Lauryl Alcohol and Amine Oxide as Foam Stabilizers in the Presence of Hardness and Oily Soil

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ABSTRACT: The effects of two potential foam boosters, n-dodecanol (or lauryl alcohol: LA) and tetradecyldimethylamine oxide (C\textsubscript{14}DMAO), were investigated for two situations in which foam made from a 0.01 wt% solution of a common alklylethoxy sulfate surfactant was highly unstable in the presence of oil drops consisting of an n-hexadecane/oleic acid mixture. In one case in which dissolved CaCl\textsubscript{2} was present at alkaline pH, insoluble calcium oleate particles formed in situ and facilitated foam breakage. In the other, a much higher concentration of calcium was present at neutral pH, and drops of a microemulsion phase formed but no calcium oleate. In both cases, 0.005 wt% LA reduced the entry coefficient, E, of the oil to the air–water surface sufficiently to prevent drop entry and stabilized the foam. In contrast, 0.005 wt% C\textsubscript{14}DMAO caused smaller reductions in E and was ineffective as a foam booster. LA was more effective because it was able to form a more compact monolayer with the surfactant than C\textsubscript{14}DMAO at the air–water surface, which led to lower surface tensions and hence lower values of E.


KEY WORDS: Antifoam, disjoining pressure isotherm, film drainage, foam boosting, foam stability, monolayer, steric effect, surfactant adsorption.

In a previous paper (1) we showed that, whereas foams made with a 0.01 wt% solution of a common alklylethoxy sulfate (AES) were relatively stable in the presence of drops consisting of a mixture of n-hexadecane and oleic acid (C\textsubscript{16}/HO\textsubscript{1}), they were highly unstable when CaCl\textsubscript{2} was added and the solution made alkaline. In the latter case, small calcium oleate particles formed at the surfaces of the oil drops and facilitated their entry into the surfaces of the foam films or Plateau borders. The result was rapid foam destruction owing to oil spreading and/or bridging.

As shown in this paper, foams of the same surfactant become unstable in the presence of the same mixed oil when sufficient CaCl\textsubscript{2} is added at neutral pH. In this case, a microemulsion phase forms at the surfaces of the oil drops and may contribute to the antifoam effect. However, formation of calcium oleate is negligible.

In some applications such as hand dishwashing, it is desirable to change the formulation slightly to maintain a stable foam under these conditions, for instance by including a relatively small amount of some additive or “foam booster.” Studies of two additives are reported and compared in this paper. One is n-dodecanol (or lauryl alcohol: LA). Such relatively long straight-chain alcohols are known to increase the surface viscosity of air–water monolayers of some anionic surfactants, e.g., sodium dodecyl sulfate, and thereby slow foam film drainage. Sometimes the mechanism of film drainage is changed from rapid and asymmetric to slow and axisymmetric (2). Some authors attribute the foam-boosting effect of these alcohols to such effects (3,4). However, Basheva \textit{et al.} (5), who recently studied the effect of adding LA to foams made with a surfactant similar to that used here in the presence of silicone oil, found that the stabilizing effect they observed was not related to film drainage but instead was the result of a highly cohesive monolayer at the air–water surfaces, which produced a large steric barrier to entry of the oil drops.

The other additive used in this study is an amine oxide, N,N\textsubscript{\textdegree},N-dimethylmyristyl amine oxide C\textsubscript{14-}\textsubscript{16}\textsuperscript{H}_{29}\textsubscript{N}(\textsubscript{CH}_{3})\textsubscript{2}\textsubscript{OH}, denoted as C\textsubscript{14}DMAO later on. Amine oxides have long been known to have surface-active and germicidal characteristics (6) and are widely used in shampoos and light-duty liquid detergents.

Matson (7) investigated and compared the foam-stabilizing efficacy of fatty amine oxides to that of alkanolamides in light-duty and heavy-duty detergents. Amine oxides were found to be much more effective foam stabilizers than amides for the detergents studied, particularly at low hardness concentrations. In shampoo applications, amine oxides are often preferred to amides as foam stabilizers. This is particularly true for acid shampoos, because amides are unstable below pH 5.5 whereas amine oxides are quite stable when the pH is as low as 3.5.

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Abbreviations: AES, alklylethoxy sulfate; C\textsubscript{14}DMAO, tetradecyldimethylamine oxide; [\textsubscript{N},\textsubscript{N},\textsubscript{N}-dimethylmyristyl amine oxide C\textsubscript{14}\textsubscript{H}_{29}\textsubscript{N}(\textsubscript{CH}_{3})\textsubscript{2}\textsubscript{OH}]; C\textsubscript{16}/HO\textsubscript{1}, mixture of n-hexadecane and oleic acid; LA, lauryl alcohol; N25-3S, an AES sodium salt with a straight C\textsubscript{12}–C15 hydrocarbon chain and an average of three ethylene oxide groups per molecule.
An important consideration in selecting an effective foam additive is the compatibility between the hydrophobes of the foaming surfactants and those of the additives. In general, a compound having a hydrocarbon chain with a length comparable to that of the hydrocarbon length of the surfactant functions as an effective foam stabilizer, probably because such compatibility promotes compact films, other things being equal. In this respect both LA and C14DMAO could be considered good candidates since the foaming surfactant, N25-SS, is an AES sodium salt with a straight C12-C15 hydrocarbon chain and an average of three ethylene oxide groups per molecule. Further discussion of foam boosters may be found in the review by Lai and Dixit (8). However, little attention has been given to the effect of boosters on the two types of unstable foams containing dispersed oil drops of interest here: one in which calcium soap is also present and greatly enhances the antifoaming effect of the oil, the other in which drops of a microemulsion phase are present at the oil-water interface. Here we investigate the effects of LA and C14DMAO on such foams and show that entry, spreading, and bridging coefficients can help explain the results.

The classical entry coefficient $E$ for an oil at an air–water surface is defined by (9)

$$ E = \gamma_{AW} + \gamma_{OW} - \gamma_{AO} \tag{1} $$

where $\gamma_{AW}$, $\gamma_{OW}$, and $\gamma_{AO}$ are the air–water, oil–water, and air–oil tensions, respectively. Positive values of $E$ indicate that entry is favored because it reduces overall interfacial free energy. Negative values imply the opposite, i.e., that entry is not possible because water spreads spontaneously at the air–oil interface ($-E$ is the spreading coefficient of water on oil). $E$ can be evaluated for either nonequilibrium or equilibrium conditions, but in the latter case Antonov’s rule requires that $E \geq 0$. However, even when $E > 0$, oil drops may never reach the air–water surface owing to repulsive effects in the aqueous pseudoemulsion film separating them. Since such effects are not included in $E$ as defined above, a generalized entry coefficient has been proposed (10). It is not often used in practice because its evaluation requires knowledge of the disjoining pressure isotherm in the pseudoemulsion film.

Figure 1 provides insight into how calcium soap particles can help oil drops destabilize foam (1). A typical disjoining pressure isotherm for the pseudoemulsion film of an ionic surfactant is shown in Figure 1C (see Refs. 11 and 12 for a general discussion of thin liquid films and disjoining pressure). Instability of the film occurs when $\Pi > \Pi^*$, so that it is negative (zero at equilibrium). As $\gamma_{AO}$ is insensitive to conventional surfactants and $\gamma_{OW}$ is typically rather small, lower values of $E$ can be achieved by decreasing the air–water tension $\gamma_{AW}$. Adding a long straight-chain alcohol such as LA produces a more compact film with lower $\gamma_{AO}$ and $\gamma_{OW}$ than the commercially available foam stabilizer C16/HOl, which is used in practice because its evaluation requires knowledge of the disjoining pressure isotherm.

In view of these considerations, possible strategies for stabilizing the foam can be visualized. One strategy is to decrease $E$, so that it is negative (zero at equilibrium). As $\gamma_{AO}$ is insensitive to conventional surfactants and $\gamma_{OW}$ is typically rather small, lower values of $E$ can be achieved by decreasing the air–water surface tension $\gamma_{AW}$. Adding a long straight-chain alcohol such as LA produces a more compact film with lower $\gamma_{AW}$. As we show below, adding 0.005 wt% LA to a system having 0.01 wt% AES surfactant and 0.01 wt% C16/HOl does, in fact, produce zero or negative values of $E$ and stable foams. In contrast, C14DMAO, which has a much smaller $\gamma_{AO}$, could be considered good candidates since the foaming surfactant, N25-SS, is an AES sodium salt with a straight C12-C15 hydrocarbon chain and an average of three ethylene oxide groups per molecule. Further discussion of foam boosters may be found in the review by Lai and Dixit (8). However, little attention has been given to the effect of boosters on the two types of unstable foams containing dispersed oil drops of interest here: one in which calcium soap is also present and greatly enhances the antifoaming effect of the oil, the other in which drops of a microemulsion phase are present at the oil-water interface. Here we investigate the effects of LA and C14DMAO on such foams and show that entry, spreading, and bridging coefficients can help explain the results.

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