

# Foam Boosting by Amphiphilic Molecules in the Presence of Silicone Oil

Elka S. Basheva,<sup>†</sup> Simeon Stoyanov,<sup>†</sup> Nikolai D. Denkov,<sup>\*,†</sup> Kenichi Kasuga,<sup>‡</sup>  
Naoki Satoh,<sup>‡</sup> and Kaoru Tsujii<sup>‡,§</sup>

Laboratory of Chemical Physics Engineering (formerly Laboratory of Thermodynamics and Physicochemical Hydrodynamics), Faculty of Chemistry, Sofia University,  
1 James Bourchier Avenue, 1164 Sofia, Bulgaria, and Research Laboratories for Hair-Care Products, KAO Corporation, 1-3, Bunka 2-Chome, Sumida-ku, Tokyo 131-8501, Japan

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The effect of several surface active additives (called for brevity “foam boosters”) on the foaming properties of solutions of the anionic surfactant sodium dodecyl polyoxyethylene-3 sulfate (SDP3S) is studied in the presence of silicone oil. As foam boosters we study lauryl amide propyl betaine (LAPB), lauryl acid diethanol amide (LADA), lauryl alcohol (LA), and a nonionic surfactant, which is a glycerin derivative (denoted as Booster A). All these substances are used or have a potential to be used as commercial foam boosters in different formulations. The silicone oil is predispersed in the foaming solution in the form of micrometer-sized droplets, which act as foam breaking entities (antifoams). A set of several experimental methods is employed to clarify the main characteristics that are affected by the boosters. Foam tests show that LADA and Booster A enhance mainly the foaminess of the solutions and that LA improves mainly the foam stability, whereas the LAPB increases both. The enhanced foam stability in the presence of LAPB and LA correlates well with the higher barriers to oil drop entry, measured by the film trapping technique (FTT). No correlation of the film stability with the so-called entry,  $E$ , spreading,  $S$ , and bridging,  $B$ , coefficients of the silicone oil is observed. Optical observations of foam films show that the boosting effect cannot be explained by a reduced rate of the foam film thinning. Only the addition of LA leads to deceleration of the final stage of the film thinning process. The obtained results demonstrate that the various boosters affect different characteristics of the foaming solution, and which of the additives is appropriate for a particular application depends strongly on the time-scale of interest.

## 1. Introduction

Mixtures of surfactants are widely used in practical applications due to their superior properties as compared to those of the individual components.<sup>1–6</sup> This synergistic action of the mixtures, if properly formulated, is used in detergency, hair-care, body-care, household, and many other surfactant-based products.<sup>2–4,6</sup> Furthermore, many of the commercial surfactants present mixtures of several individual components obtained during the manufacturing process. A classical example is the lauryl alcohol (LA) which is always present in the commercial-grade batch samples of sodium dodecyl sulfate (SDS). LA of low concentration (less than 1 molar % in the surfactant mixture) is known to affect strongly the properties of the adsorption SDS layers and to affect significantly the properties of SDS-stabilized foams.<sup>7–9</sup>

The synergism of the individual components in the surfactant mixtures is often evaluated by the so-called “molecular interaction parameters”,<sup>2–4</sup> which characterize the interaction between the surfactant molecules in the adsorption layers and in the micelles. Negative values of the interaction parameters (reflecting an attraction between the molecules) often correspond to improved properties of the mixtures. Such negative values have been experimentally determined for mixtures of anionic and cationic surfactants (the attraction could be so strong in these systems that the mixtures often precipitate) and anionic–zwitterionic mixtures. The interaction parameters for the ionic–nonionic mixtures are also negative, though smaller in magnitude—for a collection of data see ref 2. Accordingly, such surfactant mixtures are used in a variety of applications.

In the present study, we are interested in the effect of surface active additives (called for brevity foam boosters) on the foam stability and the foaminess of solutions of the anionic surfactant sodium dodecyl polyoxyethylene-3 sulfate (SDP3S) in the presence of silicone oil. Since the silicone oil is insoluble in the studied surfactant solutions, it is dispersed in the form of oil drops, which are known to affect strongly the foam stability. In fact, such oil drops are able to destroy rather efficiently the foams, which might be a desirable or undesirable effect depending on the particular application. That is why such oils are often classified as “antifoams” in the literature.<sup>10–19</sup>

\* To whom correspondence should be addressed. Phone: (+359) 2-962 5310. Fax: (+359) 2-962 5643. E-mail: ND@LTPH.BOL.BG.

<sup>†</sup> Sofia University.

<sup>‡</sup> KAO Corporation.

<sup>§</sup> Current address: Japan Marine Science and Technology Center (JAMSTEC), The DEEPSTAR Group, 2-15 Natsushima-cho, Yokosuka 237-0061, Japan.

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The presence of emulsified oil drops makes the studied systems much more complex than the simple foams. The foams produced from oil-containing solutions are, in fact, three-phase structures comprising air, water, and oil. Their overall stability depends not only on the stability of the foam films but also on the stability of the asymmetric oil–water–air films, which appear between the dispersed oil drops and the air–water interfaces.<sup>10–12,14–21</sup> The exact mechanisms of foam destruction by oil drops are still a matter of discussion in the literature.<sup>10–17</sup>

The complexity of these systems suggests another approach than just determining the interaction parameters from surface tension isotherms. Instead, we are employing in the present study a set of several experimental methods, designed to clarify the main foam characteristics that are affected by the different boosters. By standard foam tests we check whether the foaminess or the foam stability is changed by the addition of a given booster. Optical observations of the foams allow us to identify what are the structural changes in the foam, which correspond to the different stages of the foam evolution and eventually lead to foam destruction. By optical observations of foam films (both small horizontal and large vertical foam films) in model experiments, we check how the boosters affect the rate of film thinning and the film lifetime.

Since the foam destruction by the oil drops is related to the entry of the oil drops on the solution surface and the subsequent oil spreading, we characterize the surfactant solutions also with respect to the different quantities that are used in the area of antifoaming. These are the so-called entry,  $E$ , spreading,  $S$ , and bridging,  $B$ , coefficients<sup>10</sup>

$$E = \sigma_{AW} + \sigma_{OW} - \sigma_{OA} \quad (1)$$

$$S = \sigma_{AW} - \sigma_{OW} - \sigma_{OA} \quad (2)$$

$$B = \sigma_{AW}^2 + \sigma_{OW}^2 - \sigma_{OA}^2 \quad (3)$$

where  $\sigma$  are interfacial tensions and the subscripts AW, OW, and OA refer to the air–water, oil–water, and oil–air interfaces, respectively. Positive values of  $E$ ,  $S$ , and  $B$  are often considered to correspond to easy entry and spreading of the oil on the solution surface, and to unstable oil bridges, respectively (and hence to high antifoam

activity). A critical analysis of the meaning of these coefficients and their relevance to the antifoam activity of the oils can be found in refs 10, 12, and 14–18.

Another characteristic that is very important for the antifoam activity is the so-called entry barrier, which prevents the emergence of the oil drops on the solution surface. Different quantities are suggested in the literature to characterize the entry barrier,<sup>20,21</sup> but the most practical one seems to be the critical capillary pressure,  $\Delta P_{CR}$ , inducing the entry of an oil drop, which is trapped in a liquid film from the respective surfactant solution.<sup>15–18</sup>  $\Delta P_{CR}$  is accessible to direct measurement by the recently developed film trapping technique<sup>22–24</sup> (FTT) and is comparable in magnitude to the capillary pressure, which compresses the drops in the thin films or plateau borders (PBs) of the real foam.<sup>15,17</sup> A very good correlation was found in several surfactant systems between the magnitude of  $\Delta P_{CR}$  and the stability of the foams in the presence of oils.<sup>15,17,18,21,24</sup> For brevity, we call  $\Delta P_{CR}$  “the entry barrier”.

Therefore, our approach gives us the possibility to compare the studied boosters with respect to the foam formation, evolution, and destruction by silicone oil. This approach was already used<sup>15</sup> to analyze the foam boosting effect of the zwitterionic surfactant lauryl amide propyl betaine (LAPB) in SDP3S solutions, and several nontrivial conclusions were drawn from the obtained results. In particular, it was proven<sup>15</sup> that the enhanced foam stability in the presence of LAPB is related to an increased entry barrier for the oil drops, while no correlation of the foam stability with the values of the  $E$ ,  $S$ , and  $B$  coefficients was found.

In the present article, we extend the study by including several other boosters of different chemical structure. One of the boosters, alkyl acid diethanol amide, is uncharged at neutral pH, but its molecules have the ability to participate in a donor–acceptor bond through the free electron pair of the N-atom; these molecules can bind protons and are positively charged at low pH. Diethanol amide has a limited solubility in water ( $\approx 10^{-4}$  M). The other two boosters are nonionic surfactants of different solubility in water–dodecanol (LA, practically insoluble in water) and Booster A (partially soluble in water,  $4 \times 10^{-3}$  M). All these substances are well soluble in micellar solutions of SDP3S, which indicates an interaction between the molecules of SDP3S and the boosters which favors the formation of mixed micelles. These additives have been used or have a potential to be used as commercial boosters in different formulations.

On the basis of the data published in the literature<sup>2</sup> for other substances of similar chemical structure, one could expect that LAPB exhibits strongly negative interaction parameters, whereas diethanol amide and Booster A probably have moderately negative interaction parameters with SDP3S. Dodecanol is known<sup>7–9</sup> to interact very strongly with SDS in mixed adsorption layers, and one may expect that the same is true for SDP3S as well. As evidenced by the results described below, these additives can affect different characteristics of the foaming solutions, and which of the boosters is appropriate for particular application depends strongly on the requirements of the specific problem.

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## 2. Experimental Details

**2.1. Materials.** Sodium dodecyl polyoxyethylene-3 sulfate (SDP3S) of commercial grade (Kao Co., Tokyo, Japan) is used as a main surfactant. The sample presents a mixture of several species having different numbers of EO groups (2.5 on average) and different alkyl chains (mainly  $C_{12}$  and  $C_{13}$  of ratio approximately 1:1). It is worthwhile noting that the experiments in ref 15 were performed with a different batch sample of SDP3S—this explains why some slight differences in the rate of foam destruction and in the film thinning characteristics are observed in the present study as compared to the previous one. The critical micelle concentration (cmc) of SDP3S is determined as  $\approx 0.5$  mM from the surface tension isotherm.

As foam boosters we study lauryl amide propyl betaine (hereafter called LAPB), lauric acid diethanol amide (LADA), lauryl alcohol (dodecanol, LA), and one nonionic surfactant, which presents a glycerin derivative (denoted as Booster A). LAPB, LADA, and Booster A are commercial-grade products of Kao Co., Tokyo, Japan, and are used without further purification. LADA is a mixture of several diethanol amides differing in their alkyl chains ( $C_{10}/C_{12}/C_{14} \approx 1/10/1$ ). The LA is a product of Sigma Chemical Co., St. Louis, MO.

The total surfactant concentration is 0.1 M in the experiments with LAPB, Booster A, and LA and 0.02 M in the experiments with LADA. The molar ratio of surfactant to booster is 60:40 in the experiments with LAPB, LADA, and Booster A. Due to the low solubility of LA (and to its strong effect at very low concentrations), the latter is introduced as 3 molar % with respect to the main surfactant.

The commercial batches of SDP3S contain 0.063 g of NaCl and 0.024 g of  $Na_2SO_4$  per gram of surfactant. LAPB contains 0.23 g of NaCl per gram of surfactant. These electrolytes create an ionic strength of 66 mM in the solutions containing 0.1 M SDP3S, 96 mM in the solutions containing 60:40 SDP3S/LAPB, and 40 mM in the solutions containing mixtures of SDP3S and 40 molar % nonionic surfactant. All solutions are prepared with deionized water obtained from a Milli-Q Organex system (Millipore).

Silicone oil SH200 (Kao Co., Tokyo, Japan) of dynamic viscosity 5 mPa·s is used at a concentration of 0.1 wt % in the working solutions. Since the solubility of silicone oil in the surfactant solutions is very low, the oil is dispersed in the form of emulsion droplets of diameter varying between 2 and 15  $\mu$ m.

**2.2. Methods and Procedures.** *2.2.1. Foam Formation and Foam Stability Evaluation.* A Ross-Miles test is used to produce foams and to compare their stabilities. The silicone oil is emulsified in 300 mL of surfactant solution by intensive agitation for 20 min on a magnetic stirrer. The emulsion is additionally homogenized by several hand-shakes before placing it into the glass cylinder of the Ross-Miles test. The cylinder has a working volume of 1 dm<sup>3</sup> and a diameter of 37 mm. The solution is circulated (pumped) for 20 s at a debit of 125 cm<sup>3</sup>/s through an orifice (7 mm in diameter), which is placed at 23 cm above the initial level of the liquid. The change of the foam volume with time is monitored for a period of 100 min after ceasing the liquid circulation. The accuracy in the foam volume determination is  $\pm 2$  mL, whereas the reproducibility is about  $\pm 5$  mL for the final and  $\pm 10$  mL for the initial foam volume.

The bubble rearrangement, coalescence, and coarsening in the foam column are observed by a CCD camera mounted on a long-focus lens and attached to a video recorder (VCR).

*2.2.2. Size Distribution of the Emulsion Droplets.* The size distribution of the emulsion droplets is measured by video-microscopy observations in white transmitted light. A Zeiss Axioplan microscope with the objectives 50 $\times$  Epiplan LD and 100 $\times$  (immersion type) is used. The image is recorded by a CCD camera and a VCR. The videotape is afterward processed by homemade image analysis software for determination of the drop size distribution. The diameter of 100 droplets is measured in each sample.

*2.2.3. Surface and Interfacial Tension Measurements.* The surface tension of the solutions,  $\sigma_{AW}$ , is measured by the Wilhelmy plate method on a Kruss K10T digital tensiometer. The tension of the solution surface before and after its contact with silicone oil is determined. After measuring  $\sigma_{AW}$  in the absence of oil, 15–30  $\mu$ L of silicone oil is gently deposited on the solution surface

away from the Wilhelmy plate. Typically, a fast reduction of  $\sigma_{AW}$  by several millinewtons per meter is observed due to spreading of a thin layer of silicone oil on the surface. Afterward, no detectable change of  $\sigma_{AW}$  is recorded for a period of 60 min.

The surface tension of the oil,  $\sigma_{OA}$ , is measured by the Du Nouy ring technique on a Kruss K10T tensiometer. The interfacial tension of the oil–solution interface,  $\sigma_{OW}$ , is measured by the spinning drop method on a Kruss Site 04 tensiometer.

*2.2.4. Stability of Foam Films.* Horizontal foam films of sub-millimeter size are observed in the so-called Scheludko cell.<sup>25,26</sup> A foam film is formed from a biconcave drop of surfactant solution, placed in a vertical cylindrical glass capillary, by sucking out liquid through an orifice in the capillary wall. The amount of liquid in the capillary and the film radius can be varied by a pressure control system. The capillary and the foam film are kept in a closed glass container to suppress the water evaporation. The foam films are observed from above (microscope Zeiss Axioplan, objectives LD Epiplan 10 $\times$  and 50 $\times$ ) in reflected or transmitted white light. The observations in reflected light provide a clear interference picture of the thin films, while the transmitted light allows one to observe the emulsion droplets in the film or in the meniscus region surrounding it.<sup>15</sup>

*2.2.5. Rate of Thinning and Stability of Vertical Foam Films.* Vertical foam films are formed on a rectangular glass frame (5  $\times$  5 mm<sup>2</sup>). The experimental setup is closed in a transparent glass container, which ensures saturation of the atmosphere around the film with aqueous vapors. The films are observed in monochromatic light ( $\lambda = 550$  nm), which gives one the opportunity to determine the film thickness from the intensity of the light reflected by the film.<sup>26</sup> Just after film formation, one sees alternating dark and bright interference stripes moving downward, which indicate that the film thickness is of the order of several hundred nanometers and that the foam film gradually thins with time. As the thickness of the upper part of the film becomes smaller than  $\sim 100$  nm, a very thin (appearing black in reflected light) film region appears there. This thin region expands with time until it occupies the entire film area. A rupture of the foam film may occur at different stages of the film thinning process depending on the surfactants used and on the presence of silicone oil. In these experiments we are able to measure the film lifetime,  $\tau_L$ , the time needed for the appearance of a black spot inside the film,  $\tau_{DR}$ , and the velocity of black spot expansion,  $v_E$ .

In another set of experiments a different frame is used, similar in design to that reported by Koczko and Racz.<sup>27</sup> It consists of three vertical legs (1.0 cm long) which meet at the tip of a central capillary at 120°. Three films are simultaneously formed in such a frame with a Plateau border between them, which is not influenced by the solid wall of the glass frame.

*2.2.6. Critical Capillary Pressure for Drop Entry (Film Trapping Technique, FTT).* The critical capillary pressure leading to rupture of the asymmetric oil–water–air film and to subsequent oil drop entry is measured by the new version of the FTT.<sup>23</sup> Briefly, a vertical glass capillary, partially filled with the working solution, is placed in a close vicinity above a glass substrate. The capillary is connected to a pressure control system, which allows one to vary and to measure the difference,  $\Delta P = (P_{IN} - P_0)$ , between the air pressure in the capillary,  $P_{IN}$ , and the ambient atmospheric pressure,  $P_0$ , with an accuracy of  $\pm 20$  Pa. When  $P_{IN}$  increases, the air–water meniscus in the capillary is pushed against the glass substrate—a wetting film is formed, which traps some of the oil droplets dispersed in the working solution. The droplets are observed from below, through the glass substrate, by means of an inverted optical microscope. Upon further increase of  $\Delta P$ , some of the trapped drops enter the air–water interface. Hence, the equipment allows one to measure the critical capillary pressure inducing the drop entry,  $\Delta P_{CR}$ , as a function of the solution composition and drop radius. A larger pressure difference,  $\Delta P_{CR}$ , corresponds to a higher barrier (more difficult drop entry) and vice versa.

All experiments are performed at an ambient temperature of  $25 \pm 1$  °C.

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**Table 1. Effect of Boosters on the Foaminess and Foam Stability in the Presence of 0.1 wt % of Silicone Oil: Volume of the Generated Foam ( $V_{IN}$ ); Volume of the Foam That Remained after 100 min ( $V_F$ ); Onset of the Foam Destruction ( $\tau_D$ ); Rate of Foam Destruction ( $v_D$ ); Critical Capillary Pressure Leading to Entry of the Silicone Oil Drops ( $\Delta P_{CR}$ ), Which Is a Measure of the Entry Barrier, As Determined by the FTT<sup>a</sup>**

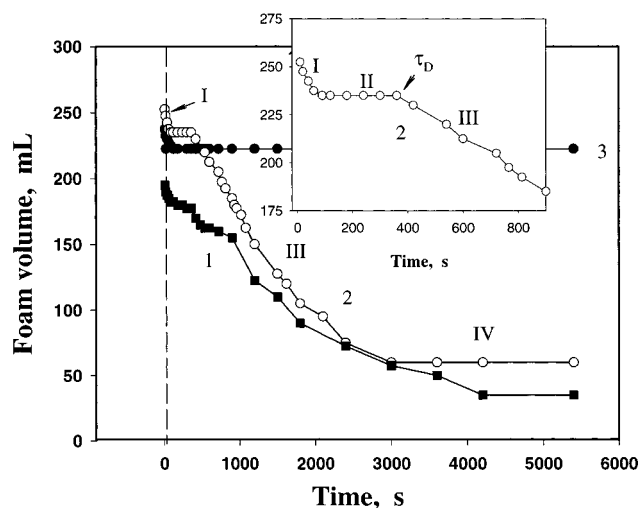
booster		$V_{IN}$ (mL)	$V_F$ (mL)	$V_F/V_{IN}$	$\tau_D$ (min)	$v_D$ (mL/min)	$\Delta P_{CR}$ (Pa)
no booster	0.1 M	195	48	0.25	<2	3	305
	0.02 M	192	45	0.23	<1	5	65
40 mol % LAPB (0.1 M)		238	190	0.80	stable foam	stable foam	1070
40 mol % Booster A (0.1 M)		252	68	0.26	7	7	700
40 mol % LADA (0.02 M)		248	55	0.22	5	12	170
3 mol % LA (0.1 M)		205	172	0.84	stable foam	stable foam	> 1500

<sup>a</sup> The composition of the solutions is described in more detail in section 2.1.

**Table 2. Interfacial Tensions<sup>a</sup> with Calculated Entry,  $E$ , Spreading,  $S$ , and Bridging,  $B$ , Coefficients for Silicone Oil in Solutions of SDP3S and Booster A (Total Surfactant Concentration 0.1 M)<sup>b</sup>**

booster A (molar fraction)	$\sigma_{AW}^{IN}$ (mN/m)	$\sigma_{AW}^{EQ}$ (mN/m)	$\sigma_{OW}$ (mN/m)	$S_{IN}$ (mN/m)	$S_{EQ}$ (mN/m)	$E_{IN}$ (mN/m)	$E_{EQ}$ (mN/m)	$B_{IN}$ (mN/m) <sup>2</sup>	$B_{EQ}$ (mN/m) <sup>2</sup>
0.0	33.2	25.8	6.8	6.6	-0.8	20.2	12.8	756.4	319.8
0.2	29.3	23.9	5.2	4.3	-1.1	14.7	9.3	493.5	206.2
0.4	25.6	20.8	3.5	2.3	-2.5	9.3	4.5	275.5	52.8
0.6	25.0	20.4	1.6	3.6	-1.0	6.8	2.2	235.5	26.7
0.8	24.4	20.1	0.8	3.8	-0.5	5.4	1.1	203.9	12.6
1.0	24.4	20.2	0.7	3.9	-0.3	5.3	1.1	203.8	16.5

<sup>a</sup> In all cases the oil–air tension,  $\sigma_{OW} = 19.8$  mN/m. <sup>b</sup>  $\sigma_{AW}^{IN}$  is the surface tension of the surfactant solution in the absence of oil, which is used to calculate the coefficients denoted by the subscript IN (see eqs 1–3);  $\sigma_{AW}^{EQ}$  is measured after spreading of silicone oil on the solution surface (section 2.2.3), and the respective coefficients are denoted by the subscript EQ.



**Figure 1.** Foam volume versus time for three different surfactant solutions: SDP3S (curve 1), SDP3S/Booster A = 60:40 (curve 2), and SDP3S/LAPB = 60:40 (curve 3). All solutions are of total surfactant concentration 0.1 M and contain 0.1 wt % of silicone oil. The roman numbers, associated with curve 2, indicate the different stages of the foam evolution. The inset shows an enlarged view of the initial periods on curve 2 ( $\tau_D$  is the onset of foam destruction).

### 3. Results and Discussion

**3.1. Foaminess and Foam Stability.** *3.1.1. Stages of the Foam Evolution.* All experiments discussed in section 3.1 are performed with surfactant solutions containing 0.1 wt % of silicone oil. In Figure 1 we present the foam volume as a function of time,  $V(t)$ , for three of the studied systems—SDP3S (no booster, curve 1), SDP3S + Booster A (curve 2), and SDP3S + LAPB (curve 3). From curve 2 one sees that, in general, the foam evolution in the studied systems can be subdivided into four periods (denoted as I–IV on curve 2). The video examination allows one to identify the elementary processes that occur within the foam column and lead to the observed changes in the foam volume.

Period I takes about 100–120 s. During this period the upper border of the foam remains still, because no

**Table 3. Initial,  $V_{IN}$ , and Final,  $V_F$ , Foam Volumes, and Onset of Foam Destruction,  $\tau_D$ , for Mixtures of SDP3S and LADA (0.02 M Total Surfactant Concentration, 0.1 wt % Silicone Oil)**

LADA molar fraction	$V_{IN}$ (mL)	$V_F$ (mL)	$V_F/V_{IN}$	$\tau_D$ (min)
0	192	45	0.23	<1
0.2	218	40	0.18	10
0.4	248	55	0.22	5
0.6	230	85	0.37	8
0.8	238	112	0.47	20
1.0	212	198	0.93	>100

coalescence of the bubbles with the air phase above the foam column is observed. The lower border of the foam rises up (which is indicated on the graph as a reduction of the foam volume by 15–20 mL), due to the drainage of water from the initially formed wet foam. Several processes are seen to take place within the foam during this period: The foam films thin down (see also section 3.2 and Tables 6 and 7); the plateau borders (PBs) and the nodes where they meet become much narrower; and the smallest bubbles shrink and disappear due to the air diffusion across the foam films (driven by the higher air pressure in the small bubbles)—cf. Figure 2A and B.

During stage II, the upper and lower borders do not change their positions, which reflects the facts that the water drainage has become very slow and that no bubble coalescence with the air phase above the foam occurs (no foam destruction is observed). However, the video observations show that an important restructuring of the foam cells takes place during this period (Figure 2B–D). The small bubbles disappear, and as a result, the density of the PBs (i.e., their total length per unit foam volume) and of the nodes (number per unit volume) decreases several times. As a result, a gradual accumulation of oil drops in the remaining nodes and PBs is observed with time, because the trapped drops cannot follow the draining water<sup>15</sup> (see also Figures 3 and 4). Also, the compressing capillary pressure, exerted by the walls of the shrinking nodes and PBs, gradually increases with time.

When a certain critical value of the compressing capillary pressure is reached (related to the entry barrier of the oil drops and depending on the surfactant composi-

**Table 4. Interfacial Tensions<sup>a</sup> with Calculated Entry, *E*, Spreading, *S*, and Bridging, *B*, Coefficients for Silicone Oil in Solutions of SDP3S and LADA (Total Surfactant Concentration 0.02 M)**

LADA molar part	$\sigma_{AW}^{IN}$ (mN/m)	$\sigma_{AW}^{EQ}$ (mN/m)	$\sigma_{OW}$ (mN/m)	$S_{IN}$ (mN/m)	$S_{EQ}$ (mN/m)	$E_{IN}$ (mN/m)	$E_{EQ}$ (mN/m)	$B_{IN}$ (mN/m) <sup>2</sup>	$B_{EQ}$ (mN/m) <sup>2</sup>
0.00	36.0	28.4	9.4	6.8	-0.8	25.6	18.0	992.3	502.9
0.20	33.4	26.7	7.0	6.6	-0.1	20.6	13.9	772.5	369.9
0.40	31.4	25.1	5.3	6.3	0.0	16.9	10.6	622.0	266.1
0.56	30.3	23.7	3.6	6.9	0.3	14.1	7.5	539.0	182.6
0.80	28.1	21.8	2.4	5.9	-0.4	10.7	4.4	403.3	89.0
1.00	26.6	20.3	0.8	6.0	-0.3	7.6	1.3	316.2	20.7

<sup>a</sup> In all cases the oil-air tension,  $\sigma_{OW} = 19.8$  mN/m.

**Table 5. Drainage of Small Foam Films (800  $\mu$ m in Diameter) in the Scheludko Cell: Time for Appearance of Black Spot in the Film ( $\tau_{SP}$ ) and Time for Black Spot Expansion ( $\tau_F$ )<sup>a</sup>**

booster	$\tau_{SP}$ (s)	$\tau_F$ (s)
no booster (0.1 M SDP3S)	55	140
no booster (0.02 M SDP3S)	39	98
40 mol % betaine (0.1 M)	50	105
40 mol % LADA (0.02 M)	68	73
40 mol % Booster A (0.1 M)	52	88
3 mol % LA (0.1 M)	53	645

<sup>a</sup> The films are formed from surfactant solutions without silicone oil.

**Table 6. Stability and Drainage Rate of Vertical Foam Films in the Absence of Oil: Film Life Time ( $\tau_L$ ); Time for Appearance of Black Film ( $\tau_{DR}$ ); Time for Black Film Expansion ( $\tau_E$ ); Velocity of the Boundary between the Thick and the Black Film Regions ( $v_E$ )**

booster	$\tau_L$ (s)	$\tau_{DR}$ (s)	$\tau_E$ (s)	$v_E$ ( $\mu$ m/s)
no booster (0.1 M SDP3S)	380	78	195	46
no booster (0.02 M SDP3S)	240	70	160	44
40 mol % betaine (0.1 M)	>900	37	142	73
40 mol % LADA (0.02 M)	720	42	95	97
40 mol % Booster A (0.1 M)	>900	30	124	74
3 mol % LA (0.1 M)	>900	75	420	39

**Table 7. Stability and Drainage Rate of Vertical Foam Films in the Presence of Silicone Oil: Film Life Time ( $\tau_L$ ) and Time for Appearance of Black Film ( $\tau_{DR}$ )<sup>a</sup>**

booster		$\tau_L$ (s)	$\tau_{DR}$ (s)
no booster (0.1 M SDP3S)	prespread layer	66 $\pm$ 15	33 $\pm$ 10
	pre-emulsified	~160	55 $\pm$ 15
no booster (0.02 M SDP3S)	prespread layer	60 $\pm$ 15	27 $\pm$ 10
	pre-emulsified	~150	97 $\pm$ 30
40 mol % betaine (0.1 M)	prespread layer	>600 <sup>b</sup>	32 $\pm$ 15
	pre-emulsified	~580	110 $\pm$ 80
40 mol % LADA (0.02 M)	prespread layer	80 $\pm$ 20	30 $\pm$ 15
	pre-emulsified	~300	120 $\pm$ 80
40 mol % Booster A (0.1 M)	prespread layer	80 $\pm$ 20	36 $\pm$ 15
	pre-emulsified	~180	~60
3 mol % LA (0.1 M)	prespread layer	66 $\pm$ 20	42 $\pm$ 15
	pre-emulsified	~150	~50

<sup>a</sup> These films typically rupture during the process of black area expansion. The reproducibility of the measured  $\tau_L$  and  $\tau_{DR}$  values in these systems is rather poor, because random factors (such as the oil drop entry) are involved. Therefore, the quoted average times indicate only the general trends. <sup>b</sup> Occasionally ruptures much earlier.

tion), the process of foam destruction is initiated, primarily through a destruction of the upper layer of bubbles—stage III (Figure 2E). Occasionally, a foam destruction within the foam column is observed (Figure 5). Note that the foam rupture is certainly caused by the droplets of silicone oil, because all of the studied surfactant solutions produce a very stable foam in the absence of oil—no destruction in the time scale of interest is observed. The onset of the foam destruction process is denoted by  $\tau_D$  (see the inset of Figure 1). The rate of foam destruction,  $v_D = -dV/dt$ ,

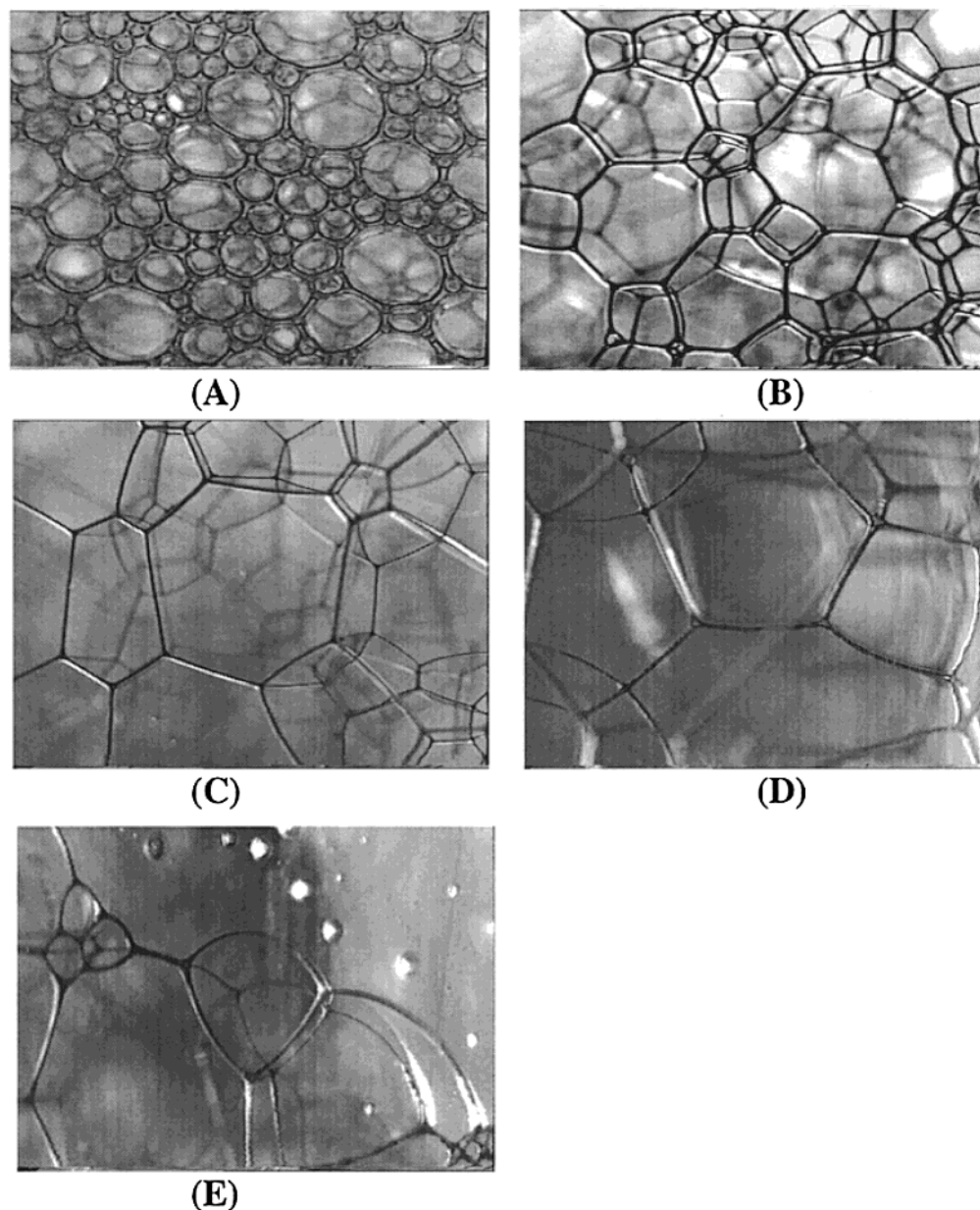
is approximately constant during the main course of period III. Afterward,  $v_D$  gradually decreases in magnitude, and stage IV is reached when the foam volume remains almost constant (Figure 1). During this period mainly large bubbles have remained and the process of bubble rearrangement is relatively slow.

The comparison of the three curves in Figure 1 shows that period II is absent in the system without boosters (only SDP3S), and the processes of liquid drainage and foam destruction are not temporarily separated in curve 1. This poor foam stability reflects the lower entry barrier of the oil droplets in the absence of boosters (see Table 1). On the contrary, period II in the system containing LAPB as a foam booster (curve 3) is very long— $\tau_D$  is longer than the time span of our observations. Again, this very good foam stability correlates with the high entry barrier for the oil drops in this system (Table 1 and ref 15).

**3.1.2. Comparison of the Booster Efficiency.** To compare the boosting effect of the different additives, we present in Table 1 the initial foam volume,  $V_{IN}$ , the final foam volume,  $V_F$ , their ratio,  $V_F/V_{IN}$ , the onset of foam destruction,  $\tau_D$ , and the rate of destruction,  $v_D$ , for all of the studied boosters. For comparison, the critical capillary pressure inducing the drop entry,  $\Delta P_{CR}$ , is also presented. As discussed in ref 15, the FTT experiments show that  $\Delta P_{CR}$  is lower for the larger drops; therefore, in Table 1 we present only the results for drops of diameter  $\approx 7$   $\mu$ m, which is close to the mean drop size in the studied solutions.

In general, the boosters can affect  $V_{IN}$  (the foaminess) or  $V_F$  (the foam stability). From this viewpoint, the studied additives can be classified as follows: LAPB improves both the foaminess and the foam stability; LADA and Booster A enhance mainly the foaminess, while the LA affects mainly the foam stability. Therefore, whether a given additive will be an efficient booster or not is strongly dependent on the time scale of interest. If this time scale is shorter than or comparable to the onset of foam destruction,  $\tau_D$ , then the relevant characteristic is  $V_{IN}$ , because the foam destruction starts too late to be of importance. On the contrary, if the time scale of observation is much longer than  $\tau_D$ , the relevant characteristic is  $V_F$ . Thus, Booster A and LADA are the best foam boosters, if one is interested in the short-term foam behavior, because they produce very voluminous foam. However, LAPB and LA are much better if one is interested in the long-term foam behavior, because they produce more stable foams.

It is worth noting for comparison that the foams produced from all these surfactant solutions are very stable (no destruction for more than 90 min) *in the absence of silicone oil*. The ratio of the final to initial foam volumes,  $V_F/V_{IN} \approx 0.80 \pm 0.04$ , is determined only by the process of water drainage from the foam column. As an example, for 0.1 M SDP3S solutions (no booster)  $V_{IN} = 165$  mL and  $V_F = 128$  mL; that is,  $V_F/V_{IN} \approx 0.78$ . Therefore, the foam collapse observed in the experiments, when silicone oil is



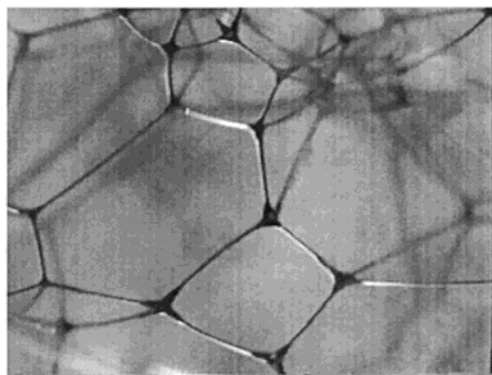
**Figure 2.** Photographs of the foam cells just below the top of a foam column at different stages of the foam evolution—cf. curve 2 in Figure 1: (A) wet foam, stage I; (B) foam at the transition between stages I and II; (C and D) air diffusion from the small bubbles toward the larger ones leads to disappearance of the smallest bubbles and to gradual accumulation of oil drops in the nodes and the plateau borders during period II; (E) when the capillary pressure at the top of the foam column exceeds a given critical value, a rupture of the upper layers of bubbles in the foam column is observed—beginning of stage III (0.1 M solution of 60:40 SDP3S/Booster A, containing 0.1 wt % silicone oil).

present in the solutions, is entirely due to the antifoam effect of the oil. These results reinforce the conclusion made in ref 15 that the main role of the foam booster in the absence of oil is to increase the initial foam volume, while in the presence of oil the booster might additionally suppress the antifoam activity of the oil.

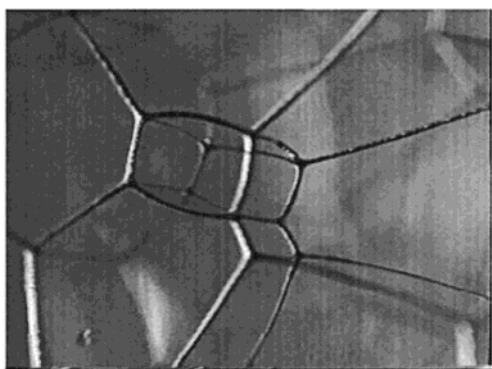
**3.1.3. Effect of the Booster Concentration.** The variations of  $V_{IN}$  and  $V_F$  as functions of the SDP3S/Booster A ratio in the surfactant mixture are shown in Figure 6. Both curves demonstrate the foam boosting effect of Booster A, which is by no means trivial. Two rather different concentration ranges could be distinguished:  $V_{IN}$  and  $V_F$  increase from 200 to 250 mL and from 45 to 65 mL, respectively, when the concentration of Booster A rises from 0 to 40 molar % in the surfactant mixture. The further increase of the concentration of Booster A leads to a sharp decrease of the initial foam volume and to a strong increase

of the foam stability,  $V_{IN} \approx V_F$ . Therefore, there is an optimum ratio of SDP3S and Booster A (60:40) with respect to the foaminess, while a long-term stability of the foam is observed only in the mixtures where Booster A prevails. No foam tests are made with solutions containing more than 70 molar % Booster A, because these solutions contain a surfactant precipitate.

The observed variation of  $V_F$  might be explained taking into account the measured values of the entry barrier,  $\Delta P_{CR}$ . As seen from Table 1, the addition of Booster A increases the entry barrier from 305 Pa (only SDP3S) up to 700 Pa (at 40% Booster A). Accordingly, there is an increase of  $V_F$  from 45 to 68 mL. The further increase of the entry barrier should affect strongly  $V_F$ , because the height of the final foam column is expected to be on the order of  $H_F \sim \Delta P_{CR}/(\rho g)$ , where  $\rho$  is the mass density of the surfactant solution and  $g$  is the acceleration of gravity.<sup>15</sup>



(A)



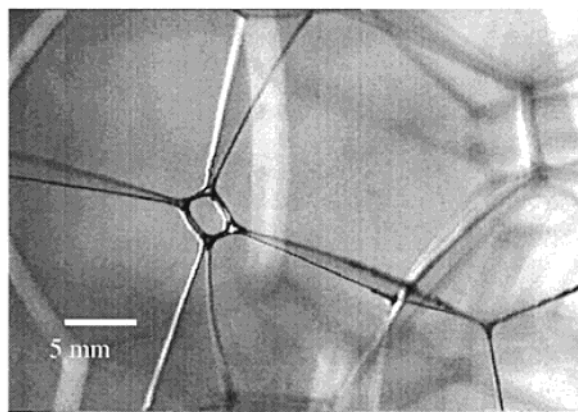
(B)

**Figure 3.** (A) Oil drops accumulate first mainly in the nodes where the plateau borders meet with each other. (B) With time both the nodes and the plateau borders at the top of the foam column become densely packed with oil drops (0.1 M SDP3S solution containing 3 molar % of LA).

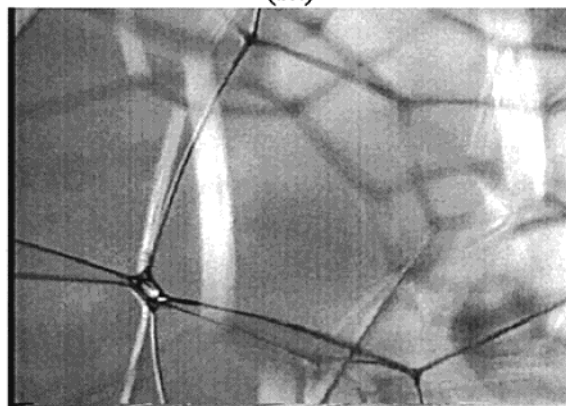
In our foam test cylinder, the increase of  $H_F$  with 1 cm (which corresponds to an increase of  $\Delta P_{CR}$  by 100 Pa) corresponds to a growth of the foam volume by 10 mL. Indeed, additional measurements by FTT showed that the entry barrier is higher than 1500 Pa for the solution containing 60% of Booster A, which correlates very well with the observed increase of  $V_F$  up to 160 mL in the solutions containing more Booster A than SDP3S.

Another factor that might also be important for the foam stability in this system is the significant change in the values of the  $E$ ,  $S$ , and  $B$  coefficients at the ratio 50:50 (see Table 2). Note that the  $E$ ,  $S$ , and  $B$  coefficients are all strongly positive when SDP3S is in excess (except the equilibrium spreading coefficient,  $S_{EQ}$ ), which implies that the oil drops are able to destroy the foam after entering the walls of the plateau borders. However, the values of the  $E_{EQ}$  and  $B_{EQ}$  coefficients are about an order of magnitude lower in the surfactant mixtures containing more Booster A than SDP3S, which might lead to a reduced antifoam activity of the silicone oil.

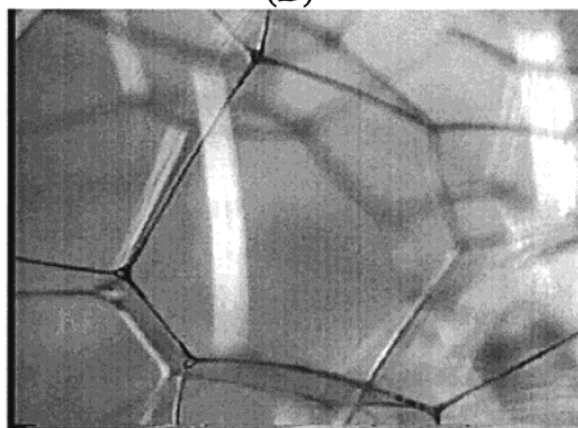
Another possible reason for the higher foam stability in this concentration range could be the very low interfacial tension  $\sigma_{OW}$  (below 1 mN/m); see Table 2. The small values of  $\sigma_{OW}$  correspond to an enhanced deformability of the oil drops, which in turn allows them to rearrange and to migrate more easily in the plateau borders during the liquid drainage from the foam, without a foam destruction. In addition, smaller oil droplets are produced during the preparation of the working solutions at lower interfacial tension. The optical observations show that the mean diameter of the oil drops in the working solutions of the



(A)



(B)

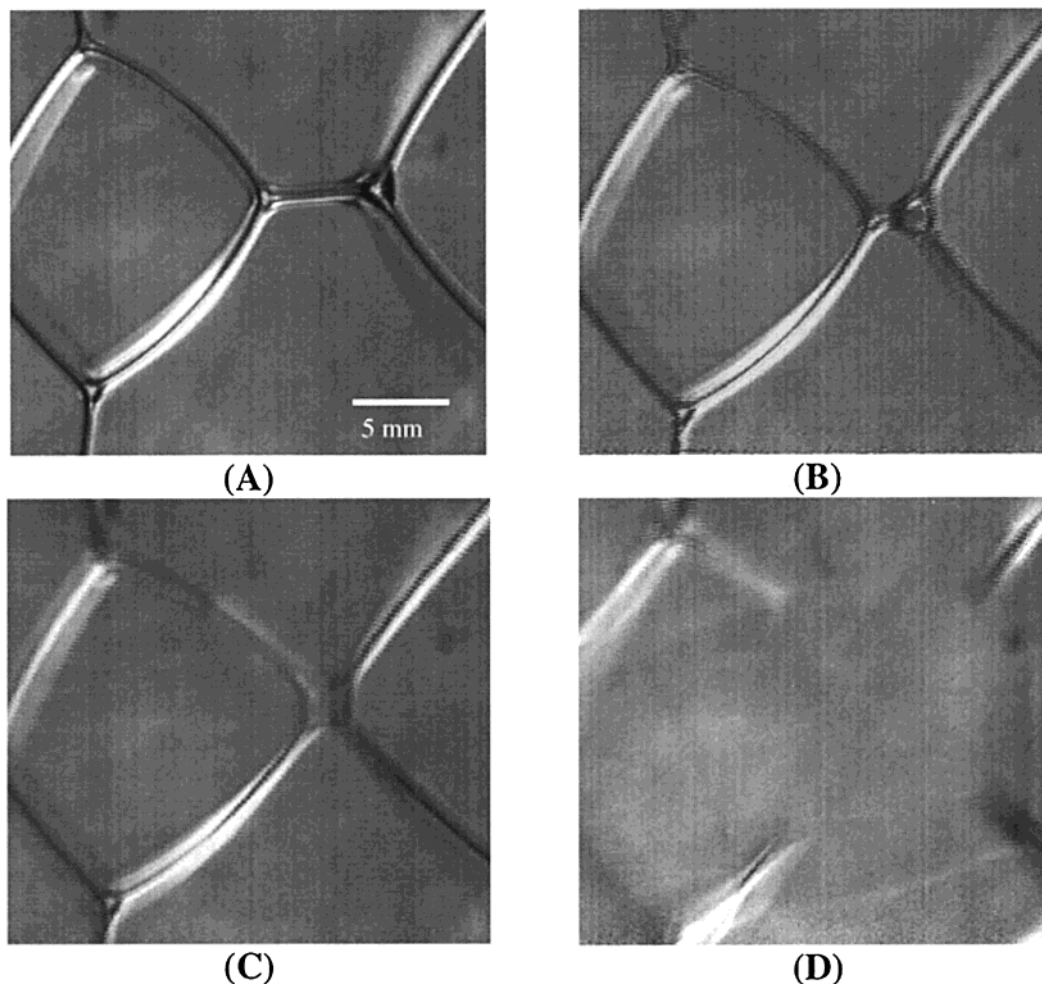


(C)

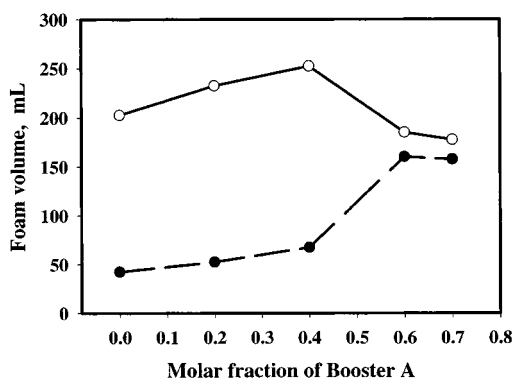
**Figure 4.** Three consecutive video-frames showing the shrinking of a small foam bubble (as a result of the air diffusion across the foam films), which leads to a local rearrangement of the foam structure and to accumulation of silicone oil in the plateau borders and nodes.

SDP3S/Booster A mixture is  $5.5 \mu\text{m}$ , with the main fraction of the drops being in the range between 2 and  $10 \mu\text{m}$ . For comparison, the average diameter of the drops in the SDP3S solution is  $8 \mu\text{m}$  with a significant fraction of the drops being up to  $15 \mu\text{m}$  large. As discussed in refs 14 and 15, the foam stability might depend strongly on the size of the oil drops.

The observed maximum in the foaminess of the surfactant mixtures is more difficult to explain, because the process of foam formation involves complex phenomena, such as the dynamics of surfactant adsorption, the stability of the foam films well before their surfaces are saturated with surfactant molecules, and others. An additional



**Figure 5.** (A–D) Consecutive video-frames showing the destruction of foam cells within a foam column in the moment, when a rearrangement of the nodes and plateau borders (containing silicone oil drops) takes place.



**Figure 6.** Initial (empty circles) and final (solid circles) foam volume as a function of the molar fraction of Booster A in the surfactant mixture (0.1 M total surfactant concentration; 0.1 wt % of silicone oil).

complication in our systems is the presence of oil, which is able to induce bubble coalescence during foaming and to affect the dynamic surface properties of the solutions. All these processes are still poorly understood, and we refrain from their detailed analysis, which would be rather speculative on the basis of the available information. Most probably, the increased foaminess of the mixtures is related to faster adsorption of the surfactant molecules, which in turn decreases the dynamic surface tension, facilitating in this way the surface expansion and bubble generation.<sup>9,28</sup> The faster adsorption should lead also to

a more rapid stabilization of the foam films intervening between the newly created bubbles<sup>29,30</sup> and of the asymmetric oil–water–air films formed between the oil drops and the solution surface.<sup>18</sup>

The foam tests with SDP3S/LADA mixtures show a qualitatively similar behavior: a maximum in the foaminess at an approximately 1:1 ratio of SDP3S and LADA, a slight increase of the foam stability in the concentration range where SDP3S prevails, and a steeper increase in the foam stability at higher booster concentrations; see Table 3. Only the foams produced from solutions of pure LADA are entirely stable in the time scale of our observation (100 min); however, these solutions are turbid due to the low solubility of LADA in water. Note that the foam boosting effect of LADA manifests itself by an increase of both  $V_{IN}$  and  $\tau_D$ , which results in a rather voluminous foam for several minutes after its generation. Therefore, the foaminess is the most important characteristic for short time scales (up to 10–15 min).

As indicated in Table 1, the addition of LADA increases the entry barrier of the oil drops from 65 to about 170 Pa. This is probably the main reason for the delay in the onset of foam destruction in the presence of LADA. The values

(28) Adamson, A. W.; Gast, A. *Physical Chemistry of Surfaces*, 6th ed.; Wiley-Interscience Publication: New York, 1997.

(29) Ivanov, I. B.; Dimitrov, D. S. In *Thin Liquid Films: Fundamentals and Applications*; Surfactant Science Series, Vol. 29; Ivanov, I. B., Ed.; Marcel Dekker: New York, 1988; Chapter 7.

(30) Kralchevsky, P. A.; Danov, K. D.; Denkov, N. D. In *Handbook of Surface and Colloid Chemistry*; Birdi, K. S., Ed.; CRC Press: New York, 1997; Chapter 11.



of the  $E$ ,  $S$ , and  $B$  coefficients (Table 4) cannot be used to explain the increase of the foam stability, because they are strongly positive (except for the pure LADA solutions). The experiments with thin liquid films demonstrate that the introduction of LADA leads to an increase of the lifetime of the foam films both in the absence and in the presence of silicone oil (see Tables 6 and 7 and section 3.2.2.4). This enhanced film stability is probably related to the specific interactions between the SDP3S and LADA molecules in the adsorption layers, but a detailed explanation of this effect is still missing.

Previous experiments<sup>15</sup> with LAPB showed different concentration trends: both  $V_{IN}$  and  $V_F$  substantially increase with the booster concentration up to the ratio of 60:40 (in the region where SDP3S is in excess). At a higher relative concentration of LAPB,  $V_{IN}$  slightly depends on the booster concentration and the foams are very stable in the time scale of interest,  $V_F/V_{IN} \approx 0.8$ . These results are explained<sup>15</sup> by the steep increase of the entry barrier in the presence of LAPB, whereas any correlation of the foam stability with the  $E$ ,  $S$ , and  $B$  coefficients is absent for this system. The experiments demonstrate that the foam films formed from LAPB-containing solutions are particularly stable in the presence of silicone oil (ref 15 and section 3.2.2.4). This effect, as well as the high entry barrier measured for these solutions, is probably related to the strong intermolecular attraction in the adsorption layers, typical for the anionic–zwitterionic mixtures.<sup>2</sup> One may expect that this attraction increases the surface dilatational elasticity of the mixed adsorption layers, which in turn reduces the probability for occurrence of large fluctuations in the density of the layers adsorbed on the film surfaces and, hence, decreases the probability for film rupture (see, e.g., the discussion in ref 31).

The increased foam stability in the presence of 3 molar % LA is also explained by the very high entry barrier (above 1500 Pa) measured with this solution; see Table 1. The oil drops are unable to enter the surfaces of the foam films and the PBs; hence, the oil remains captured in the PBs without being able to destroy the foam. In addition, the thin film studies show that the LA decelerates the final stage of the film thinning, probably due to the increased surface viscosity of the solution<sup>7,9</sup> or to increased Gibbs elasticity.<sup>29</sup> As indicated by the measured interfacial tensions and by the calculated  $E$ ,  $S$ , and  $B$  coefficients, the silicone oil must be a rather efficient antifoam, if the entry barrier was not so high:  $\sigma_{AW}^{IN} = 30.7$  mN/m,  $\sigma_{AW}^{EQ} = 25.1$  mN/m,  $\sigma_{OW} = 6.5$  mN/m,  $E^{IN} = 17.4$  mN/m,  $E^{EQ} = 11.8$  mN/m,  $S^{IN} = 4.4$  mN/m,  $S^{EQ} = -1.2$  mN/m,  $B^{IN} = 593$  (mN/m)<sup>2</sup>, and  $B^{EQ} = 280$  (mN/m)<sup>2</sup>. Besides, the reduced value of  $\sigma_{AW}^{IN}$  (as compared to that in the absence of LA, 33.2 mN/m; see Table 2), evidences that mixed adsorption layers of SDP3S and LA are formed in this system, despite the fact that the solution concentration is above the cmc.

In conclusion, we observe an increased barrier to drop entry with all booster-containing solutions (as compared to the solutions of SDP3S), which correlates well with the enhanced foam stability. If the barrier is higher than  $\sim 1000$  Pa, then the foams are stable during the time span of our observations. If the barrier is lower than 1000 Pa, there is a destruction of the foam, but the onset of this process is delayed for at least several minutes by the addition of boosters.

**3.2. Stability of Foam Films.** *3.2.1. Foam Films in the Scheludko Cell.* The general pattern of the foam film thinning in the presence of oil drops has been described in section 3.3.1 of ref 15 for SDP3S and SDP3S/LAPB

mixtures. Qualitatively the same thinning pattern is observed with the other studied additives, as well. The microscope observations show that the oil drops leave the foam films soon after their formation and virtually do not affect the stages and the rate of film thinning. The foam films in the Scheludko cell are very stable and are not destroyed by the oil drops, due to the relatively high entry barrier (above 65 Pa) for all of the studied systems. As discussed in ref 17, the entry barrier should be below  $\sim 20$  Pa for drop entry in the thinning foam films to occur—such low barriers can be achieved by using mixed solid–liquid antifoams.<sup>10,14,16–18</sup>

In principle, one possible mechanism of foam stabilization by the additives (at least for a certain period) could be the decrease of the rate of water drainage from the foam films and from the real foams. To compare the effect of the different boosters on the rate of film thinning, we show in Table 5 the following characteristics:  $\tau_{SP}$  is the time from the moment of film formation until the appearance of a thin spot corresponding to the final film thickness (therefore,  $\tau_{SP}$  characterizes the rate of film thinning);  $\tau_F$  is the time needed for expansion of the black spot until it occupies the entire film area. The data in Table 5 are obtained with surfactant solutions in the absence of silicone oil.

Remarkably, the results show that most of the boosters (LAPB, Booster A, and LA) virtually do not change the rate of film thinning— $\tau_{SP}$  is between 50 and 55 s for all surfactant solutions of total concentration of 0.1 M. Only the introduction of LADA leads to about two times longer  $\tau_{SP} = 68$  s, as compared to  $\tau_{SP} = 39$  s for solutions without booster at the same concentration (0.02 M). Furthermore, the introduction of a booster typically leads to a faster expansion of the black spot. Only LA is an exception in this aspect, because it leads to a somewhat slower rate of spot expansion. Therefore, the obtained results do not support the idea that the main role of the boosters is to decelerate the rate of liquid drainage from the liquid films. The experiments with real foams also have not revealed any significant difference in the rate of liquid drainage during stage I of the foam evolution in the presence of the studied boosters.

*3.2.2. Experiments with Vertical Foam Films and Plateau Borders (PBs).* Several series of experiments are performed with vertical films: (1) with surfactant solutions in the absence of silicone oil; (2) with solutions whose surface has been covered by a prespread layer of silicone oil; (3) with solutions containing pre-emulsified silicone oil. Series 1 and 2 are performed with films hanged on a rectangular frame, whereas series 3 is performed with the three-legs frame to observe the effect of oil droplets trapped in the PB.<sup>15</sup>

The following characteristics are measured and presented in Tables 6 and 7:  $\tau_L$  is the overall lifetime of the film;  $\tau_{DR}$  is the time needed for formation of a black (thin) spot in the upper portion of the film ( $\tau_{DR}$  is an analogue of  $\tau_{SP}$  in the experiments with horizontal films);  $\tau_E$  is the time for expansion of the black spot, that is the time elapsing from its appearance until it occupies the total film area (an analogue of  $\tau_F$ );  $v_E$  is the velocity of the line separating the thin black film from the thicker portion of the film, that is,  $v_E$  is another measure for the expansion of the thin film.<sup>32,33</sup>

*3.2.2.1. Experiments in the Absence of Silicone Oil.* As described in ref 15, the film thinning pattern in the absence

(32) Yamanaka, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1755.

(33) Stoyanov, S. D.; Paunov, V. N.; Basheva, E. S.; Ivanov, I. B.; Mehreteab, A.; Broze, G. *Langmuir* **1997**, *13*, 1400.

of silicone oil is very reproducible and the films are relatively stable. All boosters increase the lifetime of the foam films. The drainage time,  $\tau_{DR}$ , in the presence of the boosters is typically shorter (except LA, which practically does not affect it), which means that the thick films thin faster in the presence of the boosters. The time for expansion of the black film,  $\tau_E$ , decreases, which also indicates a faster process in the presence of boosters. Accordingly, the velocity  $v_E$  is larger. Again the LA is an exception with respect to the thin film dynamics, because it decelerates the expansion process ( $\tau_E$  is longer and  $v_E$  is smaller).

**3.2.2.2. Experiments with a Prespread Layer of Silicone Oil.** These experiments are aimed to compare the drainage and the stability of foam films in the presence of a spread oil layer. One should note that the reproducibility is worse than that in the experiments without oil. In general, these films live significantly shorter and rupture during the process of expansion of the thin (black) area; see Table 7. Only LAPB leads to significantly more stable films as compared to SDP3S solutions of the same concentration— $\tau_L$  is much longer, and the films “survive” the stage of black area expansion in most of the experiments,  $\tau_E \approx 100$  s. All other boosters do not improve significantly the film stability. The rate of foam film drainage is notably faster (as compared to that of the solutions in the absence of oil) and slightly depends on the composition of the surfactant mixture— $\tau_{DR}$  is around 30 s for all solutions except LA, which provides a slightly slower film drainage ( $\tau_{DR} \approx 42$  s).

**3.2.2.3. Experiments with a Pre-emulsified Silicone Oil.** As seen from Table 7, the foam films from SDP3S/LAPB solutions are relatively stable, which correlates well with the observed stable foams and reflects the high entry barriers measured with this system. The introduction of LADA also leads to somewhat more stable foam films. The films from Booster A and LA solutions have practically the same rate of drainage and stability as those without any booster. Again, the reproducibility in these experiments is low, because the process of drop entry, which leads to the film rupture, involves random factors.

**3.2.2.4. Destabilization of Foam Films by Spreading Silicone Oil.** In another series of experiments, a layer of silicone oil is spread on the solution surface during the process of film thinning, that is, after the foam film has been formed. These experiments mimic to some extent the process in which an oil drop enters the solution surface at the PB and creates a source of spreading oil. The experiments show that the spreading oil induces a film rupture in all systems, but the delay is different for the various solutions—the time elapsing from the moment of oil spreading till the moment of film rupture is about 5 s for SDP3S solutions and SDP3S/Booster A mixtures, while it is significantly longer in the presence of LADA and LA (20–25 s) and especially in the presence of LAPB (1–2 min).

In conclusion, the thin film studies show that the boosters do not decelerate the dynamics of the foam film thinning (except LA which decelerates the rate of black spot expansion). The spreading silicone oil always destabilizes the foam films, but the resistance of the films to rupture depends on the particular booster. The films formed from LAPB-containing solutions are particularly resistant to the antifoam action of silicone oil.

#### 4. Concluding Remarks

A comparison of several foam boosters of different chemical structure is performed by foam tests and model

experiments with foam films. Along with the two surfactants (SDP3S and booster), the working solutions contain also 0.1 wt % of silicone oil dispersed in the form of micrometer-sized oil droplets.

Optical observation of the foams allows one to monitor the structural changes that take place during the foam evolution. In general, four stages could be distinguished in the time scale of our observations (100 min):

(i) Fast drainage of water from the initially formed wet foam, which lasts about 1.5–2 min. The oil drops leave the foam films during this period and are trapped in the neighboring plateau borders and nodes. An intensive restructuring of the foam, due to water drainage and to diffusion of gas from the small bubbles toward the larger ones, is observed. No foam destruction, in the sense of bubble coalescence with the air phase above the foam column and ensuing lowering of the upper foam border, is detected during this period.

(ii) A period of a constant foam volume, whose duration strongly depends on the surfactant composition. The most important processes during this stage are the accumulation of oil drops in the nodes and the plateau borders, and the gradual increase of the capillary pressure which compresses these drops.

(iii) A period of a relatively rapid foam destruction, which occurs mainly through disappearance of the upper layers of bubbles. This process is related to entry of the oil drops (due to the increased capillary pressure at the top of the foam column), which leads to destruction of the neighboring foam films and plateau borders.<sup>15</sup> Occasionally, a bubble coalescence within the foam column is also observed.

(iv) A period of very slow foam destruction, when the foam volume remains virtually constant.

The obtained results demonstrate that the foam boosting effect of the studied additives cannot be explained by a simple factor—the boosters may affect different aspects of the foaming process:

One can distinguish foam boosters improving mainly the foam stability (LA), the foaminess of the solutions (Booster A and LADA), or both (LAPB).

The stable foams in the presence of LA and LAPB are explained mainly by the very high barrier to entry of the oil drops in these systems (above 1000 Pa). The oil drops remain arrested in the nodes and plateau borders and are unable to destroy the foam by the mechanisms discussed in refs 10, 15–17, and 34. In this aspect, the obtained results reinforce the conclusions about the important role of the entry barrier, drawn by Bergeron et al.<sup>21</sup> (for foams in porous media), Wasan and co-workers,<sup>19,20</sup> and other researchers.<sup>10–12,15–17,24</sup>

The high entry barriers in the systems containing LA and LAPB are probably related to a very strong attraction between the molecules of SDP3S and the boosters in the adsorption layers (negative interaction parameter). Furthermore, the foam films obtained from LAPB-containing solutions are much more stable in the presence of silicone oil spread on the solution surface, which is an additional factor leading to more stable foams in the presence of oil.

The optimal ratio corresponding to maximal foaminess of the solutions of Booster A and LADA is about 1:1. This effect is more difficult to explain because several complex dynamic processes are involved. Most probably, the enhanced foaminess is related to a reduced dynamic surface tension of the solutions,<sup>9,28</sup> but the presence of silicone oil that is able to induce a bubble coalescence

(34) Koczo, K.; Koczona, J. K.; Wasan, D. T. *J. Colloid Interface Sci.* **1994**, *166*, 225.

during foaming and affects the surface properties makes these systems rather difficult for analysis. Further experiments are planned to clarify this issue. One important element in the foam boosting effect of these additives is the delay in the onset of the foam destruction process, which is also explained by the increased entry barrier in the presence of boosters.

The introduction of a foam booster typically leads to faster foam film thinning, which means that the boosting effect cannot be explained by slower film thinning and water drainage. LA seems to be an exception (it decelerates the final stage of the film thinning process), which is explained by the very high surface viscosity of the solutions containing LA.<sup>7,9</sup>

The values of the entry,  $E$ , spreading,  $S$ , and bridging,  $B$ , coefficients cannot be used to explain the foam boosting effect, because these values are positive in most of the stable systems. We observe a significant reduction of the  $E$ ,  $S$ , and  $B$  values only at very high molar fraction of LADA and Booster A in the surfactant mixtures.

Another factor that might be important in these systems is the oil–water interfacial tension. Lower interfacial tension leads to smaller oil drops (at equivalent other

conditions) and to an enhanced deformability of the drops. Both these effects would result in more stable foams in the presence of oil.<sup>15</sup>

One of the important conclusions from this study is that the choice of the appropriate booster for a particular application strongly depends on the ratio between the time scale of interest and the onset of foam destruction,  $\tau_D$ . If the time scale of interest is shorter or close to  $\tau_D$ , the foaminess is the most important factor. On the contrary, if the time scale is much longer than  $\tau_D$ , the foaminess is of no importance, while the foam stability is the relevant characteristic of the solutions.

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