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Foam Fractionation and Drainage

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Summary

The effect of drainage on the lesser accumulation ratio $\mathcal{R}$ in foam is calculated. If time t_0 alloted to drainage is varied, $\ln(\mathcal{R} - 1)$ is expected to be, in simplest instances, proportional to t_0. The expansion factor $1/\varphi$ of the foam, when this reaches the receptacle, depends on t_0, but the product $(\mathcal{R} - 1)\varphi$ ought to be independent of t_0. These conclusions are not contradicted by the meager published data.

The efficiency of accumulation in foam depends on the rate of drainage. This dependence can be expressed in mathematical terms. Let the weight-to-volume concentration of the solute in the collapsed foam be c_f g/cm^3 and assume that the evaporation of the components is negligible. Let the corresponding concentration in the bulk liquid be c_0. In a batch experiment, this c_0 varies in time; if the solute accumulates in foam, c_0 is greater at the start than at the end of foaming. The c_0 to be used for further calculations is the time average of the bulk concentration. In a continuous separation, the value of c_0 is maintained constant by adding fresh liquid to the vessel in which foaming takes place. The ratio $\mathcal{R} = c_f/c_0$ is the lesser accumulation ratio (*1*).

A foam lamella may be approximated as a sandwich whose external layers contain mainly the solute, and the composition of the interior layer is almost identical with that of the bulk liquid. If δ is the total thickness of a foam film, and x is the thickness of each surface layer, then the amount of solute in 1 cm^2 of the film is $c_0(\delta - 2x) + 2\rho x$; ρ is the concentration (g/cm³) of the solute in the surface layer; if this layer consists practically of solute only, ρ is the density of the solute material. Thus, the solute concentration (i.e., its amount in unit volume of the lamella) is

$$c_f = c_0\left(1 - \frac{2x}{\delta}\right) + 2\rho\frac{x}{\delta} \tag{1}$$

and the accumulation ratio is

$$\mathcal{R} = \frac{c_f}{c_0} = 1 - \frac{2x}{\delta} + \frac{2\rho x}{c_0\delta} \tag{2}$$

Of the variables present in the right-hand side of Eq. (2), only δ greatly changes during drainage, whereas x, ρ, and c_0 are almost constant as long as the chemical nature of the system does not change. Hence the difference $\mathcal{R} - 1$ is mainly a function of the ratio x/δ; indeed,

$$\mathcal{R} - 1 = \frac{2x}{\delta}\left(\frac{\rho}{c_0} - 1\right) \tag{3}$$

Usually, c_0 is much smaller than ρ, so that $\rho/c_0 >> 1$; thus, $\mathcal{R} - 1$ increases with x/δ, that is, with progressing drainage.

In the usual drainage measurements, not the gradual decrease of the lamella thickness δ, but the volume V of liquid oozed out of the foam is determined. However, as long as no significant bubble bursting takes place and as long as the major part of the liquid is situated in the lamellae (rather than in the Plateau borders (*1*)), δ is proportional to $V_0 - V$, if V_0 is the liquid volume in the fresh foam. If δ_0 is the average lamella thickness before drainage, then (in a perfectly stable foam)

$$\frac{\delta}{\delta_0} = \frac{V_0 - V}{V_0} \tag{4}$$

Many empirical and semiempirical formulas have been suggested for V as a function of time (*1*). They can equally well be applied to the time dependence of δ. For instance if

$$V = V_0(1 - e^{-kt}) \tag{5}$$

where t is time and k is a constant, then

$$\frac{V_0 - V}{V_0} = \frac{\delta}{\delta_0} = e^{-kt} \tag{6}$$

Consequently, see Eq. (3),

$$\mathcal{R} - 1 = \frac{2x}{\delta_0}\left(\frac{\rho}{c_0} - 1\right)e^{kt} \tag{7}$$

that is, $\ln(\mathcal{R} - 1)$ is proportional to t. This expectation can be tested on the available experimental data, however meager they are.

In some experiments, described only in U.S. Government reports (*2*), 0.1% solutions of commercial sodium dodecyl sulfate containing also small amounts of calcium chloride were foamed (batchwise) at different rates (u cm/sec) of air flow. The distance H between the liquid–foam boundary and the outlet tube for the foam was practically constant, so that the time (t_0) available for drainage (i.e., H/u) was inversely proportional to u. When this t_0 was 370, 730, 1230, and 3450 sec, the mean values of $\mathcal{R} - 1$ were, respectively 5, 6, 10, and 18. Hence, approximately, $\ln(\mathcal{R} - 1) = 1.3 + 0.0007t_0$. The coefficient of t_0 (i.e., 0.0007 sec^{-1}) ought to be identical with the k of Eq. (5) valid for the drainage of identical solutions. Unfortunately, the time dependence of V for these liquids has not been measured, but the drainage of 0.2% sodium dodecyl sulfate solutions was investigated and presented as a curve (*3*) of $V = f(t)$. The constant k seems to be about 0.002 sec^{-1} from this curve.

In analogous experiments (*4*) on the batch accumulation of trimethylhexadecyl ammonium phenolate (0.00059 *M* aqueous solutions) in foams produced by nitrogen injection, data were obtained that satisfied the approximate equation $\ln(\mathcal{R} - 1) = 1.0 + 0.0006t_0$. No measurements of drainage rate, from which the value of k [Eq. (5)] for this phenolate could have been calculated, are known to the author.

The time t_0 alloted to drainage can be altered also by altering the height H rather than the flow rate u. A 0.009% solution of dimethylethylhexadecyl ammonium bromide was foamed (*5*) at constant u and two different heights (15 and 78 cm). When $t_0 = H/u$ was about 14 sec, $\mathcal{R}$ was near 1.6; and at $t_0 = 75$ sec, $\mathcal{R}$ was about 4.0. From these two values, $\ln(\mathcal{R} - 1) = -0.86 + 0.026t_0$. No independent value for the drainage constant k for this solution is available. The rate of drainage of 0.2% dodecylamine hydrochloride solutions was shown in a graph (*3*), from which k seems to be near 0.0035 sec^{-1}. Obviously, new measurements of $\mathcal{R}$, t_0, and k on identical systems would be highly desirable.

The dependence of $\mathcal{R}$ on the duration of drainage can be expressed also without directly referring to time. When lamellar thickness δ dedecreases, the volume φ of liquid present in unit volume of foam decreases and, naturally, the expansion factor $1/\varphi$ increases. It follows from Eq. (3) that

$$\mathcal{R} - 1 = \frac{xA}{\varphi}\left(\frac{\rho}{c_0} - 1\right) \tag{8}$$

where A is the area of the gas–liquid interfaces in unit volume of foam. Hence the product $(\mathcal{R} - 1)\varphi$ ought to be almost independent of the rate u or the time t_0 (in a stable foam). This rule is in agreement with some data in the literature (*2*).

When a solution of sodium dodecyl sulfate and ferrous sulfate was foamed at two different air rates (so that t_0 was 1100 or 2200 sec), the $\mathcal{R}$ for the surfactant was, respectively, 12 and 102, whereas the expansion factor was 1730 and 15000. Thus the product $(\mathcal{R} - 1)\varphi$ was, for the two u values, 0.0064 and 0.0067, i.e., almost constant. The confirmation was less exact but still satisfactory in the instance of a solution of Alipal CO-433 [sulfate of a poly(ethylene oxide)] and ferrous sulfate. When t_0 was raised from 1000 to 2000 sec, the accumulation ratio rose from 3.5 to 15.5, and $1/\varphi$ increased from 200 to 1580 so that $(\mathcal{R} - 1)\varphi$ changed only from 0.012 to 0.009.

The data reported by Jacobelli-Turi (*4*) exhibit an unexpected trend. When $\mathcal{R}$ decreased from 105 to 45, 28, and 12, the expansion factor decreased from 4470 to 1700, 810, and 210, so that the value of $(\mathcal{R} - 1)\varphi$ was, respectively, 0.023, 0.026, 0.033, and 0.053 for the four experiments. No convincing explanation can be offered here for this increase of the product with $1/\varphi$, but it is clear that this product varied much less than did $\mathcal{R}$ and φ separately. Repetition of these tests, with due regards to the possible evaporation of phenol and to the foam collapse at low nitrogen rates, presumably will shed light on the above trend.

At any rate, Eq. (7) and (8) seem to be helpful in understanding the accumulation in foam. If the amount of liquid present in the Plateau borders is not very small compared with that in the lamellae, the geometrical meaning of δ changes but the general relations between $\mathcal{R}$ and t_0 and between $\mathcal{R}$ and φ apparently still are valid.

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