Physical Chemistry

1957

SovietRxiv

Abstract

Full Text

Physical Chemistry

K. V. Zotova and A. A. Trapeznikov

Shear Strength of Bilateral Films and Surface Layers in Saponin Solutions

(Presented by Academician P. A. Rehbinder, June 11, 1957)

The structure, composition, and properties of adsorption layers in solutions of saponin and soap-like substances, and of the bilateral films formed from these solutions, which are elements of foam cells, are of great interest for colloid chemistry.

In previous works by one of the authors, a method was developed for studying the mechanical properties of films and surface layers in soap solutions, and some preliminary measurements of the strength properties of saponin films were carried out (⁀1). It is usually assumed that the structure and composition of adsorption layers at the surface of a solution of a surface-active substance and in a bilateral film formed from the same solution are identical. In reality, as was shown in (⁀2), they may not coincide. This is of great importance for understanding many features of the properties of films and foams, in particular the concentration dependence of their stability.

The simultaneous study of the mechanical properties of bilateral films and surface layers at different concentrations is a new method for investigating the properties and composition of bilateral films.

In the present work, a method was used for measuring the shear strength of surface layers and bilateral films (⁀3). Two concentric rings made of platinum wire 0.1 cm in diameter, with radii $R_1 = 2.738$ cm and $R_2 = 2.995$ cm, were arranged horizontally. The outer ring was rigidly fixed to the walls of a cup, which could be filled with solution from below through a tube connected to an elevated vessel containing the solution; the inner ring was suspended on an elastic tungsten wire $d = 0.01$ cm, $l = 27.0$ cm, having an elastic constant of 53.6 dyne $\cdot$ cm/rad. This entire system was enclosed under a sealing glass bell jar resting on a table placed in an air thermostat.

The method consists in either raising the level of the saponin solution in the cup exactly to the middle of the rings, which are thus placed in the surface layer of the solution, or first raising it above the rings and then lowering it far below them, after which a bilateral film is formed between the rings and detaches from the solution.

Fig. 1

Figure 1: Fig. 1

In both cases, when the inner ring is twisted, deformation is undergone either by the surface layer of the solution or by the bilateral film in the narrow annular gap between the two platinum rings. Depending on the magnitude of the resistance of the system under investigation and on the parameters of the apparatus, various types of motion of the inner ring may occur: torsional oscillatory, aperiodic, or gradual displacement as a result of applying constant or continuously (stepwise) increasing loads (angles of twisting of the thread). The latter type of motion gives deformation-stress curves corresponding to a definite (average) rate of loading.

The method for measuring mechanical properties must be sufficiently rapid. For films possessing shear strength, the most suitable is the method of gradual loading, which makes it possible to obtain the deformation curve ε—shear stress P, from which one can find the limiting strength of the structure, P_r, corresponding to the accepted deformation conditions (the increase of P is carried out periodically every 15 sec by 0.072 dyne/cm).

Fig. 1. Curves of the dependence of ε on P for double-sided films formed from saponin solutions of various concentrations.
1–0.05%; 2–0.1%; 3–0.2%; 4–0.5%; 5–1%

We investigated various saponins which, as it turned out, have a very different ability to form films and foam, as well as different mechanical properties. In this work both imported saponins, produced by firms manufacturing pure chemical reagents, and domestic saponins obtained from various plants were studied. Here data are considered for one of the imported saponins (Kalbaum), which, under the adopted measurement conditions, forms comparatively stable films between the rings, possessing high mechanical properties.

In Fig. 1 are shown curves of the dependence of ε on P for double-sided films formed from solutions with various concentrations C. Here

$$\varepsilon = \frac{2\theta R_2^2}{R_2^2 - R_1^2}$$

and

$$P = \frac{C_0(\varphi - \theta)}{2\pi R_1^2},$$

where θ is the displacement of the inner ring, φ is the angle of twist of the upper end of the thread, and C_0 is the elastic constant of the thread.

Fig. 2

Figure 2: Fig. 2

It is seen from the curves that when P reaches a certain value $P = P_r$ (found by extrapolation to the abscissa axis, but which more accurately should be determined from the maximum of the curve of the dependence of P on ε [4]), ε increases especially rapidly; this indicates the occurrence of flow connected with destruction of the structure.

In Fig. 2 are shown curves of the dependence of ε on P for surface layers in the same saponin solutions. In general they are similar to the curves for films, but differ in a less abrupt transition to the vertical portion reflecting destruction of the structure and flow. Since films at $C < 0.05\%$ are unstable in the rings, it was not possible to determine their structural shear strength. For surface layers the data were obtained for solutions down to $C = 0.001\%$.

Fig. 2. Curves of the dependence of ε on P for surface layers in saponin solutions.
1–0.005%; 2–0.01%; 3–0.05%; 4–0.1%; 5–0.2%; 6–0.5%; 7–1%

In Fig. 3 are shown curves of the dependence of P_r on C for double-sided films and for surface layers of solutions, in both cases for fresh solutions and for solutions aged for 3 days.

It follows from Figs. 1-3 that, whereas P_r of **surface layers** in fresh solutions, measured a short time after their formation, in agreement with previous data of a number of authors ([5]), increases continuously with increasing concentration, P_r of **bilateral films** formed from the same solutions passes through a sharp maximum in the region of comparatively low solution concentrations ($C = 0.1\%$). For films formed from aged solutions, this regularity is basically preserved, but the strength of the structure is increased. In the surface layers formed from aged solutions, however, an even more distinct maximum appears in the range of low concentrations ($C = 0.005\%$).

Differences in the values of P_r for films and surface layers of solutions show that at small C, where P_r of the film is 3-4 times greater than P_r of the surface (whereas the number of adsorption layers in the film is only 2 times greater than in the surface), components pass preferentially into the film that impart to it greater shear strength. The selectivity of the transfer of some components into the film is also confirmed by the shape of the $P(\varepsilon)$ curves. In films at small C, the $P(\varepsilon)$ curves pass more steeply into the region of flow associated with destruction of the structure (Fig. 2).

Fig. 3. Curves of the dependence of P_r on C for bilateral films *(1 and 2)* and surface layers *(3 and 4)*. *1* and *3*–from freshly prepared solutions; *2* and *4*–from solutions aged for 3 days.

The decrease of P_r of the films to P_r of the surface with increasing C indi-

Fig. 3. Curves of the dependence of P_r on C for bilateral films (1 and 2) and surface layers (3 and 4). 1 and 3—from freshly prepared solutions; 2 and 4—from solutions aged for 3 days.

Figure 3: Fig. 3. Curves of the dependence of P_r on C for bilateral films (1 and 2) and surface layers (3 and 4). 1 and 3—from freshly prepared solutions; 2 and 4—from solutions aged for 3 days.

cates that the strength of the adsorption layer in the film reaches only half the strength of the surface; i.e., less "strong" components now pass preferentially into the film. This indicates that in concentrated solutions the "strong," more active components are more firmly bound to the less strong components. It is possible that the latter are more hydrophilic and solubilize the less hydrophilic, more active components. At low solution concentration, dissociation of such components is possible, and the more active components, being in an isolated state, more readily pass selectively into the film. During aging of a saponin solution, accompanied by hydrolytic splitting, more active components apparently accumulate; as a result, the stability of the films increases and the shear strength of the films increases. This process is confirmed by the greater brittleness of surface layers formed from aged solutions, especially after additional aging of the layers themselves for 20 min (Fig. 4). Here the aging of the layers themselves is of greater importance at low C of the solution, where accumulation of the most active and "strong" components is possible. It is often considered that micelles are absent in saponin solutions. Indeed, micelles similar to those formed in soap solutions are probably not present here. However, phenomena of solubilization are not thereby excluded. Undoubtedly, saponins, even carefully purified ones, and still more ordinary commercial ones, contain components with different surface activity, also differing in molecular structure; therefore phenomena of solubilization or dissociation of complexes in saponin solutions must be regarded as quite possible.

In the experiments described above, the role of the middle part of the bilateral film apparently is not significant in the sum of its mechanical properties. At the same time, cases are observed when the mechanical properties and structure

the middle part of the film play a large role in comparison with the adsorption layers of the film. Thus, if several double-sided films are formed successively from aged solutions of cyclamen and gladiolus saponins, their viscosity will decrease continuously. For example, for a cyclamen solution with $C = 0.5\%$, on going from film No. 1 to film No. 12 the viscosity decreases from 1.3 to 0.016 surface poise. When the solution is allowed to rest, the viscosity of the films again increases, tending toward its initial value. These phenomena can be explained by a transition of the structure formed in the bulk of the solution into the middle part of the film. Such a structure may be thixotropically destroyed in the bulk of the solution in the process of the inevitable mixing of the solution during successive formation of films, and may be restored when the solution is

at rest, thereby affecting both the structure and the mechanical properties of the film.

Fig. 4. Curves of the dependence of ε on P for surface layers of saponin solutions of various concentrations. 1 –in the surface layer 2-3 min after its formation; 2 –in the same layer after 20 min of aging following the end of the preceding measurement. Solid lines –freshly prepared solutions; dashed lines – solution aged for 3 days.

It is interesting that, together with the decrease in viscosity of successively formed films, their stability also decreases (from 18 to 2 min). Thus, in this case a parallelism is observed between the mechanical properties of the films and their stability in rings. However, it cannot be asserted that such parallelism exists in all cases, or that the mechanical properties completely determine the stability of films and foams.

It should be borne in mind that the adsorption layers in films and on the surface of a solution, in all the cases listed, are nonequilibrium.

The differences considered here in the properties and composition of adsorption layers in double-sided films and in surface layers make it possible to explain many features of the stability of foams and the results of investigations of the mechanical properties of adsorption layers obtained by various authors.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
1 VI 1957

CITED LITERATURE

1. A. A. Trapeznikov, in: *Viscosity of Liquids and Colloidal Solutions*, 1, 1941, 67, 87.
2. A. A. Trapeznikov, *Kolloidnyi Zhurnal*, 19, 252 (1957).
3. A. A. Trapeznikov, *Kolloidnyi Zhurnal*, 12, 67 (1950).
4. A. A. Trapeznikov, V. A. Fedotova, *DAN*, 81, 1101 (1951).
5. P. A. Rebinder, A. A. Trapeznikov, *ZhFKh*, 12, 573 (1938).
6. N. M. Lubman, *ZhFKh*, 1, 730 (1930).

Note: Figure translations are in progress. See original paper for figures.