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ORIGINAL CONTRIBUTION

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The role of surface viscoelasticity in slide coating processes

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Abstract In the slide hopper coating process for simultaneously applying multiple layers of coating liquids to a moving web, surfactants must be added to the photographic emulsion to ensure a stable position of the liquid bridge formed between the lower edge of the slide hopper and the moving web. In slide coating of gelatin solutions without an added surfactant, the liquid bridge becomes instable and begins to oscillate if critical coating conditions are reached. The addition of anionic surfactants stabilizes the liquid bridge against oscillations. The action of the added surfactants is a result of their interaction with gelatin. The degree of binding can be used as a measure of the interaction. The binding of anionic and cationic surfactants to gelatin was investigated using a surfactant-selective electrode. The binding isotherms of the surfactants to an alkali-processed bone gelatin were determined and compared with the surface dilational properties of the gelatin/surfactant adsorption layers. The comparison of surface rheological data obtained by the oscillating bubble method with the results of coating experiments demonstrates that the viscoelastic properties of gelatin/anionic surfactant adsorption layers are of essential importance to the stabilization of the liquid bridge against oscillations. Pure elastic adsorption layers are not able to stabilize the liquid bridge. The mechanism of the stabilizing action is discussed.

Key words Slide coating process · Gelatin · Surfactant · Binding isotherm · Surface dilational properties

Introduction

Coating is a fundamental technological process in the silver halide photographic industry. It is a very complex operation, entailing problems of wetting, spreading, emulsifying, fluid mechanics, and rheology. The coating process is very prone to giving trouble, and the ever increasing demands for better quality products require a profound knowledge of the different steps of coating technology. Slide coating is a process by which the liquid bridge, formed between the moving web and the lower edge of the coater, begins to oscillate if critical coating conditions are reached. The instability can be observed in the coating of gelatin solutions without surfactant additives. This kind of coating defect is also called barring. Barring is a defect which causes periodic cross-web thickness variations.

The coating process is very sensitive to external disturbances. Typical excitation processes for the observed oscillations can be small pressure fluctuations in the bead vacuum system or nonuniform surface energies of the web. If the surface energy of the web is nonuniform, the static and also the dynamic contact angle will not be constant, resulting in an instable position of the three-phase contact line. The exact cause of the instability in the slide coating process is not yet completely clear.

High-rate surface extensions are typical of the slide coating process. At coating speeds of 2 m/s or higher, viscous and inertial forces become important. In particular, the effect of tangential surface forces due to surface tension gradients caused by the expansion of the free surfaces on the coating must be taken into account.

Photographic emulsions essentially consist of silver halide, color coupler, gelatin, and surfactants. The surfactants used in photographic emulsions significantly modify the dilational properties of the gelatin adsorption layers. The rheological properties of the mixed adsorption layers in general are quite different from the properties of the single components. This suggests that the interaction between gelatin and the added surfactants plays an important role in the coating process.

The purpose of this study is to present experimental results on the crucial importance of the surface dilational properties, in particular the intrinsic dilational viscosity of mixed gelatin/anionic surfactant adsorption layers, in maintaining the stability in the high-speed coating process in the manufacturing of photographic materials as well as to investigate the mechanism by which surfactants stabilize the liquid bridge against oscillations at high coating speeds and especially at thin wet thicknesses of the coated film.

Experimental

Coating experiments

The essential parts of the slide coating devices described in Refs. [1, 2] are shown in Fig. 1. In this technique, one or more coating liquids are fed through distribution cavities and slots forming a multilayer stack on an inclined plane. At the end of the inclined plane, the liquid bridges a narrow gap between the coater and the moving web. The lower edge of the coater is placed at a small distance (100–400 μm) from the moving web, which is supported by the backing roll. The liquid bridge is commonly called a bead.

At higher coating speeds, a negative pressure (suction) of about 200–400 Pa is required under the liquid bridge to ensure its stable position. In order to create this pressure difference a vacuum box is built between the coater and the backing roll.

The web is a 140-mm-wide triacetate film with a previously applied gelatin subcoating to ensure proper wettability and adhesion of the coated layers. The aqueous gelatin solutions ($\eta = 6$ mPas) were coated at speeds in the range 30–90 m/min. The specific flow rate was 1 l/hcm and the gap width was 150 μm. The suction applied was 200 Pa. All the coating experiments were carried out at 313 K. The quality of the coating was characterized by measuring the extinction fluctuations ($\Delta E\%$) at the moving web, immediately after coating. The photoelectric measuring device has been described in Ref. [3]. For measuring the changes in the wet thickness caused by instabilities, a surface-inactive water-soluble red dye was added to the gelatin solution. The changes in the wet thickness were measured as extinction fluctuations, $\Delta E\%$, with an accuracy of $\pm 0.2\%$. The frequency of the periodic thickness fluctuations was determined by enumeration of the wave amplitudes on the recorder with an accuracy of ± 1 Hz in a frequency range up to 400 Hz.

Binding experiments

Surfactant-selective electrodes can be applied as a method to study the binding of ionic surfactants to gelatin. Surfactant-selective electrodes allow the quick determination of nonbound ionic surfactant in polymer solutions. The functional liquid membrane used consists of *o*-nitrotoluene as the organic solvent. The carrier complex was prepared from equivalent amounts of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate. The complex was dissolved in the organic solvent with a concentration of about 1×10^{-3} M.

The construction principle of the surfactant-selective electrode has been described previously [4, 5]. The gelatin used was an alkali-

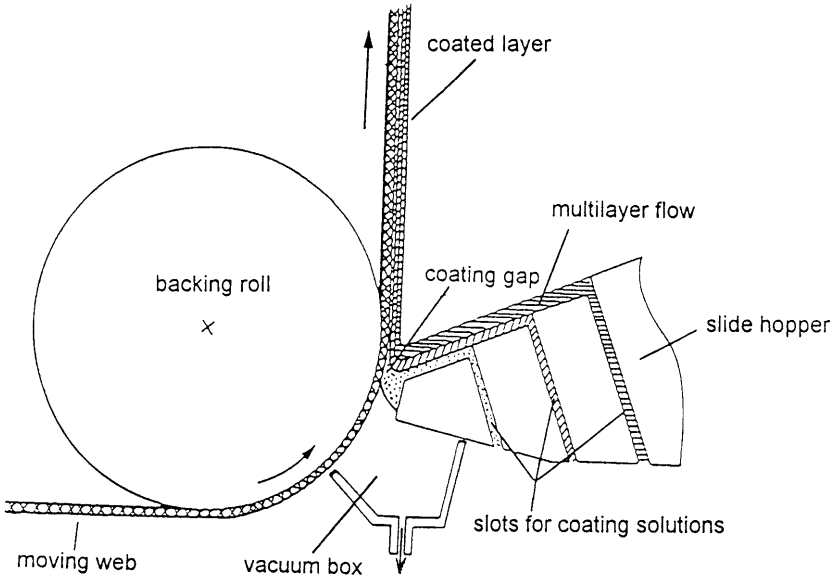

Fig. 1 Schematic diagram of a slide coating device

processed bone gelatin. The surfactants used were CTAB, sodium bis(2-ethylhexyl)sulfosuccinate and sodium alkanesulfonate.

The binding experiments were performed at a gelatin concentration of 1.0%. Successively small aliquots of a surfactant stock solution were added to 100 ml gelatin solution. After each addition the electrode potential was measured. In water the electrode showed a near-Nernstian response. The slopes were 58 mV/decade concentration with a sudden break at the critical micelle concentration (cmc). The amount of surfactant bound to gelatin was obtained by comparing the amount of added surfactant in the gelatin solution with the amount in water. The difference between the amounts added at a fixed electromotive force value corresponds to the amount of bound surfactant. Other experiments showed that the presence of gelatin does not alter the electrode response [4].

Surface rheological measurements

An oscillating bubble device was used for measuring the surface dilational properties of gelatin, surfactant, and gelatin/surfactant adsorption layers in the frequency range 3–400 Hz. This apparatus is described in Refs. [6, 7]. A closed measuring cell is filled with a surfactant solution in which a small hemispherical bubble is formed at the tip of a capillary. The capillary has a diameter of about 0.04 cm. A piezoelectric piston mounted on the measuring cell generates sinusoidal variations of the bubble volume in the frequency range 3–400 Hz. Sinusoidal changes in the bubble radius and surface area produce sinusoidal changes in the pressure within the cell. These changes in pressure are monitored by a sensitive pressure transducer which is mounted at the bottom of the cell. The pumped volume, the bubble geometry, and the frequency determine the deformation of the bubble surface and the rate of this deformation. The change in surface tension, $\Delta\gamma$, can be calculated using the change in pressure. The phase angle, φ, between deformation and dynamic surface tension can be measured. The surface rheological measurements were performed with aqueous solutions of gelatin, surfactants, and gelatin/surfactant mixtures. The measurements were carried out at 298 K.

With these results the complex surface (elasticity) dilational modulus $\varepsilon(f,c_i)$ can be determined. It is defined by the equation

$$\Delta\gamma = \varepsilon(f,c_i)\frac{\Delta A}{A} = E(f,c_i)\exp[i\Phi(f,c_i)]\frac{\Delta A}{A} \quad . \tag{1}$$

Here, γ describes the dynamic surface tension, $\Delta A/A$ the relative change in surface area, $\Phi(f,c_i)$ the phase angle between the oscillations of $\Delta\gamma$ and $\Delta A/A$, and $E(f,c_i)$ the amount of the modulus $\varepsilon(f,c_i)$. The real part of $\varepsilon(f,c_i)$ represents the surface elasticity and the dilational viscosity is proportional to the imaginary part. The modulus depends on the frequency, f, and the bulk concentration, c_i, of the components. The knowledge of $\varepsilon(f,c_i)$ in a broad frequency range allows the determination of surface rheological parameters, such as the surface dilational viscosity, the molecular exchange parameters, and the experimental Gibbs elasticity (limit value of the elastic term of the modulus).

Results and discussion

Results of the coating experiments

In aqueous coating solutions of photosensitive materials, added surfactants have several functions [8].

1. Surfactants must be able to avoid local defects caused by hydrophobic impurities in the coating solution.
2. Surfactants stabilize the multilayer flow on the slide. To ensure a stable flow it is important that the top layer has the lowest dynamic surface tension; however, it should be mentioned that the dynamic surface tension is not easy to measure.
3. Surfactants ensure the wettability on the inclined plane, on the web, and especially at the dynamic contact line.
4. Surfactants can stabilize the liquid bridge against oscillations when attaining a critical wet thickness at high coating speeds.

The last aspect was investigated in this work. We performed coating experiments and binding studies to determine the interaction between gelatin and several surfactants, and we compared these results with the dilational properties of gelatin and gelatin/surfactant adsorption layers.

The effect of different types of surfactants on the onset of oscillations of the liquid bridge was investigated by one-layer coating experiments. First, gelatin solutions ($\eta = 6$ mPas) without surfactants were coated. At a constant flow rate of the coating liquid the coating speed was successively increased, whereby the wet thickness decreased. At a fixed wet thickness, the liquid bridge becomes instable and begins to oscillate and the thickness of the coated layer varies periodically, whereby the extinction fluctuations can increase up to several tens of percentage points. The critical wet thickness depends on the suction applied. At an applied suction of 200 Pa the critical wet thickness is about 30 μm. At a higher suction the critical wet thickness is decreased.

To avoid this instability, surfactants must be added to the gelatin solution. The addition of 0.5–1 g/l surfactant lowers the surface tension of the gelatin solution by about 6–10 mN/m; however, this lowering of the surface tension does not stabilize the liquid bridge. The stability of the liquid bridge was characterized by measuring the extinction fluctuations, $\Delta E\%$, at the moving web. The values of $\Delta E\%$ serve as a measure of coating uniformity. The thickness variations should not exceed 1–2%. The results of some coating experiments are presented in Fig. 2. The experiments demonstrate that only the anionic surfactants used are able to stabilize the liquid bridge at high coating speeds or, to be precise, at thin wet thicknesses of the coated film. Gelatin solutions and gelatin solutions with added cationic surfactant (CTAB) lead to oscillations of the liquid bridge. As a result of this the thickness of the coated layer varies periodically across the web with a wavelength of about 0.5–1 cm. The added anionic surfactants sodium bis(2-ethylhexyl)sulfosuccinate and sodium alkanesulfonate prevent the onset of oscillations very effectively, so very thin layers of 15–20-μm wet thickness can be obtained which have good uniformity.

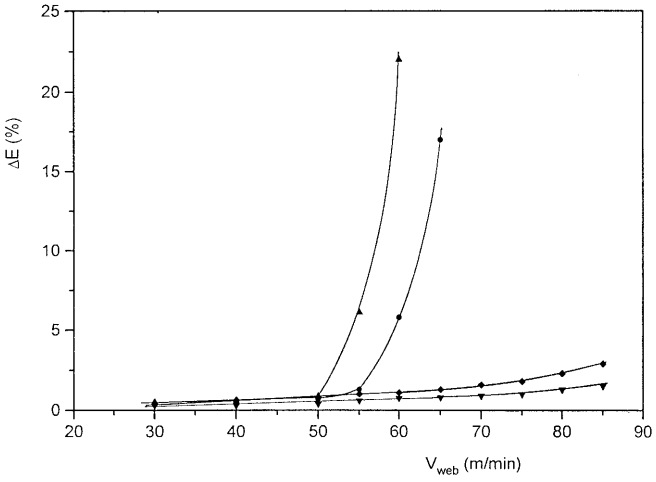

Fig. 2 Stabilizing action of different surfactants on the liquid bridge. Flow rate: $v = 1$ l/hcm; bulk viscosity: $\eta = 6$ mPas; suction: $\Delta P = 200$ Pa; surfactant concentration: $c = 0.5$ g/dm^3, gelatin solution (▲), gelatin solution + cetyltrimethylammonium bromide (*CTAB*) (●), gelatin solution + sodium bis(2-ethylhexyl)sulfosuccinate (◆), gelatin solution + sodium alkanesulfonate (▼)

Coating experiments show that the oscillations have a fixed frequency which depends on the coating conditions. The most important influencing factors are the suction applied and the type and concentration of the surfactant added [9]. The dependence of the oscillation frequency on the concentration of different added surfactants is shown in Fig. 3. The experiments were carried out at a constant suction of 200 Pa. If a critical wet thickness is reached, the gelatin solution oscillates with a frequency of about 155 Hz. The addition of the

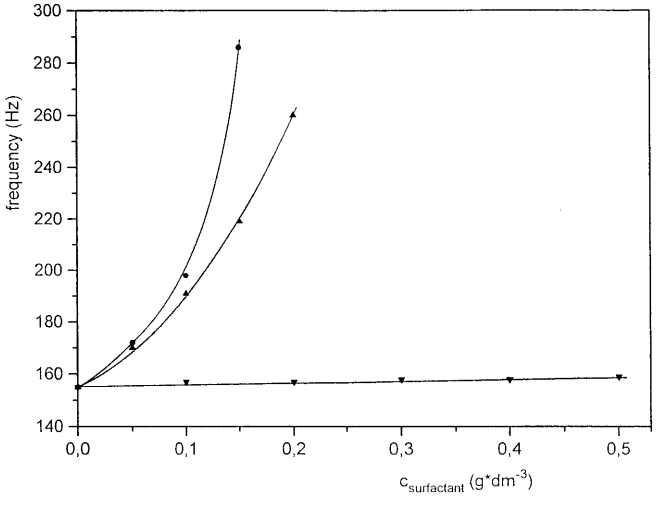

Fig. 3 Influence of the addition of different surfactants on the resonance frequency of the liquid bridge. $v = 1$ l/hcm; $\eta = 6$ mPas; $\Delta P = 200$ Pa, sodium bis(2-ethylhexyl)sulfosuccinate (●), sodium alkanesulfonate (▲), CTAB (▼)

ineffective cationic surfactant CTAB has no significant effect on the frequency. The addition of the highly active anionic surfactants sodium bis(2-ethylhexyl)sulfosuccinate and sodium alkanesulfonate increases the frequency at already very low concentrations of 0.1–0.2 g/l up to 250–300 Hz. With increasing surfactant concentration, the frequencies increase up to about 400 Hz or higher. In this frequency range the extinction fluctuations are very small, so the determination of the frequency becomes difficult. At anionic surfactant concentrations above 0.5 g/l, wavelike coating defects are not detectable. The liquid bridge is stable against oscillations, as frequencies above 500 Hz are not excited. An additional increase in frequency can be reached by applying a higher suction below the liquid bridge; therefore, the suction applied is an additional stabilizing factor.

The purpose of this work is to study how surfactants stabilize the liquid bridge against oscillations.

The effect of small amounts of added surfactants on the bulk properties of gelatin solutions is negligible. A change in viscosity can only be measured at higher surfactant concentrations [5].

The stabilizing action of the surfactants is localized on the upper surface of the liquid bridge. In this region, the surface strain rate is of the order of 2000–3000 s^{-1} [8]. The liquid bridge has two menisci: the upper, film-forming meniscus and the lower, wetting meniscus. Two-layer coating experiments showed that the stabilizing effect of surfactants is located on the upper surface. An adsorption time of a few seconds is long enough to form a gelatin/surfactant adsorption layer. On the lower meniscus, the flow in the narrow gap is very rapid and the residence time of a surface element amounts to a few milliseconds. This time is too short to form an adsorption layer [10]. The lower surface adheres to the moving web and the adsorbed molecules are transferred to the web.

The lowest oscillation frequencies were observed by coating glycerol/water mixtures. Under comparable coating conditions, frequencies of about 40 Hz were measured. The addition of anionic surfactants increases the frequency only to a small degree. Gelatin solutions oscillate with a higher frequency of about 155 Hz. The liquid bridge of both systems is instable. The slide coating process only works when the dilational properties of the upper gelatin adsorption layer are modified by anionic surfactants.

Gelatin is a surface-active substance. A gelatin solution (2 wt%) reaches a surface tension of about 40 mN/m. Its surface elasticity value is found to be in the range of about 30–60 mN/m. The values depend on the age of the adsorption layer. Gelatin adsorption layers are nearly pure elastic, the measured phase angles are approximately 0°.

In spite of the comparatively high elasticity values the gelatin adsorption layers are not able to stabilize the liquid bridge.

Coating experiments with glycerol/water mixtures ($\eta = 6$ mPas) showed that the liquid bridge is instable, and the addition of anionic surfactants did not lead to stable conditions. Only the addition of a small amount of gelatin (about 2 wt%) to a glycerol/water mixture containing anionic surfactant leads to a stable liquid bridge and a good coating quality. These experiments demonstrate the great importance of the presence of gelatin in the coating solution and indicate that the elasticity values are not of essential importance for the stabilizing action. A stable position of the liquid bridge requires viscoelastic properties in the upper adsorption layer.

Coating experiments demonstrate that only the mixed gelatin/anionic surfactant layers are able to stabilize the liquid bridge at critical coating conditions.

Because the single components (gelatin, surfactant) are not able to prevent oscillations, the stabilizing effect of the mixture must be the result of the interaction between gelatin and surfactant. Surfactants tend to associate with gelatin. However, the diversity of the types of surfactants produces a wide variety of interactions in the bulk as well as in the interface.

Results of the binding experiments

The degree of binding between gelatin and surfactant serves as a measure of the interaction between the components. The degree of binding between gelatin and different types of surfactants, sodium bis(2-ethylhexyl)sulfosuccinate, sodium alkanesulfonate, CTAB, was determined using a surfactant-selective liquid membrane electrode. The binding isotherms of the three surfactants to gelatin are presented in Fig. 4. Through comparison it can be shown that the interaction between cationics and gelatin is significantly weaker than those of anionics and gelatin. For the same alkyl chain length, cationics generally show much weaker interaction [4]. Binding studies indicate that both the head group and the hydrophobic part are involved in the interaction. The binding process is controlled by hydrophobic and other types of cooperative interactions, which are characterized by the exposure of new binding sites by unfolding. The binding of surfactants depends on their ability to unfold the proteins [11]. One of the main problems remaining in this field is the elucidation of the precise manner in which the surfactant and polymer are bound.

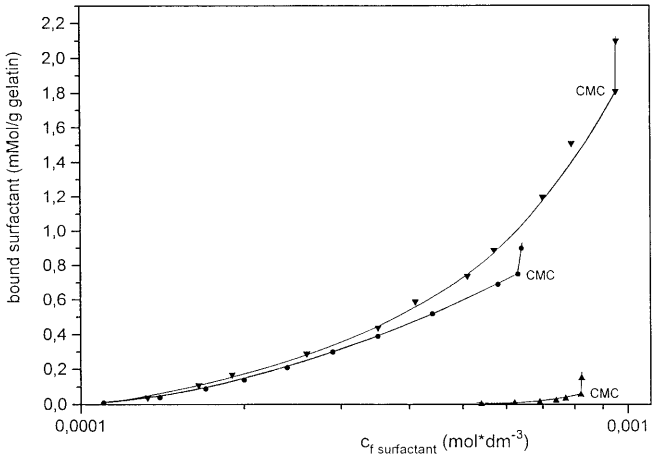

Fig. 4 Binding isotherms of different surfactants at pH 5.8 to alkali-processed gelatin. Sodium alkanesulfonate (▼), sodium bis(2-ethylhexyl)sulfosuccinate (●), CTAB (▲)

The binding isotherms obtained are not of the classical Langmuir type. They are characterized by their highly cooperative nature which is well known in polymer–surfactant interaction. The breaks in the binding isotherms do not indicate the saturation of gelatin molecules by the surfactant. The breaks indicate that the cmc of the surfactant ions in the bulk is reached. Above the cmc, the concentration of monomeric surfactant ions is constant. The surfactant bound at this concentration corresponds to the amount bound at the cmc. The electrode does not give information about binding above the cmc. In most cases the onset of micelle formation prevents the saturation level of binding from being reached. The binding of surfactants depends on their ability to unfold the gelatin. In the case of short-chain alkylsulfates (sodium octylsulfate) the ability to unfold gelatin is very low. This compound shows a very low level of binding even at low pH [4]. It may be assumed that the initial interaction between anionic surfactants and gelatin consists of an ionic binding of the $-SO_3$ groups to cationic groups of gelatin. The number of positively charged binding sites on the gelatin increases with decreasing pH. These binding sites act as nuclei for the formation of clusterlike aggregates on the gelatin. The first bound surfactant molecule favors the binding of additional molecules in its vicinity by hydrophobic interaction between the hydrocarbon chains of the surfactant and the hydrophobic sections of the gelatin. The aggregates formed show a lower degree of order than micelles. A comparison shows that several factors influence the binding of surfactants to proteins in the same way as they affect the formation of micelles, suggesting some similarity of the two processes. However, the binding of surfactants to gelatin is slightly favored, as the presence of protein facilitates the aggregation of surfactant [11].

Changes in the bulk viscosity, which are measured at higher surfactant concentrations, are caused by structural changes in the gelatin/surfactant associates, for example, by formation of intermolecular cross-bonds. The surface rheolgical properties of gelatin/surfactant adsorption layers differ significantly from those of the

bulk phase and can be explained by quite different ratios of concentration in the adsorption layer corresponding to the different surface activity of the components and the structures formed in the layer [12].

Figure 4 clearly demonstrates that only anionic surfactants exhibit strong interactions with gelatin. For example, 1 g gelatin binds about 500 mg sodium alkanesulfonate. Other binding studies using the surfactant-selective electrode also showed a strong binding of anionic surfactants to gelatin. Surfactants are bound in the form of clusterlike aggregates on the gelatin and not as single surfactant molecules. The adsorption of the strong surface-active gelatin/surfactant associates leads to a marked accumulation of surfactant near the surface, and surface rheological measurements show that the exchange of matter is increased at low frequencies. Figure 4 also demonstrates that the binding of CTAB to gelatin is negligible.

Most nonionic surfactants likewise show no detectable interaction with gelatin [13]. Generally, nonionics are not able to stabilize the liquid bridge against oscillations; however, they are used as coating aids to improve the wettability on the inclined plane, on the web, and at the dynamic contact line.

Results of the surface rheological measurements

Parallel to the binding studies, the surface dilational properties of the gelatin/surfactant adsorption layers were investigated using the oscillating bubble method. The results demonstrate the, in part, considerable modification of the dilational properties of gelatin adsorption layers by means of added surfactants.

For this reason the experimental curves $\varepsilon(f,c_i)$ were evaluated using an established surface rheological model. The results of this procedure are the insoluble limit values of the modulus, $\varepsilon_m = E(f \to \infty)$ (experimental Gibbs elasticity), the molecular exchange parameters, ω_m, and the intrinsic surface dilational viscosity, κ. The values of these parameters determine the frequency behavior of the complex dilational modulus $\varepsilon(f,c_i)$.

A pure elastic surface ($\kappa = 0$, $\omega_m < 2\pi f$) yields $E =$ constant and $\Phi = 0$ in the complete frequency range. In the molecular exchange area ($\omega_m \sim 2\pi f$) E increases and Φ decreases with increasing frequency, whereas a measurable κ prevents the disappearance of the phase angle and the reaching of a constant elasticity level at higher frequencies. These criteria can be used for a simple evaluation of Figs. 5, 6, and 7.

Figure 5 represents the frequency dependence of the complex elasticity of 0.8% aqueous gelatin solution, 3×10^{-4} M sodium bis(2-ethylhexyl)sulfosuccinate, and the mixture 0.8% gelatin + 1.8×10^{-3} M sodium bis(2-ethylhexyl)sulfosuccinate. The surfactant concentration of the gelatin solution is higher (1.8×10^{-3} M) because

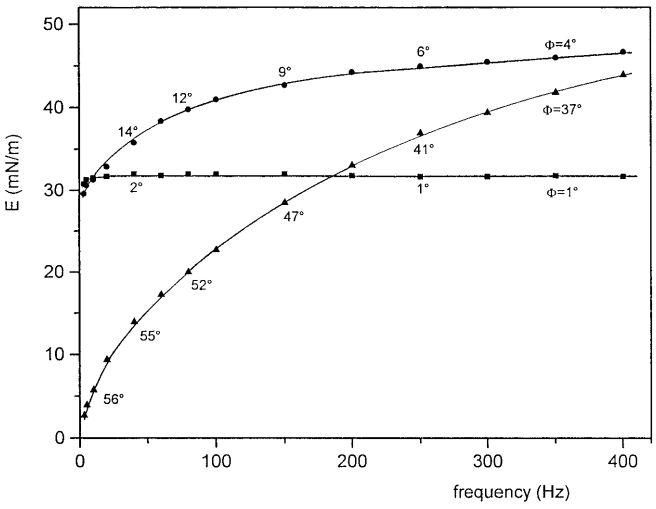

Fig. 5 Complex surface elasticities of gelatin, sodium bis(2-ethylhexyl)sulfosuccinate, and gelatin/sodium bis(2-ethylhexyl)sulfosuccinate solutions at 298 K. 0.8% gelatin solution (■), 3×10^{-4} M sodium bis(2-ethylhexyl)sulfosuccinate (●), 0.8% gelatin + 1.8×10^{-3} M sodium bis(2-ethylhexyl)sulfosuccinate (▲)

binding experiments showed that gelatin binds about 85% of the added surfactant under these conditions. This means that the free surfactant concentration in the gelatin solution is also about 3×10^{-4} M.

The gelatin adsorption layer behaves as an almost insoluble layer. The exchange of matter is negligible, and an intrinsic viscosity is not detectable. The measured phase angles are 1–2°, which means that the layer has nearly pure elastic properties. The elasticity level

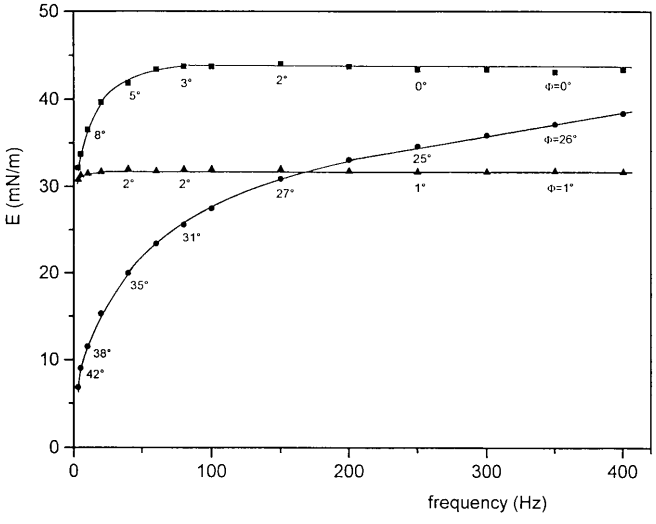

Fig. 6 Complex surface elasticities of gelatin, sodium alkanesulfonate, and gelatin/sodium alkanesulfonate solutions at 298 K. 0.8% gelatin solution (▲), 3×10^{-4} M sodium alkanesulfonate (■), 0.8% gelatin + 3×10^{-3} M sodium alkanesulfonate (●)

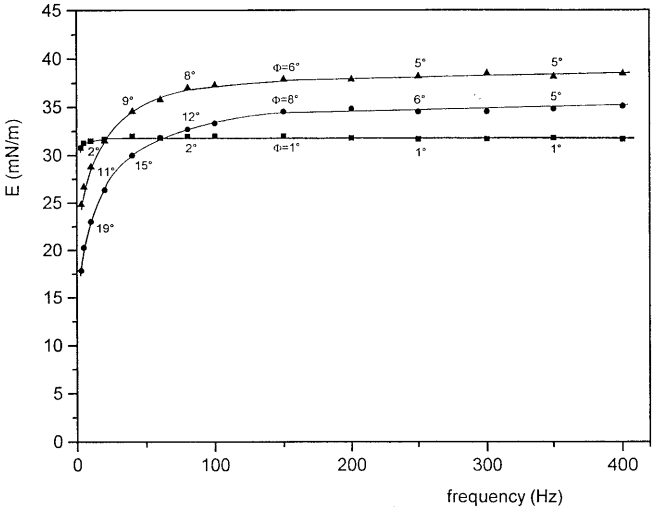

Fig. 7 Complex surface elasticities of gelatin, CTAB and gelatin/CTAB solutions at 298 K. 0.8% gelatin solution (■), 5×10^{-4} M CTAB (●), 0.8% gelatin + 5×10^{-4} M CTAB (▲)

depends on the age of the layer. Constant values were reached after about 30 min, suggesting that the elasticity level is influenced by the formation of structures within the layer.

The 3×10^{-4} M surfactant solution shows the influence of the diffusion exchange of matter on the complex elasticity values. The diffusion exchange leads to a decrease in the amount E of the elasticity values at low frequencies ($f \to 0$) and the phase angles increase up to 15°. At higher frequencies the amount E of the complex dilational modulus tends to level off. The phase angles were found to be about 5°, indicating a small degree of viscoelasticity.

The mixed system shows a remarkable frequency dependence which cannot be explained by a diffusion exchange of matter alone. At frequencies below 100 Hz the phase angles increase up to 56°. At frequencies above 200 Hz, we observe a marked increase in the magnitude E of the complex elasticity ε, whereby the phase angles reach values of about 40°. Under the same conditions the pure surfactant solution shows a phase angle of 5°.

As mentioned earlier, the steeply increasing tension (stress) amplitude ($\Delta\gamma$) with the deformation rate is a characteristic feature of an intrinsic viscosity. The dynamic surface tension amplitudes measured are caused by a change in surface concentration, Γ, and an additional part which is proportional to the rate of deformation, dA/dt, or frequency. The ratio of these two terms can be used as a scale of the degree of viscoelasticity of the adsorption layer. The degree of viscoelasticity depends to a high degree on the mixing proportion and the concentration of the components (gelatin/surfactant).

As demonstrated in Fig. 6 the system 0.8% gelatin + 3×10^{-3} M sodium alkanesulfonate shows similar properties. The aqueous surfactant solution ($c = 3 \times 10^{-4}$ M) exhibits elasticity values leveling off at frequencies higher than 80 Hz. The phase angles measured in this frequency range are practically 0°, which means that the adsorption layer is pure elastic. Under the measuring conditions gelatin binds about 90% of the alkanesulfonate added. To measure at a comparable monomer surfactant concentration, the surfactant concentration in the mixture was 3×10^{-3} M. The mixed system shows an almost linear increase in the magnitude E in the frequency range 200–400 Hz. The phase angles measured are about 25°, indicating marked viscoelastic properties.

The frequency dependence of the complex elasticity of 0.8% gelatin solution, 5×10^{-4} M CTAB, and the mixture 0.8% gelatin + 5×10^{-4} M CTAB is presented in Fig. 7. The surfactant concentration in the mixture was not increased, as gelatin does not bind measurable amounts of CTAB.

The gelatin adsorption layer shows pure elastic properties with vanishing phase angle. The magnitude E of the 5×10^{-4} M CTAB solution levels off at frequencies above 150 Hz and the phase angles were found to be about 5–6°, indicating a small degree of viscoelasticity. At frequencies $f < 100$ Hz we obtain increasing phase angles with decreasing frequency as a result of the exchange of matter.

In contrast to the gelatin/anionic systems, the magnitude E and the phase angles of the gelatin/CTAB mixed system are not increased compared to the aqueous CTAB solution. The mixed adsorption layer also shows a very small degree of viscoelasticity and, therefore, it is not able to stabilize the liquid bridge against oscillations. In comparison to the gelatin solution, the oscillation frequency of the gelatin/CTAB solution is not increased (Fig. 3). At low frequencies, the phase angles of the mixed layer are considerably smaller than those of the aqueous CTAB solution owing to the simultaneous adsorption of gelatin and surfactant.

The results obtained with the cationic surfactant emphasize that the level of elasticity or that the elasticity by itself are not crucially important to the stability of the liquid bridge.

The nature of the relaxation mechanism responsible for the surface dilational viscosity has not been clear until now. The availability of clusterlike aggregates of surfactant on the adsorbed gelatin layers leads to a considerable accumulation of surfactant molecules near the surface. These clusters are highly dynamic aggregates with a very short half-life for formation and breakdown, and this has important consequences for diffusion processes near the surface. On the other hand, the formation of intermolecular cross-bonds within the mixed adsorption layers could also produce viscoelastic properties.

According to the established model we can assume that a vanishing phase angle of the dilational modulus in the higher frequency range ($\phi \to 0$ for $f \to \infty$) hints at a bulk diffusion-controlled molecular exchange mechanism between surface and bulk. This means, the dissipative processes are located within the bulk, whereas the intrinsic surface dilational viscosity, detectable by a phase angle ($\phi > 0$) in the frequency range $f > 100$ Hz, is caused by dissipative losses within the surface layer [7]. Molecular dynamics processes in a nonequilibrium state can lead to this effect. Obviously, in the case of pure gelatin solutions the relaxation dynamics within the adsorption layer is too fast for a measurable effect in the considered time window; therefore, we think that the contribution of entanglements, junction points, or specific polymer interactions to the surface dilational viscosity is small. A possible explanation of the viscous effect of the mixture could be the disturbed thermodynamic equilibrium of the molecular distribution of surfactant and gelatin within the surface layer due to the surface dilatation.

This interpretation seems to be reasonable because anionic surfactants form strong surface-active gelatin/surfactant associates in gelatin solutions, which leads to a considerably increased surfactant concentration within and near below the surface layer. In a nonequilibrium state molecular exchange processes within such a surface layer are normally connected with a dissipative process.

For modeling the influence of the adjacent bulk phase the thickness of the surface layer can be extended until the pure bulk properties describe the boundary conditions between both phases [7]. Then, the correlation between the bulk and the surface is determined by the bulk diffusion process, caused by the disturbed thermodynamic equilibrium between both phases, and the boundary condition of the Navier–Stokes equations. An exact description of these conditions requires a detailed investigation of the force balance and the molecular exchange mechanisms at the surface [7]. This represents a current field of research; however, the known calculations of the hydrodynamics of coating processes are based on idealized boundary conditions which neglect some mechanisms [8]. A closer combination of surface rheological models and bulk hydrodynamic calculations should be realized in the future also for the description of coating processes; however, the exact calculation of the fluid mechanics of the liquid bridge under coating conditions is complicated.

Discussion of the frequency behavior of the liquid bridge

The stabilizing action of added surfactants depends to a high degree on the type of surfactant or, to be precise, its binding to gelatin. Binding experiments show that the binding between gelatin and anionic surfactants is significantly higher than that between gelatin and cationic surfactants, as well as between gelatin and most nonionic surfactants.

There is good correlation between the degree of binding as a measure of the interaction, the dilational properties of the mixed adsorption layers, and the stabilizing action in the coating process. The mechanism of the stabilizing effect is related to a strong increase in the resonance frequency. If the resonance frequency of the liquid bridge reaches a value of about 400–500 Hz, the moving web is not able to excite oscillations, which means the bead zone is also stable at critical coating conditions. As shown in Fig. 3 the addition of small amounts of anionic surfactant increases the frequency at very low concentrations (0.2 g/dm^3) up to 300 Hz with a steeply rising slope. An additional increase in frequency is reached by the applied suction.

It should be mentioned here that a marked additional stabilizing effect was detected when the lowermost layer showed viscoelastic flow properties [14]. Coating experiments showed that already in a lower range of viscoelasticity (Φ about 3–5°), the stability of the liquid bridge against oscillations and the disturbing influence of wetting inhomogeneities on the web is markedly increased. A small degree of viscoelasticity in the bulk was obtained by adding small amounts of a water-soluble polyacrylamide.

The reason for the increase in frequency is not an effect of the elastic term of the dilational modulus, ε. The ineffective cationic surfactant CTAB exhibits the same elasticity values as the anionic surfactants used. The determination of technically important values of the surface elasticity in the bead region is difficult because the modulus ε depends on the surface concentration, Γ, and this value is far from equilibrium. On the other hand, measurements of the surface elasticity performed at adsorption equilibrium at frequencies of 2 Hz or smaller are not representative for the bead region with very high strain rates [10].

At coating speeds of 2–3 m/s, viscous forces become important. In the bead region, where most of the stretching of the surface occurs, the surface strain rate is about 2000–3000 s^{-1} [8]. The surface strain rate is the gradient of surface speed. In the oscillating bubble experiments a surface deformation rate of 130 s^{-1} was found at a frequency of 400 Hz. The calculated surface dilational viscosity of the system 0.8% gelatin + 1.8×10^{-3} M sodium bis(2-ethylhexyl)sulfosuccinate amounts to 0.011 g/s. The contribution of the surface viscosity to the dynamic surface tension amounts to 1.45 mN/m. At the essentially higher strain rates in the bead region of about 2500–3000 s^{-1}, the viscous stress component of the surface tension can reach several tens of millinewtons per meter and this could be the reason for the observed increase in the resonance frequency.

Several authors [10] assume that the elasticity of the uppermost adsorption layer is an important factor for the stability of the liquid bridge. However, a direct relation between the elasticity values and the stabilizing effect could not be detected. The elasticity values of effective and ineffective gelatin/surfactant solutions were found to be in the same range, and these results suggest that the level of elasticity does not have a crucial influence on the stability of the liquid bridge. Only systems with a marked viscoelasticity of the upper adsorption layer showed a stable liquid bridge at critical coating conditions.

The results obtained suggest that in order to explain the large differences between the stabilizing action of the different surfactants the intrinsic dilational viscosity of the uppermost gelatin/surfactant adsorption layer must be taken into account; however, a detailed study of the dynamic behavior of the liquid bridge is very difficult. Nevertheless, some experimental facts point out to a simple dominant mechanism of these dynamics and, therefore, its modeling should be possible using reasonable simplifications. In a model of this process the following effects should be taken into account:

1. Small disturbances in the coating of gelatin solutions lead to oscillations of the liquid bridge at critical coating conditions.
2. The amplitudes and the frequencies of these oscillations can be influenced to a high degree by the addition of surfactants to the gelatin solutions.
3. The values of the bulk viscosity of different gelatin/surfactant solutions are similar.
4. The surface rheological properties of these solutions exhibit a large variation and a strong influence on the amplitude and the frequency of the oscillations.
5. The equilibrium surface tensions of these solutions are not very different.
6. The frequency of the oscillations increases and the amplitude decreases if the dynamic surface tension shows an intrinsic surface dilational viscosity effect.
7. For gelatin solutions the frequency of the liquid bridge depends linearly on the pressure difference over the bead.

To model the process we try to describe the dynamic properties of the liquid bridge by an oscillation equation. The amplitude of the oscillation can be characterized by the deviation, Δh, of the film element in the center of the bridge from its mean position or by the change in the radius, ΔR, of this element. A linear relation exists between Δh and ΔR for small deviations. In the first approximation, Δh and ΔR must satisfy an inhomogeneous oscillation equation,:

$$m\Delta\ddot{R} + b\Delta\dot{R} + k\Delta R = F(t) = \sum_n d_n \sin(\omega_n t + \beta_n) \ , \quad (2)$$

where m represents a mass parameter, b the dissipative term, and k the parameter of the back driving force of the oscillation. The excitation function $F(t)$ is characterized by the sum of the oscillating disturbances with the amplitude d_n. Then, the solution of Eq. (2) is given by

$$\Delta R(t) = \sum_n D_n \sin(\omega_n t + \delta_n) \ , \quad (3)$$

with

$$D_n = \frac{d_n}{m\sqrt{\left(\omega^2 - \omega_n^2\right)^2 + (b\omega_n/m)^2}} \quad (4)$$

and

$$\omega^2 = k/m \ . \quad (5)$$

The coefficient function, D_n, adopts its largest value, D_max, for $\omega_\mathrm{n} \sim \omega$ if the magnitudes $d_\mathrm{n} = d$ of the disturbances are approximately equal (assumption of a white noise function). The disturbances can be caused by small pressure fluctuations in the bead vacuum system or nonuniform surface energies of the web; therefore, the coefficient

$$D_\mathrm{max} = d/(b\omega) \quad (6)$$

is a scale for the amplitude of the oscillation. This simple model can be verified by using the results of the theory of membranes or strings. In such a framework, m represents a mass density combined with a geometric factor, b a sum of dissipative losses, and $k\Delta R$ the back driving force, which is proportional to the change in curvature, $\Delta\rho$ ($\Delta\rho \cong \Delta R/R^2$), and to the difference $\gamma' - \lambda$. Therefore we obtain

$$k = q^2(\gamma' - \lambda)/R^2 \ ,$$

where q represents a proportional constant, $\lambda \cong v^2$ the coefficient of the centrifugal forces, v the mean velocity, and γ' the dynamic film tension. γ' describes the sum of the surface tension and the same oriented tension within the bulk phase which is caused by the stretch resistance. We assume that the constants m and d are independent of the surface properties. According to Eq. (5), the resonance frequency is then given by

$$\omega(p) \cong \frac{q\sqrt{(\gamma' - \lambda)/m}}{R(p)} \ , \quad (7)$$

where $R(p)$ represents the mean radius of the film element which depends on the subpressure $p - p_0 < 0$ and the coating speed. The force balance equation [15]

$$p - p_0 \cong -(\gamma' - \lambda)/R(p) \quad (8)$$

(p_0 is the air pressure) and Eq. (7) lead to the relation

$$\omega_0(p) \cong -G(\gamma' - \lambda)(p - p_0) \ . \quad (9)$$

Only the upper surface and the bulk stretching are taken into account in Eq. (8); however, Eq. (8) is only a rough approximation of the force balance at the liquid bridge, because the influence of the bulk stretching in the bead zone on the value of $\gamma'-\lambda$ and the function $G(\gamma'-\lambda)$ must be considered as being not exactly known.

The measurements exhibit a linear dependence of the frequency on the suction. The measured dependence of the frequency on the applied suction by coating a 6% gelatin solution and a gelatin solution $+0.15$ g/dm^3 sodium alkanesulfonate is represented in Fig. 8. The slope of the straight line increases steeply with increasing surfactant concentration. As shown in Fig. 3, the addition of a small amount of 0.2 g/dm^3 sodium alkanesulfonate to a gelatin solution increases the frequency of the liquid bridge up to 260 Hz with a strongly increasing slope. At a surfactant concentration of 0.35 g/dm^3 the oscillation frequency is about 400 Hz; however, in this frequency range the oscillation amplitude is already considerably decreased, and it is difficult to enumerate the waves on the web. Figure 3 demonstrates the strong influence of the type of the surfactant added on the frequency response using the same subpressure and expansion rate. The contribution of the extensional stress of the bulk to the tension of the liquid bridge is in all cases similar, and the dynamic film tension can be approximated by the equation

$$\gamma' = \gamma_0(\alpha) + \kappa'\alpha \ . \tag{10}$$

Here, $\gamma_0(\alpha)$ describes the sum of the constant term of the surface tension and the bulk contribution to the film tension, and κ' the surface dilational viscosity. The influence of the different surfactants added on the equilibrium surface tension of the gelatin solutions is small, and we consider $\gamma_0(\alpha)$ also as approximately equal for all solutions as long as the expansion rate, α, is similar. However, the oscillating bubble experiments demonstrate a strong influence of the added surfactant on the measured surface dilational viscosity, κ. This value should correlate with the effective surface viscosity, κ', for the higher expansion rate at high coating speeds. Therefore, the very different frequencies of the liquid bridge can result mainly from different surface dilational viscosity values $\kappa' = \kappa'(c)$ (where c is the surfactant concentration) owing to its influence on the dynamic surface tension. For a constant suction Eq. (7) yields

$$\omega \cong \frac{q}{R}\sqrt{\frac{\gamma_0(\alpha)-\lambda+\kappa'\alpha}{m}} = \omega_0\sqrt{1+\frac{\kappa'\alpha}{\gamma_0(\alpha)-\lambda}} \ , \tag{11}$$

where ω_0 represents the oscillation frequency for $\kappa' = 0$, which corresponds to a gelatin solution without added surfactant. By transformation of this relation we obtain

$$\kappa' \cong \frac{\gamma_0(\alpha)-\lambda}{\alpha}\left[\left(\frac{\omega}{\omega_0}\right)^2 - 1\right] \ , \tag{12}$$

which can be used for a rough, independent estimation of the effective surface dilational viscosity, κ'. In the case of a very low coating speed, a subpressure of 200 Pa is compensated by a film pressure of about $\gamma^* \cong 40$ mN/m if the mean radius of the liquid bridge amounts to 0.2 mm. This value is probably smaller than the dynamic film tension, $\gamma_0(\alpha)$; however, according to Eq. (8), it must be of the order of the difference $\gamma_0(\alpha)$–λ, and we apply it for the estimation of κ'. With an expansion rate of $\alpha \sim 2500$ s^{-1}, $\omega_0 = 2\pi$*155 Hz (Fig. 3), and γ_0–$\lambda \cong 40$ mN/m Eq. (12) leads for a frequency $f = 219$ Hz to a dilational viscosity of $\kappa' \cong 0.016$ mNs/m. This is the same order of magnitude which was found by independent determination of the dilational surface viscosity using the oscillating bubble method. The fit procedure of the measurements demonstrated in Fig. 5 yields the value $\kappa \cong 0.011$ mNs/m for the surface dilational viscosity of a gelatin/anionic surfactant solution. A value of $\kappa \cong 0.011$, and the parameters $\alpha = 2500$ s^{-1}, and γ_0–$\lambda = 40$ mN/m lead to a frequency of about 200 Hz according to Eq. (11). We also obtain oscillation frequencies in the observed frequency range for other realistic values of the surface viscosity. For example, the viscosity values $\kappa =$ 0.005 mN/m, 0.02 mN/m, and 0.05 mN/m result in frequencies $f = 178$ Hz, 232 Hz, and 315 Hz, respectively. However, we must bear in mind that the expansion rate of the oscillating bubble method is much smaller than 2500 s^{-1}, and the viscosity is not independent of the frequency. In addition, a real quantitative verification of the model is difficult owing to the uncertain knowledge of the difference $\gamma_0(\alpha)$–λ.

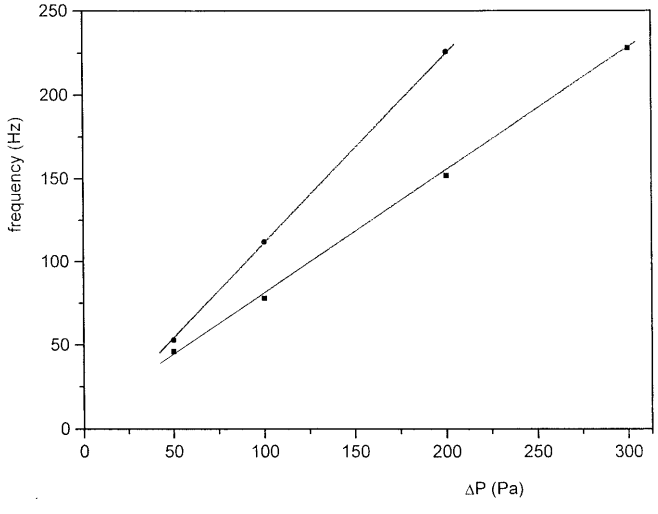

Fig. 8 Influence of the suction applied, ΔP, on the oscillation frequency. 6% gelatin solution (■) and 6% gelatin solution + 0.15 g/dm^3 sodium alkanesulfonate (●)

An increasing surface dilational viscosity causes not only a higher resonance frequency of the liquid bridge, but also a reduction of the oscillation amplitude according to Eq. (6) because of the influence of the surface dilational viscosity and the bulk viscosity on the damping parameter b. This could be the reason for the end of the oscillation in the frequency range $f > 500$ Hz.

Conclusions

In slide coating of gelatin solutions without added surfactants or with ineffective surfactants, the liquid bridge, formed between the lower edge of the slide coater and the moving web, becomes instable and begins to oscillate if critical coating conditions are reached. The instability occurs at low wet thicknesses. Coating experiments show that only the addition of anionic surfactants to a gelatinous coating solution leads to stability against oscillations.

The single components (gelatin, surfactant) are not capable of preventing oscillations; therefore, the stabilizing effect of the mixture must be a result of the interaction between gelatin and surfactant.

Binding studies were carried out to characterize the interaction between gelatin and several surfactants. These studies indicate that only anionic surfactants show strong binding to gelatin. The binding of the cationic surfactant CTAB to gelatin is negligible.

Investigations of the surface dilational properties of gelatin and gelatin/surfactant adsorption layers demonstrate a partially considerable modification of the dilational properties of gelatin adsorption layers by means of added anionic surfactants. Gelatin adsorption layers are nearly pure elastic, whereas gelatin/anionic surfactant layers exhibit a marked viscoelasticity.

At the high strain rates in the bead zone the contribution of the surface dilational viscosity to the dynamic surface tension can reach several ten of millinewtons per meter and this leads to the observed strong increase in the resonance frequency. The reason for the increase in the frequency is not a low or a higher value of the surface dilational elasticity. The elasticity values of adsorption layers of effective, as well as ineffective, surfactants were found to be in the same range. A direct relation between the elasticity values and the stabilizing effect could not be detected. These results suggest that the surface dilational elasticity does not have a crucial influence on the stability.

Coating experiments demonstrate that the liquid bridge of solutions which have pure elastic adsorption layers oscillates if critical coating conditions are reached. Only coating solutions with a marked viscoelasticity of the upper adsorption layer also show a stable liquid bridge at very thin wet thicknesses. High values of the surface dilational viscosity cause a high resonance frequency of the liquid bridge and a marked reduction in the oscillation amplitude. In the frequency range $f > 500$ Hz the liquid bridge becomes stable against oscillations.

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