Collapse of polyhedral two-dimensional foams

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The comparative experiments with monolayer and bulk foams of the same composition gave the reliable evidence of collective effects at the collapse of bulk foams.

It is well known that the lifetime of a foam depends on the pressure drop across the liquid phase of the foam.[1] Moreover, a critical pressure drop at which a foam was completely broken in 0.5–2.5 min was found for many foams.[1–3] In foams stabilised with non-ionic surfactants like oxyethyl derivatives of alcohols, acids and alkylphenols, this critical pressure strongly depends on temperature.

The properties of films in a three-dimensional foam are different from the properties of individual (model) foam films. This difference results form the fact that the size and shape of films in a foam are different, and the kinetics of attaining hydrostatic equilibrium in the films is more complicated in comparison with free films. In addition, co-operative effects occur in foams. These effects are a consequence of the transfer of local perturbations, caused by ruptures of particular films and by the disturbance of a local balance, to neighbouring films and bubbles.[1]

The aim of this work was to examine the effect of pressure drop in the liquid phase of a foam at constant temperature ($T = \text{const}$) and the effect of temperature at $\Delta P = \text{const}$ on the lifetime of a two-dimensional (monolayer) foam and to compare the obtained data to the analogous properties of three-dimensional foams for revealing the role of co-operative effects in the collapse (break) of a foam column.

The foam was produced by bubbling a gas through a porous membrane (the filter pore diameter was 40 mm) into a surfactant solution. The average diameter of the generated bubbles was about 0.9 mm.

The foam was arranged on a glass filter between two glass plates placed in a plane 1 cm apart and covered with a cover glass at the top. Thus, the foam was in contact with the porous membrane on one side and with glass plates on other three sides. In different experiments, the glass thickness (and, correspondingly, the foam layer thickness) was 1, 2 or 4 mm. The entire system was placed in a thermostatted jacket to maintain a required constant temperature. This method for studying a foam monolayer differs from known methods,[1,4] in particular, from the method of studying a dynamic (renewable) bubble monolayer on the surface of a surfactant solution.[5] The method used allowed us to produce a fully polyhedral foam throughout the height of the monolayer with a controlled positive (capillary) pressure of the liquid phase; the pressure could be varied in particular experiments.

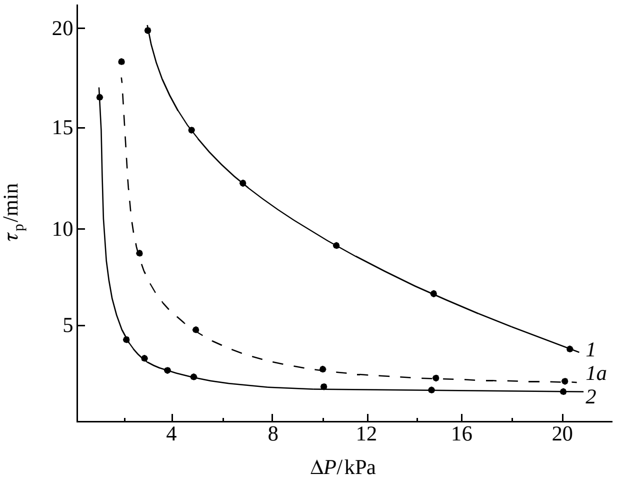

Figure 1 The lifetime of foams as a function of the pressure drop for foams prepared of a mixture (2:1) of OP-7 and OP-4 solutions (c_{total} = = 0.3 wt% + 0.2 mol dm^{-3} NaCl): (*1*) two-dimensional foam, (*1a*) bilayer foam and (*2*) three-dimensional foam (h = 2 cm).

The kinetics of attaining steady-state pressure in the borders of a monolayer foam is beyond the scope of this work since it is well known that the equilibrium capillary pressure was attained rather rapidly (in 1–1.5 min) in a porous membrane even at high pressure drops (up to 10 kPa)[1] and in a monolayer foam.[6]

We studied monolayer foams of solutions for which three-dimensional foams exhibited different break patterns when a reduced pressure was produced in the liquid phase of the foams.

Three-dimensional foams were examined in a thermostatted cell; a Por 40 filter served as the bottom of the cell. In the gravitational field (without a pressure drop applied), monolayer foams of non-ionic surfactants on a porous membrane at 20 °C and a foam of a lysozyme solution exhibited the lifetimes of longer than a hour and about 0.5 h, respectively. The previously developed method[1] was used for producing a pressure drop in the foam and the corresponding equilibrium capillary (and disjoining) pressure. According to this method, the foam was brought into contact with a porous membrane the pressure beneath which was reduced. The difference in the pressures above the foam and below the porous membrane was no higher than the capillary pressure in the filter pores in order for only the liquid and not the gas can pass through the pores.

Figure 1 demonstrates the functions $\tau_p = f(\Delta P)$, where τ_p is the foam lifetime at the pressure drop, for monolayer, bilayer and three-dimensional foams produced from a mixture of OP-7 and OP-4 (commercial oxyethylated octylphenols) solutions in the ratio 1:2 ($c_{\text{total}} = 0.3$ wt%) with the addition of NaCl (0.2 mol dm^{-3}) at 20 °C. The break of the three-dimensional foam of this solution was avalanche-like at pressure drops higher than 3.5 kPa. A further increase in the pressure did almost not shorten the foam lifetime.

As can be seen in Figure 1, the lifetime of monolayer foams of the non-ionic surfactants progressively decreased as the pressure was increased from 2 to 20 kPa. In this case, only a

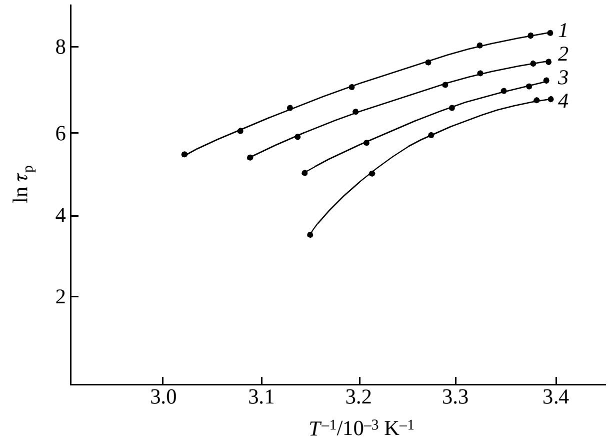

Figure 2 The function $\tau_p = f(1/T)$ for monolayer foams prepared of a mixture (2:1) of OP-7 and OP-4 solutions; ΔP = (*1*) 2, (*2*) 3, (*3*) 5 and (*4*) 7 kPa.

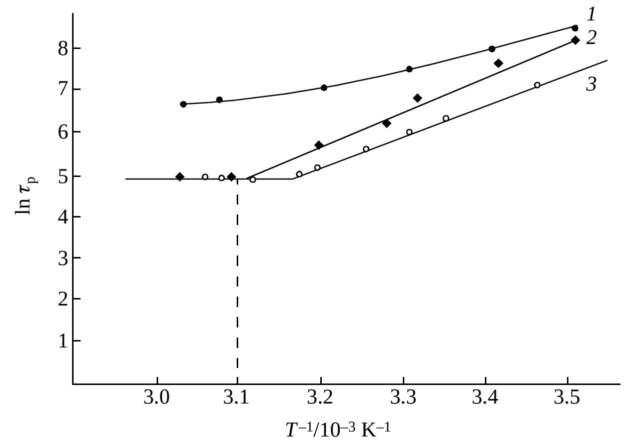

Figure 3 The function $\tau_p = f(1/T)$ for three-dimensional foams prepared of a mixture (2:1) of OP-7 and OP-4 solutions at different capillary pressures; ΔP = (*1*) 0.5, (*2*) 1 and (*3*) 2 kPa.

decrease in the average degree of dispersity of the foam was observed over a long time as a consequence of the diffusive gas transfer from small to larger bubbles, which were further combined by lateral coalescence to form two-dimensional cavities.

The lifetime of foam monolayers shortened from 25 to 5 min as the pressure was increased from 2 to 10 kPa. The lifetime of a foam microvolume (of an approximately bilayer foam) was closer to the lifetime of a three-dimensional foam.

In going to microvolumes (a foam height of 2 mm) at T = 20 °C and ΔP = 2–10 kPa, a decrease in the foam lifetime to 10 or 3–4 min was observed at ΔP = 2 or 10 kPa, respectively, for the mixture of OP-7 and OP-4 solutions. As the pressure was increased, the formation of cavities, which occupied 1/4 to 1/3 of the total foam volume, was occasionally observed on the periphery of a microvolume; these cavities were formed very rapidly (like an avalanche).

The monolayer foams of lysozyme solutions exhibited a different behaviour. Thus, at ΔP = 1 kPa, initially, the bubbles rapidly enlarged by diffusion within the first minute; next, intense coalescence primarily on the periphery of the monolayer was observed in 3–4 min. The foam was completely broken by five minutes. Lysozyme foam microvolumes were broken at and separated from the filter. The lifetime of these foams was no longer than 2 min.

Figure 2 demonstrates a semilogarithmic plot of the lifetime of monolayer foams as a function of the reciprocal of temperature ($1/T$) at different pressure drops. The foams were obtained from a mixture of OP-7 and OP-4 solutions in the ratio 2:1 (c_{total} = 0.3 wt%) with NaCl added (0.2 mol dm^{-3}). The experiments were performed at temperatures below the cloud point, which is 58 °C for the above mixture.

It can be seen in Figure 2 that the lifetime of the two-dimensional foam shortened with increasing pressure drop in the liquid phase and with increasing temperature. However, a critical temperature at which the break becomes avalanche-like was not observed.

Similar $\tau_p(1/T)$ functions were obtained for a foam of a Triton X-100 solution (5×10^{-3} mol dm^{-3} + 0.4 mol dm^{-3} KCl). The lifetimes of two-dimensional foams prepared from this solution shortened with increasing pressure drop at T = const. For example, at 40 °C, τ_p = 720, 620 and 210 s at ΔP = 3, 5 and 10 kPa, respectively.

As was mentioned above, the critical pressure for a foam of a mixture of OP-7 and OP-4 at T = 20 °C was equal to ΔP = 3.5 kPa. Because of this, the temperature dependence of the lifetime of these foams at a height of 2 cm was studied at $\Delta P < \Delta P_c$; this dependence is shown in Figure 3. As can be seen, the pressure drop ΔP = 0.5 kPa was not critical at any temperature up to the cloud point. At a pressure drop of 1 or 2 kPa, the break of the foam became avalanche-like at T = 50 or 44.5 °C, respectively. Curves *2* and *3* in Figure 3 exhibit inflection points, which were shifted towards lower temperatures with decreasing capillary pressure.

The temperature function $\tau_p(1/T)$ for non-ionic surfactants is the exponential, which is typical of activation processes with overcoming energy barriers,[1,7,8]

$$\tau_p = \tau_p^0 \exp(E_p/RT),$$

where E_p is the effective (apparent) activation energy of the break of foams; R is the gas constant; and T is the absolute temperature.

This function corresponds to the linear portions of the curves to the right of the inflection points.

The E_p values for foams of a mixture of OP-7 and OP-4 were graphically found from the slopes of the linear portions of curves *2* and *3* to be equal to 70.63 and 62.33 kJ mol^{-1} (at ΔP = = 1 and 2 kPa, respectively).

To elucidate the mechanism of the break of foams of Triton X-100 solutions, in addition to a monolayer foam, foam microvolumes 2 and 4 mm in height (which correspond to ~2 and 4 bubble layers) were also examined. The $\tau_p(1/T)$ curves also exhibited inflection points typical of three-dimensional foams prepared from the same solution.[7,8]

The lifetimes of foams shortened with increasing thickness of the layer at constant temperature.

We found that an increase in the positive (capillary) pressure in the liquid phase resulted in a decrease in the lifetime of all foams. However, the lifetime of a monolayer foam was significantly longer at all pressure drops, and the mechanism of breaking was different from that in three-dimensional foams.

In a monolayer foam, the lifetime shortened as the pressure was increased because of accelerating outflow of the liquid and attaining successively higher disjoining pressures. This resulted in a decrease in the film thickness and the activation barrier of rupture. For this reason, the diffusive gas transfer (diffusion enlargement of the average size) and the lateral coalescence were accelerated. However, a critical pressure with the instantaneous break of the entire foam was not attained in solutions of the non-ionic surfactants examined.

It is evident that this behaviour of monolayer foams is due to restricted possibilities for the transfer of local perturbations from one bubble to another in the course of the film rupture because of fixation of the Plateau–Gibbs borders of the foam by a solid support on all sides.

On the other hand, the lifetime and the character of breaking were almost identical in monolayer and three-dimensional foams with structured adsorption layers having high surface viscosity.

Thus, comparative experiments with monolayer and three-dimensional foams provided a convincing demonstration of the occurrence of co-operative effects which come into play in a foam even in thin layers, beginning with a foam bilayer.

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