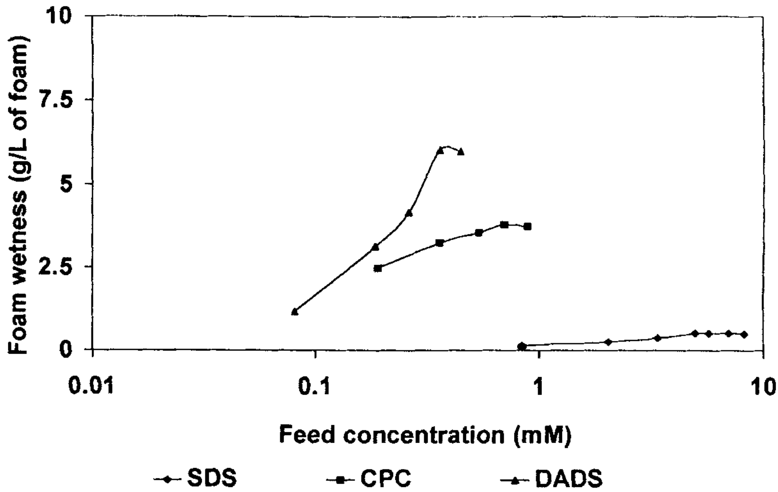


FIG. 18 Effect of surfactant feed concentration on foam wetness.



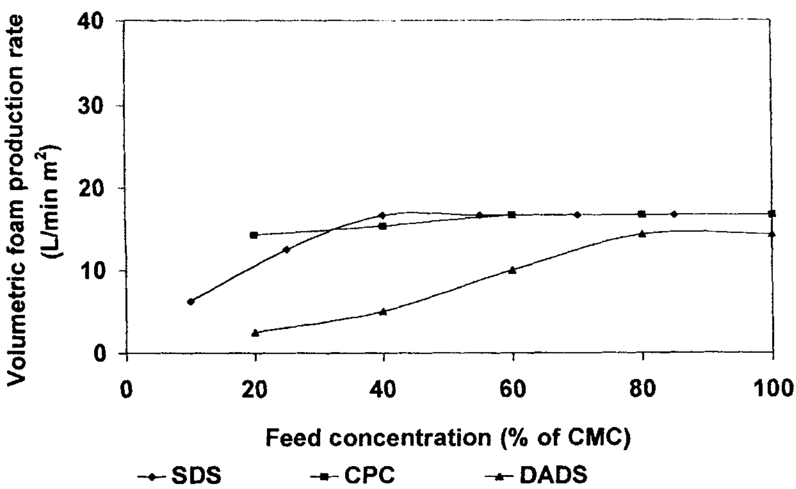


FIG. 19 Effect of surfactant feed concentration (% of CMC) on volumetric foam production rate.

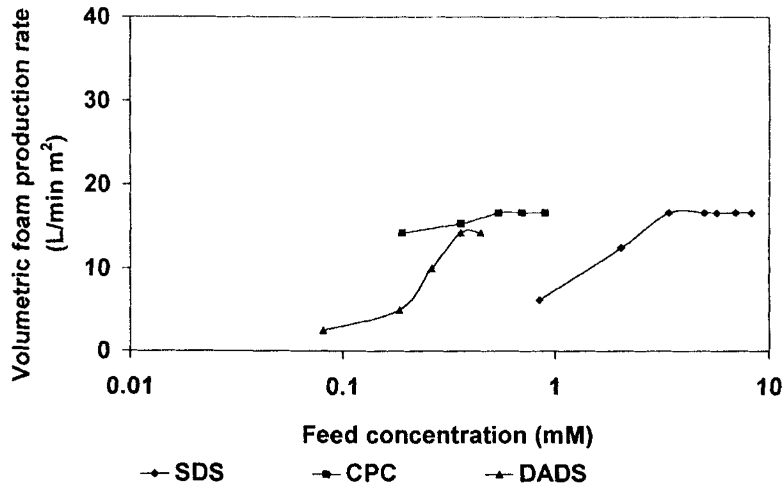


FIG. 20 Effect of surfactant feed concentration on volumetric foam production rate.



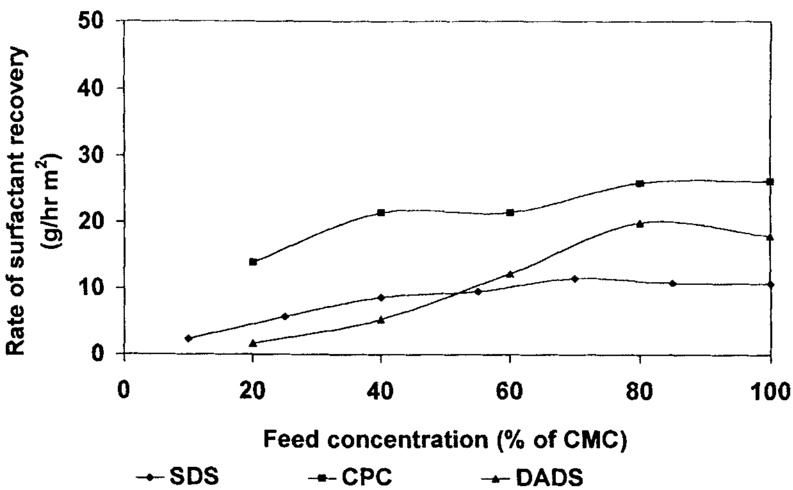


FIG. 21 Effect of surfactant feed concentration (% of CMC) on rate of surfactant recovery.

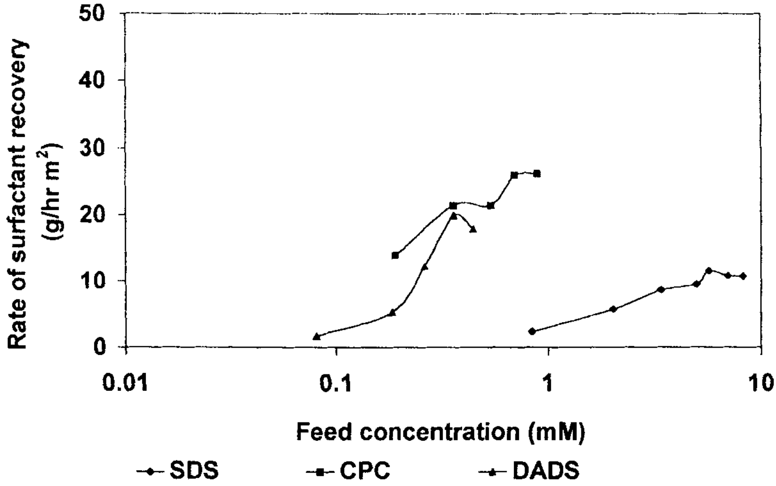


FIG. 22 Effect of surfactant feed concentration on rate of surfactant recovery.



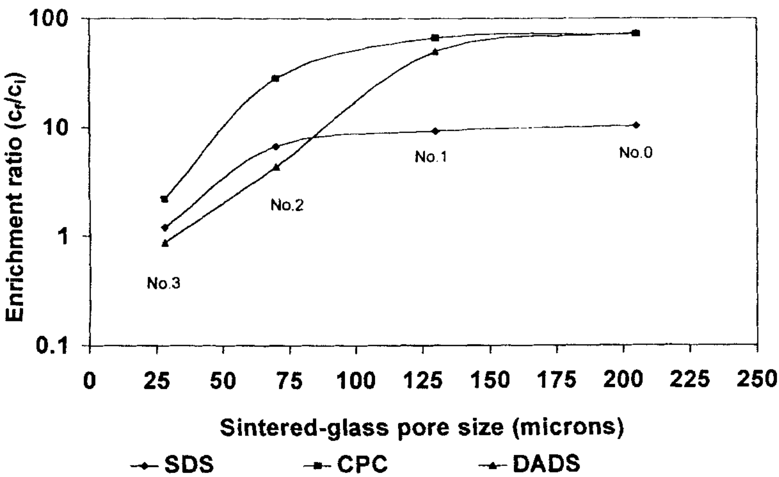


FIG. 23 Effect of sintered-glass porosity on enrichment ratio.

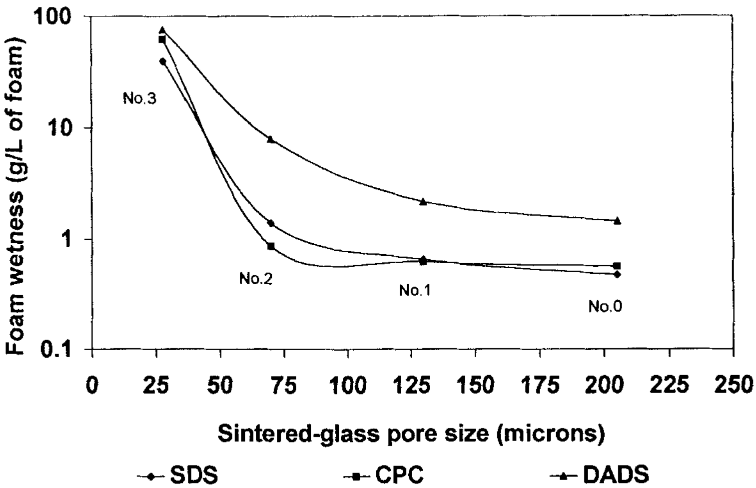


FIG. 24 Effect of sintered-glass porosity on foam wetness.

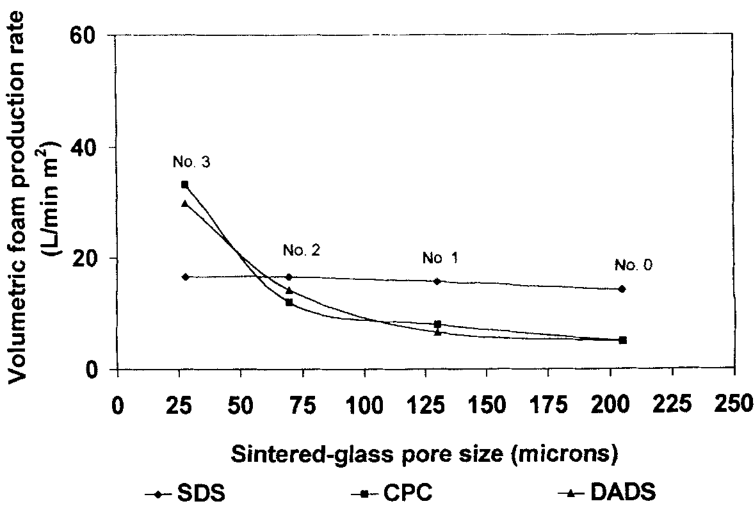


FIG. 25 Effect of sintered-glass porosity on volumetric foam production rate.

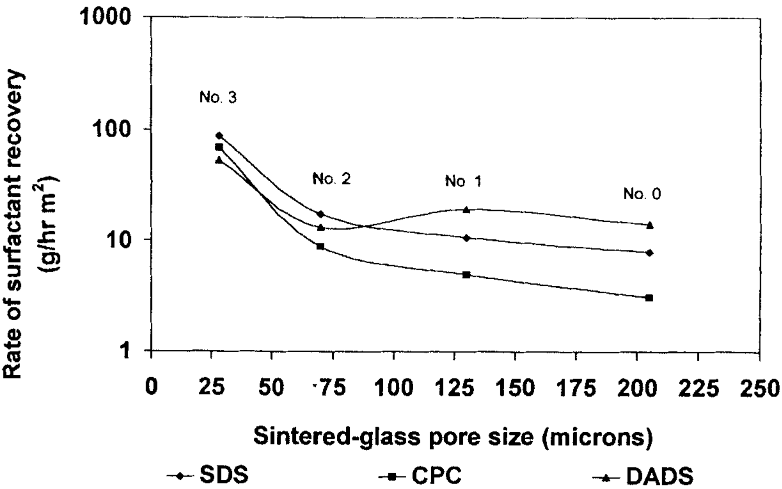


FIG. 26 Effect of sintered-glass porosity on rate of surfactant recovery.



foam. This more than compensates for the increased surface area of the bubble formed, resulting in a decreased enrichment ratio (Fig. 23). The result is in disagreement with some work done by Konduru (10), probably because this effect is very system-dependent. The rate of surfactant recovery is highest for the lowest pore size studied because of the greater foam production rate.

The effects of the variables studied are summarized in Tables 3 and 4. It can be concluded that CPC is the surfactant most efficiently recovered by foam fractionation with the highest enrichment ratio and highest recov-

TABLE 3
Effect of Variables[a]

| | Enrichment ratio | | | Foam wetness | | | Foam flow rate | | | Rate of recovery | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Increasing variable | SDS | CPC | DADS | SDS | CPC | DADS | SDS | CPC | DADS | SDS | CPC | DADS |
| Air flow rate | ⇓ | ⇓ | ⇓ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ |
| Foam height | ⇑ | ⇑ | ⇑ | ⇓ | ⇓ | ⇓ | ⇓ | ⇓ | ⇓ | ⇓ | ⇓ | ⇓ |
| Liquid height | ⇔ | ⇑ | ⇔ | ⇔ | ⇓ | ⇔ | ⇔ | ⇔ | ⇔ | ⇔ | ⇔ | ⇔ |
| Sparger pore size | ⇑ | ⇑ | ⇑ | ⇓ | ⇓ | ⇓ | ⇔ | ⇓ | ⇓ | ⇓ | ⇓ | ⇔ |
| Surfactant concentration | ⇓ | ⇓ | ⇓ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ |

[a] ⇑ = increase, ⇓ = decrease, ⇔ = no substantial change or change not monotonic.

TABLE 4
Effect of Surfactant Type for Base Case Conditions
(in decreasing order)

| | |
|---|---|
| Enrichment ratio | CPC > DADS > SDS |
| Foam wetness | DADS > CPC > SDS |
| Foam flow rate | SDS ~ CPC > DADS |
| Surfactant recovery | CPC > DADS > SDS |

ery rate for base case conditions. Increasing air flow rate or decreasing foam height or decreasing sparger pore size increases surfactant recovery rate but decreases enrichment ratio, so these design parameters would need to be optimized for a specific system. Liquid height has little effect on performance.

As the fractionation progresses with increasing time for a batch system or increasing number of stages for a continuous system resulting in a surfactant concentration decrease, the enrichment ratio increases and the recovery rate decreases. In order to indicate the effectiveness of this process and to compare the different surfactants over a range of concentrations, staging calculations were performed for a steady-state fractionation train. Base case conditions were used except for surfactant concentration, which was assumed to be equal to the CMC in the feed and at 10% of the CMC in the process effluent. The "overall" enrichment ratio is defined by the surfactant concentration in the total collapsed foam collected from all the stages divided by surfactant concentration in the feed to the first stage. The number of stages required for this 90% reduction in concentration is 165, 8, and 27, and the overall enrichment ratio is 9.93, 21.50, and 16.13 for SDS, CPC, and DADS, respectively. This confirms that CPC is the most readily removed of the three surfactants studied, as suggested from raw data earlier.

It is not surprising that SDS requires more stages for removal since more moles or grams of surfactant per liter of solution treated is being removed. However, it has already been stated that the effluent to be treated often has a surfactant concentration around the CMC from surfactant-based separations, so the use of a high CMC surfactant in a surfactant-based separation is a disadvantage. Therefore, comparing conditions required to treat different surfactants at feed concentrations corresponding to their CMC values is reasonable. It should be noted that this staging calculation is valid for the liquid feed rate used, which corresponds to a liquid residence time for the base case of 45.93 minutes. For a given diameter column per stage and overall percent surfactant removal, if the feed flow rate were less, the residence time per stage would be greater and the number of stages less. On the other hand, if the number of stages were reduced at constant feed flow rate and overall percent surfactant removal, the column diameter for each stage would be greater and the residence time per stage increased. As an example, for the CPC staging calculation just discussed, if the liquid residence time were increased to 375 minutes, the 90% surfactant removal could be achieved in one stage compared to eight stages corresponding to the 46 minute residence time per stage.

## CONCLUSIONS

1. Foam fractionation can be effective in the separation of surfactant from aqueous solution. For example, for conditions used here, 90% removal of CPC can be obtained in a single stage with a liquid residence time of 375 minutes. From this study, the effectiveness of the foam fractionation process in recovering CPC is better than for DADS or SDS.
2. An increase in the air flow results in a decrease in the enrichment ratio and an increase in the surfactant recovery rate.
3. A greater foam height produces a higher enrichment ratio and a lower surfactant recovery rate.
4. Liquid height has little effect on the separation process.
5. The enrichment ratio decreases and the surfactant recovery rate increases as feed liquid surfactant concentration increases.
6. A decrease in the pore size of the porous sparger results in a decrease in the enrichment ratio and an increase in the surfactant recovery rate.



## ACKNOWLEDGMENTS

Financial support for this work was provided by National Science Foundation Grant CBT 8814147, an Applied Research Grant from the Oklahoma Center for the Advancement of Science and Technology, the Center for Waste Reduction Technologies of the American Institute of Chemical Engineers, Agreement N12-N10, the TAPPI Foundation, the National Research Council of Thailand, Thailand National Science and Technology Development Agency, and US AID (University Development Linkages Project). In addition, support was received from the industrial sponsors of the Institute for Applied Surfactant Research including Akzo Nobel, Amway, Colgate-Palmolive, Dow, Dowelanco, DuPont, Henkel, ICI, Kerr-McGee, Reckitt and Colman, Lubrizol, Phillips Petroleum, Pilot

Chemical, Shell, Sun, and Witco. Surfactant was provided by Kao Industries Co. Ltd., Zealand Chemical, and Dow Chemical.

## REFERENCES

1. J. F. Scamehorn and J. H. Harwell (Eds.), *Surfactant-Based Separation Processes*, Dekker, New York, 1992.
2. J. F. Scamehorn, S. D. Christian, and R. T. Ellington, in *Surfactant-Based Separation Processes* (J. F. Scamehorn and J. H. Harwell, Eds.), Dekker, New York, 1992, Ch. 2.
3. B. L. Roberts, Ph.D. Dissertation, University of Oklahoma, 1993.
4. T. E. Carleson, in *Surfactant-Based Separation Processes* (J. F. Scamehorn and J. H. Harwell, Eds.), Dekker, New York, 1992, Ch. 10.
5. P. J. Elving, *Treatise on Analytical Chemistry, Part I, Vol. 5*, 2nd ed., Wiley, New York, 1982.
6. Y. Okamoto and E. J. Chou, in *Handbook of Separation Techniques for Chemical Engineers* (P. A. Schweitzer, Ed.), McGraw-Hill, New York, 1979, Sec. 2.5.
7. F. Sebba, *Foams and Biliquid Foams—Aphrons*, Wiley, New York, 1987.
8. M. J. Rosen, *Surfactants and Interfacial Phenomena*, 2nd ed., Wiley, New York, 1988, Ch. 7.
9. R. B. Grieves, S. Kelman, W. K. Obermann, and R. K. Wood, *Can. J. Chem. Eng.*, *41*, 252 (1963).
10. R. Konduru, *J. Chem. Eng. Jpn.*, *25*, 548 (1992).
11. S. N. Hsu and J. R. Maa, *Ind. Eng. Chem., Process Des. Dev.*, *24*, 38 (1985).
12. R. Lemlich and E. Lavi, *Science*, *134*, 191 (1961).
13. C. A. Brunner and R. Lemlich, *Ind. Eng. Chem., Fundam.*, *2*, 297 (1963).
14. D. O. Harper and R. Lemlich, *Ind. Eng. Chem., Process Des. Dev.*, *4*, 13 (1965).
15. K. Kubota, A. Yasui, and S. Hayashi, *Can. J. Chem. Eng.*, *55*, 96 (1977).
16. S. A. Zeiminski, M. M. Caron, and R. B. Blackmore, *Ind. Eng. Chem., Fundam.*, *6*, 233 (1967).
17. M. S. Hoffer and E. Rubin, *Ibid.*, *8*, 483 (1969).
18. K. Koczo and G. Racz, *Colloids Surf.*, *56*, 59 (1991).
19. F. Uraizee and N. Ganesan, *Sep. Sci. Technol.*, *27*, 937 (1992).
20. R. D. Sil and F. D. Talbot, *Can. J. Chem. Eng.*, *55*, 67 (1977).
21. R. B. Grieves and K. E. Burton, *Sep. Sci. Technol.*, *22*, 1597 (1987).
22. M. Moussavi, *Ibid.*, *27*, 783 (1992).
23. M. Moussavi, *Ibid.*, *29*, 1087 (1994).
24. F. F. Peng and P. Di, *Ind. Eng. Chem. Res.*, *33*, 922 (1994).
25. M. M. Koutlemani, P. Mavros, A. I. Zouboulis, and K. A. Matis, *Sep. Sci. Technol.*, *29*, 867 (1994).
26. F. Kepak and J. Kriva, *Sep. Sci.*, *5*, 385 (1970).
27. M. H. Leu, J. E. Chang, and M. S. Ko, *Sep. Sci. Technol.*, *29*, 2245 (1994).
28. K. Kubota, H. Kawanoue, and S. Hayashi, *Can. J. Chem. Eng.*, *55*, 101 (1977).
29. K. Kubota and S. Hayashi, *Ibid.*, *55*, 286 (1977).
30. D. Berk, J. E. Zajic, and L. A. Behie, *Ibid.*, *57*, 327 (1979).
31. K. Kubota, S. Hayashi, and Y. Takubo, *Ibid.*, *57*, 591 (1979).
32. Y. Okamoto and E. J. Chou, *Sep. Sci.*, *10*, 741 (1975).
33. R. B. Grieves, D. Bhattacharyya, and P. I. W. The, *Can. J. Chem. Eng.*, *51*, 173 (1973).

34. R. C. Huang and F. D. Talbot, *Ibid.*, *51*, 709 (1973).
35. R. B. Grieves and D. Bhattacharyya, *Sep. Sci.*, *7*, 115 (1972).
36. R. B. Grieves and R. K. Wood, *AIChE J.*, *10*, 456 (1964).
37. R. B. Grieves, I. U. Ogbu, D. Bhattacharyya, and W. L. Conger, *Sep. Sci.*, 5, 583 (1970).
38. R. B. Grieves and D. Bhattacharyya, *J. Am. Oil Chem. Soc.*, *42*, 174 (1965).
39. D. J. Brash and K. R. Robilliard, *Sep. Sci. Technol.*, *14*, 699 (1979).
40. R. Konduru, *J. Chem. Eng. Jpn.*, *25*, 555 (1992).
41. T. A. Pinfold, *Sep. Sci.*, *5*, 379 (1970).
42. R. K. Wood and T. Tran, *Can. J. Chem. Eng.*, *44*, 322 (1966).
43. P. Bhattacharyya, S. K. Ghosal, and K. Sep, *Sep. Sci. Technol.*, *26*, 1279 (1991).
44. P. Somasundaran, *Sep. Sci.*, *10*, 93 (1975).
45. E. J. Chou and Y. Okamoto, *Sep. Sci. Technol.*, *13*, 439 (1978).
46. E. Rubin and J. Jone, *Ind. Eng. Chem., Fundam.*, *8*, 474 (1969).
47. K. B. Medrzychka and W. Zwierzykowski, *Sep. Sci. Technol.*, *16*, 185 (1981).
48. J. D. Rouse, D. A. Sabatini, and J. H. Harwell, *Environ. Sci. Technol.*, *27*, 2027 (1993).

*Received by editor August 10, 1995*