Effects of Counterions and Co-ions on the Drainage and Stability of Liquid Films and Foams

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The influence of various electrolytes on the thinning of foam films and the decay of foams stabilized with sodium dodecyl sulfate (SDS) is investigated. The ionic strength was kept constant, 0.024 M, in all experiments. Sodium salts, Na_2SO_4, $NaNO_3$, $NaCl$, Na_2CO_3, Na_3PO_4, and sodium citrate, as well as magnesium salts, $MgSO_4$, $Mg(NO_3)_2$, $MgCl_2$, and $Mg(OOCCH_3)_2$, are used. The lifetime and the critical thickness of rupture of the unstable films, as well as the equilibrium thickness of the stable films, are measured. The rate of drainage of the liquid from the foams and their decay time are also measured. The influence of the bivalent counterion, Mg^{2+}, is related to two major effects influencing the film stability in the opposite directions: (i) increase of the surface elasticity and viscosity due to connections between neighboring surfactant headgroups produced by Mg^{2+} and (ii) enhancement of the ionic correlation attraction between the film surfaces. The data show also an unexpectedly large influence of the co-ions on the film and foam stability. Carbonates, phosphates, and citrates have the most significant stabilizing effect. At least two effects may be responsible for the larger stability of the films with co-ions of weak acids: (i) The dissolved carbonate and phosphate salts spontaneously adjust to pH 11.4 in the solution, which leads to hydrolysis of SDS to dodecanol. The latter increases the surface elasticity, viscosity, and kinetic stability of films and foams. (ii) The molecules of the carbonic, phosphoric, or citric acid can interconnect headgroups of neighboring SDS molecules in the surface adsorption monolayers by formation of multiple H-bonds. Such a linking also enhances the kinetic stability. These hypotheses agree well with the accumulated experimental data and can be helpful for a better understanding of the role of citrates, phosphates, and other electrolytes in body-care and household detergency.   © 1998 Academic Press

Key Words: detergency: effect of citrates, phosphates; foam films, kinetic stability; foams, effect of co-ions and Mg^{2+}; H-bonds: SDS with weak acids; hydrolysis of SDS; ionic correlations: effect on film stability; liquid films, drainage and stability; surface elasticity: effect of linkers; surface forces: ionic correlations; syneresis of foams, effect of electrolytes.

1. INTRODUCTION

The great importance of foams in various fields of practice has stimulated studies of foam systems for many years (1). The stability and the lifetime of foams are governed by the properties of their structural units: thin liquid films (TLF) and Plateau borders (1–3). The latter are influenced by the rheological properties of the surfactant adsorption monolayers and their interaction across the TLF. The electrostatic interaction, which gives rise to long-range double-layer forces (2) and to short-range hydration repulsion (4), plays an important role in the stability of foam films. The effect of electrostatics was studied experimentally by variation of electrolyte concentration (2, 5, 6). Sharma and Khilar (7) established that the addition of electrolyte affects the surface mobility. As a rule 1:1 electrolytes were used in these studies. There are only few works on the effect of bivalent *counterions* on the process of film thinning (8, 9). It was observed (9) that the type of film rupture depends to some extent also on the type of *co-ions*.

The influence of co-ions (monovalent or bivalent) has been studied mainly with respect to the properties of sodium dodecyl sulfate (SDS) adsorption *monolayers* (10–12). Yamanaka (13) investigated the properties of vertical films and foams containing sodium salts with various anions. These films and foams were stabilized by a nonionic surfactant (polyoxyethylene nonylphenyl ether) instead of SDS. It was experimentally established that the stability of the studied foams depends on the type of the anion in the solution.

According to the DLVO theory (14), at a fixed ionic strength of the solution the type of co-ion should not affect the double layer interaction in so far as the co-ions are repelled by the charged film surfaces and do not enter the Stern layers. On the other hand, in our preliminary experiments we observed that the drainage and stability of foam films depend strongly on the type of the co-ion at a given counterion and total ionic strength. This intriguing observation stimulated us to extend the study, whose results are the subject of the present article.

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We investigated foam films and foams stabilized by SDS in the presence of a variety of electrolytes at constant ionic strength $I = 0.024$ M. The latter value of I was chosen because it belongs to the concentration range typical of the formulations used in household and personal-care detergency. The co-ions were provided by either sodium salts, Na_2SO_4, $NaNO_3$, $NaCl$, Na_2CO_3, Na_3PO_4, and sodium citrate, or magnesium salts, $MgSO_4$, $Mg(NO_3)_2$, $MgCl_2$, and $Mg(OOCCH_3)_2$. When preparing a solution we accounted for the fact that the co-ions corresponding to a weak acid are present in the solution as anions of different valence, depending on the pH. The lifetime and the critical thickness of rupture (or the equilibrium thickness, if any) of single films have been determined. The kinetics of the foam drainage was also studied by measuring the volume of liquid drained out of the foam as a function of time. Correlations between the drainage and stability of the separate films and of the foams formed from the same solution were sought and the factors causing the established effect of the co-ions were examined.

The paper is structured as follows. Section 2 describes the experiments. Section 3 presents and discusses the experimental results for single foam films (formed in the Scheludko cell). Likewise, Section 4 is devoted to experimental results with foams and their interpretation. We believe that the unexpectedly large effect of the co-ions on the properties of the films and foams and the proposed hypotheses for their explanation will provoke additional studies in this field.

2. EXPERIMENTAL CONDITIONS

(a) Methods and Experimental Procedures

We studied single horizontal foam films formed in a standard Scheludko cell (3) by sucking the liquid out of a biconcave droplet contained in a cylindrical capillary. The films were observed with an optical microscope in reflected monochromatic light of wavelength 551 nm. The critical film thickness of rupture h_{cr}, as well as the equilibrium film thickness h_f, was determined interferometrically from the intensity of the reflected light (3, 15). The thinning of unstable films was observed visually and their lifetime was measured by an electronic chronometer. Description of the experimental setup used for the study of thin liquid films and details about the experimental procedure can be found in Refs. (8, 16).

In the parallel experiments with foams we generated wet foam by the method of Bartsch by shaking the solution in a glass cylinder of total volume 150 cm³. Each solution investigated (with a volume of 20 cm³) was shaken 20 times by hand as reproducibly as possible. Immediately after that the cylinder was put in a vertical position and the volume of the liquid under the foam (the so-called ''initial volume,'' V_0) was recorded as a function of time. At least five indepen-

dent measurements of the foam drainage were carried out for each investigated solution. The data were then averaged. We measured also the full time of foam destruction (foam breakage), τ_{br}. It is defined as the time needed for the height of the foam column in the center of the cylinder to decrease from its initial value down to zero.

The volume of the liquid drained out of the foam as a function of time was fitted by a double exponential equation (17–19),

$$V(t) = V_\infty - V_1\exp\left(-\frac{t}{\tau_1}\right) - V_2\exp\left(-\frac{t}{\tau_2}\right), \quad [1]$$

where $V_\infty = 20$ ml is the liquid volume flowed out for $t \to \infty$, V_1 and V_2 are parameters obeying the condition $V_1 + V_2 = V_\infty - V_0$, and τ_1 and τ_2 are characteristic times of the foam drainage. The time constant τ_1 is believed to account for the drainage of the liquid from the foam due to the gravity, whereas τ_2 is considered a characteristic time for the coalescence of foam bubbles due either to the diffusion of air across the foam films or to the rupture of these films (17–19). In the present study the four parameters V_1, V_2, τ_1, and τ_2 were obtained by means of the least-squares method from the best fit of the experimental data for $V(t)$.

For the time being there is no general theory of the foam drainage. Therefore to characterize this process one is to apply either empirical equations, such as Eq. [1], or to use quantities, which are directly measurable, such as τ_{br}. In fact, the experiments with foams, reported in the present paper, have an auxiliary role: their purpose is to demonstrate whether or not the properties and stability of single films, formed in the Scheludko cell (3), correlate with the properties of the real foams.

The equilibrium surface tension of the SDS solutions was measured by the Wilhelmy plate method. All experiments with films and foams were carried out at 30°C.

(b) Materials

Two series of SDS (p.a. grade, Sigma) solutions were used. In the first one the surfactant solutions contained added sodium salts $NaCl$, $NaNO_3$, Na_2CO_3, Na_2SO_4, Na_3PO_4, or sodium citrate. The second series of solutions contained magnesium salts $MgCl_2$, $Mg(NO_3)_2$, $Mg(OOCCH_3)_2$, or $MgSO_4$ at constant Mg concentration, 0.006 M. Most of the electrolytes (p.a. grade) were purchased from Teokom (Bulgaria). NaCl was from Merck. The $NaH_2PO_4 \cdot H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ were from Ciech (Poland). The citric acid was kindly provided by Colgate–Palmolive and the sodium citrate (purum) was from Chemapol (Prague).

As already mentioned, the total ionic strength of all SDS-containing solutions was kept constant, $I = 24$ mM. At this ionic strength the CMC of the solutions was measured to be 3 mM SDS irrespective of the type of the added electrolyte.

For the solutions of monovalent electrolytes we achieved $I = 24$ mM by adding the respective amount of sodium salts while the solutions of magnesium salts were with constant concentration (0.006 M) with an addition of NaCl (when needed). On the other hand, anions of different valence are present in the solutions of salts of weak acids. Their exact concentrations, as well as the concentration of the nondissociated molecules, had been taken into account when solutions of fixed ionic strength, $I = 0.024$ M, were prepared. The input concentrations of the solutes in solutions containing phosphate and citrate salts at different pH were determined by using the set of equations

$$K_w = [H^+][OH^-] \qquad [2]$$

$$K_1 = \frac{[H_2A^-][H^+]}{[H_3A]} \qquad [3]$$

$$K_2 = \frac{[HA^{2-}][H^+]}{[H_2A^-]} \qquad [4]$$

$$K_3 = \frac{[A^{3-}][H^+]}{[HA^{2-}]} \qquad [5]$$

$$[Na^+] + [H^+]$$
$$= [OH^-] + [H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] \qquad [6]$$

$$C_a + C_{salt} = [H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}], \qquad [7]$$

where K_w is the ionization equilibrium constant of water, K_1, K_2, and K_3 are the dissociation constants of the acid, and C_a and C_{salt} are the molar concentrations of the acid and the salt (say citric acid and citrate), correspondingly. Equation [6] expresses the electroneutrality condition, and Eq. [7] expresses the mass balance of the anion. The above set of equations was solved using the optimization procedure SOLVER of Microsoft Excel 5.0; see Ref. (20). Thus the exact concentrations of all ionic species present in the solution can be calculated for a given pH, and the type of the predominant co-ion can be determined.

Since the magnesium salts are highly hygroscopic, for a better precision stock solutions were prepared. The exact concentration of Mg^{2+} ions in these solutions was determined by titration. All solutions were prepared with double distilled water.

3. FOAM FILMS: RESULTS AND DISCUSSION

(a) Experimental Data

In order to check how the type of the co-ion influences the properties of the TLF we measured the lifetime and the critical thickness of film rupture of *unstable* films or, alternatively, the equilibrium thickness of the *stable* films. The films were obtained from solutions of SDS with concentration below CMC (2×10^{-4} and 4.3×10^{-4} M) and above

CMC (5.8×10^{-3} M). The same experiments were carried out with films formed from solutions containing magnesium salts. Comparing the results for the two series of salts one can distinguish the contributions of the co-ion and the counterion to the observed effects.

Visual observations of the thinning of unstable foam films revealed that films consecutively formed in the same experiment exhibit various types of rupture. The alternative types of film rupture with *sodium* salts are:

(i) Rupture of *bright* films. These films ruptured at thickness of about 80 nm. In reflected light they looked bright and often broke after formation of small, very mobile darker spot(s). The film ruptured 2–3 s later.

(ii) Rupture of *gray* films. They reached smaller thickness of nearly 50 nm. These films looked gray in reflected light and had uneven thickness. Sometimes, before the film rupturing, black (thinner) spots appeared in the film.

(iii) Rupture of *dark gray* films. Among the unstable films they had the longest lifetime. They reached a constant thickness of about 35 nm and in this state existed from 45 s up to several minutes.

One can distinguish five types of rupture for films formed from solutions containing *magnesium* salts; they are similar to those previously described in Ref. (9):

(i) Rupture of bright film preceded by the formation of small gray spot(s). This type of film rupture is frequent at low SDS concentrations. When the film reaches a thickness ≥ 50 nm, small dark gray spots appear near the film periphery; they quickly and randomly move throughout the film area for about 1–2 s; immediately after that the film breaks down.

(ii) Rupture of gray film. The film thins gradually to a thickness ranging from 15 to 36 nm for several dozens of seconds and suddenly ruptures. Sometimes the appearance of darker spots was observed just before the breakage of a gray film.

(iii) Rupture of black film containing *lenses*. Lenses of diameter several micrometers appear in a group during the transition from gray to black film. They are dispersed mainly in the central zone of the film and move randomly throughout the film area. Their size varies with time and their number decreases due to coalescence. The film ruptures when only a few lenses are still present in the film. This type of film rupture is observed at the higher SDS concentrations.

(iv) Rupture of black film. The film thins gradually to black film of thickness between 14 and 19 nm, which suddenly ruptures.

(v) Rupture of black film with the appearance of *spots*. Lenses appear during the transition to a film of thickness about 18 nm. The lenses are better visible than in films type (iii) and live longer (up to 3–4 min). Once the lenses disappear the transition from primary (common black) film

to secondary (Newton black) film begins with the appearance of spots [cf., e.g., Refs. (2, 6)]. The film ruptures soon after that, never reaching the equilibrium state of secondary black film.

The thinning of the films with magnesium salts, especially at the higher concentration of SDS (4.3×10^{-4} M), took longer than for the films with sodium salts.
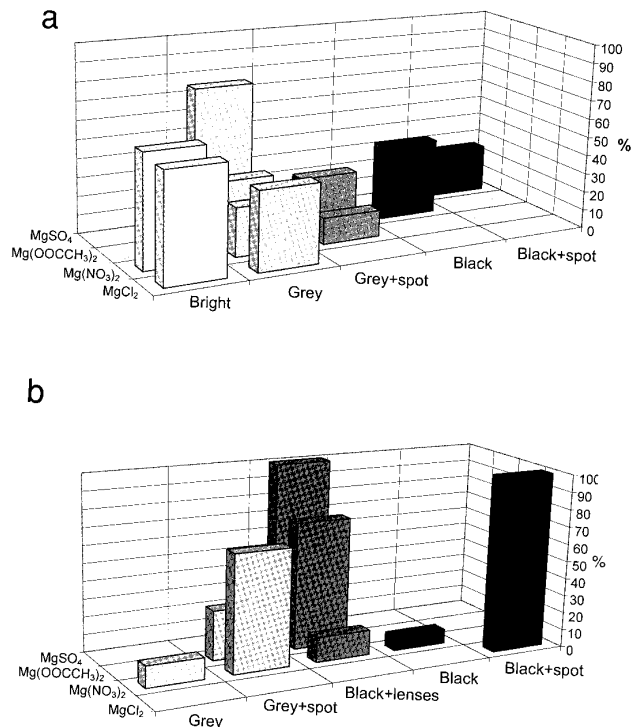
At least 50 films were formed from each solution of a given SDS concentration and type of electrolyte. Their lifetimes were recorded and then split into groups corresponding to the types of rupture. The mean lifetime as well as the percentage of the films in each group were calculated.

Figures 1 and 2 present the experimentally determined percentage of the films belonging to the various types of rupture described above. The color of the bars resembles the color of the respective films at their final state (just before their rupture or at the stable state). Darker color corresponds to smaller film thickness.

The horizontal rows in Figs. 1 and 2 characterize the various alternative ways of film rupture with their probability. In Fig. 1a one sees that in the case of co-ions (anions) corresponding to a strong acid (Cl^-, NO_3^-, SO_4^{2-}) the films
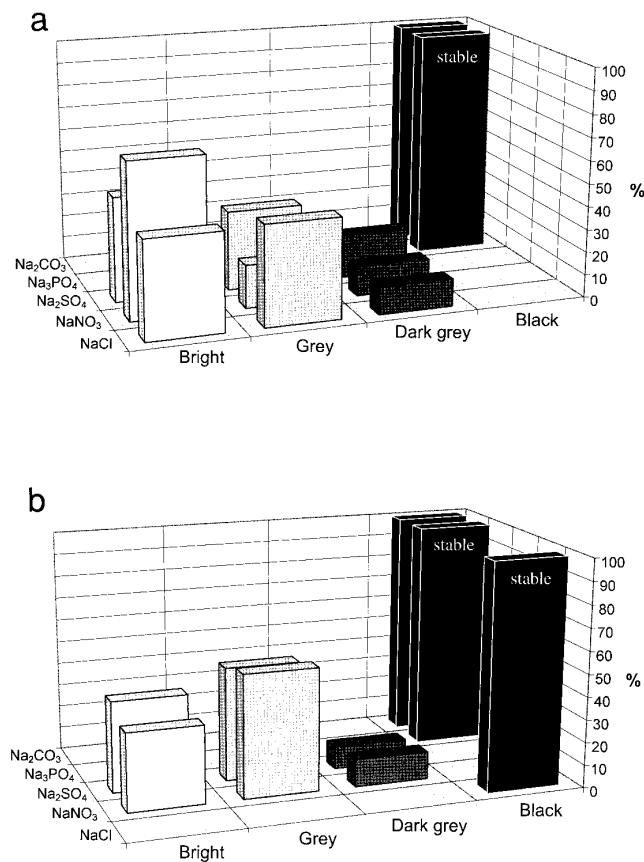
FIG. 2. Histogram of the ways of film rupture depending on the type of co-ion for Mg salts. (a) SDS concentration 2×10^{-4} M; (b) SDS concentration 4.3×10^{-4} M.

are relatively unstable, as compared to the markedly different behavior of the stable films with co-ions corresponding to weak acids (carbonate and phosphate).

For the higher SDS concentration (Fig. 1b) the films from solutions with Cl^- behave similar to those with carbonate and phosphate, i.e., they reach a state of stable black film, whereas the films with NO_3^- and SO_4^{2-} are unstable as in the case of the lower SDS concentration in Fig. 1a.

Comparing Fig. 1a with Fig. 1b and Fig. 2a with Fig. 2b one can see that the number of longer living films increases with the SDS concentration (the heights of the brighter bars decrease). With the raise of the SDS concentration the number of alternative ways of rupture decreases (cf. Fig. 2a and Fig. 2b). It can be seen that the films in the presence of magnesium salts at concentration of SDS below CMC are not stable.

From the results shown in Figs. 1 and 2 one can conclude that there is a predominant type of film rupture at given experimental conditions: SDS concentration, type of counterion and co-ion. Tables 1 and 2 list the mean lifetimes and thicknesses of these predominant films. In particular, when the films are unstable, Tables 1 and 2 contain their critical thickness, h_{cr}, measured just before their rupture. If the film is stable (life time $\tau = \infty$) Tables 1 and 2 show its equilibrium thickness. One can see in Table 1 that for the SDS concentrations lower than CMC (2×10^{-4} and 4.3×10^{-4} M) the films are unstable and rupture relatively thick in the

FIG. 1. Histogram of the ways of film rupture depending on the type of co-ion for Na salts. (a) SDS concentration 2×10^{-4} M; (b) SDS concentration 4.3×10^{-4} M. The black films are stable.

TABLE 1

Characteristic Parameters of the Predominant Type of Films Formed from SDS Solutions with Various Sodium Salts Added

Electrolytes	Film parameters	SDS 2.0×10^{-4} M	SDS 4.3×10^{-4} M	SDS 5.8×10^{-3} M
Na_2SO_4	type of film	bright	gray	black
	lifetime τ	15.2 s	16.0 s	∞
	thickness	84.8 nm	62.9 nm	24.2 nm
$NaNO_3$	type of film	bright	gray	black
	lifetime τ	9.7 s	18.9 s	∞
	thickness	81.7 nm	52.9 nm	22.2 nm
$NaCl$	type of film	gray	black	black
	lifetime τ	32.2 s	∞	∞
	thickness	53.5 nm	23.5 nm	19.2 nm
Na_3PO_4	type of film	black, stable	black, stable	black, stable
	thickness	17.8 nm	20.0 nm	18.7 nm
Na_2CO_3	type of film	black, stable	black, stable	black, stable
	thickness	20.8 nm	20.9 nm	20.1 nm

presence of Na_2SO_4 and $NaNO_3$ ($h_{cr} \approx 50–80$ nm). Their lifetime is short, about 10–20 s. The films with NaCl have the longer lifetime ($\tau \approx 32$ s) and their critical thickness of rupture is smaller; at 4.3×10^{-4} M SDS these films become stable with equilibrium thickness $h_{eq} = 23$ nm. Na_3PO_4 and Na_2CO_3 have a pronounced stabilizing effect on the films. In the presence of these electrolytes the films remain stable even at the lowest surfactant concentration ($h_{eq} \approx 18–21$ nm). All of the films obtained at SDS concentration above CMC (5.8×10^{-3} M) are stable and their equilibrium thickness is about 19–24 nm.

Table 2 gives the measured characteristic parameters of the films containing Mg salts. The co-ions of the investigated magnesium salts are the same as the co-ions of Na salts in Table 1, except $Mg(OOCCH_3)_2$, which was used as a representative of the salts of weak acids instead of the insoluble $MgCO_3$. When the concentration of SDS is below CMC all films with Mg salts are unstable. It should be noted that

the films with $Mg(OOCCH_3)_2$ typically have the longest lifetime and can reach the smallest critical thickness (of about 15 nm). The replacement of the Cl^- and NO_3^- ion by SO_4^{2-} ion noticeably decelerates the film thinning and increases the film lifetime. These facts can be related to the observation that during the film thinning lenses are formed inside the films with $MgSO_4$ and $Mg(OOCCH_3)_2$; these lenses are found (9) to serve as reservoirs of solution, which is supplied to the draining film thus decreasing the rate of its thinning.

(b) Kinetic and Thermodynamic Stability of Foam Films

As all values of the film thickness given in Tables 1 and 2 are greater than 12–14 nm, one may conclude that we deal either with the electrostatically stabilized primary films or with films which rupture while approaching this equilibrium state. To interpret the data in Figs. 1 and 2 and Tables

TABLE 2

Characteristic Parameters of the Predominant Type of Films Formed from SDS Solutions with Various Magnesium Salts Added

Electrolytes	Film parameters	SDS 2.0×10^{-4} M	SDS 4.3×10^{-4} M	SDS 5.8×10^{-3} M
$MgCl_2$	type of film	gray	black + spot	black
	lifetime τ	21.0 s	64.2 s	∞
	thickness	44.1 nm	13.2 nm	16.1 nm
$Mg(NO_3)_2$	type of film	bright	gray	black
	lifetime τ	11.4 s	32.2 s	∞
	thickness	80.0 nm	53.3 nm	12.0 nm
$Mg(OOCCH_3)_2$	type of film	black	black + lenses	black
	lifetime τ	56.2 s	81.5 s	∞
	thickness	14.9 nm	12.8 nm	14.8 nm
$MgSO_4$	type of film	gray	black + lenses	black
	lifetime τ	38.4 s	238 s	∞
	thickness	36.1 nm	18.4 nm	18.7 nm

TABLE 3
Parameters of the Foam Films Containing 2×10^{-4} M SDS in the Presence of Different Co-ions as a Function of pH

	h_{eq} (nm)			τ (s)			h_{cr} (nm)		
pH	NaCl	Na_3PO_4	Citrate	NaCl	Na_3PO_4	Citrate	NaCl	Na_3PO_4	Citrate
4.6	19.22	20.5	21.0	30.2	242.1	186.7	40.3	22.0	24.3
	(6%)	(20%)	(17%)				(42%)	(58%)	(54%)
6.9	19.05	21.0	27.9	128.2	∞	∞	20.4	—	—
	(16%)	(100%)	(100%)				(72%)		
11.4*	16.27	17.8	28.6	∞	∞	∞	—	—	—

Note. pH 7.8 for the films with citrate co-ions.

1 and 2, we utilize the concept of *thermodynamic* and *kinetic* stability of liquid films; see, e.g., Ref. (21). This concept is based on the understanding that the mere fact of existence of *thermodynamic* stable state(s) of a thin liquid film does not guarantee that the film can ''safely'' reach this state. Indeed, the film thinning is accompanied with convective and diffusion fluxes, vortices and instabilities, nonuniform surfactant adsorption, etc. Each of these factors, or their combination, may lead to the rupture of the film before reaching the equilibrium state.

The notion of *kinetic stability* of thin liquid films is used to denote the resistance of the film against rupture during the thinning. The kinetic stability can be characterized by the lifetime of the *draining* film, τ. The major factors determining the kinetic stability of the foam films are the rheological properties of the surfactant adsorption monolayers and especially their Gibbs (surface) *elasticity,* E_G, the surface *viscosity,* and the diffusion (adsorption) *relaxation time*. Especially, it is established that all factors and additives leading to increase of E_G lead also to longer lifetimes of the draining films and increase the chance for them to reach the equilibrium state (22).

Let us first have a look at the *thermodynamically* stable films in Table 1. The magnitude of their thickness suggests that they are stabilized by the repulsive electrostatic disjoining pressure, Π_{el}. The magnitude of Π_{el} is affected by the type of the electrolyte (1:1, 1:2, etc.) even at the same ionic strength. Indeed, for a 1:1 electrolyte one may estimate Π_{el} by means of the formula by Verwey and Overbeek (23):

$$\Pi_{el}(1:1) = 64n_0kT\left(\tanh\frac{\Phi_s}{4}\right)^2 e^{-\kappa h},$$

$$\Phi_s \equiv \frac{e\varphi_s}{kT}, \; \kappa^2 \equiv \frac{8\pi e^2 I}{\varepsilon kT}. \quad [8]$$

Here n_0 is the concentration of a 1:1 electrolyte, k is the Boltzmann constant, T is the temperature, κ^{-1} is the Debye screening length, $I = \frac{1}{2}\Sigma Z_i^2 n_i$ is the ionic strength, h is the film thickness, ε is the dielectric permittivity of water, e is

the electronic charge, and φ_s is the surface potential. An analogue of Eq. [8] has been derived by Muller (24) for the case of a 2:1 electrolyte (bivalent counterion) and a 1:2 electrolyte (bivalent co-ion),

$$\Pi_{el}(i:j) = 432n_{(2)}kT\left(\tanh\frac{\nu_{i:j}}{4}\right)^2 e^{-\kappa h}, \quad [9]$$

where $n_{(2)}$ is the concentration of the bivalent ions, the subscript $i:j$ takes value 2:1 or 1:2, and

$$\nu_{2:1} = \ln[3/(1 + 2e^{-\Phi_s})], \; \nu_{1:2} = \ln[(2e^{\Phi_s} + 1)/3]. \quad [10]$$

Next, let us clarify how Eq. [9] incorporates the valency effects of a co-ion in a double layer framework. We note that at the same ionic strength I (at the same κ) one has $n_0 = 3n_{(2)}$. Then from Eqs. [8] and [9] one obtains

$$\frac{\Pi(1:2)}{\Pi(1:1)} = 2.25, \quad [11]$$

where we have taken into account that at high surface potentials, $\Phi_s \geq 4$, the hyperbolic tangents in Eqs. [8] and [9] are equal to 1. If this condition is fulfilled, then Eq. [11] predicts stronger repulsion in the films with a 1:2 electrolyte as compared to those with a 1:1 electrolyte. This prediction is consonant with the fact that in Table 1 the stable ($\tau = \infty$) films with Na_2SO_4 are thicker than the respective films with $NaNO_3$ and NaCl, but the effect is not so strong.

In the films with Mg^{2+} the ionic correlation attraction becomes important (25–27). This can be the explanation of the fact that the thickness of the films with Mg^{2+} is systematically smaller than that of the films with Na^+, cf. Tables 1 and 2. (See also Eq. [15] below.)

On the other hand, the theoretical expressions for Π_{el} are not sensitive to the chemical nature of the co-ion and cannot explain the difference between the evolution of the films with Cl^- and NO_3^- (see Fig. 1b), and especially, the markedly greater stability of the films with carbonates and phos-

phates. Therefore, the only reasonable explanation of the latter fact is that the films with carbonates and phosphates exhibit an enhanced *kinetic* stability, which is most probably due to the greater Gibbs elasticity, E_G, of the surfactant adsorption monolayers.

(c) Effect of Hydrolysis of SDS to Dodecanol

It is known that even a very small amount of dodecyl (lauryl) alcohol, dodecanol (DOH), strongly increases the Gibbs elasticity, E_G, and the stability of films and foams from SDS solutions (28). Bergeron (29) reported that microscopic films formed from aged SDS solutions are thinner than those from fresh solutions, which can be attributed to the partial hydrolysis of SDS to DOH. In Ref. (30) the effect of dodecanol on the stability of foams stabilized with SDS was studied. It was found that even when the dodecanol concentration is 100 times lower than the concentration of SDS, the foam lifetime is 10 times longer compared to that in the absence of DOH. These effects of dodecanol can be attributed to the fact that the surface activity (the constant in the Langmuir adsorption isotherm) of dodecanol is 500 times larger than the corresponding constant of SDS, see Ref. (31), as well as to the fact that a small addition of DOH significantly increases the Gibbs elasticity, E_G, of the SDS adsorption monolayers, i.e.,

$$(E_G)_{SDS} \ll (E_G)_{SDS+DOH}, \quad E_G \equiv -\Gamma\left(\frac{\partial\sigma}{\partial\Gamma}\right),$$

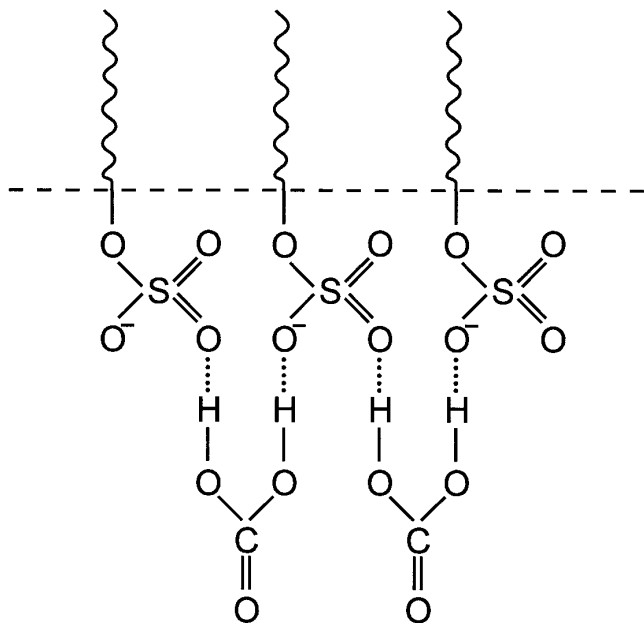where Γ is surfactant adsorption and σ is surface tension.

FIG. 3. Interconnection of neighboring SDS headgroups due to the formation of H-bonds with molecules of the carbonic acid.

TABLE 4

Measured Gibbs Elasticity, E_G, and Surface Shear Viscosity, η_{sh}, of 0.2 mM SDS Solutions

Solution	E_G (mN/m)	η_{sh} ($\times 10^{-7}$ N s m^{-1}) from Ref. (35)
SDS/NaCl	17.6	3.9
SDS/Na–citrate	30.1	13.0

The solutions with Na_2CO_3 and Na_3PO_4, from which stable films and foams are formed, are alkaline with pH 11.3. At this pH hydrolysis of SDS to DOH can take place:

$$D{-}O{-}SO_3^- + OH^- \rightarrow D{-}OH + SO_4^{2-} \quad [12]$$
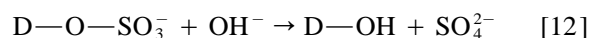
(D symbolizes the dodecyl chain). One may expect hydrolysis of SDS also at acidic pH. To check whether hydrolysis takes place, we carried out additional experiments with films and foams in the presence of phosphate and citrate salts at various pH. Experiments with carbonate salts have not been performed as their solutions are not stable in the whole studied range of pH values. The citrate salt was chosen as this is a salt with properties similar to the phosphates and carbonates. (Moreover, citrates are widely used in detergent chemistry.)

Experiments with solutions containing NaCl in alkaline, neutral, and acidic solutions have also been carried out. The properties of the films and foams from these solutions are compared with those formed from solutions containing phosphates or citrates. If a similar behavior is observed one can conclude that the pH of the solution determines the film stability, irrespective of the type of co-ion (phosphate, citrate, carbonate, etc.).

The results from the additional experiments with films at three different pH values are presented in Table 3. It contains the experimentally measured

(i) values of the equilibrium thickness, h_{eq}; the percentage of the films which reach the equilibrium state is shown in parentheses;

(ii) values of the life-time τ of the unstable films; $\tau = \infty$ symbolizes that the film is stable;

(iii) values of the critical film thickness, h_{cr}, measured just before the film rupture and the percentage (in parentheses) of the films which rupture with this thickness.

One sees (Table 3) that in the case of *acidic* solutions (pH 4.6) the predominant number of films are unstable; the films from the phosphate and citrate solutions are found to live markedly longer than the films formed from the chloride solutions. In the case of *neutral* solutions (pH 6.9) the films with phosphates and citrates are already 100% stable, whereas the films with chloride are still predominantly unsta-
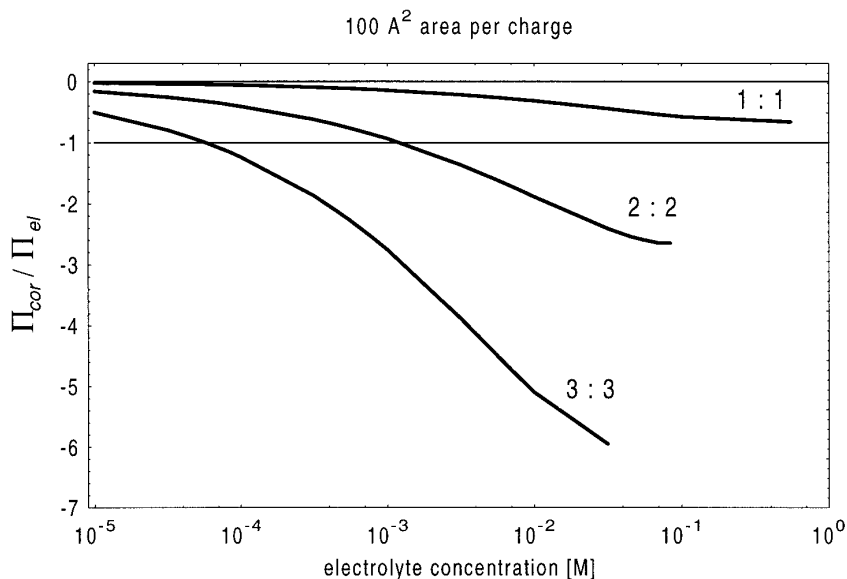
FIG. 4. Theoretical plot of Π_{cor}/Π_{el} vs the electrolyte concentration for 1:1, 2:2, and 3:3 electrolytes calculated by means of Eq. [15]; the area per surface charge is $|e/\sigma_s| = 100 \text{ Å}^2$.

ble. Finally, in the case of *alkaline* solutions all films reach the equilibrium state, irrespective of the type of the co-ion.
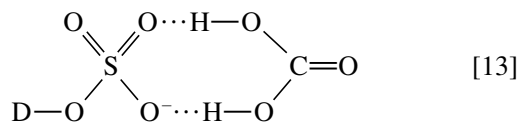
The most probable explanation of the enhanced kinetic stability of the films formed from *alkaline* solutions (Table 3) is the increased Gibbs elasticity of the adsorption monolayers due to the partial hydrolysis of SDS to DOH, Eq. [12]. In fact, the presence of DOH leads to immobilization of the film surfaces and suppresses the growth of surface instabilities which would bring about film rupturing. Thus the foam film can gradually thin down to its equilibrium thickness.

The most probable explanation of the instability of the films formed from *acidic* solution (pH 4.6, Table 3) is the specific adsorption of H^+ ions to the sulfate headgroups of SDS. This leads to a greater degree of neutralization of the surface electric charge and to the growth of surface instabilities driven by the attractive van der Waals forces (32).
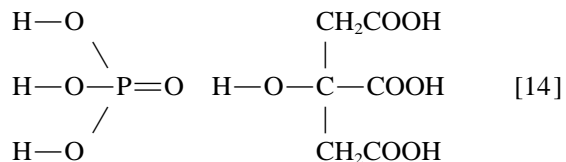
(d) Multiple H-bonding Due to Weak Acids

The data in Table 3 show an effect that cannot be explained by the presence of DOH: one sees that the films containing co-ions of *weak* acids are *systematically* more stable than those containing co-ions of *strong* acids (this is evidenced also by the data in Figs. 1 and 2 and Tables 1 and 2). Even in the case of acidic solutions (pH 4.6 in Table 3) the films containing co-ions of weak acids live longer and can survive to reach smaller thickness. All the data presented above leads to the conclusion that the presence of a weak acid in the solution increases the *kinetic* stability of the foam films. From a theoretical viewpoint this means that the weak acids somehow increase the surface elasticity and viscosity. A possible mechanism is proposed below.

As known, a portion of a weak acid is present in the solution in nondissociated, electroneutral form. The H atoms of the nondissociated molecules of the weak acids are known to be active in H-bonding; for example, such H-bonding is known to be responsible for the dimerisation of the acetic acid in solution. Therefore, we may expect that nondissociated molecules of a weak acid can form also H-bonds with the sulfate headgroups of SDS. As an example let us consider the H-bonding of carbonic acid to SDS:

$$
\begin{array}{c}
\text{O}\diagdown \quad \text{O} \cdots \text{H—O} \diagdown \\
\text{S} \qquad\qquad\quad \text{C}{=}\text{O} \qquad [13]\\
\text{D—O}\diagup \quad \text{O}^- \cdots \text{H—O} \diagup
\end{array}
$$

The two H-bonds are shown dotted; the H-bond with $—\text{O}^-$ is expected to be stronger than that with $={}$O, both of them on the order of dozens kT (33). Since one molecule carbonic acid can form two H-bonds, the molecules of the carbonic acid are able to *interconnect* headgroups of neighboring SDS molecules in a surface adsorption monolayer; see Fig. 3. Such a linking between the SDS molecules should certainly cause an increase of the surface elasticity and viscosity. Having in mind the structure of the phosphoric and the citric acid,
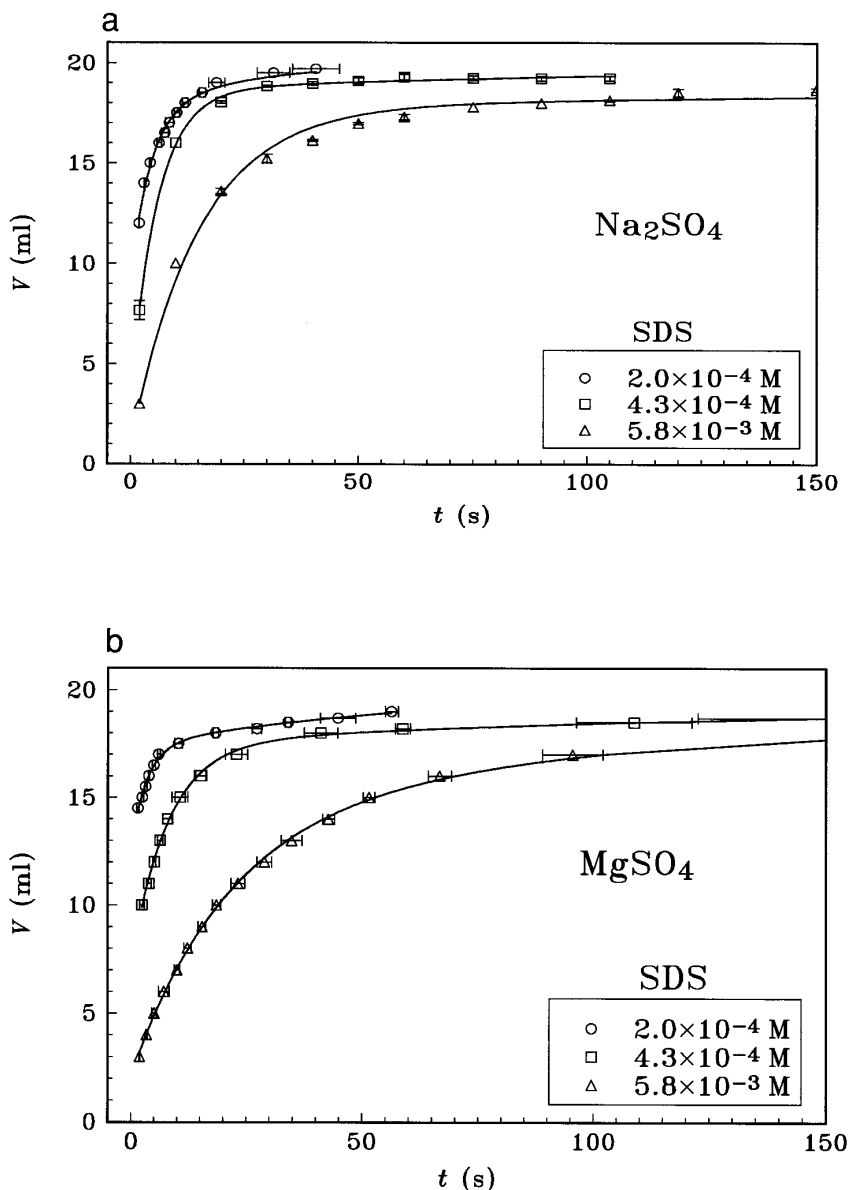
$$
\begin{array}{ll}
\text{H—O} & \text{CH}_2\text{COOH}\\
\quad\diagdown & \qquad |\\
\text{H—O—P}{=}\text{O} \quad \text{H—O—C—COOH} & \quad [14]\\
\quad\diagup & \qquad |\\
\text{H—O} & \text{CH}_2\text{COOH}
\end{array}
$$

FIG. 5. Plot of the volume, V, of the liquid drained out of a foam vs time t. The different curves correspond to solutions of different SDS concentration with (a) Na_2SO_4 and (b) $MgSO_4$.

one concludes that the phosphoric acid can realize up to three H-bonds, whereas the citric acid is able to realize up to four H-bonds with the SDS headgroups. To connect two SDS headgroups at least two —OH groups per acidic molecule must be available, see Eq. [14]; i.e., some of the partially dissociated forms of the phosphoric and citric acids could be also able to interconnect the surfactant headgroups. This will strongly affect the surface rheological properties.

To verify the above hypothesis experimental measurements of surface elasticity and viscosity in the presence of co-ions of weak and strong acids are needed. We already have preliminary data in this aspect. The surface (Gibbs)

elasticity, E_G, and the surface shear viscosity, η_{sh}, have been measured for the solutions of sodium chloride and citrate corresponding to the second row of Table 3 (pH 6.9). Table 4 summarizes our preliminary data for E_G and η_{sh}. The values of the Gibbs elasticity, E_G, in Table 4 are obtained from experimental σ vs ln c_{SDS} equilibrium isotherms, fitted by means of the van der Waals adsorption isotherm. In addition, η_{sh} was measured by means of the sliding particle method (34). The larger values of both E_G and η_{sh} measured for the citrate solutions (Table 4) are consonant with the above hypothesis. Of course, more data and a systematic study of these effects is needed, which is now under way.

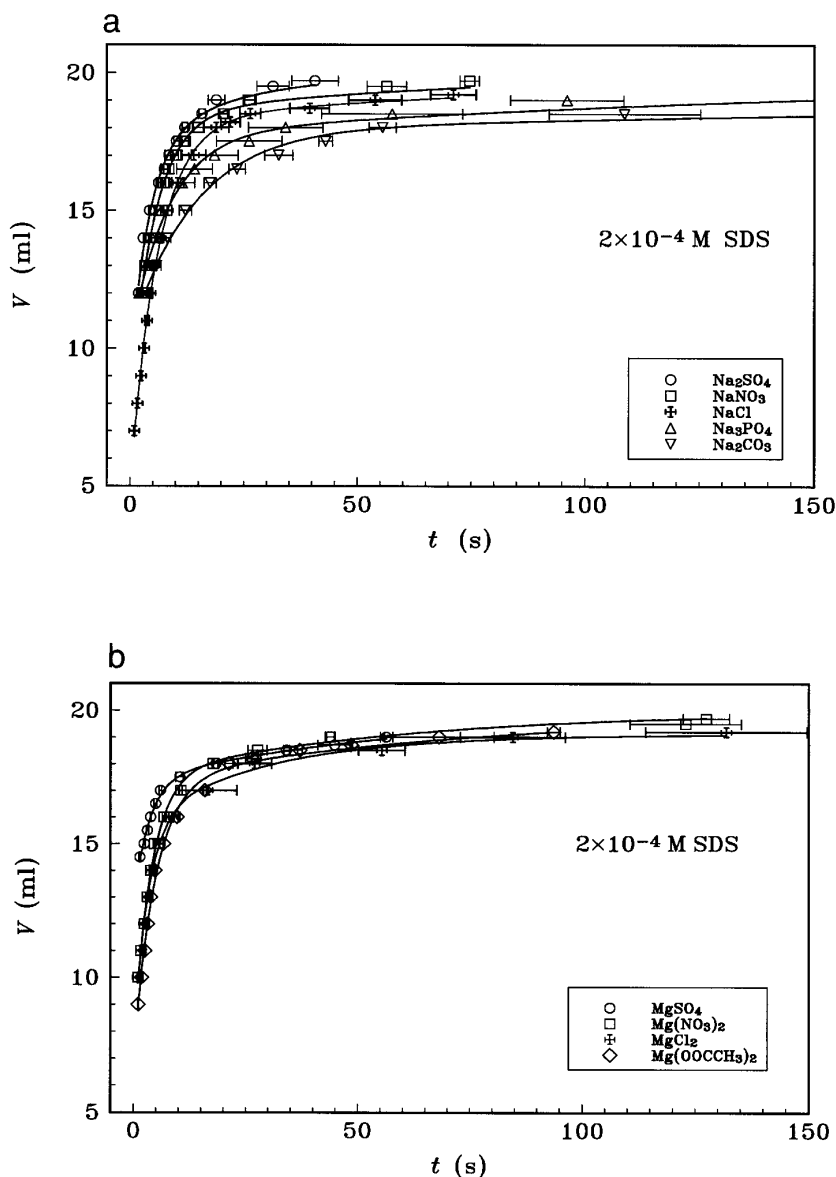For the time being we may note that the hypothesis about

FIG. 6. Plot of the volume, V, of the liquid drained out of a foam vs time t for solutions with 2×10^{-4} M SDS and various electrolytes, all of them of ionic strength 0.024 M. (a) Sodium salts and (b) magnesium salts.

the multiple H-bonding agrees qualitatively with the following experimental observations:

(i) The enhanced stability of the films with co-ions of weak acids can be attributed to the fact that only the weak acids can exist in solution in nondissociated H-bonding form, cf. Eqs. [13–14]. (ii) The molecules in the latter form are electroneutral and are not repelled from the charged adsorption monolayers as the charged co-ions are. This repulsion is believed to cause the weak effect of the usual co-ions on the properties of the electric double layers and thin liquid films. (iii) Moreover, the acetic acid, which may realize one H-bond per molecule with SDS, is not able to interconnect the SDS headgroups (as illustrated in

Fig. 3) and to affect the surface rheology. The experiment shows that the presence of acetate really does not stabilize the foams.

In reality, the kinetic stability of the foam films is most probably affected by the interplay of the stabilizing effects of H-bonding and hydrolysis of SDS to DOH. For pH > 7 the concentration of the nondissociated form of the acid decreases with the increase of pH; the stabilizing effect of H-bonding should diminish, but this can be compensated by the increase of the hydrolysis of SDS. One may in principle discriminate between the two effects by comparative experiments with dodecyl sulfates and sulfonates; the latter do not hydrolyze, but can take part in H-bonding.

(e) Effects Due to Bivalent Counterions (Mg^{2+})

Returning to the data for the films with Mg (Table 2 and Fig. 2) we have to mention that for the observed film thicknesses the presence of Mg^{2+} ions affects the film stability in the following three ways:

(i) The bivalent Mg^{2+} ions in the subsurface Stern layer (unlike the monovalent Na^+ ions) are able to connect couples of neighboring surfactants headgroups thus increasing the surface elasticity and viscosity. This effect should lead to an *increase* of the kinetic stability of films and foams.

(ii) The Mg^{2+} ions adsorb more strongly in the Stern layer than the Na^+ ions and thus decrease the surface charge density. This can have *either stabilizing or destabilizing* effects on films and foams depending on whether the ionic correlation attraction or the double layer repulsion prevails (see below).

(iii) The presence of Mg^{2+} ions (or any other bivalent counterion) greatly enhances the ionic correlation attraction. For electrolyte concentrations above a certain *critical* value the ionic correlation attraction becomes greater than the double layer repulsion, which leads to *destabilization* of films and foams. In particular, the predominant ionic correlation attraction facilitates the growth of thermally excited fluctuation capillary waves, which cause rupturing of the films.

To illustrate the latter effect we will make use of the formula derived by Attard *et al.* (26) for the case when $\exp(-\kappa h) \ll 1$ and the electrolyte is symmetrical ($Z:Z$):

$$\Pi_{cor} = \Pi_{el} \frac{Z^2 e^2 \kappa}{4\epsilon kT} (\ln 2 + 2I_C) + O(e^{-2\kappa h}). \quad [15]$$

Here Π_{el} is the conventional DLVO electrostatic disjoining pressure

$$I_C = \frac{1}{2}(1 + J)\ln 2 + \frac{2 - 2z^3 + z}{2z(2z^2 - 1)^2}$$
$$- \frac{1}{2}(1 - J)\ln(z + z^2) - \frac{\sqrt{z^2 - 1}}{z}$$
$$\times [1 + J + 4(2z^2 - 1)^{-3}]\arctan\sqrt{\frac{z - 1}{z + 1}}$$
$$J \equiv \frac{2z^2 - 3}{(2z^2 - 1)^3}, \ z \equiv \left[1 + \left(\frac{2\pi e \sigma_s}{\epsilon kT \kappa}\right)^2\right]^{1/2},$$

Π_{cor} is the ionic correlation component of disjoining pressure, and σ_s is the surface charge density. The calculation from Eq. [15]'s theoretical dependence of the ratio Π_{cor}/Π_{el} vs the electrolyte concentration is plotted in Fig. 4 for 1:1, 2:2, and 3:3 electrolytes; we have used the value $|e/\sigma_s| = 100$ Å^2 for the area per surface charge. The "critical" electrolyte concentration corresponds to the intersection points of the curves with the horizontal line at -1 in Fig. 4 (for electrolyte concentrations above the critical the ionic correlation attraction becomes greater by magnitude than the double layer repulsion). One sees in Fig. 4 that for a 2:2 electrolyte the critical concentration is about 0.001 *M* for $|e/\sigma_s| = 100$ Å^2. As the concentration of Mg^{2+} in our solutions is 0.006 *M,* an important destabilizing effect from the ionic correlations should be expected. The latter effect might be partially neutralized by the increase of the surface elasticity and viscosity caused by the adsorption of Mg^{2+} ions.

The fact that the films with Mg^{2+} ions are stable at 5.8×10^{-3} *M* SDS (slightly above CMC; see the last column in Table 2) deserves a special discussion. If the bulk concentration of Mg^{2+} ions were above the critical one, such thick equilibrium films could not exist. The most probable explanation can be given by the strong adsorption of Mg^{2+} ions in the *micelle* Stern layers. As the input concentrations of SDS and Mg in these solutions are comparable, the adsorption of Mg^{2+} ions will considerably decrease the bulk concentration of the free Mg^{2+} ions, which could become *smaller* than the critical one. To verify quantitatively this explanation one needs data for the adsorption of Mg^{2+} ions in the Stern layers of the micelles and solution surface, which might be a subject of a subsequent study.

4. FOAMS: RESULTS AND DISCUSSION

(a) Experimental Data

Figure 5 shows our results for the drainage of foams in the presence of Na and Mg sulfates with the same ionic strength, $I = 0.024$ M. Each curve represents the increase of the volume, *V*, of the liquid drained out of the foam as a function of time, t. The different curves correspond to different surfactant concentrations. One sees that with the increase of the surfactant concentration the drainage rate of the foams decreases; this can be attributed to the increasing immobilization of the surfaces by the adsorption monolayers. In addition, a comparison between the curves in Fig. 5a and 5b shows that the liquid drains more slowly from the foams with Mg than from those with Na, especially at the later stages of drainage. This is most probably due to the fact that liquid lenses are captured in the films with MgSO$_4$ (see above), which serve as reservoirs slowly supplying liquid to the draining foam. Moreover, as mentioned above the bivalent Mg^{2+} ions in the subsurface Stern layer (unlike the monovalent Na^+ ions) are able to connect couples of neighboring surfactant headgroups thus increasing the surface elasticity and viscosity.

Figure 6 shows experimental $V(t)$ curves measured with 2×10^{-4} M SDS solution in the presence of various added electrolytes, all of them of ionic strength 0.024 M. Figure 6a

TABLE 5
Characteristic Times, τ_1 and τ_2 (See Eq. [1]) of Liquid Drainage out of SDS Foams
from Various Electrolyte Solutions of the Same Ionic Strength, 0.024 M

Electrolyte	SDS 2.0×10^{-4} M		SDS 4.3×10^{-4} M		SDS 5.8×10^{-3} M	
	τ_1 (s)	τ_2 (s)	τ_1 (s)	τ_2 (s)	τ_1 (s)	τ_2 (s)
NaCl	6.1	110.1	11.4	396.2	21.1	1192.9
NaNO$_3$	5.4	68.5	6.7	239.6	14.6	277.4
Na$_2$CO$_3$	13.9	498.3	8.8	406.4	15.8	241.3
Na$_3$PO$_4$	8.3	176.2	8.1	583.1	14.0	320.6
Na$_2$SO$_4$	4.2	23.1	5.9	134.6	14.3	320.1
MgCl$_2$	3.3	29.0	9.9	636.6	11.9	57.1
Mg(NO$_3$)$_2$	3.9	58.2	8.0	550.2	21.0	384.4
Mg(OOCCH$_3$)$_2$	4.5	59.8	7.8	362.6	20.7	394.5
MgSO$_4$	3.4	61.5	7.9	123.8	21.2	107.1

contains data for the sodium salts. One sees that the drainage of the liquid out of the foams with carbonates and phosphates is the slowest. This finding correlates with the fact that the single foam films with carbonates and phosphates are the most stable (Fig. 1a). It is consonant also with the hypothesis that the carbonates and phosphates increase the surface elasticity and viscosity because of interconnection of neighboring surfactant headgroups (cf. Fig. 3), as well as because of hydrolysis of SDS to DOH. The increased surface elasticity and viscosity not only decelerate the film thinning, but also oppose the drainage of the liquid through the Plateau borders (channels). The data for the foams with Mg salts in Fig. 6b do not show a pronounced difference between the foams containing different co-ions. Note however, that none of the co-ions of the Mg salts (including that of the acetic acid) is able to create *multiple* H-bonds. In addition, it is also possible for the strong effect of the Mg^{2+} counterion (see Section 3e above) to dominate the effect of the co-ions.

(b) Fits with Semiempirical Curves

The solid lines in Figs. 5 and 6 represent the best fits of the experimental data by means of Eq. [1]. One sees that the latter semiempirical equation compares very well with the experimental data. This is true for the three SDS concentrations studied and for all added electrolytes. From the best fits we determined the values of the adjustable parameters τ_1 and τ_2, which are listed in Table 5. The good agreement between Eq. [1] and the experiment implies that the empirical parameters τ_1 and τ_2 should have some physical meaning. To reveal it we compare the magnitude of τ_1 and τ_2 with the time scales of the real processes observed with the draining foams.

(i) After the shaking of the surfactant solution we first observe the motion of an ensemble of almost spherical bubbles

of various sizes upward under the action of the buoyancy force. At the upper part of solution the bubbles are collected to form a wet foam. In our experiments this first stage of foam formation took between 5 and 20 s, depending on the specific solution. A look at Table 5 suggests that τ_1 can be identified with the characteristic time of this stage. Note that τ_1 is not so sensitive to the type of the ions in the solution (Table 5), which can be attributed to the fact that in the process of bubble raising (related mainly to the buoyancy force and to long-range hydrodynamic interactions between the bubbles), the bubble surfaces behave as tangentially immobile.

(ii) Next, the wet foam gradually transforms into a dry foam, which is accompanied by thinning of the films, drainage of the liquid through the Plateau borders, breakage of films, and reorganization of the network of Plateau borders. The rate of this process might be markedly decreased if liquid lenses are captured inside the foam films. The experimental characteristic time of this process is on the order of the values of τ_2 listed in Table 5. The best correlation between the values of τ_2 and the stability of single foam films (Figs. 1 and 2) is observed for the lowest SDS concentration, 2×10^{-4} M; one observes that the foams with carbonate and phosphate have the greatest τ_1 and τ_2, which can be an effect of the greatest surface elasticity of the respective surfactant adsorption monolayers. For the higher surfactant concentrations the effect of surface elasticity should be suppressed by the increased surface immobilization of the denser monolayers and dominated in some cases by the presence of lenses in the films. Probably that is the reason why one cannot establish any systematic dependence of τ_2 on the type of co-ion from the data for 4.3×10^{-4} and 5.8×10^{-3} M SDS in Table 5.

(c) Correlation between the Stability of Films and Foams

We measured also the full time of the foam destruction (breakage), τ_{br}; see Fig. 7. As mentioned earlier, it is defined
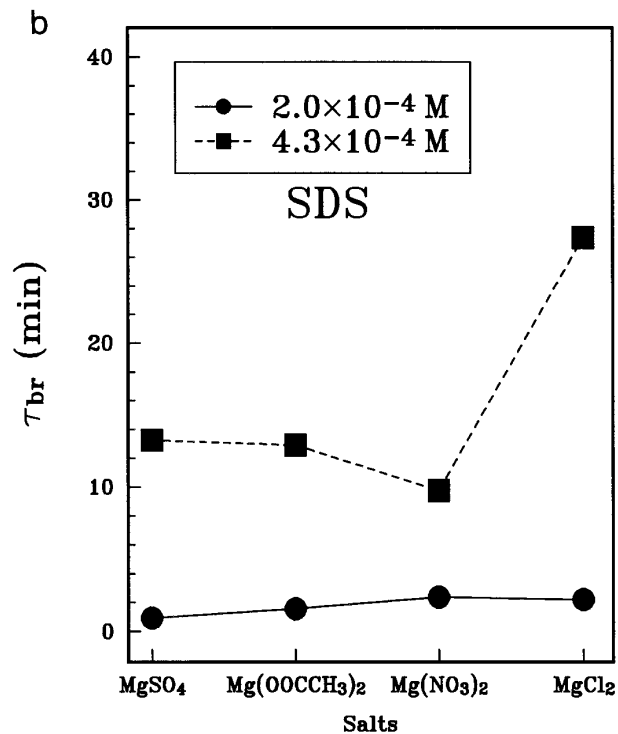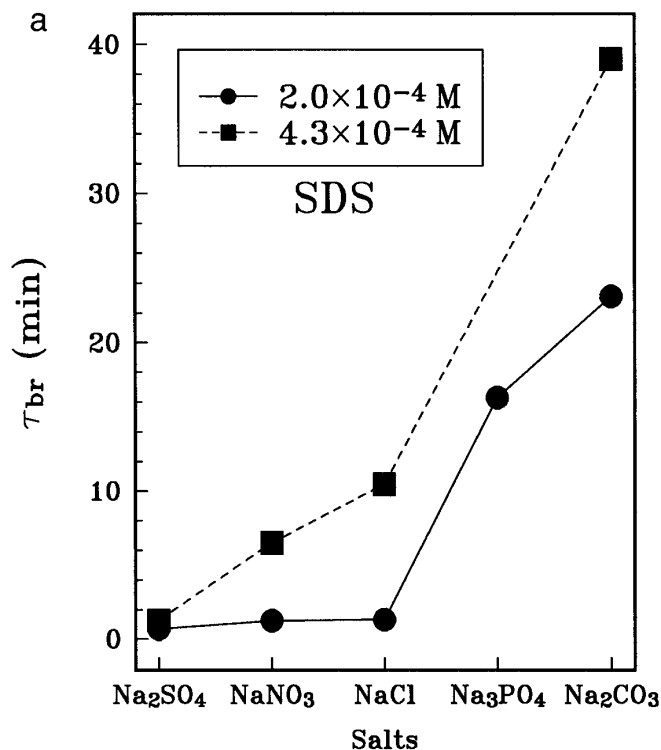
FIG. 7. Total time of foam destruction, τ_{br}, vs the type of the co-ion for (a) Na salts and (b) Mg salts at two different SDS concentrations: 2 $\times 10^{-4}$ and 4.3 $\times 10^{-4}$ M.

TABLE 6

Correlation between the Stability of Separate Foam Films and Foams in the Presence of Various Co-ions Provided by Sodium and Magnesium Salts

Co-ions	Film	Foam
SO_4^{2-}	the most unstable	the most unstable
NO_3^-	highly unstable	highly unstable
CH_3COO^-	unstable	unstable
Cl^-	unstable (stable)[a]	unstable
Carbonate	stable	less unstable
Phosphate	stable	less unstable

[a] For NaCl.

as the time elapsed from the formation of the foam to the appearance of a spot of bare solution surface at the center of the decaying foam column. In the case of foams with Na$^+$ counterions one observes a pronounced deceleration of the foam destruction when phosphate or carbonate is present in the solution (Fig. 7a). On the other hand, in spite of being a co-ion of a weak acid, the acetate does not specifically affect the lifetime of the foams; see Fig. 7b. The latter is evidenced also by the comparison of the properties of single films and foams in Table 6. As already mentioned, one can attribute the difference between the effects of acetate and the of other two weak acids (carbonate and phosphate) to the fact that the acetic acid can form a single H-bond with the surfactant sulfate headgroups and consequently, the acetic acid cannot interconnect the neighboring headgroups and thus to affect the surface rheology (in contrast with the carbonic and phosphoric acids).

In fact, we establish a good correlation between the stability of single films and foams; see Table 6. To make the comparison we have summarized all results for film thinning and rupture, as well as for the drainage of liquid from a foam and for the foam destruction. The correlation is almost perfect, except for the fact that the single films with carbonates or phosphates are stable, whereas the corresponding foams are unstable (although more stable than the foams with the other co-ions). A possible explanation is that the films in the Scheludko cell (diameter about 200 μm) are much smaller than the films in the real foams (diameter on the order of millimeters). It is known that the probability of film rupturing increases with the increase of the film area (32).

Table 7 contains data for the effect of pH on the drainage of the liquid out of the foam. The SDS concentration is 2 $\times 10^{-4}$ M. The parameters τ_1 and τ_2 are determined from the best fits of the data with Eq. [1]. One sees that τ_1, τ_2, and τ_{br} increase with the increase of pH for all three types of co-ions. For pH 4.6 and 6.9 the values of τ_2 and τ_{br} are greater for the foams with phosphate and citrate in comparison with the foams with chloride. The latter effect can be

TABLE 7

Characteristic Times, τ_1 and τ_2 (Eq. [1]) of Liquid Drainage from SDS Foams as Functions of pH;
all Solutions Contain 2×10^{-4} M SDS and Electrolyte of Ionic Strength 0.024 M

	Sodium chloride			Sodium phosphate			Sodium citrate		
pH	τ_1 (s)	τ_2 (s)	τ_{br} (s)	τ_1 (s)	τ_2 (s)	τ_{br} (s)	τ_1 (s)	τ_2 (s)	τ_{br} (s)
4.6	5.5	19.8	319	3.4	22.7	331	3.1	35.8	463
6.9	9.8	64.4	357	6.0	100.1	528	3.7	96.9	479
11.4	9.6	135.0	1954	9.4	153.9	1197	—	—	—

attributed to kinetic stabilization due to the multiple H-bonding (Fig. 3). At pH 11.4 the hydrolysis of SDS to DOH seems to be the predominant stabilizing effect; this leads to a comparable stability of the foams with chloride and phosphate. The data for foams in Table 7 correlate well with the analogous data for the stability of single films in Table 3.

CONCLUDING REMARKS

It is not an easy task to understand and predict the properties and stability of foams. To a great extent this is due to the fact that the foam properties are determined by an interplay of many factors. In the present article we focus our attention on some of these factors, viz. the effect of the type of the counterion and co-ion. The main contributions of our study can be summarized as follows:

A detailed set of experimental data is obtained for the evolution of foam films and foams in the presence of various co-ions, two types of counterions at three surfactant concentrations, and various pH; see Figs. 1, 2, 5–7 and Tables 1–7. The unstable films are characterized by their lifetime and critical thickness of rupture, whereas the stable films are characterized by their equilibrium thickness.

The data show an unexpectedly large influence of the co-ions on the foam film and foam stability; see Figs. 1, 2, and Tables 1, 2, 6, and 7. Such an influence cannot be explained by the DLVO theory of liquid film stability (14, 23). The analysis of our data suggests that at least two effects are responsible for the larger stability of the films with co-ions of weak acids.

(i) The dissolved carbonate and phosphate salts spontaneously adjust a higher value of the solution pH (pH 11.4), which leads to hydrolysis of SDS to dodecanol. The dodecanol increases the surface elasticity and viscosity, and thus enhances the kinetic stability of the films and foams. Enhanced stability exhibit also the foams with other co-ions (say chlorides) if the value of pH is higher; see Table 7.

(ii) The H atoms of the nondissociated molecules of the weak acids are known to be active in H-bonding. Since one molecule of carbonic, phosphoric, or citric acid can, respectively, form up to two, three and four H-bonds, the molecules of these acids are able to *interconnect* headgroups of neighboring SDS molecules in a surface adsorption monolayer; cf. Fig. 3. Such a linking between the SDS molecules causes an increase of the surface elasticity and viscosity and enhances the kinetic stability of the films and foams. This hypothesis agrees well with the accumulated experimental data (see Section 3d). It can be helpful for a better understanding of the role of the citrates and phosphates in body care and household detergency.

The influence of a bivalent counterion (in our case Mg^{2+}) on the film and foam stability has been also studied. It is interesting to note that the bivalent counterions give rise to two major effects which influence the film stability in the opposite directions:

(i) The bivalent counterions in the subsurface Stern layer (unlike the monovalent ions) are able to connect couples of neighboring surfactants headgroups thus increasing the surface elasticity and viscosity, and the kinetic stability of films and foams. This leads to longer lifetimes and smaller critical thicknesses of the unstable films with Mg in comparison to that with Na counterions; cf. Tables 1 and 2.

(ii) The presence of bivalent counterions greatly enhances the ionic correlation attraction. For electrolyte concentrations above a certain *critical* value the ionic correlation attraction becomes greater than the double layer repulsion, which leads to *destabilization* of films and foams. This leads to the absence of an equilibrium state of primary (common black) film and rupturing of the films with Mg ions for SDS concentrations below CMC.

The latter two effects seem to counterbalance each other and the foams with Mg behave similarly to those with Na; see Figs. 5 and 6. In general, there is a good correlation between the experimental results for the stability of films and foams; cf. Table 6.

Two of the effects discussed in the present article, the multiple H-bonding of the SDS headgroups by molecules of weak acids (Section 3d) and the critical concentration of bivalent counterions (Section 3e), deserve special attention and additional studies, which are now under way.

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