

DEFOAMING

Theory and Industrial Applications

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Preface

Problems associated with excessive foaming occur in a surprisingly wide range of situations. Development of suitable antifoams has therefore been a necessity for the successful solution of foaming problems in industries as different as textile dyeing and detergent manufacture. Arguably, the problem of controlling excessive foam is generally of equal importance to that of generating stable foams. Yet this problem usually receives scant attention in the few textbooks that deal with the subject of foams. It seems timely, therefore, to redress the balance and devote a text exclusively to the subject of defoaming.

In many areas of surface and colloid science, the sheer complexity of phenomena often means that technology has actually led scientific understanding. The development of antifoams involving the interaction of one disperse phase (gas) with at least one other disperse phase (emulsion droplets or particles) is perhaps such an area. By including a chapter in this volume concerning the current theoretical understanding of the mode of action of antifoams, it is hoped that some of the association of the subject with the mysterious arts will be dispelled.

In many cases, the selection of an antifoam that will adequately control the foam is only the beginning of a solution to a foaming problem. Attendant considerations include the amount of antifoam required, the state of dispersion of the antifoam, and the possibility of the antifoam interacting adversely with some aspect of a process. These considerations may often be of overriding importance and may therefore affect the selection of the antifoam. They are also usually specific to particular applications. For this reason the

volume is divided into chapters concerning different industrial applications of antifoams so that detailed descriptions of the problems and solutions specific to given industries may be dealt with. Not all such applications are covered in this one volume, but a sufficiently wide range is included to give some indication of the appropriate approaches for any foam control problem. Also, a measure of coherence is maintained throughout the book despite the varied nature of the industries considered so that nomenclature and definitions of terms are consistent.

This book would not have been possible without the timely contributions of the various authors. Their patience in enduring the many editorial changes, which a volume such as this entails, is gratefully acknowledged. Finally, gratitude is due to Unilever Research for the provision of secretarial assistance which greatly facilitated the preparation of this volume.

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1

The Mode of Action of Antifoams

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I. INTRODUCTION

This chapter attempts a complete review of the various mechanisms proposed for the action of antifoams over the past half-century. It is a feature of this subject that these mechanisms, although plausible, are often speculative. Thus, unequivocal experimental evidence is often lacking. Indeed, the full theoretical implications of proposed mechanisms are also often not fully developed. In the main, all of this derives from the extreme complexity of the relevant phenomena. Foam is itself extremely complex, consisting of (usually) polydisperse gas bubbles separated by draining films. These films exhibit complicated hydrodynamics involving the distinct rheology of air-liquid surfaces and, for thin films, colloidal interaction forces. The nature of the foam film collapse processes which are intrinsic to a foam are still imperfectly understood.

Antifoams are usually hydrophobic, finely divided, insoluble materials. Their presence therefore further complicates the complexities associated with foam. Indeed commercial antifoams for aqueous solutions usually consist of hydrophobic particles dispersed in hydrophobic oils. The action of such antifoams concerns the effect of a dispersion (of antifoam in foaming liquid) of a dispersion (the antifoam) on yet a third dispersion (the foam).

Theories of antifoam mechanism appear to fall into two broad categories: those which require the antifoam to be surface active at the air-liquid surfaces of the foaming liquid, and those which do not. Theories which require the antifoam to be surface active associate antifoam behavior with an effect on surface tension in the foam films which leads to film rupture. Theories which do not require the antifoam to be surface active usually concern the hydrophobic nature of the antifoam. They suppose that dewetting of antifoam entities in foam films produces capillary instabilities which lead to film rupture.

The chapter is divided into four sections. The first concerns an outline of the main processes which are believed to contribute to the stability of foam films in the absence of antifoam. The second examines the relationship between antifoam effects and surface activity of the antifoam. The third section concerns inert hydrophobic particles and capillary theories of antifoam action in aqueous solutions. The last section concerns the mode of

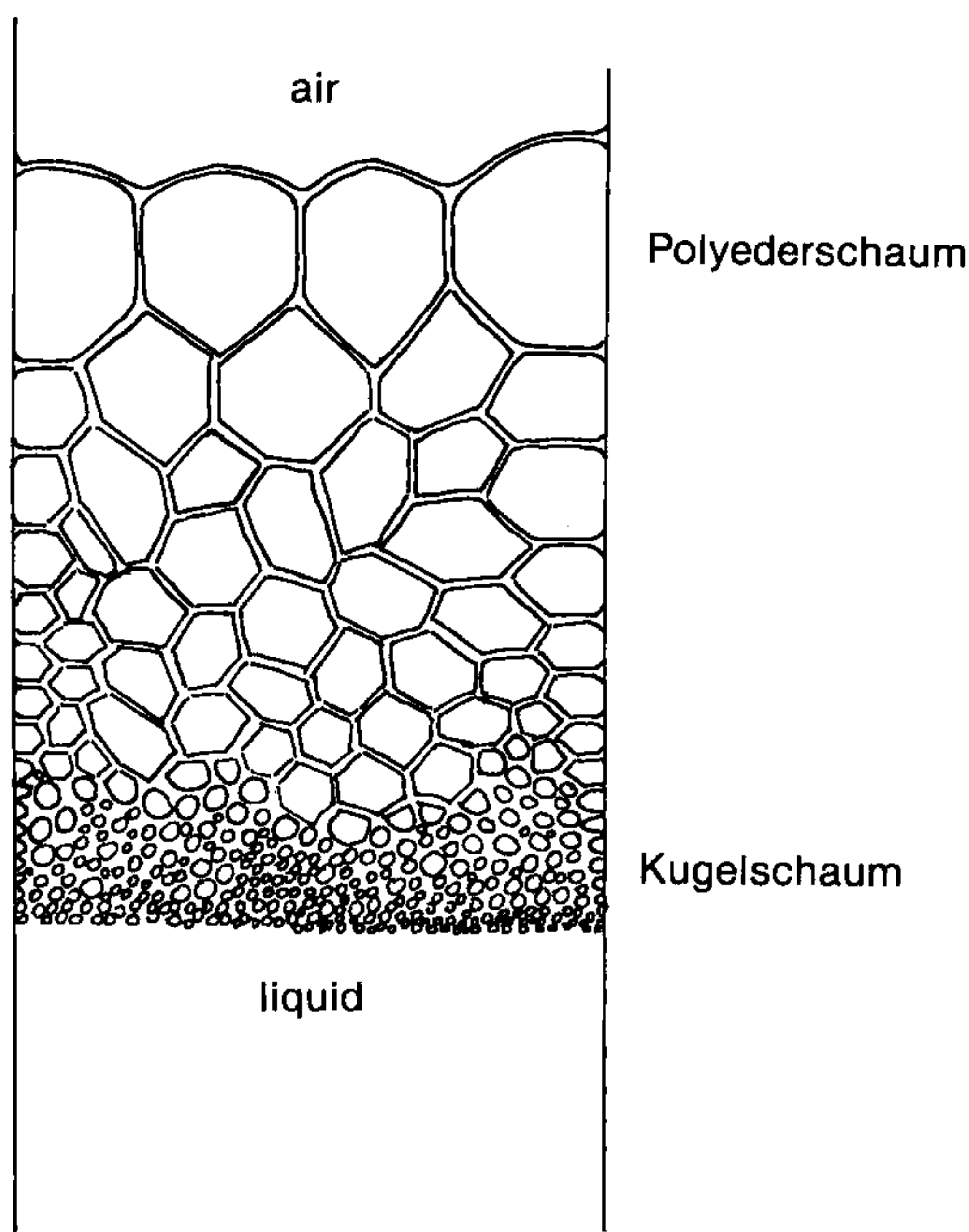


FIG. 1 Foam structure.

action of the mixtures of hydrophobic particles and oils which form the basis of many of the commercial antifoam concoctions proposed for aqueous foams.

II. THE STABILITY OF FOAMS

Before considering the mode of action of antifoams, we review the factors which contribute to the stability of a foam. A brief summary only is given here. For more complete accounts the reader is referred to the many reviews on the subject [1–5]. Our summary closely follows the excellent review by Lucassen [2].

The structure of a typical foam formed by, say, shaking a surfactant solution in a cylindrical vessel is shown schematically in Fig. 1. In the lower part of the foam, bubbles are spherical (so-called *kugelschaum*) and of small size with a relatively low gas volume fraction. As the liquid drains out of the foam, the bubbles distort to form polyhedra. This polyhedral foam (*polyederschaum*) consists of plane-parallel films joined by channels called plateau borders. The gas volume fraction is here relatively high and the density low so that polyhedra first form at the top of the foam column.

Throughout the foam there are differences in the sizes of adjacent bubbles. This will mean that differences in capillary pressure will exist between the adjacent bubbles so that gas will diffuse from small to large bubbles. The more soluble the gas in the continuous phase or the higher the partial vapor pressure of the continuous phase the faster this process of bubble disproportionation will proceed. There is no arrangement of bubbles in a foam which permits elimination of this process. Thus, for example, if there is free headspace above the foam the upper surface will consist of films of curved section. This will mean diffusion of gas out of the upper layer of bubbles into the headspace because of the capillary pressure implied by the curved surface.

As the films at the top of the foam thin, they become more susceptible to rupture by mechanical shock or vibration. Moreover, with some foams rupture of films at a certain thickness is spontaneous. Films at the top of the foam then tend to break first, and the foam collapses from the top downward in a catastrophic cascade.

A. Surface Tension Gradients and Foam Film Stability

Films formed by adjacent bubbles in a pure liquid are extremely unstable. Pure liquids therefore do not form foams. This arises in part because of the response of the films to any external force such as gravity. Consider, for example, a vertical plane-parallel film in a gravity field. There is no reason why any element of that film should move in response to the applied gravitational force with a velocity different from that of any adjacent element. No velocity gradients in a direction perpendicular to the plane of the film surface against the air will therefore exist. There will then be no viscous shear forces opposing the effect of gravity. The film will exhibit plug flow (resisted only by extensional viscous forces) with elements accelerated downward tearing it apart. The process is depicted in Fig. 2a.

This behavior can be drastically altered if we arrange for a tangential force to act in the plane of the liquid-air surface so that the surface is essentially rigid. In the case of a vertical plane-parallel film of a viscous liquid with such rigid surfaces, subject to gravity, a parabolic velocity profile will develop as shown in Fig. 2b. This means that velocity gradients will exist in a direction perpendicular to the film surfaces. A viscous stress will therefore be exerted at the air-liquid surface. This stress must be balanced by the tangential force acting in the plane of the surface. That force can only be a gradient of surface tension. This balance of viscous forces and surface tension gradients at the liquid-air surface can be written as

$$\frac{d\gamma_{AF}}{dy} = \eta_F \left(\frac{du_y}{dx} \right)_{x=0} \quad (1)$$

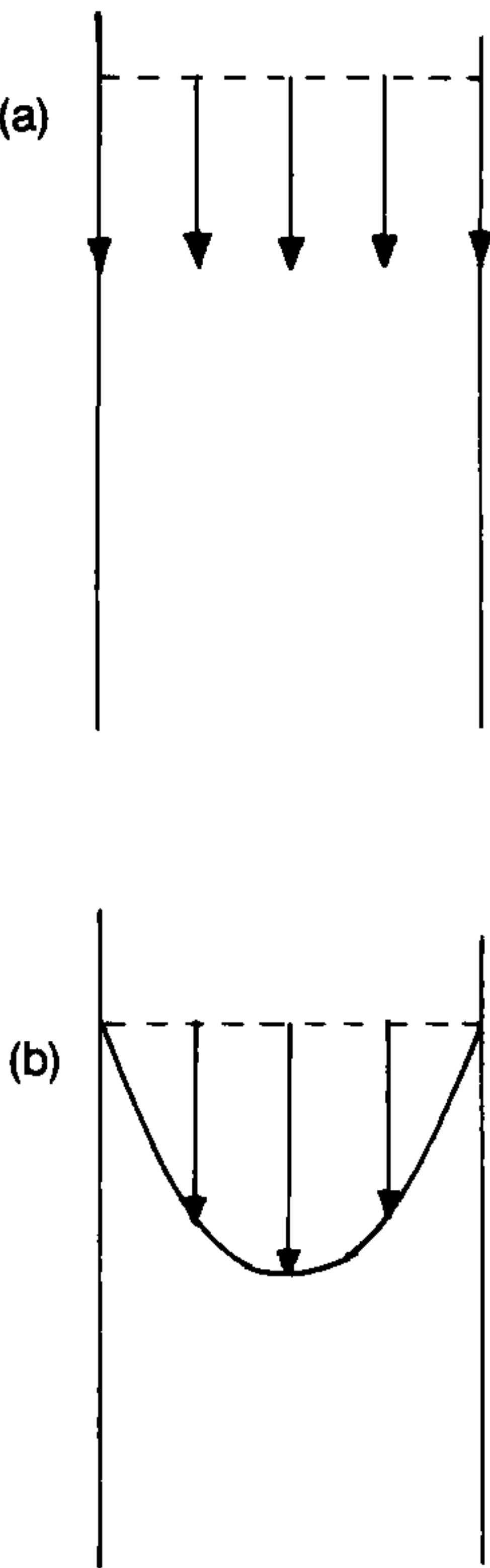


FIG. 2 Velocity profiles in draining foam films: (a) plug flow; (b) flow with parabolic velocity profile when film surfaces are immobile.

where γ_{AF} is the air-liquid surface tension of the foaming liquid, η_F is the viscosity, u_y is the velocity of flow in the y direction, y is the vertical distance, and x is the horizontal distance in the film.

Thus, we find that if the force of gravity (or indeed any other force such as that due to the capillary pressure caused by the curved plateau borders) is to be resisted by the film, then a surface tension gradient must exist at the air-liquid surface. In the case of a vertical film in the gravity field the gradient is [2]

$$\frac{d\gamma_{AF}}{dy} = \frac{\rho gh}{2} \tag{2}$$

where h is the film thickness, ρ is the liquid density, and g is the acceleration due to gravity. This gradient can only exist where differences of surface composition can occur. We therefore require the presence of more than one

component in the film. Indeed, it is possible to speculate that in the case of, say, aqueous foams diffusion of water through the gas phase may rapidly remove any differences in concentration between different parts of a foam film if only one solute is present. In this case at least two solutes (or three components) would be required.

Surface tension gradients due to differences in the surface excess of soluble surface-active components may exist only when either the surface is not in equilibrium with the bulk composition or there are concomitant differences in bulk composition parallel to the surface. In the case of the former the magnitudes of the gradients are of course determined by the rate of transport of surfactant to the relevant surfaces. With concentrated surfactant solutions transport rates by diffusion will be rapid and surface tension gradients will tend to be eliminated. Thus, it has occasionally been reported that foamabilities decline at extremely high concentrations of surfactant in aqueous solution. Conversely, however, if foam films are denuded of surfactant because of extremely slow transport rates, then the maximum surface tension gradients which can be achieved will be small. Such films will therefore be susceptible to rupture when exposed to external stress. However, the complex problem of assessing both the effect of rate of transport on the surface tension gradients in foam films and the overall resultant impact upon foam film stability, when subject to an external stress, has not apparently been fully addressed.

Differences in bulk composition are possible in a thin foam film as a result of stretching the film. If the film is sufficiently thin, then any stretching causes a depletion of the bulk phase surfactant solution between the air-liquid surfaces of the foam film as more surfactant adsorbs on those surfaces. Distances perpendicular to the film are small so that, provided the stretching occurs reasonably slowly, equilibrium inside the film element may be always maintained. Depletion of bulk phase surfactant concentration will therefore necessarily mean an increase of the surface tension of the film as it is stretched. This will, however, only occur if reduction of surfactant concentration causes a concomitant increase in surface tension. In the case of a pure surfactant at concentrations above the critical micelle concentration (cmc), this may not always happen.

We find then that it is possible to generate a surface tension gradient in a foam film by stretching various elements of the film to different extents. The increase in surface tension due to stretching imparts an elasticity to the film. This property of foam films was first recognized by Gibbs [6] and is usually referred to as the Gibbs elasticity ϵ_G . It is defined as

$$\epsilon_G = \frac{2d\gamma_{AF}}{d \ln A} = - \frac{2d\gamma_{AF}}{d \ln h} \quad (3)$$

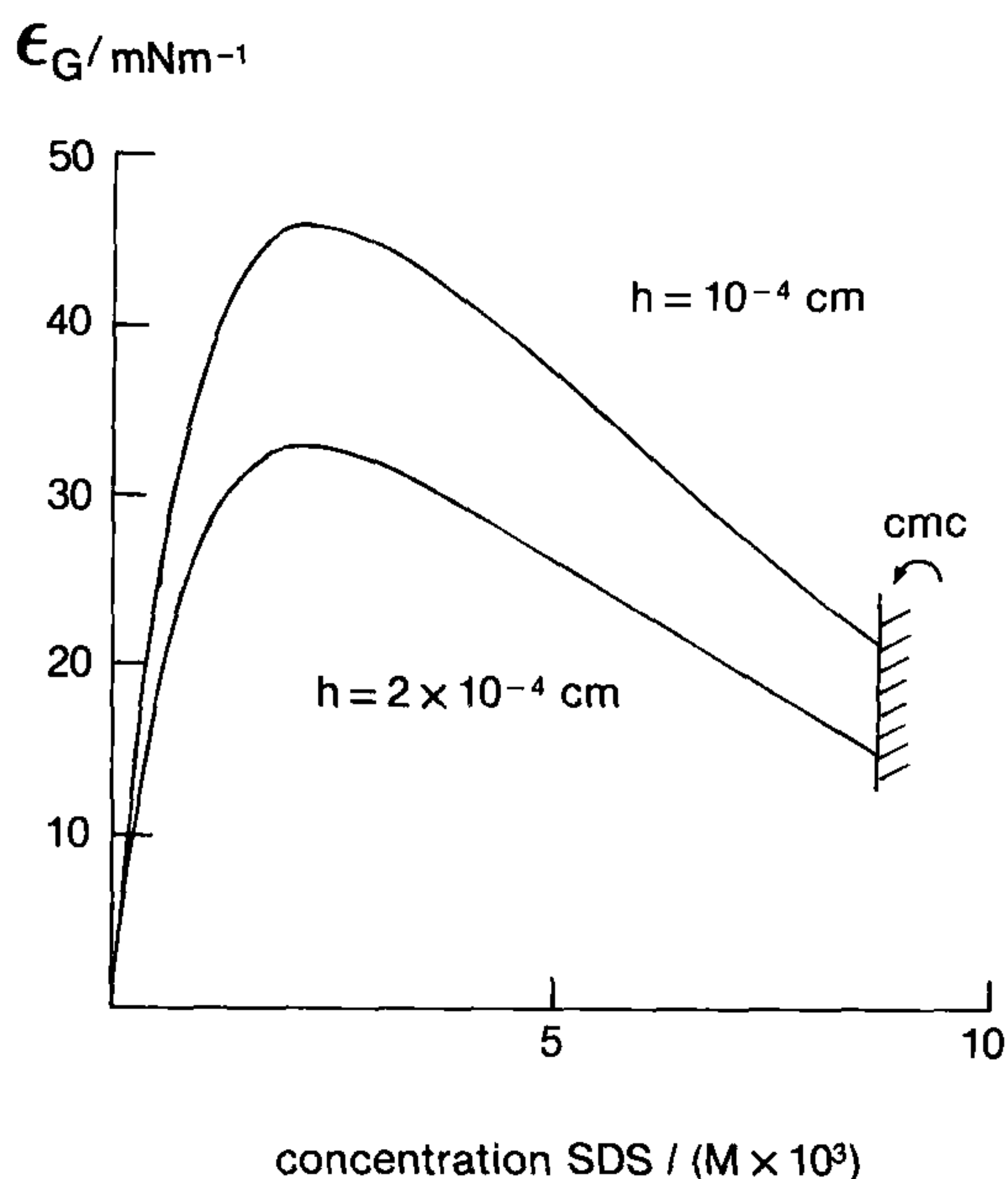


FIG. 3 Gibbs elasticities of submicellar sodium dodecylsulfate solutions. (From Ref. 2.)

where A is the film area and the factor 2 arises because of the two surfaces.

A plot of ϵ_G against concentration for a submicellar aqueous solution of sodium dodecylsulfate (SDS) is shown in Fig. 3 by way of example. Here we see that, except at very low concentrations, decreases in film thickness at constant concentration produce increases in Gibbs elasticity so that $(\partial \epsilon_G / \partial h)_c \leq 0$. Thus, as the film becomes thinner stretching will cause a relatively greater depletion of surfactant in the intralamellar liquid and the surface tension will rise to a greater extent.

The plot of Gibbs elasticity against concentration shown in Fig. 3 clearly reveals a maximum at concentration c_{\max} . At extremely low concentrations of surfactant we find that upon stretching of the film there is essentially no contribution from the intralamellar liquid, and the surfactant behaves as an insoluble monolayer. Here with increase in surfactant concentration both the surface excess and the elasticity of the monolayer increase. However, further increases in the surfactant concentration will eventually mean that it significantly exceeds that required to compensate for stretching of the air-liquid surface, so $\epsilon_G \rightarrow 0$. These two opposing consequences of increasing concentration conspire to produce the maximum in a plot of Gibbs elasticity.