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A new method for studying foaminess

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A new method for studying the foaminess of surfactant solutions has been elaborated based on investigating a completely uniform foam bubble monolayer on the solution surface; the experimental technique and results for an aqueous solution of sodium dodecylsulfate are described.

The term ‘foaminess’ has been introduced by Bikerman[1] who defined this property as follows. When a steady stream of bubbles passes through a layer of a foaming solution a stationary height of a foam column is produced which can be measured. The foaminess is defined as:

$$\Sigma = V/w \qquad (1)$$

where V is the foam volume and w is the volume gas rate which should be chosen so as to attain the adsorption equilibrium between the surfactant solution and moving bubbles. Bikerman’s definition, however, cannot be considered as satisfactory. For example, the V/w ratio depends on w. It then follows from the fact of the existence of a critical value w_c that the volume V increases without limit as w approaches w_c (the theory relating to w_c has been formulated in detail[2]). A stationary value for V is also impossible for another reason. The bubble stream with a surfactant adsorbed extracts the surfactant from solution, and the foam, moving upward to the boundary of its stability, carries the surfactant to this boundary. As a result, a surface excess of the surfactant,

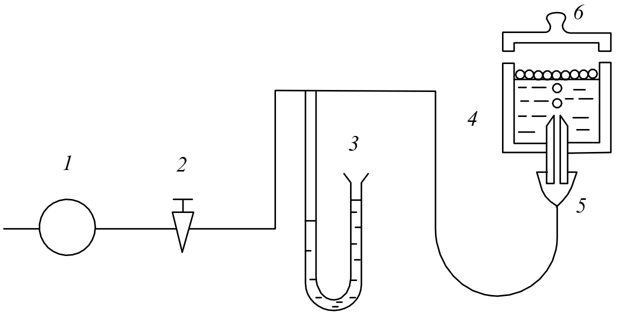

Figure 1 Experimental set-up for measuring foaminess by the foam monolayer method: *1,* microcompressor; *2*, stopcock; *3*, manometer; *4*, measuring cell; *5*, glass capillary; *6*, cover.

typically of low solubility in the dispersed medium of the foam, does not return to the solution.

It is of note that destruction of the foam proceeds not only at the foam surface, but also in the foam bulk. This leads to a change in foam dispersity along the column height, so that the most powerful mechanism of the surface foam destruction (responsible for the foam volume) is related to the degree of dispersion which is strongly different from the initial one. If the foam was initially monodisperse, the change in the dispersion degree would proceed through the state of polydispersity, making the situation still more complex. Thus, the above definition of foaminess as a physical notion seems to be incorrect. We need a clearer and more definite definition of the foaminess (foamability) of a solution.

We define foaminess as the foam bubble life-time. The principal distinction of our method is: (a) all bubbles are produced with a capillary tube and thus have the same size, (b) not a foam column, but a foam monolayer on a surfactant solution is under observation, (c) the bubble radius is chosen to be equal to the Laplace capillary constant for a pure solvent in order to create a polyhedral foam monolayer as predicted by the theory of foams.[2,3] In our method, the bubble size and the height of foam are fixed, and only the bubble frequency is variable and is chosen to maintain a stationary foam monolayer of complete coverage. The foam monolayer has a hexagonal packing of bubbles, possessing all typical-for-foam structure elements: films, channels and knots.

The use of a foam monolayer has a number of advantages as compared with its multilayer variant. The excess surfactant returns to the solution after the destruction of the bubbles of monolayer. As experiments show, there is no bubble coalescence in the foam monolayer: only upper (but not lateral) films of the foam monolayer break, so that the dispersity of the two-dimensional foam is maintained constant during the process of foam destruction. Each elementary process of bursting a bubble creates a vacancy in the bubble monolayer which can be occupied by a new bubble of the same size. The number of such bubbles per unit time, n, is a directly measurable quantity. The bubble life-time, τ, characterising the foaminess of a solution is determined from the relationship

$$\tau = N/n \tag{2}$$

where N is the total number of the foam cells on the solution surface, which is kept constant by the bubble flow rate n. Since the destruction of the upper films of the monolayer is of stochastic nature, all the bubbles, including very new ones, are in the same 'starting' positions: the probability of bursting for any of them is the same. From here, but not from a completely definite life-time for each bubble, equation (2) follows (the number of 'marked' bubbles diminishes by e times per time τ).

By multiplying the numerator and denominator of the right-hand-side of equation (2) by the bubble volume, we obtain the right-hand side of equation (1) where V is the volume of the foam monolayer. Thus, the definition expressed in equation (2) is a limiting form of Bikerman's definition, but with a clear physical meaning, not withstanding the fact that the experimental method is quite different from that of Bikerman. In addition to the above, it could be noted that, in contrast with a monolayer, a three-dimensional foam in the state of destruction does not even have an upper flat surface to measure the foam height since gravity only slightly influences, in the direction of smoothing, the upper foam boundary.

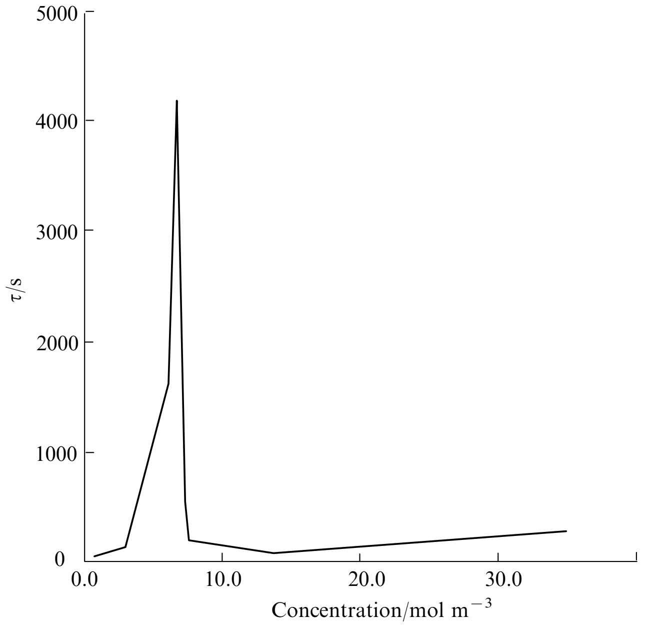

Figure 2 The foaminess, τ, as a concentration function for an aqueous solution of sodium dodecylsulfate.

The scheme of our experimental set-up for measuring the foaminess of surfactant solutions is shown in Figure 1. The air from a microcompressor *1* passes though the regulating valve *2* to the end of a glass capillary *5* in the measuring cell *4*. A solution under investigation is placed in the measuring cell and the bubble monolayer is formed on the solution surface with the aid of the capillary *5*. The air pressure at the capillary end is controlled by the U-shaped water manometer *3*. The cover *6* prevents evaporation. The whole system can be placed in a thermostat if necessary.

The experimental procedure used depends on the bubble life-time, *i.e.* on the surfactant concentration. At a high concentration (well above the critical micelle concentration in the case of colloidal surfactants) when foam bubbles are long-lived, the bubbles are produced one by one sufficiently seldom, and every vacancy formed should be filled by a new bubble individually by moving the capillary tip to a free spot in the foam monolayer. At a lower concentration (close to the critical micelle concentration), bubbles are produced frequently (but still in a discrete way). The bubble monolayer is thus more mobile and there is no need to transport a bubble to a corresponding spot: all the bubbles easily replace each other. Finally, at a very low concentration (much smaller than the critical micelle concentration) when the bubble life-time is very short we move from the production of discrete bubbles to a continuous air stream. The bubble life-time can be measured as the ratio of the bubble monolayer height and the air stream front velocity. The latter is measured as follows. For a given gas flow rate, a system under investigation is replaced by a system with very stable foam. In the same measuring cell, the movement of the foam front corresponds to the air stream front velocity and can be measured directly. As experiments show, the new method proposed for measuring foaminess can be used for a wide range of surfactant concentration.

For the sake of illustration we present in Figure 2 the experimental results obtained for an aqueous solution of commercial sodium dodecylsulfate (Fluka, >99% grade) using the above, new method for studying foaminess. As is clearly seen in Figure 2, a sharp maximum of foaminess appears in the critical-micelle-concentration region. Similar maxima, but not so well pronounced as demostrated by this new method, have been reported in the literature, dodecylsulfate being the most active among alkylsulfates at room temperature.[1,4] Since we used sodium dodecylsulfate without further purification, the effect observed is probably strengthened by the presence of a highly surface-active impurity (like dodecanol which is a typical admixture to sodium dodecylsulfate), which leads, as is well known, to a minimum of the surface tension of a surfactant solution in the critical-micelle-concentration region.

References

1 J. J. Bikerman, *Foams*, Springer, Heidelberg, 1973.
2 V. V. Krotov, *Kolloidn. Zh.*, 1980, **42**, 1081; 1092 [*Colloid J. USSR* (*Engl. Transl.*), 1980, **42**, 903].
3 V. V. Krotov, *Kolloidn. Zh.*, 1986, **48**, 1170 [*Colloid J. USSR* (*Engl. Transl.*), 1986, **48**, 97].
4 E. Gotte, *Kolloid-Z.*, 1933, **64**, 327.

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