The Molecular Mechanism for Destabilization of Foams by Organic Ions

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The effect of tetraalkylammonium ions on the destabilization of foam has been studied by measuring the half-life of foam ($\tau_{1/2}$), area/molecule at the air/water interface, surface viscosity and critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS). The area/molecule of SDS in organic salt solutions, calculated from the Gibbs isotherm, increases as the size of organic ion increases, and surface viscosity of the film decreases with the size of organic ions. The interaction of tetraalkylammonium ions with SDS decreases the CMC of the solution, and hence the concentration of SDS monomers decreases. The CMC of SDS decreases with the increase in the size and concentration of organic ions. The decrease in the CMC, increase in the area/molecule of SDS at the air/water interface and the decrease in surface viscosity by tetraalkylammonium ions all work to decrease the foam stability. The results indicate that the change in intermolecular distance between surfactant molecules in the adsorbed film by organic ions can significantly influence the surface viscosity and foam stability. The foam destabilizing efficiency of tetraalkylammonium ions was superior or equivalent to that of tributyl phosphate and 2-ethyl hexanol, which are used in many antifoaming formulations.

KEY WORDS: 2-Ethyl hexanol, foam stability, half-life of foam($\tau_{1/2}$), intermolecular distance, sodium dodecyl sulfate, surface concentration, surface viscosity, tetraalkylammonium ions, tributyl phosphate (TBP).

The effects of adding electrolyte to foams stabilized by ionic surfactants may be difficult to predict due to several counteracting mechanisms (1). One contribution to film stability is due to electrical repulsions between the ionic double layers associated with adsorbed ionic surfactants on the two sides of the liquid film. Because addition of electrolyte causes compression of the electrical double layers, it may decrease the stability of the foam. On the other hand, the presence of electrolyte reduces repulsions between adjacent surfactant head-groups at the air/water interface, thus promoting formation of more condensed films with higher surface viscosity. Hence, the latter mechanism is associated with an increase in foam stability by electrolytes. A third mechanism that may be important is that the electrolyte affects the solubility of the surfactant. The concentration of surfactant may either be enhanced or reduced at the air/water interface when electrolyte is added.

The nature of the electrolyte is, of course, important in this context. Electrolytes containing multivalent metal ions can be anticipated to cause larger effects on foam stability compared to those with monovalent ions, specially for ionic surfactants. Even when comparing the influence of a set of alkali metal chlorides, distinct differences in foam stabilities are observed (2). In the present study, electrolytes containing organic ions have been investigated. A mechanism that is not common to inorganic electrolytes may be important here: Larger organic ions adsorbed at the air/water interface may alter the packing of surfactant molecules and, hence, influence surface viscosities and foam stability.

To study the relationship between the structure and the foam inhibiting effects of organic ions, electrolytes containing tetraalkylammonium ions of different sizes have been investigated. A previous study concerning o/w (oil-in-water) emulsions has shown that tetraalkylammonium ions are efficient demulsifiers (3), which make them interesting to study with regard to their antifoaming properties.

The foam destabilizing efficiency of the organic salts has been compared to those of tributyl phosphate (TBP) and 2-ethyl hexanol (EH), which are well-known antifoaming substances used in several commercial formulations. The reason why this comparison was made is that the foam-inhibiting properties of tributyl phosphate and 2-ethyl hexanol have been attributed to their ability to reduce the surface viscosity of foam films (4,5), which we also believe is an important mechanism for the tetraalkylammonium salts.

MATERIALS AND METHODS

Materials. Sodium dodecyl sulfate, (SDS; $C_{12}H_{25}OSO_3Na$, 99.9%, Merck, Darmstadt, Germany) and hexaoxyethylene dodecyl ether, [$C_{12}E_6$ ($C_{12}H_{25}(OCH_2CH_2)^6OH$)], 99%; Nikko Chemicals Tokyo, Japan) were used as received. The following materials were also used: tetramethylammonium bromide [TMAB; prosynthesis (p s), (Merck); tetraethylammonium bromide (TEAB; p s), (Merck); tetrapropylammonium bromide (TPrAB), (Fisher Scientific, Cincinnati, OH); tetrabutylammonium bromide (TBAB; p s), (Merck); tetrapentylammonium bromide (TPAB, > 99%), (Aldrich Chemical Company, Milwaukee, WI); tetrabutylammonium chloride (purum), (Fluka AG, Buchs, Switzerland); EH (p s), (Merck); TBP (p s), (Merck); and sodium bromide [NaBr; proanalysis (p a)], (Merck)]. All chemicals were used as supplied.

Methods. The foam destabilizing efficiency of different additives were quantitated by generating foam and measuring the half-life of the foam $\tau_{1/2}$, corresponding to the time for the reduction of the foam volume to half of the initial volume. Two different methods were used to produce the foam. In the first method, the Ross-Miles procedure (6) was used to produce the foam. In a second method, the foaming solution (50 mL) was foamed at a constant gas flow rate (2.7 L/h) through a glass frit, in a 900-mL graduated cylinder. After 10 min of gas flow, the gas was turned off and $\tau_{1/2}$ was measured. If not otherwise stated, the second method was used in the experiments.

The $\tau_{1/2}$ values given in this paper correspond to average values of three to five independent experiments. The accuracy is estimated to be within 5%. All measurements were carried out at 22–23°C.

Surface tensions were measured by a deNoüy ring or Wilhelmy plate method to calculate the area/molecule at the air/water interface and the critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) in the presence of various organic salts.

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The deep-channel surface viscometer was used to measure the surface viscosity of SDS solutions in the presence and absence of organic salts, as described in a previous paper (7). In the deep-channel surface viscometer, the channel walls are stationary concentric cylinders; the floor of the viscometer moves with a constant angular velocity. After measuring the center-line velocity of the air/water interface, the surface viscosity can be calculated with the following equation:

$$\varepsilon = \frac{\eta y_0}{\pi}\left[\frac{8V_b}{\pi V e^{\pi D}} - 1\right] \qquad [1]$$

where ε is the surface viscosity, η is the bulk viscosity of subphase, y_0 is the channel width, V_b is the plate rotational speed, V is the center-line velocity of the interface, and D is the ratio of depth to width of the liquid channel. To measure the center-line velocity, a small Teflon particle was placed at the interface, and the time for that particle to make one complete revolution under a certain plate angular velocity was recorded from visual observations.

RESULTS AND DISCUSSION

Symmetrical tetraalkylammonium bromide salts. Table 1 shows the initial foam heights, as determined by the Ross–Miles procedure (6), of foams stabilized by the anionic surfactant SDS in the presence of various electrolytes. Figure 1 displays the $\tau_{1/2}$ of these foams. The surfactant concentration is 14 mM, which is above the CMC of the pure surfactant (8 mM).

Figure 1 shows that the influence of NaBr on the foam stability was minor, below a 1:1 ratio of NaBr/SDS. By contrast, drastic reductions in $\tau_{1/2}$ were observed even with only a small addition of an electrolyte containing large tetraalkylammonium ions. The $\tau_{1/2}$ values are in the order TEAB > TBAB > TPAB. Hence, a correlation was observed between the size of the tetraalkylammonium ion and its destabilizing effect on the foam. Contrary to what was observed with regard to foam stability, the initial foam heights were not significantly influenced by tetraalkylammonium bromide electrolytes. Only for TPAB could a substantial reduction in the initial foam volume be observed (Table 1).

There are several mechanisms that may be important in explaining the correlation between the size of the organic cations and the destabilizing effect on an ionic foam:

(i) *Reduced electric repulsions between surfactant layers.* From nuclear magnetic resonance (NMR) self-diffusion measurements, it is known that the attractive interactions between tetraalkylammonium ions and ionic surfactants increase with the size of the ion (8). This is due to an increase in the hydrophobicity of the ions with the size of the alkyl chains. Hence, the surface potential, as well as the electrical double layer repulsions that contribute to foam stability, are lower in the presence of hydrophobic organic ions than in systems with less hydrophobic ions.

(ii) *Reduced surface viscosity.* Qualitatively, foam stability has been correlated with the surface viscosity of adsorbed films. It is accepted that if the surface viscosity is low, the foam produced will be unstable (1,9,10). Shah *et al.* showed that the surface viscosity in mixed surfactant systems was maximum at the 1:3 molecular ratio because of the two-dimensional hexagonal arrangement of molecules at the interface. The maximum surface viscosity at 1:3 molecular ratio produced the most stable foams. The presence of large tetraalkylammonium ions at the air/water interface may perturb the packing of surfactants, thus producing noncoherent films with low surface viscosity and low stability. The surface viscosity of SDS (14 mM) solution in the presence of various salts (3 mM) decreased with an increase in the size of organic ions (Table

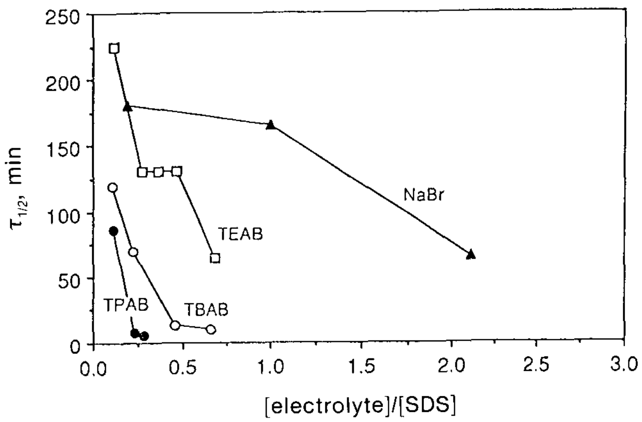

FIG. 1. The half-life ($\tau_{1/2}$), of sodium dodecyl sulfate (SDS) foams in the presence of different electrolytes *vs.* the electrolyte/SDS molar ratio. The electrolytes are tetrapentylammonium bromide (TPAB), tetrabutylammonium bromide (TBAB), tetraethylammonium bromide (TEAB) and sodium bromide (NaBr). The SDS concentration was 14 mM. The foams were produced by the Ross–Miles procedure. The $\tau_{1/2}$ of SDS foams at zero electrolyte concentration was 225 min for all curves.

TABLE 1

Initial Foam Heights, Obtained with the Ross–Miles Method, of SDS in the Presence of Different Electrolytes[a]

$X_{NaBr/SDS}$	H (mm)	$X_{TEAB/SDS}$	H (mm)	$X_{TBAB/SDS}$	H (mm)	$X_{TPAB/SDS}$	H (mm)
0	180	0	180	0	180	0	180
0.19	170	0.11	180	0.11	172	0.11	160
1.00	175	0.28	172	0.23	170	0.29	147
2.11	175	0.47	175	0.46	175		
		0.69	175	0.66	172		

[a] The foam heights are given for some different electrolyte/surfactant molar ratios (X). SDS, sodium dodecyl sulfate; NaBr, sodium bromide; TEAB, tetraethylammonium bromide; TBAB, tetrabutylammonium bromide; TPAB, tetraphenylammonium bromide.

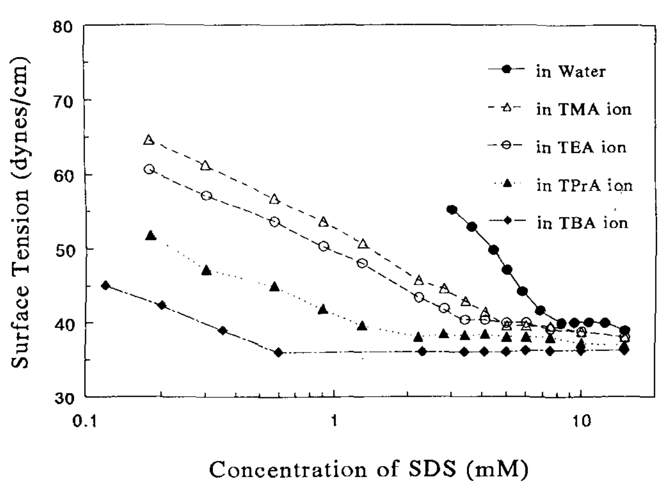

FIG. 2. The surface tension of sodium dodecyl sulfate (SDS) solutions containing tetraalkylammonium ion. The concentration of organic salt was kept as 3 mM in all cases. TMA, tetramethylammonium; TEA, tetraethylammonium; TPrA, tetrapropylammonium; TBA, tetrabutylammonium.

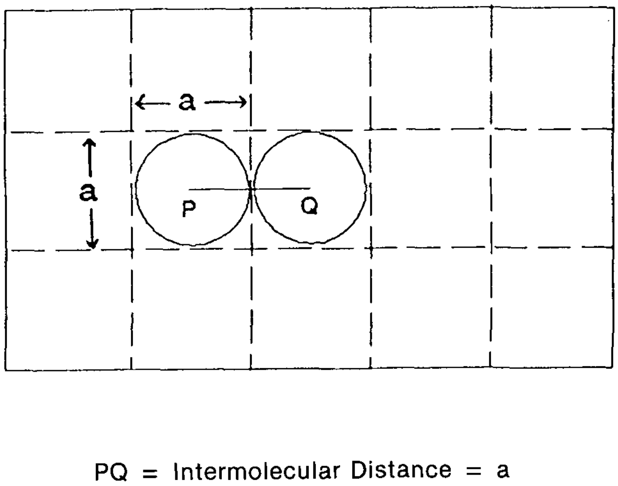

FIG. 3. The square lattice model for the adsorbed monolayer of sodium dodecyl sulfate at the interface to calculate the intermolecular distance.

2). The lower surface viscosity in the presence of large organic ions will enhance the collapse of foam.

(iii) *Reduced surface concentrations.* The larger tetraalkylammonium ions form hydrophobic complexes with SDS molecules (13), which may lead to an inactivation of the foam-stabilizing ability of the surfactant. Tetrapentylammonium ion formed complexes with SDS molecules in our experimental concentration range. Therefore, the CMC of SDS in the presence of this ion could not be measured. The concentration of SDS at the air/water interface can be calculated from the following Gibbs adsorption equation:

$$\Gamma = \frac{-1}{2RT}\,\frac{d\gamma}{d\ln C} \qquad [2]$$

The concentration of SDS at the air/water interface (Γ) was calculated with Equation 2. Therefore, the area/molecule of SDS at the air/water interface is given by $1/\Gamma$. The slope ($d\gamma/d\ln C$) near the CMC can be obtained from Figure 2 when the salt concentration in the subsolution is 3 mM. This is the concentration at which defoaming experiments were carried out. The area/molecule increases as the size of organic ions increases (Table 2).

(iv) *Increased intermolecular distance between surfactant molecules in the adsorbed film.* The intermolecular distance of SDS at the interface can be calculated as follows. Let us assume that each SDS molecule at the interface occupies the square lattice with side "a", as shown in Figure 3. Thus, the area of square lattice for a molecule is a^2, and the distance of two adjacent squares is "a". The area/molecule of SDS calculated as described in (iii) can be equated with a^2, and, hence, the intermolecular distance "a" can be obtained by taking the square root of the area/molecule.

The intermolecular distance between SDS molecules at the air/water interface increases with an increase in the size of organic ions (7.2 Å in aqueous solution, 10.5 Å in TMAB, 10.9 Å in TEAB, 11.5 Å in TPAB and 12.4 Å in TBAB solution when organic salt concentration is 3 mM), as shown in Figure 4. This small increase in the intermolecular distance leads to dramatic decreases in surface viscosity of the SDS solution in the presence of organic ions (Table 2). It has been reported that the average area/molecule of stearic acid in a buffer solution was maximum at pH 9.0 because of the strongest repulsion between molecules or the penetration of buffer ions (14). The maximum area/molecule of the decanoic acid at pH 9.0 resulted in the most unstable foam. However, addition of decanol to decanoic acid in the molar ratio of 3:1 strikingly improved the foam stability at pH 9.0 (15). Reduction in the interlayer electrical repulsions in the presence of large tetraalkylammonium ions most certainly contributes to destabilization of the foam. Because tetraalkylammonium ions also substantially decrease the stability of nonionic foams, the adsorption of these organic ions to surfactant films may be common to both ionic and nonionic surfactants. For SDS films, ionic interaction between surfactants and organic cations may enhance the adsorption of ion to film. For nonionic film, the surface activity of organic cations could drive the cations to adsorb at the nonionic film.

(v) *Reduced CMC.* Tetraalkylammonium ions are water structure formers, and their effectiveness increases with increasing length of the alkyl group (16). Moreover, the degree of counterion association to the ionic surfactant

TABLE 2

The Area/Molecule of Sodium Dodecyl Sulfate (SDS) and Surface Shear Viscosity of the Film When Salt Concentration is 3 mM and Concentration of SDS is 14 mM

	Area/molecule (Å^2/molecule)	Surface viscosity (cP)
In aqueous solution	51.8	0.11
$(CH_3)_4N^+$	110.6	0.06
$(CH_3CH_2)_4N^+$	118.3	0.054
$(CH_3CH_2CH_2)_4N^+$	133.0	0.049
$(CH_3CH_2CH_2CH_2)_4N^+$	153.8	0.02
$(CH_3CH_2CH_2CH_2CH_2)_4N^+$	—	0.009

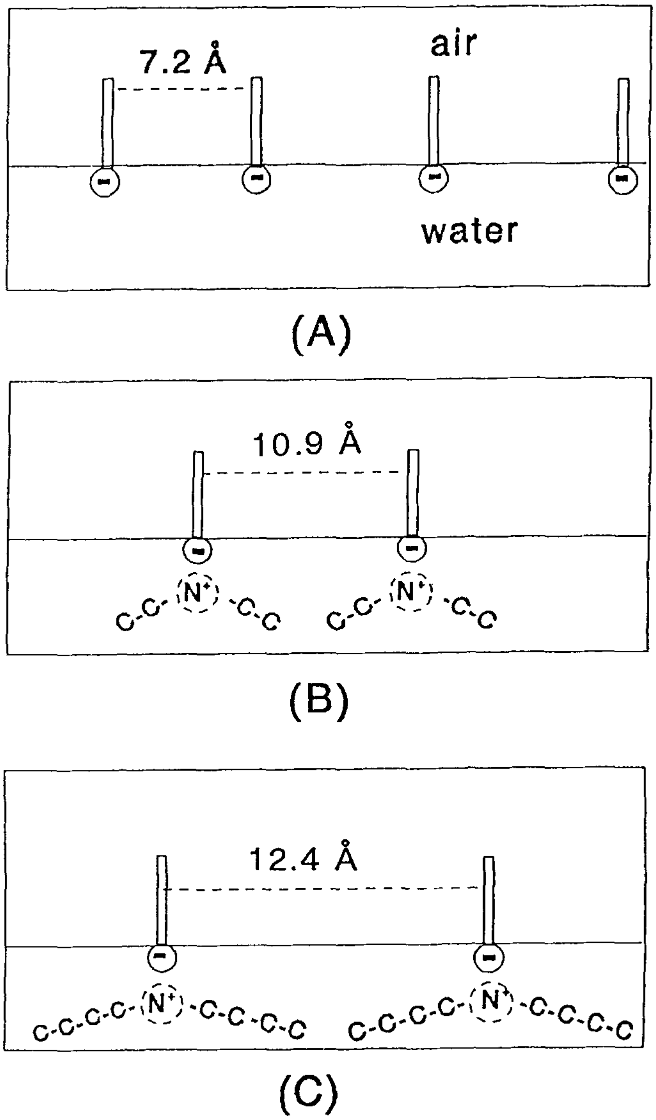

FIG. 4. The average intermolecular distance for sodium dodecyl sulfate films on water (A), 3 mM tetraethylammonium (B) and 3 mM tetrabutylammonium ionic solutions (C).

TABLE 3

CMC Values of SDS Solutions in Variouis Organic Salt Solutions of Different Concentrations[a]

Concentration of organic ion	3 mM	10 mM	50 mM
$(CH_3)_4N^+$	5.0 mM	2.3 mM	1.3 mM
$(CH_3CH_2)_4N^+$	3.4	2.2	0.9
$(CH_3CH_2CH_2)_4N^+$	1.6	1.0	0.36
$(CH_3CH_2CH_2CH_2)_4N^+$	0.62	0.31	0.12

[a] The critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) in pure aqueous solution is 8.2 mM.

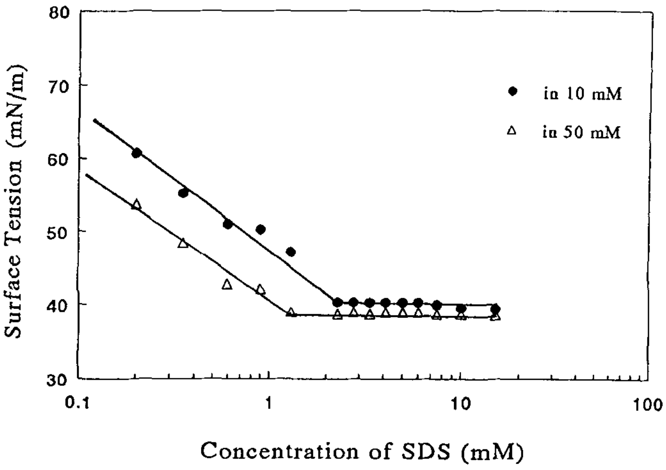

FIG. 5. The surface tension of sodium dodecyl sulfate (SDS) solutions at 10 mM and 50 mM tetramethylammonium ionic concentration.

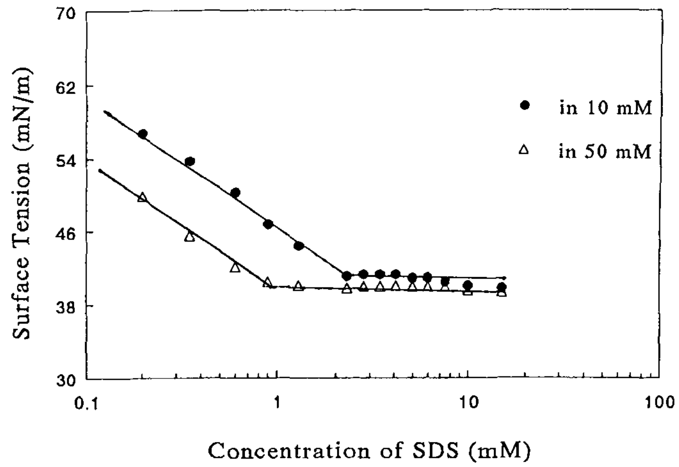

FIG. 6. The surface tension of sodium dodecyl sulfate (SDS) solutions at 10 mM and 50 mM tetraethylammonium ionic concentration.

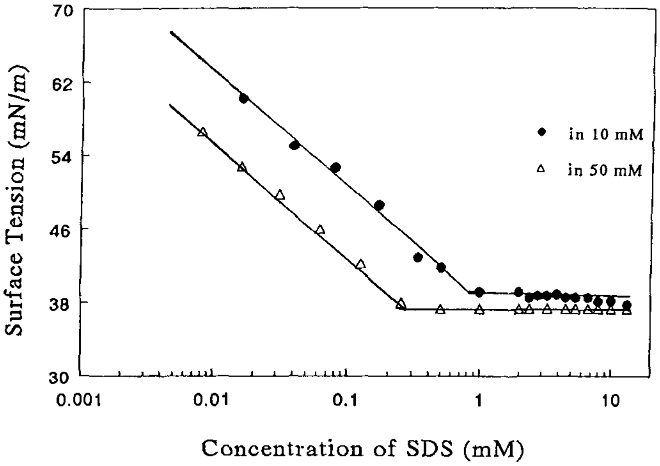

FIG. 7. The surface tension of sodium dodecyl sulfate (SDS) solutions at 10 mM and 50 mM tetrapropylammonium ionic concentration.

layer increases with the size of ions (8). Therefore, the CMC of SDS in the 3 mM tetraalkylammonium solutions decreases as the size of the organic ion increases. The CMC also decreases as the concentration of organic salts increases (Table 3 and Figures 5–8). The liquid film in foam must have a film elasticity such that mechanical shocks

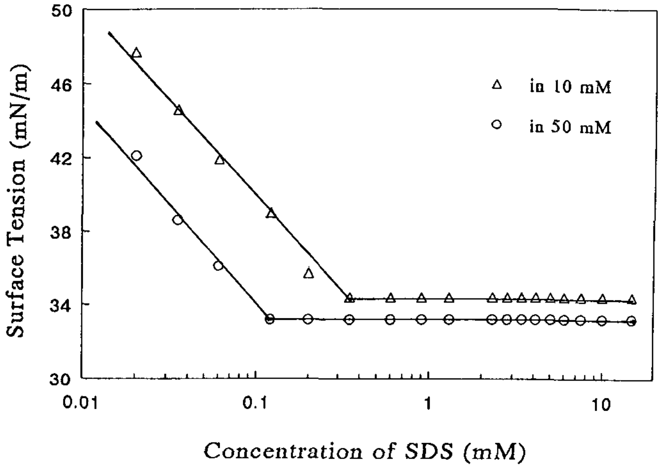

FIG. 8. The surface tension of sodium dodecyl sulfate (SDS) solutions at 10 mM and 50 mM tetrabutylammonium ionic concentration.

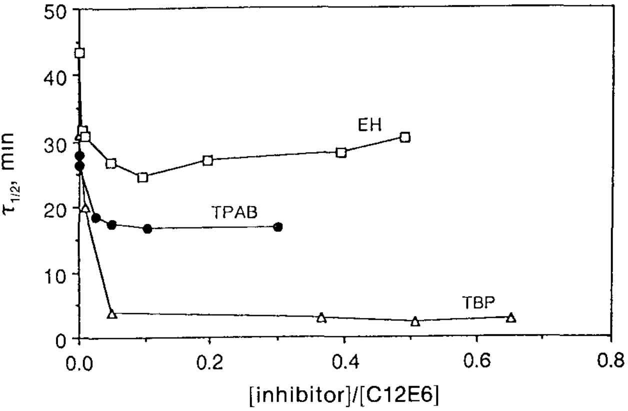

FIG. 10. The half-life, ($\tau_{1/2}$), of $C_{12}E_6$ foams in the presence of different foam inhibitors *vs.* the inhibitor/surfactant molar ratio. The $C_{12}E_6$ concentration was 0.14 mM. Abbreviations as in Figure 9.

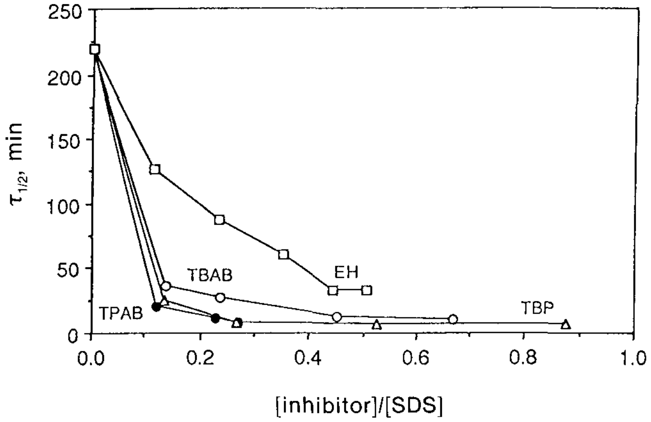

FIG. 9. The half-life, ($\tau_{1/2}$), of SDS foams in the presence of different foam inhibitors *vs.* the inhibitor/surfactant molar ratio. The SDS concentration was 14 mM. In absence of electrolyte, $\tau_{1/2}$ was 225 min. Abbreviations as in Figure 1. EH, 2-ethyl hexanol; TBP, tributyl phosphate.

that tend to cause a local thinning or stretching of the liquid film are rapidly opposed and counterbalanced by the restoring forces generated during the initial stage of distortion. The mechanism concerning operation of this film elasticity depends on two phenomena—the adsorption of surfactant monomers from the bulk to the air/water interface to restore the surface tension in expanding regions (Gibbs effect); and the movement of liquid to restore the thinning process by the surface tension gradient (Marangoni effect) (16). When the CMC is low (*i.e.*, the concentration of monomers is low), the surfactant monomers cannot adsorb quickly from the bulk to the air/water interface. This slow adsorption of monomer results in less film elasticity and foam stability in the solution of SDS and tetraalkylammonium ions.

Comparison with other antifoaming substances. The foam-destabilizing efficiency of electrolytes with the largest tetraalkylammonium ions, TBAB and TPAB, were compared with some other well-known antifoaming substances, TBP and EH. Figure 9 shows the half-life of foams stabilized by SDS in the presence of different foam-inhibiting substances. It is interesting that both cationic and anionic salts decrease the foam stability of SDS, a negatively charged surfactant. The $\tau_{1/2}$ values obtained for the foams in the presence of TBP and the organic salts are rather similar, however. Because TBP acts by promoting drainage of the lamella and reducing the surface viscosity of the surfactant films (1), a similar mechanism may be attributed to the tetraalkylammonium ions. The surface tension of TBP is 27 mN/m, whereas the surface tension of a 1 M solution of TBAB is 46 mM/m. Figure 10 shows the half-lives of foams produced with hexaethylene dodecyl ether, $C_{12}E_6$, and TBP is much more effective in destabilizing the nonionic surfactant system than TPAB. This may be attributed to a lower surface concentration of TPAB as compared to TBP in this system, which does not include the coulombic attraction between SDS and TPAB as in the previous system.

In both anionic and nonionic surfactant systems, EH is less efficient in destabilizing foams than the organic salts are. Although the surface activity is higher for EH (the surface tension is 26 mN/m), it may not expand the area/molecule as efficiently as tetraalkylammonium ions because of its molecular shape. Therefore, it is not effective as an antifoaming agent.

In many practical applications, foams are stabilized by mixtures of ionic and nonionic surfactants. The influence of TPAB and TBP on the foam stability of mixed SDS and $C_{12}E_6$ surfactant systems was therefore studied. The ratio between SDS and $C_{12}E_6$ was altered, but the total surfactant concentration and the concentration of foam inhibitor were kept constant. In agreement with what was observed, TPAB was more efficient in destabilizing the foam in a pure ionic system than TBP, whereas the opposite was true in the pure nonionic system, as shown in Figure 11. In a mixed surfactant system, no distinct differences were observed between the two systems. Hence, it appears that, even at moderate surface potentials, TPAB is as efficient as TBP is in destabilizing these foams.

Comparison of the foam-destabilizing efficiency of the tetraalkylammonium bromide salts with TBP and EH,

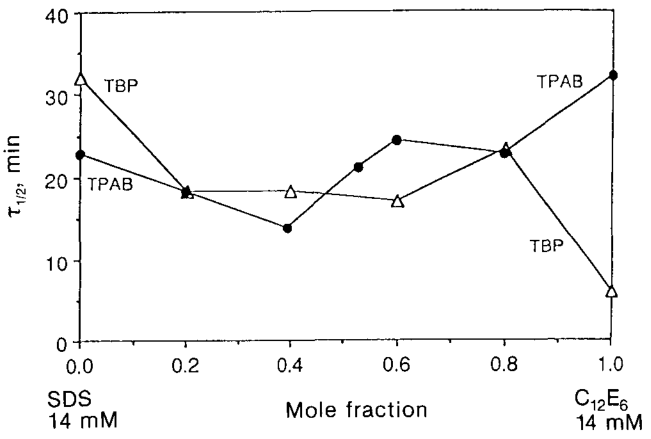

FIG. 11. The half-life, ($\tau_{1/2}$), of foams stabilized by mixtures of $C_{12}E_6$ and SDS in the presence of different foam inhibitors. The ratio between SDS and $C_{12}E_6$ was altered, whereas the total surfactant concentration, 14 mM, and the concentration of foam inhibitors, 3 mM, were kept constant. Abbreviations as in Figure 9.

which are used in many commercial foam, inhibiting formulations, demonstrates that the organic salts have potential for use in technical applications involving foam inhibition. Unlike most defoamers/antifoamers used commercially, the tetraalkylammonium salts are water-soluble. From the technical point of view, this may be relevant, as it will facilitate the distribution of the foam inhibitor into the solutions that must be protected from foaming.

ACKNOWLEDGMENTS

The authors thank the Swedish Research Council for Engineering Sciences, Procter & Gamble Company, Alcoa Foundation and the National Science Foundation (Grant NSF-CPE 8005851) for their support.

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[Received February 19, 1993; accepted August 10, 1993]