Juvenescent Soap Films. The Evaporative Stabilization of a Film by a Volatile Surfactant

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Abstract

In the absence of evaporation, soap films may be preserved indefinitely after a rapid evolution to an equilibrium thickness, the black film. This evolution can be slowed down enormously so that the appearance of a recently formed thick and colored film can be preserved for hours or weeks. Such juvenescent films form when the evaporation of water is prevented and that of a minor but highly surface-active component is favored. For example, a solution of sodium dodecyl sulfate containing decyl or octyl alcohol gives juvenescent films in a thermostated enclosure, containing also a micellar solution which is initially free of the alcohol and is capable of absorbing it from the vapor phase. Juvenescence depends on a pseudo-steady state in which the surface tension of a film element increase on account of evaporation of the alcohol, and this causes contraction and thickening, return to the bulk liquid, and replacement by a fresh film element rich in alcohol. The analogy to "tears of strong wine" is marked. Quantitative experiments, using octyl alcohol, are also described.

Any condition favoring this effect must be eliminated if accurate equilbrium film-thickness measurements are to be obtained.

Introduction

PERHAPS THE EARLIEST account of the effect of a volatile component on soap films is that of Draper in 1836 (1). He observed that ammonia gas would diffuse rapidly through a soap film and also cause it to thin, resulting in an intensification of the interference colors. Gibbs (2) commented on the topic, and the effect of ether vapor as a defoamer has been known since the work of Van der Mensbrugghe (3) in 1869.

Interest in this problem developed when certain puzzling film drainage patterns were traced to the presence of volatile surface-active components, namely, small amounts of aliphatic alcohols such as decanol.

The Thinning of Soap Films

As normally observed, soap bubbles show interference colors in reflected light and eventually burst because of evaporation. If evaporation is prevented by forming bubbles in a closed and preferably thermostated chamber or, more conveniently, forming thin soap films on glass frames in such a container, then it is possible to observe the colors and motions in the film by reflected light. Such films thin during a few minutes or, at most, hours and ultimately reach an equilibrium thickness which is generally so thin that they no longer reflect much light and appear black. As thinning proceeds, the thin black film grows downwards from the top of the glass frame. This process has been described in detail by Mysels et al. (4), and the factors governing the equilibrium thickness of the black films are a current topic of modern soap film research (5–9). The black film is a typical metastable state, and such films have been known to last for periods up to three years (10) although once they start bursting, the process is completed within a millisecond (11).

Most solutions give soap films which are "mobile" and display rapid streaming during the thinning stages. This can be accounted for by a) gravity convection, which causes an upward flow of thinner film elements, and by b) marginal regeneration, during which thicker film elements are sucked into the Plateau Border (the thickening where a film meets another film or a support or the bulk solution) and are replaced by equal areas of thinner film pulled out of the border (4). As differences of thickness correspond to differences of colors in reflected light, these streamings are easily visible. Some solutions containing aliphatic alcohols or fatty acids form rigid films (12,4), in which the streamings are extremely slow and irregular. In these films the viscous flow of liquid between the two surface monolayers plays a large part in thinning (4).

Marginal regeneration and gravity convection are efficient thinning mechanisms so that moble films become black in a matter of minutes. Rigid films, on the other hand, change much more slowly, and the process takes hours. In either case, once equilibrium is reached, no further streaming occurs.

Two types of black films have been distinguished in these films, the first, where thickness depends greatly on the ionic strength of the solution and is always above about 80A, and the second, where thickness is constant at about 45A. The latter forms only in the presence of high concentrations of certain ions such as Na^+ or K^+ but then grows very rapidly (13).

Juvenescent Films

It is possible to obtain a film which will come to an apparent state of equilibrium when it is only partly black and while marginal regeneration and gravity convection persist in the colored portions so that it keeps the appearance of having been formed only a minute or two earlier. Such films, which might be called "juvenescent," were produced in a brass chamber (volume 1100 cc) with a glass window, as illustrated in Figure 1, and fitted with a cuvette 2 set in a flat dish 1. The apparatus was immersed in a thermostat at 25C. The films were made by drawing up the glass frame through the liquid by means of a stainless steel rod, which passed through a Teflon sleeve in the top of the chamber and was attached to the glass rod of the frame by a Perspex screw clamp. The films were illuminated with a fluorescent lamp and observed in the reflected light.

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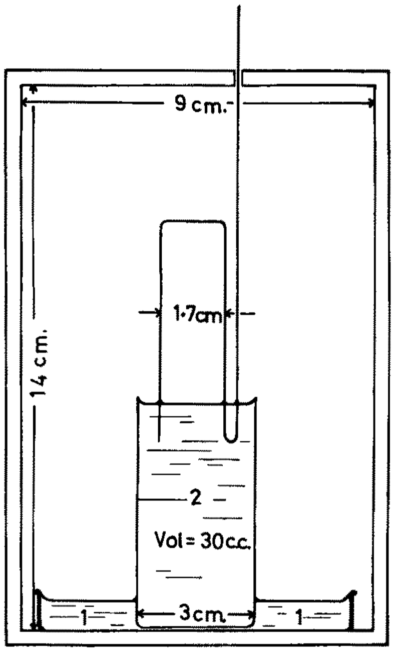

FIG. 1. The Apparatus. The soap film is formed within a brass enclosure by lifting a glass frame from cuvette 2 which contains a solution different from that in the flat dish 1.

The necessary condition for obtaining juvenescent films was that the solution in the flat dish 1 differ from that in the cell 2 and that it have a lower concentration (or at least activity) of a volatile surface-active compound. Thus it was found that when a few drops of decyl alcohol were added to a solution of sodium decyl sulfate (0.87% w/v) in the cell and sodium decyl sulfate solution (0.87% w/v) was placed in the flat dish, a juvenescent film formed. This film had a tendency to become partly rigid, but marginal regeneration could still be observed in the more mobile regions. It was found that systems containing sodium decyl, dodecyl, and tetradecyl sulfates all exhibited this phenomenon when sufficient decyl alcohol was added. This was also true for systems containing 0.15 M sodium chloride. Because of the tendency of these films to become partially rigid, quantitative experiments were carried out by using octyl alcohol as the volatile component.

This phenomenon occurs only when there is a difference in the concentration of a surface-active volatile component between the cell solution and that in the dish. If the two solutions are made the same, or if such a solution is put in a stoppered bottle containing a glass frame of the type used by Miles (12), no juvenescent behavior results.

Proposed Mechanism

An explanation of this effect may be given as follows. The system will tend to approach equilibrium by evaporation of the alcohol from the surface of the film. Since the addition of alcohol to a solution of the surfactant lowers the surface tension, the surface tension of the film will increase as the alcohol evaporates and the film element involved will tend to contract. Such a contraction will result in the thickening of this film and simultaneously in pulling up fresh film and liquid from the bulk solution and the border. The thickened film, which has been depleted of the volatile alcohol, then moves down under the influence of gravity and returns to the bulk solution. This process gives rise to a cyclic pumping action which can be observed in the colored region of the film. In the films under observation thick film was drawn out of the Plateau Borders at the sides of the frame and also sometimes in the center of the meniscus at the base of the film, giving rise to a two-dimensional fountain-type motion as can be seen in Figure 2. In this way the bulk solution in the cell is depleted of alcohol, but this occurs at an extremely slow rate because of the relatively small volume of solution in the film compared with the bulk solution. At the same time the solution in the bottom compartment becomes enriched in alcohol but, because of the small amount of alcohol involved, this also occurs at an extremely slow rate. This whole process, which may be called

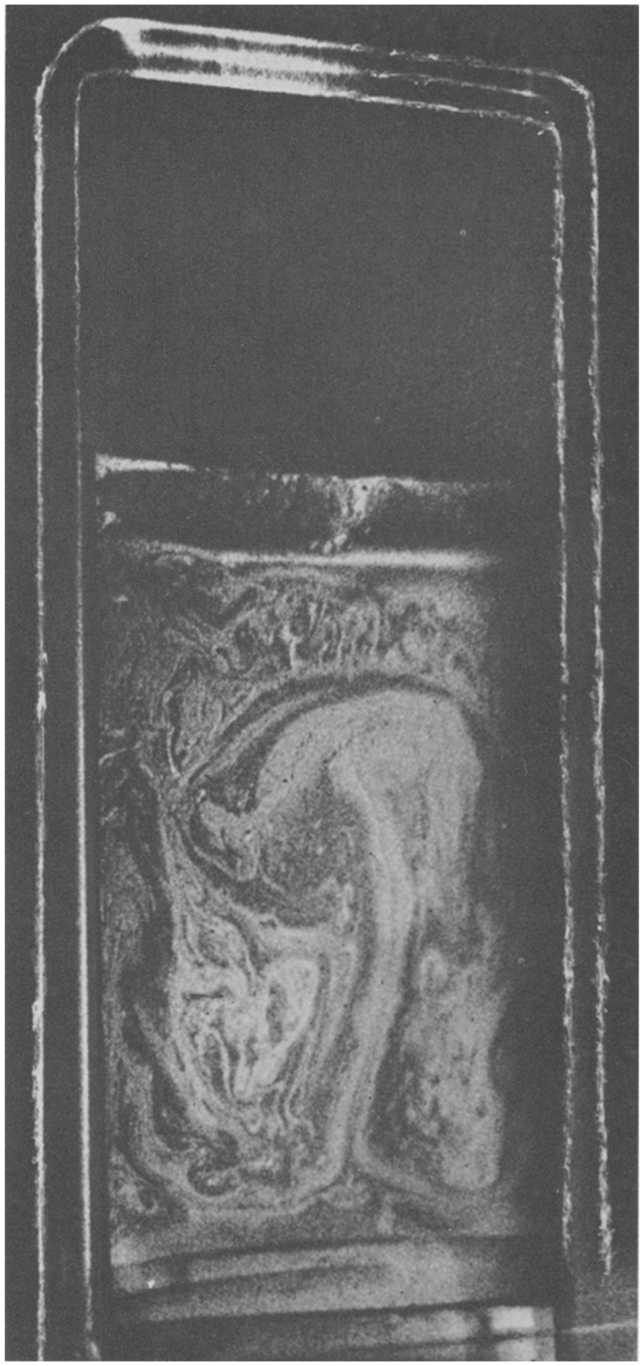

FIG. 2. Juvenescent film several days old, showing black film in the top one-third of the frame and colored film with vigorous streaming in the lower two-thirds. Thicker film is being pulled out from the center of the bottom meniscus.

evaporative stabilization, will compete with the marginal regeneration and gravity convection tending to thin the film, giving rise to a pseudo-steady state and juvenescent appearance. The rate of approach to equilibrium by gradual changes in this pseudo-steady state will depend on the volatility of the alcohol and on the capacity of the two solutions.

Perhaps the closest analogy to juvenescent films previously reported is in the behavior of "tears of strong wine"—the streaming on the sides of a glass containing alcoholic beverages—which has been discussed by Boys and was first explained by James Thompson in 1855 (14). This process, which involves a complete circulation of the fluid and can be stopped by placing a cover over the glass to prevent evaporation, differs from a juvenescent film mainly in that one side of the film is completely rigid.

These ideas are supported by the following measurements and observations, in which the height occupied by the black film was determined by using a cathetometer through windows in the chamber and in the constant temperature bath.

Black Film Area

If other factors are equal, the fraction of the total area of the juvenescent film which is occupied by the black film varies markedly with the total height of the film as shown in Figure 3. This result is to be expected since the black film area present during the pseudo-steady state will depend on the relative rates of thinning and thickening processes. Increased hydrostatic suction accelerates thinning and should interfere with thickening.

The diameter of the glass rods forming the frame did not affect the process; the results obtained in Figure 3 were essentially the same as when a frame 0.1 cm larger in diameter was used.

The amount of black film formed at a given total height changes as the system approaches equilibrium. Thus, in the system sodium dodecyl sulfate-octyl alcohol, the ratio of black film to the total area five hours after setting up the experiment was 0.03 and increased to 0.16 after 21 hr.

The approach to equilibrium is much faster with octyl alcohol than with decyl alcohol because of the higher vapor pressure of the octyl alcohol.

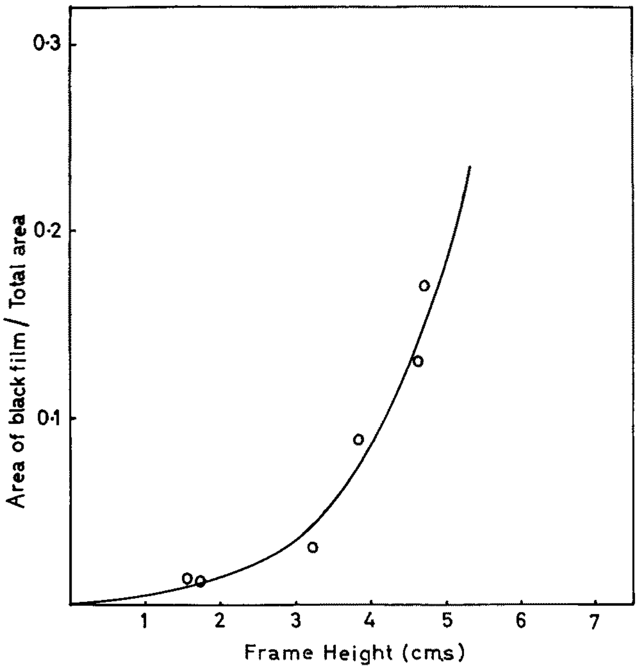

FIG. 3. The effect of frame height upon the fraction of the frame area occupied by black film during pseudo-steady state. 9.7×10^{-4} M sodium dodecyl sulphate in 0.15 M sodium chloride half-saturated with n-octyl alcohol at 25C. Frame diameter 1.5 mm, width 1.7 cm.

Effect of Alcohol Concentration

In order to determine the effect of concentration of alcohol upon juvenescent behavior, experiments were carried out on the system sodium dodecyl sulfate-sodium chloride-octyl alcohol. The experiments were set up so solutions in 1 and 2 differed only in that 2 contained the stated alcohol concentration and 1 was initially free of it. Measurements were made after allowing at least 3 hr for the system to come to thermal equilibrium. Figure 4 gives the ratio of the area of black film to the total film area at constant total film height of 3.5 cm. Two solutions, one above and one below the critical micelle concentration for sodium dodecyl sulfate in 0.15 M sodium chloride, were investigated. The octyl alcohol was added to the solution, using an "Agla" micrometer syringe. The regions of intersection of

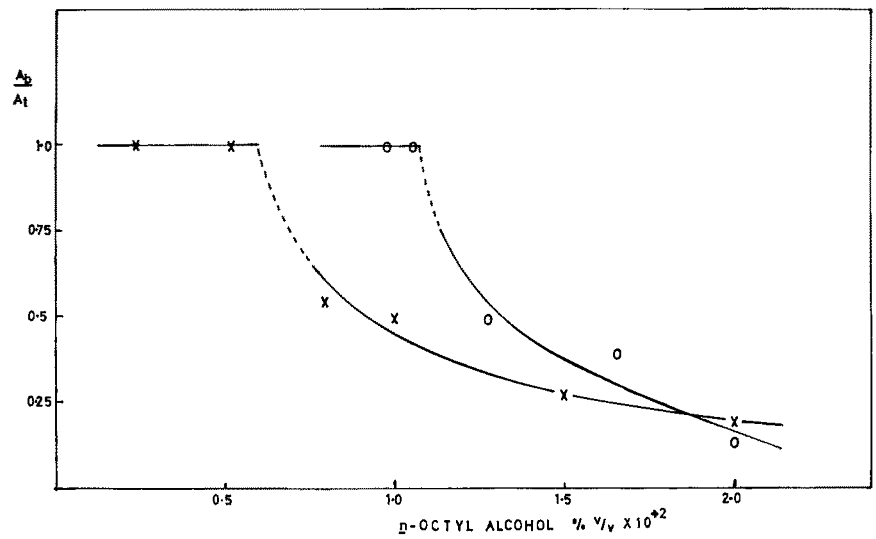

FIG. 4. The effect of alcohol concentration upon black film development for solutions below and above the CMC. Film height 3.5 cm. 0.15 M NaCl containing ○ 8.67×10^{-4} and X 2.02×10^{-3}M sodium dodecyl sulfate.

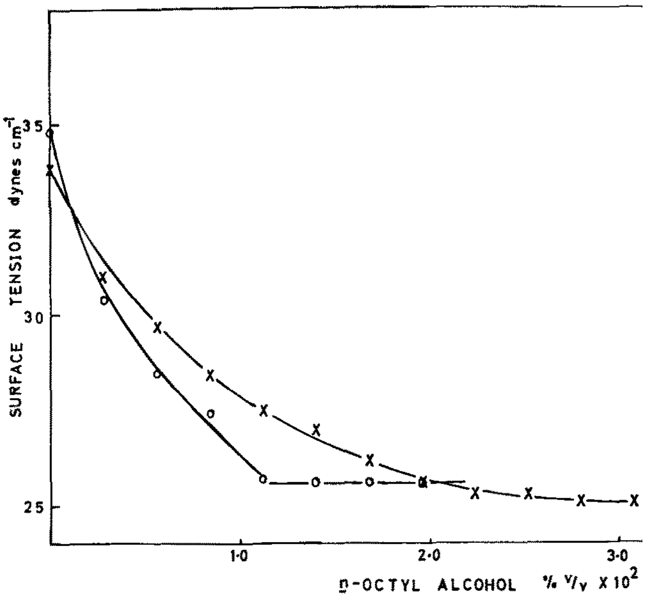

FIG. 5. The effect of concentration of n-octyl alcohol upon the surface tension of sodium dodecyl sulfate solutions ○ 8.46×10^{-4} M, X 2.02×10^{-3} M in 0.15 M NaCl.

the horizontal lines with the curves give the alcohol concentration required to produce visibly juvenescent films under these conditions. Two other solutions above the CMC, one 0.0105 M NaLS and another 0.01 M NaLS—0.01 M NaCl, both showed juvenescent behavior when the alcohol concentration was in the region of 0.007% v/v. The higher alcohol requirement of the solution below the CMC may be explained by the lower absorbing capacity of the micelle-free solution in 1.

It must be noted that, in both solutions of Figure 3, the black film formed was a second black film. This shows that octyl alcohol both promotes and stabilizes the second black film since, as has been shown previously (13), second black film formation does not occur in the absence of alcohol until a sodium chloride concentration of 0.225 M is reached. The minimum alcohol concentration for juvenescent film formation is not dependent on the type of black film formed since the other solutions of lower ionic strength mentioned above formed a first black film.

The alcohol concentration not only affected the steady state position of the boundary between colored and black film but, as might be expected, affected also the rate at which this boundary descended even when it did not lead to visible juvenescence after 3 hr. Thus, above the CMC, when the alcohol concentration was 0.0024% v/v, it took 17 min for the black film to fill the frame, but at 0.0052% v/v it took 35 min.

Solubility and Surface Tension Effect of Alcohol

It was of interest to establish whether the onset of juvenescent film formation was related to the solubility of the alcohol in the detergent solutions. The solubility of octyl alcohol in water at 20C was found by Addison to be 0.042% w/v (15). The method was to measure the surface tension as a function of alcohol concentration and hence find above what concentration the surface tension remained constant. Yasunaga (16) however reports that the solubility of octyl alcohol in water depends on the method of preparation of the solution because of the formation of colloidal particles of alcohol, which is consistent with Addison's observation that "vigorous agitation of the solution gave a semipermanent emulsion which upset the surface tension measurements".

The surface tension of two solutions of sodium dodecyl sulfate in 0.15 M sodium chloride was measured as a function of the alcohol concentration; the results plotted in Figure 4 confirm, of course, that additions of alcohol reduce the surface tension. Two distinct types of curve are obtained however. Below the CMC a sharp transition is found. It was also observed that, when the alcohol concentration exceeded about 0.015% v/v, gel particles appeared and the solution became turbid. These observations indicate that the determination of "saturation" in these systems is not simple. Below the CMC it would seem reasonable to regard the transition in surface tension as a saturation concentration, but above the CMC no such point can be clearly defined. It is interesting that below the CMC the transition in surface tension corresponds closely to the onset of juvenescent film formation. Above the CMC no such correlation exists.

Foam Breaking

During these investigations it was also observed that octyl alcohol acted as a foam breaker when it was added to a foam containing no octyl alcohol. Thus addition of as little as 0.0023% v/v octyl alcohol to a foam resulted in almost instantaneous collapse. However a foam formed from a solution already containing 0.0028% v/v alcohol was not collapsed by the addition of more alcohol. These observations are consistent with the work of Sasaki and Okazaki (17), who report that butyl alcohol, when added to a foam, is a defoamer but, when present from the beginning, is a foam stabilizer.

Detergent-Free Systems

It would seem reasonable to infer that, if evaporative stabilization is responsible for juvenescent films, then the presence of the surfactant may not be essential. In fact, it is possible to observe a similar effect by using a solution of ethyl alcohol in water, provided only very small films, about 1 to 2 mm high, are made. In the apparatus, when the ethyl alcohol concentration in the cell was greater than 0.17 mole fraction, with water in the base of the cell, a transient film, showing vigorous motions and interference colors, could be observed. When the film was not more than about 1 mm high, it would remain stable for several minutes but, on increasing the size, the vigor of the motions increased and the film burst. Such a system reaches equilibrium more rapidly (approximately 12 hr) as the ethyl alcohol distills into the water in the flat dish and then it is impossible to observe such effects.

Neville and Hazlehurst (18) have reported similar behavior in films of pure liquids and attributed the existence of "stable" films to uniform evaporation from the whole surface of the film, which results in a cooling. Since the cooling is greatest where the film is thinnest, there is an increase in surface tension and a flow of liquid into the thinner region, which leads to stabilization of the film. The motions of the colored films they describe seem similar to those observed; however they report that the most stable films are made with kerosene, which is not a pure liquid, but consists of hydrocarbons ranging in chain length from about C_8 to C_{14} (boiling point range 175–325C). In this case it would seem more likely that the main factor influencing the stability is the evaporation of the lower molecular-weight species, which would give rise to the kind of phenomena described in this paper and the temperature effect may well be of secondary importance.

Importance in Equilibrium Studies

Visible juvenescence is not likely to be present in experiments designed to study equilibrium films. However volatile surfactants are often present in such studies, either as accidental impurities or added purposefully, for example, to produce rigid films. Unless the whole system is then at equilibrium with respect to these impurities, there is the danger that an incipient form of juvenescence—a slowly evolving steady state departing slightly from equilibrium—prevails and leads to anomalous behavior, e.g., to greater of lesser thicknesses than corresponds to true equilibrium. The presence of such impurities may have been the source of difficulties noted by Lyklema and Mysels (8), which were always eliminated by thorough cleaning of the apparatus and were attributed by them to heavy metal contaminations.

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