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Enrichment and Fractionation by Foaming*

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Summary

In a binary mixture of surface-active sodium salts of dodecylsulfate, benzenesulfonate and dodecylbenzenesulfonate, each substance appeared to act independently over the range of concentrations examined. There was no evidence of competition like that reported earlier for a system that involved ion-pairing. In cases such as those in the present study, degradation of the separation may result when the less surface-active species is initially much lower in concentration. Measurements of the volume of solution in the flask during a foaming experiment confirmed the expectation that faster gas flows and higher concentrations of surface-active species lead to higher holdup and longer time to reach a steady state.

INTRODUCTION

The foaming process, including the reflux operation, is carried out in much the same way as a distillation, so it has been customary to assume that a foam fractionation of two or more substances would behave in a parallel fashion. Recent studies of foam processes have emphasized the enhancements in enrichment ratios that accrue from reflux (*1–4*), and the implication has been that the fractionation also would be improved. In an earlier study (*5*), in which a cationic foaming agent was used to separate two anionic species, it was suggested that competition for the interface resulted in a more favorable fractionation than calculated on

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the basis of the behavior of the individual species. A later study (*6*) appeared to confirm the existence of competition in fractionation and pointed out the difficulty in isolating the contributions of reflux and drainage when enrichment ratios for a single compound were examined.

In the present study, an attempt has been made to evaluate the possible role of competition for the interface in the fractionation process by using two compounds that were capable of forming stable foams without an added agent and also one compound that, by itself, was incapable of forming a stable foam. Because formation of relatively stable ion pairs should be a much less significant factor than it was in the earlier study, any other interfacial effect should be easier to detect. In addition, new data were obtained that illustrate the complexity of the drainage problem.

EXPERIMENTAL

Reagents

Radioactive sodium dodecylsulfate (sulfur-35) was obtained from New England Nuclear Corporation. The nonradioactive sodium dodecylsulfate (Matheson, Coleman and Bell) and sodium dodecylbenzene sulfonate (Tennessee Corporation) were recrystallized twice from 95% ethanol. All other reagents were reagent grade and were used without further treatment.

Apparatus

The foaming apparatus consisted of a 55-cm length of 25 mm o.d. glass tubing fitted at the bottom with a rubber stopper that held an inverted gas-dispersion tube. Doubly purified, water-saturated tank nitrogen was used to produce the foam. Foam samples were taken directly from the top of the column by means of 5-ml pipets.

A multilayer, 15-cm strip of fine-mesh copper screen placed in the top of the column caused enough disruption and breakage of the bubbles to accomplish reflux. This simple system was not successful in producing reflux with fast-rising foams (high gas-flow rate) or very stable foams (high surfactant concentrations); however, it was preferred to other techniques of foam breakage, such as using heat or additives, because of the smaller possibility of contamination or evaporative loss.

Concentrations of sodium dodecylbenzenesulfonate and sodium benzenesulfonate were measured by ultraviolet absorption using a Beckman DU spectrophotometer. Concentrations of sodium dodecylsulfate were measured using an ordinary isotope-dilution technique (*7*) employing a Radiation Instrument Development Laboratory Designer Series liquid scintillation counter. The stock sodium dodecylsulfate solution contained a small amount of the reagent tagged with radioactive sulfur-35. Since aqueous samples were involved, a basic dioxane–napthalene scintillating solvent system was used (*7*).

Surface tensions were measured using a Cenco Model 70535 duNuoy-type tensiometer.

Procedures

In quantitative measurements, sodium dodecylsulfate was found to have negligible absorption throughout the ultraviolet region where sodium dodecylbenzenesulfonate and sodium benzenesulfonate absorbed. In turn, sodium dodecylbenzenesulfonate, sodium benzenesulfonate, and sodium dodecylsulfate, at the concentrations used in these studies, had no effect on the counting efficiency of radioactive sodium dodecylsulfate.

The final foaming, sampling, and assay procedures for most of the experiments were done in the following way: A 60-ml sample was transferred into the column for foaming. The nitrogen flow was adjusted to 42 ml/min, which brought the foam to the top of the column in about 4 min. When reflux was desired, the copper screen was inserted in the top of the column. Foam samples were removed from the top of the column using 5-ml pipets at different time intervals that began when the foam had reached the top of the column. The foam samples in the pipets were allowed to collapse and drain into small test tubes. The volume of collapsed foam varied from 100 to 500 μl depending primarily on the wetness of the foam.

A sample of collapsed foam was transferred to 1-cm ultraviolet absorption cell by means of a 100-μl syringe and diluted with distilled water to 2.50 ml. After mixing, the absorbance was measured at 224 nm (sodium dodecylbenzenesulfonate) or 220 nm (sodium benzenesulfonate), and the concentration was determined from an appropriate standard curve.

Another portion of the sample (50–500 μl) was transferred to a counting bottle. Since water affected the counting efficiency, the volume in all samples was kept constant by adding distilled water to bring the voulme to 1.0 ml. Then scintillation solution was added, and, after mixing, the samples were counted over a 10-min interval. After correcting for background, the concentration of radioactive sulfur-35 was determined from a calibration graph of average number of counts per minute (CPM) versus concentration. That value was corrected for sample size, and the concentration of sodium dodecylsulfate (SDS) in the foam was calculated from the equation

$$\text{conc SDS (foam)} = \text{conc SDS (bulk)} \times \frac{\text{CPM (sample)}}{\text{CPM (bulk)}}$$

Use of this equation eliminated the necessity of a decay correction, providing the bulk solution was counted the same day as the samples.

Enrichment ratios were calculated by dividing the concentration of surfactant in the foam and its concentration in the *initial* bulk solution.

RESULTS

Preliminary Experiments

Curves of surface tension versus concentration for the three surface-active reagents are shown in Fig. 1. Sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) are much more surface active than sodium benzenesulfonate (SBS). Although the surface tensions for SDS and SDBS look significantly different, their enrichment ratios later showed them to be nearly the same in foaming behavior.

Table 1 shows the enrichment behavior of SDS and SDBS when each was present alone after 0 and 30 min of reflux. Changes in surfactant

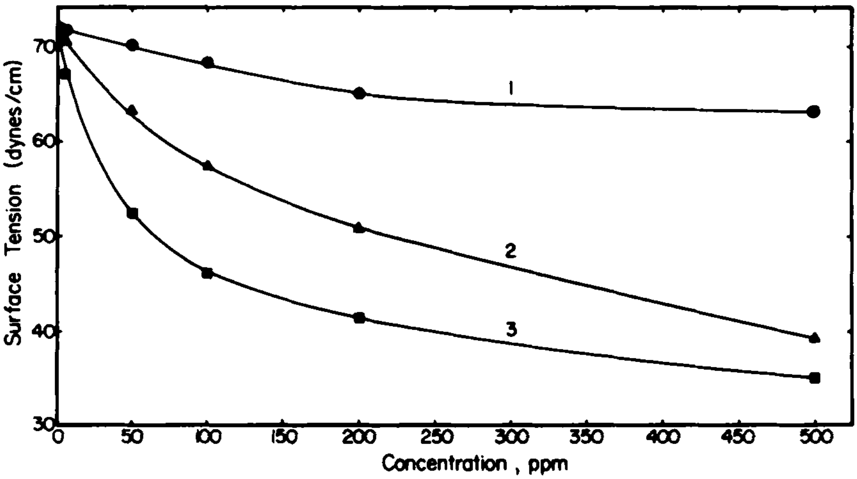

FIG. 1. Surface tension curves: (1) sodium benzenesulfonate; (2) sodium dodecylsulfate; (3) sodium dodecylbenzenesulfonate.

TABLE 1

Foam Composition at the Top of the 40-cm Column

Experiment	Initial solution	Reflux time (min)	Ppm in foam ($\times 10^{-2}$) SBS	Ppm in foam ($\times 10^{-2}$) SDS	$\frac{\text{ppm SDS}}{\text{ppm SBS}}$	E_R SBS	E_R SDS	$\frac{E_R\ (\text{SDS})}{E_R\ (\text{SBS})}$
1a	300 ppm SDS	0	—	14.5	—	—	4.8	—
1b	300 ppm SDS	30	—	21.2	—	—	7.1	—
2a	300 ppm SBS +300 ppm SDS	0	3.48	14.3	4.1	1.16	4.8	4.1
2b	300 ppm SBS +300 ppm SDS	30	3.91	23.0	5.9	1.30	7.7	5.9
3	100 ppm SBS +300 ppm SDS	30	3.81	21.2	5.6	3.8	7.1	1.85
4	45 ppm SBS +300 ppm SDS	30	2.68	18.9	7.1	6.0	6.3	1.06
5	150 ppm SBS +150 ppm SDS	30	2.98	16.7	5.6	1.99	11.1	5.6
6a	200 ppm SDBS	0	10.1[a]	—	—	5.1[a]	—	—
6b	200 ppm SDBS	30	15.7[a]	—	—	7.8[a]	—	—
7	200 ppm SDBS +300 ppm SDS	0	9.1[a]	1.37	1.51[a]	4.5[a]	4.6	1.00[a]
8	5000 ppm SDBS +7500 ppm SDS	0	169[a]	256	1.51[a]	3.4[a]	3.4	1.01[a]

[a] SDBS substituted for SBS.

concentrations in the foam were not significant after about 25 min, indicating some limiting steady-state condition had been reached. The limits of reproducibility of concentrations obtained in these and other similar experiments were usually ±5% and rarely worse than ±10%. Data for SBS alone are not presented because the foam was not stable enough to allow samples to be taken.

Mixtures

The importance of interfacial competition was tested by examining the enrichment and fractionation behavior of mixtures of SBS and SDS (two compounds that are very different in surface activity). The data, summarized in Table 1, show the expected increase in enrichment of each component with reflux time. Likewise, the ratio of enrichment ratios, increased with reflux time, indicating that the fractionation was improving. It is interesting to note, however, that the presence of SBS had no significant effect on the enrichment of SDS.

Decreasing the initial concentrations of these two reagents (experiments 2b and 5) resulted in the expected higher enrichment ratios (*5*), but the fractionation remained unchanged. When only the SBS concentration was decreased (experiments 2b, 3, and 4) the enrichment ratios for SBS increased as expected, but the fractionation *decreased*. The enrichments of the SDS were lower but probably not significantly (i.e., within ±10%). Lower SDS enrichments might be expected if there was "repulsion" at the interface as suggested by Karger and Rogers (*5*) in another study. However, that was tested by using higher concentrations of surfactants, including SDBS in place of SBS, because its greater surface activity should increase the importance of any competition factor. Table 1 shows the enrichment data for these mixtures at two different concentration levels (experiments 7 and 8). No reflux was used because the foam produced from the high surfactant concentrations was too stable. At the very high concentrations the enrichment ratios (E_R) were somewhat smaller, but there was absolutely no fractionation. In addition, the behavior of SDS and SDBS in mixtures appeared to be unchanged from when they were present alone. One can only conclude that competition for the interface, especially since the capacity was very much greater at the high concentrations, was not an important factor for repulsion in the interface. Hence, the earlier results of Karger and Rogers (*5*) and Rogers and Olver (*6*) may not be a general one. In those cases, the competition may have reflected the existence of a reaction involving ion-pair formation.

During the above experiments it was noted that different volumes of solution remained in the column after the steady state had been reached. That solution volume was related to the wetness of the foam and therefore to drainage. The volume changes were studied in more detail, and some of the data are illustrated in Fig. 2. Curves 1, 2, and 3, all obtained at the same flow rate of gas, showed that the most dilute solution reached a steady state sooner and that it produced the foam that contained the least liquid in the column at the steady state. The hold-up at the steady state was divided in an unknown way between two factors relating to the presence of more and smaller bubbles in the concentrated systems: (a) greater foam area, and (b) slower drainage through that foam. Evidence for greater importance of the latter is the greater depth of the minimum below the steady-state volume and the longer time required to reach that minimum.

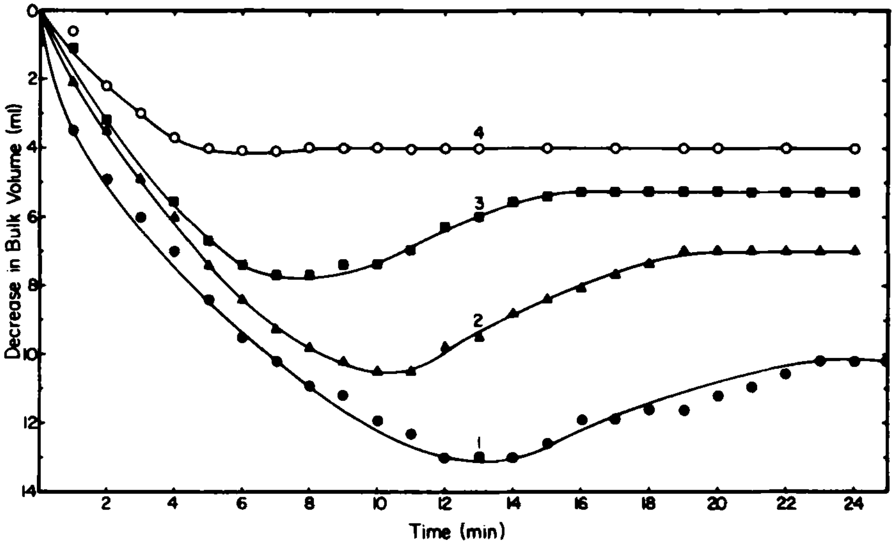

FIG. 2. Effect of foaming time and gas-flow rate on bulk volume: (1) 300 ppm SBS + 300 ppm SDS, flow rate = 42 ml/min; (2) 150 ppm SBS + 150 ppm SDS, flow rate = 42 ml/min; (3) 100 ppm SBS + 100 ppm SDS, flow rate = 42 ml/min; (4) 100 ppm SBS + 100 ppm SDS, flow rate = 21 ml/min.

Figure 2 emphasizes the desirability of establishing the steady state before sampling the foam for analysis. Curve 4 in the figure also shows an effect that has been widely recognized in foam work—namely, that slower gas-flow rates produce drier (better-drained) foams.

It has also long been recognized that foaming of more dilute solutions produces higher enrichments as in experiments 2b vs. 5. Since lower surfactant concentrations produce drier foams, drainage alone could conceivably account for the increased enrichments. Experiments 2b, 3, and 4 showed that drainage did not always account for the increased enrichments. In those experiments, the concentration of highly surface-active SDS was held constant while that of the almost non-surface-active SBS was decreased. The foam wetness and stability depended almost entirely on the SDS, which remained unchanged; however, the enrichment of SBS increased significantly as its concentration was reduced. These results support similar data obtained by Karger and Rogers (*5*) for a more complicated system involving ion-pairing.

DISCUSSION

Our studies showed no evidence for decrease of one enrichment ratio due to the presence of a second surface-active compound. Furthermore, a few experiments showed that the interface could easily tolerate much larger concentrations of two species than have been reported in Table 1, again with no evidence that one species was affected by the presence of the second. Hence it appears that in the absence of a reaction such as ion-pairing, competition for the interface will not have an effect on the fractionation.

On the other hand, it is important to recognize a limitation inherent foam fractionation that may at first appear to be anomalous. The data from experiments 2b, 3, and 4 in Table 1 can be used as an indication of what may happen in an attempt to fractionate a mixture of two components that have widely different surface activities. To anticipate the conclusion, it appears that because the enrichment ratio for a surface-active substance is higher at lower concentration levels, the attempted separation of a larger concentration of a more surface-active substance from a small concentration of a less active substance may result in almost complete removal of the latter in the foam along with only part of the more active species. For example, starting with a 1:1 mixture of the two components as in experiment 2b and foaming once will produce a foam more enriched in the more surface-active component. The relative composition of the foam could be similar to the solution used in experiment 3. Thus, if the collected foam was first collapsed and then foamed in turn, one would still obtain fractionation favoring the more surface-active component. However, the ratio of concentrations in the foam would remain nearly the same because of the larger enrichment ratio for the less surface-active component. If that sequence were repeated until the composition of the foam was similar to the initial solution used in experiment 4, one would find that the concentration in the pot of the less surface-active component was actually *much* lower than in the initial solution (experiment 2b) while its concentration in the foam was only slightly lower than before. If that sequence were indeed followed in a column as in repeated foam fractionations, it is evident that the less surface-active material might be carried over almost completely, with part of the more surface-active component, during the early stages of a foam fractionation. As a result, there would be left *behind* a more nearly pure fraction of the more surface-active component. Again, this result would come about because of independent behavior of the surface-active species and failure of the less active species to be displaced from the interface.

In that case, columns should be able to improve fractionations only to a certain extent, depending on the ratio of the initial concentrations and surface activities of the species, before the separation would degrade. Such behavior is not what one would expect to find for a distillation column operated under nearly ideal conditions.

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