Notes

Experimental Observations on Drainage of Foams Generated Using Micellar Solutions of Anionic, Cationic, and Nonionic Surfactants

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1. Introduction

The stability of foams and foamlike dispersions is an important consideration in the design of many foam-based operations and processes in food, pharmaceutical, biochemical, chemical, and petroleum engineering. In previous articles of this continuing work, it has been shown that water-soluble polymers and hydrocolloids can be conveniently used to significantly enhance the stability of aqueous foams, including the foams generated at higher temperatures and pressures.[1-3] Extending this study, we investigate the stability of foams generated with ionic and nonionic surfactant solutions at concentrations higher than the critical micelle concentration (CMC) (we shall call these foams micellar foams) and the influence of polymer addition on the stability of these foams. The study of the stability of these foams, in particular, is useful in applications such as the manufacture of ultrafine carbonate particles, in formulations of food and pharmaceutical products, and in many industrial foams where the concentration of surfactant species is high.[4]

In a systematic study, it is shown that the stability of swollen micellar foams decreases with the decrease in second virial coefficient of the liquid phase.[5] The decrease in the second virial coefficient is related to the decrease in repulsive interactions between the micelles and hence it is shown that the lower the repulsive intermicellar interactions, the less stable is the foam. There have been a significant number of studies conducted on the drainage/thinning of micellar foam films, since the pioneering work of Johnott and Perrin.[6,7] Recently, Wasan and co-workers have both theoretically and experimentally shown that the stepwise thinning of a thin film formed from micellar solutions of sodium dodecyl sulfate is governed by a long range electrostatic repulsion by ionic micelles and the restricted volume effect in the film.[8-11] Similar findings

have also been obtained by Radke and co-workers, who attribute the origin of this phenomenon to the existence of an oscillatory structural force.[12,13] Recent simulation studies have shown that structuring of micelles occurs in thin micellar films (thicknesses less than 100 nm), which in essence gives rise to stepwise thinning or sheeting phenomena.[14-17] In this study the liquid drainage and foam decay characteristics of foams generated using micellar solutions, of both ionic and nonionic surfactants have been investigated. Furthermore, the influences of addition of a water soluble polymer and an oil phase have been noted for surfactant systems studied.

2. Experimental Studies

The experimental work conducted in this study is the preparation of micellar solutions and the liquid drainage, the foam decay, and the bubble size measurements of foams generated using the solutions as well as solutions with polymer additives. The pertinent phase diagrams and viscosity measurements were also conducted.

2.1. Materials, Equipment, and Experimental Setup. The surfactants used in this work are sodium dodecyl sulfate (SDS), benzalkonium chloride (BKC), and Triton X-100 (TX100). The cosurfactant and the polymer used in this work are lauryl alcohol (LA) and sodium carboxymethyl cellulose (SCMC), respectively. These materials were of the same specification as in our previous studies.[1-3] The organic phase used was analytical grade cyclohexane.

The micellar solutions were prepared using the following concentrations

surfactant	concentration (wt %)
1. SDS	0.17 (0.75 CMC), 0.23 (1 CMC), 2.3 (10 CMC), 4.6 (20 CMC), 9.2 (40 CMC), 13.8 (60 CMC)
2. BKC	0.17 (1 CMC), 1.7 (10 CMC), 3.4 (20 CMC), 6.8 (40 CMC)
3. TX100	0.02 (1 CMC), 0.2 (10 CMC), 0.4 (20 CMC), 0.8 (40 CMC)

The concentrations are also shown in terms of critical micellar concentration, CMC, and the surfactant concentration will be expressed in CMC henceforth. The range of surfactant concentration is selected by keeping in mind that the micelles formed are of globular type. It has been shown in a previous study that, at higher concentrations of surfactant, the foams are stable due to the formation of a liquid crystalline phase.[18] The concentration of SCMC was varied from 0.1 to 0.75 wt %. The cyclohexane to surfactant ratio used was 2 to 5.

A simple experimental setup similar to that of Maskara and Khilar (1993) was used to generate as well as study the drainage

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Table 1. Liquid Drainage Time Constants for Foams Generated Using Different Surfactants at Different Concentrations

surfactant	concn (CMC)	$\tau_{0.5}$ (s)	$\tau_{0.8}$ (s)
SDS	0.75	110	360
	1.00	110	370
	10.00	100	325
	20.00	100	330
	40.00	110	350
	60.00	120	410
BKC	1.00	85	290
	10.00	75	230
	20.00	70	180
	40.00	90	240
Triton X100	1.00	65	225
	10.00	90	265
	20.00	95	270
	40.00	95	260

behavior of micellar foams.[19] This setup consists of a graduated glass tube of 1.25 m length and 36 mm inside diameter with a side tube at the bottom to pour solution as well as to introduce air. A drain valve and a washing nozzle are also provided. The other components include a rotameter to measure the air flow rate, a diffuser stone at the bottom of the tube to distribute the air, and a small compressor with a bypass valve.
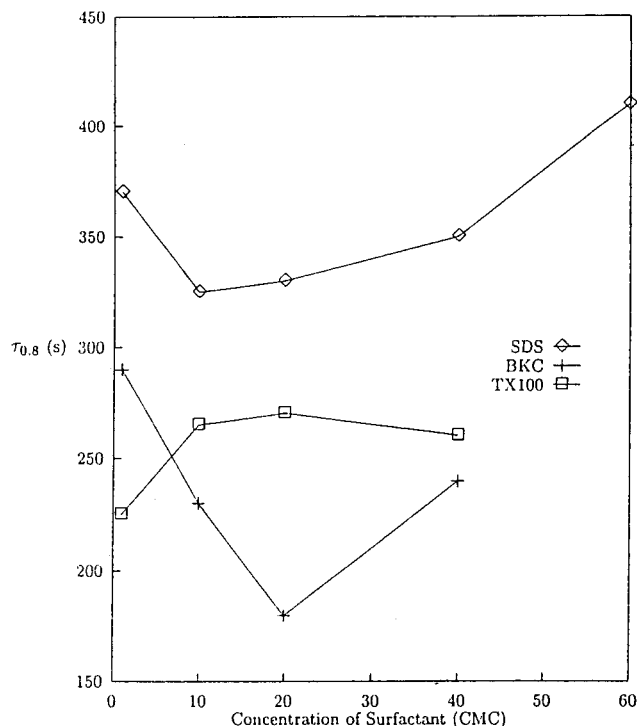
The level of the solution in the tube was maintained constant at 18 cm in all the drainage runs. The generating air flow rateused in all the experiments was 5×10^{-5} m^3 s^{-1}. All the drainage runs were repeated and some more than twice to check the reproducibility, which was found to be reasonably good, at ±3% in the drainage time. The initial gas volume fraction was measured by breaking the foam completely using a few drops of isopropyl alcohol. A Ubbelhode viscometer was used to measure the viscosity of the solutions. For polymer-added solutions, a Brookfield viscometer was used.

2.2. Measurement Procedures. Measurements were carried out in three areas: liquid drainage, foam volume decay, and foam bubble size. The measurement procedures involved were exactly similar to those in our previous study.[3] The time lag between foam generation and taking exposure (of photographs) was less than 15 s.

The detailed measurement procedure is presented elsewhere.[20] In liquid drainage measurements, typically, the drainage half-life, $\tau_{0.5}$, is obtained from the drainage plots to compare the stability of foams generated at different conditions. At this rather early stage of drainage, the foam film is not thin enough (thickness less than 100 nm) for micellar phenomena such as micellar structuring to affect the drainage process. Simple calculations were done to estimate the initial film thickness. It can be estimated by the following equation (1) based on a spherical bubble and spherical shell of the liquid film.

$$1 - \phi = 30h/(a + 3h) \tag{1}$$

Here ϕ is the gas volume fraction, a is the average bubble radius, and h is the film thickness. Implicit assumptions are that only 10% of the liquid in the foam constitutes lamellae,[21] that h is much smaller than a, and that the foam bubble is nearly spherical in shape. Taking a typical value for the bubble radius as 150 μm and ϕ as 0.92, we obtain h as approximately 400 nm. After 50% drainage of the liquid, the film thickness will be greater than 100 nm and micellar effects will not be manifested in the drainage phenomenon. On the other hand, drainage becomes very slow beyond 90% drainage and the bubble size may change due to interbubble diffusion during this period. We have therefore chosen a drainage time in this study as the 80% drainage time, $\tau_{0.8}$, i.e., the time during which 80% of the original amount of liquid drains and the film thins to below 100 nm. Both the values

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Figure 1. $\tau_{0.8}$ vs concentration plots for SDS, BKC, and TX100.

of $\tau_{0.5}$ and $\tau_{0.8}$ are determined in each case. A better way is probably to compare the drainage time period between 80% and 90% drainage for during this period; the film is likely to be thin enough to be affected by micellar interactions. Our measurements showed that the trend is qualitatively the same as the 80% drainage time, and hence we have adopted the 80% drainage time as a parameter to represent the stability of micellar foams by the liquid drainage technique.

3. Results and Discussion

3.1. Drainage of Micellar Foams. Both the values of 50% and 80% drainage life ($\tau_{0.5}$ and $\tau_{0.8}$) of micellar foams of ionic and nonionic surfactants are presented in Table 1. Figure 1 shows the nature of variation of $\tau_{0.8}$ of foams generated at different concentrations of three surfactants, i.e., SDS, BKC, and TX100. It also shows the difference in variations of $\tau_{0.8}$ with concentration between ionic and nonionic surfactants. The following interesting observations can be made from the table and the figure.

1. Comparing the values for drainage half-life from Table 1, we note that there is virtually little or no variation in $\tau_{0.5}$ with concentration in the case of ionic surfactants, SDS and BKC.

2. Unlike $\tau_{0.5}$, we observe from Table 1 that the 80% drainage life, $\tau_{0.8}$, varies substantially both for ionic and nonionic surfactants. Figure 1 presents the variation of $\tau_{0.8}$ with surfactant concentration greater than the CMC. We observe from this figure that the natures of variations for ionic and nonionic surfactants are different. For ionic surfactants, $\tau_{0.8}$ first decreases up to a concentration of 20 CMC and then increases, while for nonionic surfactant, $\tau_{0.8}$ increases and levels off at higher concentrations. (For BKC, the decrease is significant, while the decrease is weak in the case of SDS.) The increase in $\tau_{0.8}$ at a higher concentration of the surfactant is attributed to a change in morphology of the micelles, e.g., the change from globular to cylindrical micelles. (In the case of SDS, the transition in morphology of micelles occurs at 30 CMC.[8])

3. We further observe for the case of nonionic surfactant, TX100, that the drainage half-life, $\tau_{0.5}$, increases by about
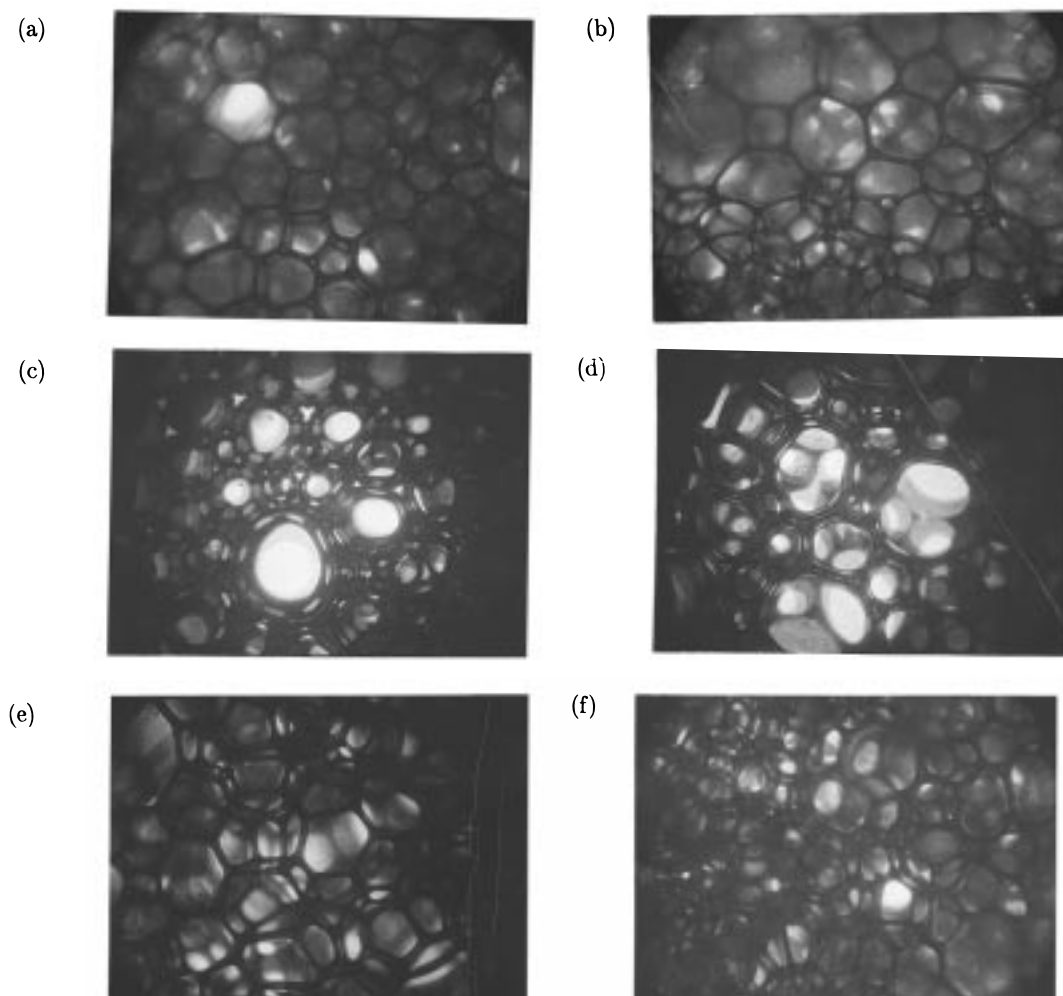
Figure 2. Typical transmission photomicrographs of a thin layer of foam samples generated using different surfactant solutions: (a) SDS (1 CMC); (b) SDS (40 CMC); (c) BKC (1 CMC); (d) BKC (40 CMC); (e) TX100 (1 CMC); (f) TX100 (40 CMC).

Table 2. Bubble Size and Viscosity Data[a]

surfactant	concn (CMC)	viscosity (Pa·s) $\times 10^{-3}$	sauter mean bubble diameter (μm)
SDS	1.00	1.00	280 (90−450)
	20.00	1.15	260 (130−340)
	40.00	1.32	320 (130−430)
BKC	1.00	1.05	280 (85−390)
	20.00	1.07	270 (95−360)
	40.00	1.10	340 (100−400)
TX100	1.00	1.00	350 (160−390)
	20.00	1.03	230 (85−285)
	40.00	1.05	220 (65−300)

[a] The numbers given in the parentheses represent the range of bubble size measured.

40% while the 80% drainage life, $\tau_{0.8}$, increases by about 20% at higher concentrations.

In order to further understand this drainage behavior and explain the above interesting observations, we have carried out several other measurements that are presented next.

3.2. Bubble Size and Viscosity Measurements. Figure 2 shows the photographs of thin layers of foam bubbles taken by means of transmitted light. The photographs look somewhat cluttered with bubbles, with the top and bottom layers appearing in view. Nevertheless, we observe from these photographs that the bubbles are in general polyhedral in shape, having different sizes. From these photographs, the sauter mean bubble size (diameter) was calculated for foams generated at different surfactant concentrations of the three surfactants used in this study.

Table 2 presents the values of the sauter mean size, the range in size along with the measured values for the viscosity of the surfactant solutions. We observe from this table that the variations in bulk viscosity of the surfactant solutions are virtually negligible up to a surfactant concentration of 40 CMC. Below about 40 CMC, it is known that most surfactant solutions form globular micelles having volume phase fractions below 0.1 and, therefore, the viscosity increase is insignificant. The viscosity, however, increases when the structure of the micelles changes from the globular to cylindrical and others.

We further observe from the table that there is not much variation in the mean bubble size of foam produced with ionic surfactants up to 20 CMC; however, at higher concentrations, the mean bubble size increases slightly. But for foams from nonionic surfactant, the mean bubble size decreases substantially. Without the knowledge of dynamic surface tension, it will not be possible to explain these interesting observations. This observation on the mean bubble size, however, partly explains the observations related to drainage half-life, $\tau_{0.5}$, which is presented in what follows.

Network modeling studies on the drainage of a static foam column have shown that bubble size is an important parameter that significantly affects the drainage behavior
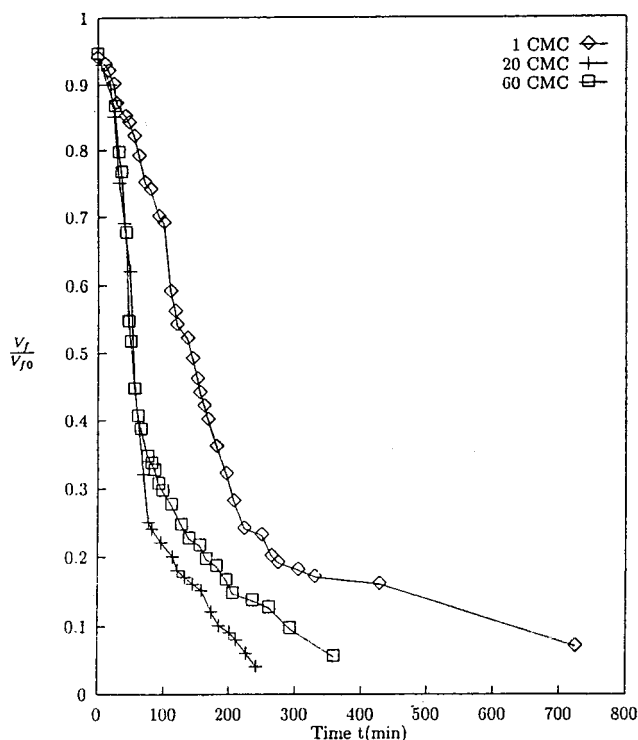
Figure 3. Effect of surfactant (SDS) concentration on foam decay.

Table 3. Liquid Drainage Time Constants for Foams Generated with Surfactant Solutions Doped with SCMC

solutions	viscosity (Pa·s) $\times 10^{-3}$	$\tau_{0.5}$ (s)	$\tau_{0.8}$ (s)
SDS (1 CMC)	1.00	110	370
SDS (1 CMC) + 0.75 wt % SCMC	36.50	990	1930
SDS (40 CMC)	1.32	110	350
SDS (40 CMC) + 0.75 wt % SCMC	37.00	170	420
TX100 (1 CMC)	1.00	65	225
TX100 (1 CMC) + 0.1 wt % SCMC	28.00	245	850
TX100 (40 CMC)	1.05	95	260
TX100 (40 CMC) + 0.1 wt % SCMC	30.00	360	1260

3.3. Foam Decay Measurements. Figure 3 shows the foam volume decay curves generated at the concentrations of 1 CMC, 20 CMC, and 60 CMC of SDS. This experiment was repeated thrice, and the values of the volume decay varied within ±3%. Average values are shown in Figure 3. We observe from the figure that the foam generated from an SDS concentration of 1 CMC decays more slowly than those generated at the concentrations of 20 CMC and 60 CMC. Furthermore, the foam generated at 60 CMC decays relatively slowly compared to that generated at 20 CMC. We therefore conclude that micellar foams are relatively less stable than that produced at 1 CMC. This trend observed in the foam decay experiments is similar to that observed in liquid drainage results; i.e., the foam stability decreases and then increases. We believe that the increase in stability at 60 CMC is due to the change in the morphology of micelles at higher surfactant concentration.

3.4. Effect of Addition of Sodium Carboxymethyl Cellulose (SCMC). Continuing with our previous studies concerning the enhancement of stability by the addition of water soluble polymers, we have conducted drainage studies of foams generated from the micellar solutions of SDS and TX100 doped with SCMC.[1-3] Table 3 presents the values of $\tau_{0.5}$ and $\tau_{0.8}$ for different cases. The addition of SCMC (in the weight percent range used in the present study) to the surfactant solution is believed to have a negligible effect on the CMC of the surfactant by means of associating with the surfactant molecules. The study of interaction between poly(*N*-vinylpyrrolidone) with SDS shows that addition of about 400 g of polymer to 1 L of surfactant solution would change the CMC by 5%.[25]

We observe from this table that both $\tau_{0.5}$ and $\tau_{0.8}$ values for foams generated with SDS at 1 CMC are significantly increased due to the addition of 0.75 wt % of SCMC. This observation is consistent with previously reported studies and has been primarily attributed to the fact that the bulk viscosity increases significantly due to the addition of SCMC.[1] We, however, observe that there is a small increase in $\tau_{0.5}$ and $\tau_{0.8}$ values for foams generated from SDS solution at 40 CMC doped with 0.75 wt % SCMC. Such weak enhancement in stability indicates that the drainage of foams generated from micellar solutions of anionic surfactant are not entirely governed by a viscous drainage mechanism. On the other hand, considering the increase in $\tau_{0.5}$ and $\tau_{0.8}$ values for foams generated from solutions of TX100, enhancements are significant for foams generated from TX100 at both 1 CMC and at 40 CMC. Consequently, it can be concluded that for a micellar solution of a nonionic surfactant, such as TX100, the drainage process is affected by the increase in viscosity.

3.5. Effect of the Addition of an Oil Phase (Microemulsion Foam). In order to investigate the drainage of microemulsion foams, cyclohexane was added to a micellar solution of 20 CMC of SDS with 2.8 mM of lauryl alcohol.

since it determines the hydraulic resistance.[22,23] In fact, simulations using the Bhakta and Khilar model have shown that the drainage half-life is approximately inversely proportional to the square of the bubble size for a monosized foam.[24] Furthermore, it is shown that the drainage half-life is directly proportional to the viscosity of the liquid phase. The values of interfacial viscosity and elasticity are not available in the literature for all the three systems studied. It is, however, expected that these parameters which significantly affect the drainage rate will not alter substantially with surfactant concentration for globular micellar solutions without any other additives; the micelles are believed to be in the bulk of the film rather than at the film–gas interface. On the basis of these theoretical results, we infer that the observed increase in $\tau_{0.5}$ for foams of nonionic surfactant TX100 results from the decrease in bubble size. In other cases, the changes in viscosity and bubble size are small and consequently the variation in $\tau_{0.5}$ is small. It should be noted that in addition to these considerations, interbubble diffusion and collapse of bubbles may also influence $\tau_{0.5}$.

The variation in the values of $\tau_{0.8}$ is considered next. By the time 80% of the liquid has drained, the film has thinned to below 100 nm. Below 100 nm, a micellar film of anionic surfactant, SDS, has been observed to show stratification and drain through sheeting.[8,12,13] Therefore, the observation of a difference in the variation in $\tau_{0.8}$ values between ionic and nonionic values indicates the possible effects of a stratification phenomenon. Without a study at the foam film level it will not, however, be possible to delineate the cause of this difference in drainage characteristics between micellar foams generated using ionic and nonionic surfactants. To further investigate the stability of micellar foams, we have carried out the foam decay experiments for the ionic surfactants.

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The $\tau_{0.5}$ and $\tau_{0.8}$ values for the oil to surfactant ratios of 2, 5, 10, 15, and 20 are 50 and 100 s, 45 and 90 s, 40 and 90 s, 23 and 50 s, and 12 and 35 s, respectively. These values are substantially lower than the values of 100 and 330 s for a foam generated with 20 CMC SDS solution. (Lauryl alcohol being a cosurfactant, on addition of 2.8 mM of lauryl alcohol to 20 CMC SDS solution, the $\tau_{0.5}$ and $\tau_{0.8}$ values are expected to increase from 100 and 330 s, respectively.) Furthermore, it can be noted that, as the oil to surfactant ratio is increased, the drainage time decreases, indicating a decrease in the stability of the foam. At an oil to surfactant ratio of 20, $\tau_{0.5}$ and $\tau_{0.8}$ values for foams generated with 0.75 wt % of SCMC are found to be 30 and 70 s, respectively. Such an increase in drainage times is comparable to that of micellar foams and is much less than what is obtained for foams below the CMC. Large size bubbles of about $1-2$ mm were found to form, particularly at high oil to surfactant ratios. These observations also indicate the effect of micellar interactions on the drainage process. With the addition of an oil phase, the micellar globules swell, with a possible increase in intermicellar interactions, particularly at low oil to surfactant ratios. Consequently, the drainage process is significantly affected. This result is consistent with the results obtained by other investigators.[5]

4. Conclusions

1. The 80% drainage life, $\tau_{0.8}$, can be used as a parameter for studying the stability of micellar foams from ionic surfactants, such as SDS. The $\tau_{0.8}$ for drainage of foams generated using SDS shows an initial decrease and then increases with an increase in concentration. The foam decay measurements also confirm this trend.

2. Both $\tau_{0.5}$ and $\tau_{0.8}$ for foams generated from a nonionic surfactant (TX100) increase with a surfactant concentration beyond the CMC and level off at a higher concentration within the range studied.

3. Addition of water soluble polymer increases the drainage half-life of micellar foams of anionic surfactant (SDS) but not as significantly as is observed for aqueous foams at or below the CMC, which can be as high as 15 times.[1] However, for micellar foams of nonionic surfactant (TX100), the increase in half-life is as significant as is observed for aqueous foams below the CMC.

4. Both $\tau_{0.5}$ and $\tau_{0.8}$ are found to decrease for foams produced from a micellar solution of SDS (20 CMC) in the presence of an oil phase (cyclohexane). With an increase in oil phase content, both values are found to decrease further.