STUDY OF GAS EXCHANGE BETWEEN BUBBLES IN FOAM

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Gas diffusion in foam through the liquid film that separates bubbles due to the capillary pressure difference in different-size bubbles is considered. The system of integral equations is obtained which determines the interdependent bubble size variation. The process is numerically modeled, which shows that gas exchange is important in the foam destruction process.

Foams that appear due to the mixing of gas and liquid on the surface of natural pools or in processing plants are highly concentrated complex-structure dispersed systems that consist of many thin liquid film-separated different-size bubbles having an irregular shape [1, 2]. An extremely developed interphase surface provides free energy excess, thus causing constant structure deformation and rapid foam destruction that visually manifest in disappearing fine and then in growing and destructing coarse bubbles. In this process, called syneresis, the effects bound up with the liquid flowing in films and channels that separate the bubbles have been well studied. The role of gas exchange between the bubbles has been hardly investigated. At the same time, to control the properties of the foam, first, the existence time necessary to perform technological processes requires rather complete knowledge of the interdependence between the foam structure parameters and the characteristics of the liquid and the bubbles that form the foam.

Until now, in modeling the foam dynamics [3], account of the role of gas exchange between the bubbles is based on the data of [4] where the bubble completion time in the boundless liquid is estimated or on the results of [5] where the diffusional growth of an isolated bubble is considered with regard to the gas concentration change in the surrounding liquid. In either case, the most essential factors that specify gas exchange have been omitted. These are the thickness and properties of the film separating the bubbles and the size ratio of the neighboring bubbles. In the present article, based both on the schematic presentation of the foam structure and on the assumption that the diffusional gas flow is constant over the film thickness, the physical model of the process is constructed and a system of equations is obtained which characterizes the bubble size variation due to gas diffusion from a smaller to a larger bubble.

Figure 1a is a schematic of the real foam structure. Its specific features are approximately the same film thickness of the liquid between the bubbles, which reduces the free surface energy of the system [2] to minimum, and the wide size spectrum of the bubbles having a very irregular shape. In constructing the model for diffusional exchange adequate to the real foam structure, the latter circumstance requires all foam elements to be included into it, which is impossible in practice. For the problem considered it is expedient to model the foam structure by spherical bubble aggregation and to examine the elementary volume of the foam (Fig. 1b) that contains a central coarse bubble with a radius R_l and finer bubbles with a radius R_s uniformly distributed over the coarse bubble surface. A third row is located behind the fine bubbles, whose role is taken into account in the mathematical model by making a correction for the gas flow. In this case, the liquid film between the bubbles has a variable thickness taken into account in the model by some mean ("effective") quantity δ_e. It is assumed that the number of fine bubbles being in contact with the coarse bubble is determined from the following condition: on the surface of the sphere with a radius $R_l + R_s$ the fine bubble occupies an area equal to the area of the hexagon covering its circumference $2\sqrt{3}R_s^2$, i.e.,

$$n = \operatorname{int}\left[\frac{2\sqrt{3}\pi}{3}\left(1+\frac{R_l}{R_s}\right)^2\right]. \tag{1}$$

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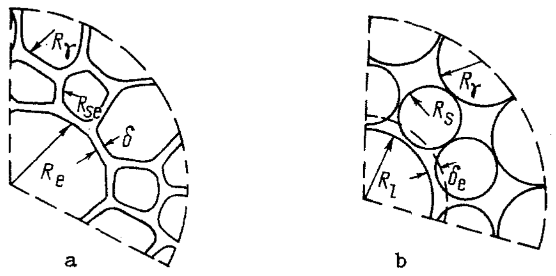

Fig. 1. Structure (two-dimensional representation) of the real foam (a) and its schematic representation by spherical bubbles (b).

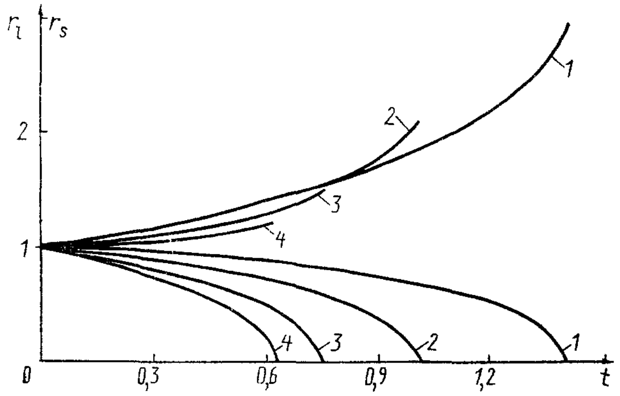

Fig. 2. Dimensionless time variation of the relative sizes of the coarse and small bubbles at different initial size ratios: 1) $r_0 = 1.5$; 2) 2.5; 3) 5.0; 4) $r_0 = 10$.

With an increase in the ratio R_l/R_s, the number of fine bubbles being in contact with the coarse one must increase due to the movement from the third row to the second. It should be noted that an alternative model for the foam structure can be given in the form of cubes (or similar figures). In this case, the constant thickness of the film separating the bubbles corresponding to the real foam is preserved but calculation of the capillary pressure requires one to include some "effective" radius of a "cubic bubble," which is no less conventional than the concept of "effective" film thickness in the accepted model.

We shall present the gas pressure in a spherical bubble as the sum of the external and capillary pressures minus the liquid vapor elasticity

$$P_g = P_\infty - P_v + \frac{2G}{R}. \tag{2}$$

By using the Mendeleev–Clapeyron equation, it is possible to determine the gas mass in a bubble

$$m_g = \frac{4}{3}\pi R^3 \left(P_\infty - P_v + \frac{2G}{R}\right)\left(\frac{BT}{\mu}\right)^{-1}. \tag{3}$$

We shall give the gas flow into the bubble through the unit surface according to the Fick law as a product of the gas diffusion coefficient through the bubble boundary and the gas concentration gradient at the boundary [6]

$$\frac{dm}{dt} = 4\pi R^2 D \left(\frac{\partial C}{\partial r}\right)_{r=R}.$$

This expression enables one to determine the amount of gas diffused into the bubble (or from it) during the time t as follows:

$$\Delta m_g = 4\pi D \int_0^t R^2 \left(\frac{\partial C}{\partial r}\right)_{r=R} dt. \tag{4}$$

By referring expression (3) to the initial conditions and by using the last expression, let us give the gas mass variation in the bubble vs. time as follows:

$$m_g(t) = \frac{4}{3}\pi R_0^3 \left(P_\infty - P_v + \frac{2G}{R_0}\right)\left(\frac{BT}{\mu}\right)^{-1} + 4\pi D \int_0^t R^2 \left(\frac{\partial C}{\partial r}\right)_{r=R} dt.$$

Now, using this expression and formula (3), it is possible to determine the time variation of the gas pressure in the bubble

$$P_g(t) = \left(P_\infty - P_v + \frac{2G}{R_0}\right)\frac{R_0^3}{R^3} + \frac{3BTD}{\mu R^3}\int_0^t R^2 \left(\frac{\partial C}{\partial r}\right)_{r=R} dt. \tag{5}$$

Once more applying formula (2) in order to exclude $P_g(t)$ from (5) and solving it with respect to the bubble radius, the following equation is obtained:

$$\begin{gathered}\frac{R^3}{R_0^3} + \frac{2G}{R_0(P_\infty - P_v)}\left(\frac{R^2}{R_0^2} - 1\right) - \frac{3BTD}{\mu R_0 (P_\infty - P_v)} \times \\ \times \int_0^t \frac{R^2}{R_0^2}\left(\frac{\partial C}{\partial r}\right)_{r=R} dt - 1 = 0.\end{gathered} \tag{6}$$

This equation determines the isolated bubble radius variation in the boundless liquid depending on the sign and the value of the gas concentration gradient at the bubble boundary.

Now, let us analyze the specific features of gas diffusion through the bubble boundary in the foam. Let us consider the gas concentration at the bubble boundary to be equal to its saturation value for the gas pressure in the bubble, i.e.,

$$C_{r=R} = C_s = \alpha_{sa}\frac{P_g}{P_a}\rho_{ga}. \tag{7}$$

Taking into account that the bubbles are separated by thin films in the foam, we shall consider this gas diffusion process through the film separating the bubbles steady-state, i.e., we shall assume the gas concentration flow over the film thickness to be the same. Then it may be considered that the concentration gradient is equal to the concentration difference at the boundaries of the film based on its thickness:

$$\frac{\partial C}{\partial r} = \frac{\Delta C_s}{\delta_e}. \tag{8}$$

The gas concentration gradients at the boundary of the contacting bubbles under the accepted assumptions are equal in magnitude and different in sign. Hence, for coarse and fine bubbles, substituting (7) into (8) yields the same expression

$$\left(\frac{\partial C}{\partial r}\right)_{r=R_l} = -\left(\frac{\partial C}{\partial r}\right)_{r=R_s} = \frac{\alpha_{sa}\rho_{ga}}{\delta_e P_a}(P_{gs} - P_{gl}).$$

(Here the ordinate r refers to a system with the origin at the centers in each of the bubbles.) The gas moves from the smaller to the larger bubble since in the smaller bubble the gas pressure is high because of the higher capillary pressure. Using formula (2), we shall find

$$\Delta m_{gl} = \frac{8\pi\alpha_{sa} D\rho\mathrm{ga} G}{\delta_e P_a} \int_0^t R_l^2 \left(\frac{1}{R_s} - \frac{1}{R_l}\right) dt.$$

Substituting this expression into (4) determines the gas mass increment in a coarse bubble

$$\left(\frac{\partial C}{\partial r}\right)_{r=R_l} = \frac{2\alpha_{sa}\rho\mathrm{ga}\, G}{\delta_e P_a} \left(\frac{1}{R_s} - \frac{1}{R_l}\right). \tag{9}$$

The gas mass increment in a small bubble may be given as the 1/n fraction of Δm_{gl}, i.e., as the fraction of one of the n bubbles that surround the central coarse bubble. Let us introduce the coefficient $1 \leq \gamma \leq 2$ that determines the gas flow into the third row: at $\gamma = 1$ the gas does not diffuse into the third row, and at $\gamma = 2$ the flows into the central bubble and into the third row are the same. With the aforesaid taken into account, using (9) and determining n by formula (1), we obtain the following expression:

$$\Delta m_{gs} = \frac{8\pi\gamma\alpha_{sa}\rho\mathrm{ga} GD}{\delta_e P_a} \int_0^t \frac{R_l^2}{\operatorname{int}\left[\frac{2\pi}{\sqrt{3}}\left(1 + \frac{R_l}{R_s}\right)^2\right]} \left(\frac{1}{R_s} - \frac{1}{R_l}\right) dt. \tag{10}$$

Now we can return to Eq. (6), and applying it alternatively to the coarse and fine bubble, by substitution of expressions (9) and (10) we arrive at the system of the integral equations that determines the interdependent bubble size variation in the foam:

$$\begin{gathered}
\left(\frac{R_l}{R_{l0}}\right)^3 + \frac{2G}{R_{l0}(P_\infty - P_v)}\left(\left(\frac{R_l}{R_{l0}}\right)^2 - 1\right) - \frac{6\alpha_{sa}\rho\mathrm{ga} GDBT}{\mu R_{l0}(P_\infty - P_v) P_a \delta_e} \times \\
\times \int_0^t \left(\frac{R_l}{R_{l0}}\right)^2 \left(\frac{1}{R_s} - \frac{1}{R_l}\right) dt - 1 = 0, \\
\left(\frac{R_s}{R_{s0}}\right)^3 + \frac{2G}{R_{s0}(P_\infty - P_v)}\left(\left(\frac{R_s}{R_{s0}}\right)^2 - 1\right) - \frac{6\gamma\alpha_{sa}\rho\mathrm{ga} GDBT}{\mu R_{s0}(P_\infty - P_v) P_a \delta_e} \times \\
\times \int_0^t \frac{R_l^2}{\operatorname{int}\left[\frac{2\pi}{\sqrt{3}}\left(1 + \frac{R_l}{R_s}\right)^2\right]} \left(\frac{1}{R_s} - \frac{1}{R_l}\right) dt - 1 = 0.
\end{gathered} \tag{11}$$

Numerical integration of this system makes it possible to follow the size variation of the neighboring bubbles in the foam due to gas diffusion through the film separating them. In what follows, decreasing the smaller bubble to some minimum size under the assigned values that determine the liquid properties and the bubble parameters, as compared to the experimentally found foam existence time, will permit one to evaluate the role of diffusional gas exchange in the foam destruction process.

If we consider water and water-based solutions as the liquid, assuming that the process proceeds at normal atmospheric pressure and normal temperature, then the system of equations (11) can be essentially reduced. Under the mentioned conditions $P_\infty = P_a >> P_v$. For the bubbles $R > 10^{-5}$ m the magnitude $2G/RP_a << 1$. Passing to the relative values of the bubble radii yields

$$\begin{gathered}
r_l = \left(1 + \frac{6\alpha_{sa}\rho\mathrm{ga} GDBT}{\mu R_{l0}^2 P_a^2 \delta_e} \int_0^t r_l^2 \left(\frac{r_0}{r_s} - \frac{1}{r_l}\right) dt\right)^{1/3}, \\
r_s = \left(1 - \frac{6\gamma\alpha_{sa}\rho\mathrm{ga} GDBT}{\mu R_{s0} P_a^2 \delta_e R_{l0}} \int_0^t \frac{r_l^2 r_0^2 \left(\frac{r_0}{r_s} - \frac{1}{r_l}\right) dt}{\operatorname{int}\left[\frac{2\pi}{\sqrt{3}}\left(1 + r_0 \frac{r_l}{r_s}\right)^2\right]}\right)^{1/3}.
\end{gathered} \tag{12}$$

We shall include, in the equations, the time scale

$$t_0 = \frac{P_a^2 \delta_e R_{s0}^2 \mu}{\rho_{\text{г.a}} G D B T \alpha_{sa}}, \quad t = t_0 \tau \tag{13}$$

and we shall obtain the following rather simple system of integral equations:

$$\begin{gathered} r_l = \left(1 + \frac{6}{r_0^2} \int_0^\tau r_l^2 \left(\frac{r_0}{r_s} - \frac{1}{r_l} \right) d\tau \right)^{1/3}, \\ r_s = \left(1 - 6\gamma r_0 \int_0^\tau \frac{r_l^2 \left(\frac{r_0}{r_s} - \frac{1}{r_l} \right) d\tau}{\operatorname{int} \left[\frac{2\pi}{\sqrt{3}} \left(1 + r_0 \frac{r_l}{r_s} \right)^2 \right]} \right)^{1/3}. \end{gathered} \tag{14}$$

This system was solved on a computer by the iteration method: we specified $\gamma = 1.5$ and only varied the initial bubble size ratio as it was possible to represent all remaining parameters by one generalized time scale t_0. Figure 2 plots the results of modeling the bubble size variation by using the system of equations (14).

Now we shall estimate the time necessary to decrease a small bubble two times, assuming that $r_0 = 1.5$ and 10.0, i.e., at $R_{s0} = 1 \cdot 10^{-3}$ m, $R_{l0} = 1.5 \times 10^{-3}$ and $1 \cdot 10^{-2}$ m. By Fig. 2 for $r_s = 0.5$ we find $\tau_{0.5/1.5} = 1.205$ and $\tau_{0.5/10} = 0.500$. For sweet water and air ($P_a = 1.01 \times 10^5$ Pa, $T = 290$ K, $\rho_{ga} = 1.19$ kg·m^{-3}, $G = 73.5 \times 10^{-4}$ N·m^{-1}, $\mu = 2.9 \times 10^{-2}$ kg·mole^{-1}, $D = 2 \cdot 10^{-9}$ m^2·sec^{-1}, and $\alpha_{sa} = 0.022$) at $\delta_e = 10^{-7}$ m we find $t_{0.5} = 37.8$ and 15.6 sec, respectively, by formula (14). It is much greater than the foam existence time in pure water [1]; hence, gas exchange plays no essential role during foam destruction in pure water. The structure of expression (13) for the time scale shows that as for the case considered the time necessary to decrease a smaller bubble by two times is reduced proportionally to the decrease of the thickness of the film separating the bubbles, directly proportionally to the square of its initial radius, and inversely proportionally to the decrease of the capillary constant, diffusion coefficient, and temperature. The external pressure exerts a considerable stabilizing influence on the foam. For example, decreasing the film up to $\delta_e = 10^{-6}$ cm at a two-fold reduction of the capillary constant shortens $t_{0.5}$ five times up to $t_{0.5/1.5} = 7.6$ sec and $t_{0.5/10} = 30$ sec, and in this case gas exchange is predominant in the foam destruction.

The similar analysis by using formulas (13) and Fig. 2 may be made for different foam-forming liquids and gases. Solving the complete system of equations (12) has yielded results slightly differing from the solution of simplified system (14).

Thus, this study has enabled one to obtain the system of integral equations that can model the interdependent size variation of the bubbles in the foam due to gas exchange through the liquid film separating them. Including the generalized parameter, i.e., the time scale, combining all characteristics of the liquid, the bubbles, and the gas filling them that affect the considered process, has allowed one to easily estimate the conditions by numerical modeling when gas exchange between the bubbles is of considerable importance for the foam destruction. The obtained results essentially supplement the available representations of syneresis and can be used to predict the characteristics of the foams created in the technological processes and observed on the pool surface. In particular, the results of the present study allow the conclusion to be made that the monodispersed foams (i.e., those composed of the same bubbles) must possess the highest stability as diffusional gas exchange must be absent in them.

NOTATION

r, radius in the spherical coordinate system; t, time; t_0, time scale; R and R_0, bubble radius and initial value of the bubble for the boundless liquid; R_l, R_{l0} and $r_l = R_l/R_{l0}$, radius of a coarse bubble, its initial and relative values; R_s, R_{s0} and $r_s = R_s/R_{s0}$, radius of a small bubble in the foam, its initial and relative values; $r_0 = R_{l0}/R_{s0}$, initial bubble size ratio; R_γ, bubble radius in the 3rd row; R_e, "effective" bubble radius in the "real" foam; δ_e, mean "effective" thickness of the film separating the bubbles; P_∞, P_a, P_g, P_v, external and atmospheric pressure, gas pressure, elasticity of the vapors of the surrounding liquid in a bubble; m_g, gas mass in a bubble; μ, gas gram-mole; ρ_{ga}, gas density at atmospheric pressure; C and C_s, concentration and saturation concentration of the gas; α_{sa}, bulk saturation concentration of the gas at atmospheric pressure; T, temperature; B, universal gas constant; D, gas diffusion coefficient; n, number of small bubbles surrounding the coarse one; γ, coefficient allowing for the existence of the bubble row behind the small ones.

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