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# COALESCENCE OF COARSELY DISPERSED CONCENTRATED EMULSIONS WITH TURBULENT AGITATION

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The coalescence of drops, larger than microscale vortices, induced by velocity pulsations in concentrated emulsions is examined based on the theory of locally isotropic turbulence.

Intensification of the interaction of drops with the dispersed phase accompanying turbulent motion of fluid emulsions is widely used to increase the efficiency of different technological processes. However, under real conditions, it is difficult to establish reasonable regimes due to the nonunique relationship between the basic technological parameters. Thus, turbulent agitation increases the frequency of collisions between drops, the rate of mass transfer, the rate of chemical reactions in the dispersed phase, but, on the other hand, it decreases the dispersity and complicates the subsequent separation of phases in the emulsion system. In its turn, the dispersity of the emulsion determines the mechanisms for interaction and destruction of drops, as well as the nature of the reverse effect of the dispersed phase on the hydrodynamic parameters of the continuous medium. In this respect, the least studied are turbulent flows of unstable concentrated emulsions with a nonequilibrium dispersed phase, i.e., capable of coalescence or fragmentation.

Since the drop-size distribution in a turbulent flow of unstable emulsions is the subject of separate investigation, the effect of polydispersity is not examined in this work. It is assumed that in the range studied, changes in the concentration of the emulsion do not exhibit anomalous rheological properties, while the coalescence of drops does not create any difficulties in examining the two-phase system as a homogeneous fluid with the use of a simple quasihomogeneous model. The analysis of the coupling between the hydrodynamic and viscous characteristics of emulsions and the concentration of the dispersed phase is based on A. N.

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Kolmogorov's theory of locally isotropic turbulence and the results of experimental studies of fragmentation and coalescence processes in concentrated systems. Within the scope of the assumptions adopted, a quantitative estimate is made of the reverse effect of drops of the dispersed phase that are larger than the microscale of turbulence on the averaged velocity pulsations in the continuous medium, which is necessary to determine the rate of coalescence in coarsely dispersed emulsions.

*Fragmentation of Drops in the Dispersed Phase in a Turbulent Flow of Concentrated Emulsions.* Breakdown of drops accompanying turbulent motion of a two-phase system occurs mainly under the action of dynamic and shear stresses of the continuous medium. In the inertial interval of the homogeneous turbulent flow, the maximum size of drops, stable relative to fragmentation, which satisfy the condition $\lambda_0 \leqslant d \leqslant L$, is established in accordance with the equilibrium of dynamic and surface forces [1, 2]

$$\rho_c \bar{v}^2 d_m/\sigma = \text{const.} \tag{1}$$

Expression (1) is applicable, generally speaking, to dilute emulsions. As the concentration of drops in the dispersed phase increases, it has been established experimentally that the equilibrium size, which limits the process of coalescence in emulsions, increases [3-7]. The experiments were carried out in standard, geometrically similar agitating apparatuses, equipped with a six-blade agitator turbine and four deflecting barriers in a turbulent flow regime that is self-similar relative to the Reynolds number of the agitator. For the conditions of the agitating apparatus, Eq. (1), averaged over the drop sizes, was used in the form

$$d_{32}(W) = Cf(W)\, D_T (\rho_c N^2 D_T^3/\sigma)^{-0.6}, \tag{2}$$

where f(W) reflects the effect of the concentration of the dispersed phase on the averaged size of the equilibrium drops.

According to the data in [8], the equilibrium values of $d_{32}$ and $d_m$ differ by a numerical coefficient close to unity. For this reason, in Eq. (1), rewritten for a concentrated emulsion, after substituting $d_{32}$, only the magnitude of the constants to be determined on the right side changes:

$$\rho_e \bar{v}^2(W)\, f(W)\, D_T (\rho_c N^2 D_T^3/\sigma)^{-0.6}/\sigma = \text{const}, \tag{3}$$

where $\rho_e = \rho_c(1 - W) + \rho_d W$. Table 1 presents some of the empirical expressions for f(W), as well as the hydrodynamic characteristics of the agitating apparatuses and experimental data on the measurements of the coalescence rate in the emulsion system studied.

The generally accepted explanation of the mechanism for increasing the equilibrium size of drops is coalescence, which competes more effectively with fragmentation processes as the concentration of the dispersed phase increases [5-7, 9, 10]. Thus, with the help of the dynamic equilibrium model for fragmentation and coalescence processes for concentrated emulsions it was shown in [9] that an increase in the stable, relative to fragmentation, size of drops must be related only to coalescence, while the extinction of turbulence must be relegated to a secondary role. The validity of this assertion, obtained as a result of a very large number of assumptions, is not confirmed, e.g., by the data in [4], where a practically noncoalescing kerosene–water system was studied. In addition, the theoretical model using expressions for the coalescence and fragmentation rates that are valid for dilute systems may turn out to be inadequate for concentrated emulsions.

Another explanation of the physical essence of the phenomenon, which reflects f(W), depends on the increased effectiveness of viscosity of an emulsion system with increasing concentration of the dispersed phase. For example, in [11], the function f(W) = 1 + 3W was obtained based on the theory of the universal Kolmogorov equilibrium [1] with the help of only a linear dependence of the viscosity of the emulsion on concentration. Although this fact gives serious justification for not completely rejecting the contribution of extinction of turbulence to the increase in the size of equilibrium drops in concentrated emulsions, such an approach is very limited from the theoretical point of view. The point is that the effective viscosity of a concentrated emulsion is not a real physical parameter, especially since the linear law was obtained for completely laminar motion of the two-phase system with a very low concentration of the dispersed phase.

An estimate of the possible role of coalescence in establishing the equilibrium sizes of drops in agitators gives a comparison of the rates of coalescence and circulation. It is

TABLE 1. Characteristics of Fragmentation and Coalescence Processes for Concentrated Emulsions in Agitators (according to data from different papers)

| Composition of the emulsion system and source in the literature | Constant C in Eq. (2) | Form of the function f(W) | Range of variation of W | Dispersity | Rate of circulation $\theta_c$, 1/sec | Rate of coalescence of drops $\theta$, 1/sec |
|---|---|---|---|---|---|---|
| Toluene, benzene, xylene, chlorobenzene, $CCl_4$–water [3] | 0,060 | $1+9,0\ W$ | 0,0 –0,20 | — | — | — |
| Kerosene–water[4] | 0,051 | $1+3,14\ W$ | 0,05 –0,30 | — | 0,58–1,04 | 0 |
| Mixture of $CCl_4$ with benzene–$H_2O$ [5] | 0,058 | $1+5,4\ W$ | 0,025–0,34 | $d_{32}\sim\lambda_0$ | 0,35–1,20 | 0,00058–0,0024 |
| Mixture of kerosene with dichlorobenzene–$H_2O$ [6] | 0,081 | $1+4,47\ W$ | 0,025–0,15 | $d_{32}>\lambda_0$ | 0,66–1,05 | 0,0012–0,02 |
| 12 different organic fluids–water and a water solution of 2 M–NaOH [7] | 0,052 | exp (4 $W$) | 0,025–0,50 | — | 0,22–4,67 | — |
|  | 0,39 | 1, for We$>10^4$ | 0,025–0,50 | — | 0,22–4,67 | — |
| Mixture of $CCl_4$ with benzene–water [18] | — | Not studied | 0,10 –0,25 | $d_{32}>\lambda_0$ | 0,55–1,81 | 0,002–0,038 |
| Aqueous solution of $Na_2SO_4$–mixture of perchloroethylene with kerosene [20] | — | $W^{0,4-0,5}$ | 0,003–0,04 | $d_{32}>\lambda_0$ | 0,70–2,51 | — |

well known that the flow of fluid in an agitator moves along closed trajectories in a vertical plane, passing through the blade zone of the agitator, where drops break down. For this reason, a decrease in the number of drops due to coalescence $dn/dt = -\theta n$ is manifested only over the period of time necessary for a unit volume of the emulsion to complete a single circulation, which is determined from the equation $t_c = 0.83(D/D_t)^2/N$ [12]. The transition to finite differences with the help of the replacement of $\Delta t$ by $t_c = 1/\theta_c$ gives $\Delta n/n = -\theta/\theta_c$. Substituting from Table 1 the values of $\theta$ and $\theta_c$ obtained by different researchers, it is possible to clarify the real effect of coalescence in an agitator. In this case, it is not very great.

Extinction of Pulsations in Homogeneous Turbulent Flow. It is evident that the reverse effect of the concentration of the dispersed phase on the velocity field of the continuous medium for $d \leqslant \lambda_0$ is reflected quite completely by the viscous properties of the emulsion. In this case, the nature of the interaction of turbulent vortices with small drops depends on the averaged gradient of pulsations and as a whole is determined by the effective viscosity [13]. In coarsely dispersed emulsions, when $d > \lambda_0$, the viscous nature is retained only for the interaction of drops with pulsations whose scale exceeds that of the drops. For vortices close and smaller in size, the viscous nature of the interaction of drops gradually goes over into a dynamic nature, which is related to the redistribution of the kinetic energy from the continuous medium to the dispersed phase. In the averaged description of turbulence, this is essentially the physical meaning of the extinction of pulsations.

The maximum level of extinction of pulsations, starting from such a simplified model of turbulence in an emulsion flow, must be expected when the equilibrium drop diameters approach the upper limit of the inertial interval. Thus, even in the absence of coalescence, variation of the average drop sizes in a real polydispersed emulsion relative to the interval between the minimum and maximum vortices, having sufficient kinetic energy, can change the numerical coefficient in the linear dependence for f(W).

In this paper, in order to make a quantitative estimate of the effect of the concentration of the dispersed phase on the magnitude of the averaged pulsations, we used the following facts. The hydrodynamics of the agitating apparatus with standard construction, used in [3-8] to study fragmentation, has been well studied [14]. For $Re_M = \rho_e N D_T^2/\mu_e \geqslant 10{,}000$, the turbulent flow in the agitator becomes homogeneous, while the dissipation of energy does not depend on $Re_M$, i.e., on the viscosity of the medium being agitated. It follows from here that expression (3) represents the relationship between the concentration of the dispersed phase of the emulsion and the magnitude of the averaged pulsations. The constant on the right side of this equation is determined from the condition that the equality is conserved for $W \simeq 0$ taking into account the dependence for velocity pulsations in a homogeneous fluid in a standard agitator [15]

$$\bar{v} = 0.73\, N D_T^2 / (D^2 H)^{1/3}. \tag{4}$$

After simple transformations, for emulsions with nearby equal fluid densities ($\rho_e \approx \rho_c$), the final dependence is written in the form

$$\bar{v}(W)/\bar{v} = f(W)^{-0.5}. \tag{5}$$

Rate of Coalescence of Coarsely Dispersed Drops. In a homogeneous turbulent flow, nonequilibrium drops, larger than the microscale of turbulence, collide and coalesce under the action of velocity pulsations. For dilute monodispersed emulsions, the rate of collision between drops is determined based on turbulent diffusion of colloidal particles [16] or elements of the fluid making up the continuous medium [17], as well as with the help of the kinetic theory of gases [18]. In all cases, the following dependence is valid with an insignificant difference in the numerical coefficient:

$$\bar{\theta} \simeq \bar{v} W / d_{32}. \tag{6}$$

We note that the power 0.5 of W in [17] was obtained based on an erroneous assumption concerning the coincidence of the time scale of collisions between drops and the time scale of the diffusion of fluid elements. Actually, the rate of collisions between drops, which is the inverse of the collision time, in addition, is proportional to the concentration of the dispersed phase of the emulsion W, which gives Eq. (6) to within a constant.

Comparison of direct experimental measurements of the rate of coalescence of drops in agitators having standard construction [3, 6, 17, 19] showed that for concentrated emulsions, for $d_{32} > \lambda_0$, the power of W differs considerably from unit. The experimental values 0.5 [3], 0.45 [6], 0.6 [17], and 0.5-0.6 [19] clearly contradicts the theoretical expression (6). In order to explain this experimentally established fact, we shall use relations (2) and (5). Substituting into Eq. (6) the expressions for $d_{32}$ and $\bar{v}$ taking into account their concentration dependences, we separate out all terms explicitly depending on W:

$$F_v(W) = W / f(W)^{1.5}. \tag{7}$$

In order that the relation between the coalescence rate and the drop concentration not be studied again in this expression, in carrying out the following calculations, we shall assume that $f(W) = 1 + 3.14W$ [4].

Comparison of the functional relation $F_V(W)$ with experimentally established expressions, presented in Fig. 1, indicates that they agree quite well. The correspondence between the experimental curves I and II and the computed data 1, 2, obtained by an approximation with the help of curve V and the coefficients of proportionality 5.47 and 4.09, is convincing evidence for the validity of Eq. (5). Thus, the adequacy of the model adopted for the interaction of coarsely dispersed drops with homogeneous turbulent flow in agitators with high Reynolds numbers has been demonstrated.

The empirical dependence $W^{0.8}$ [5], which was obtained under the condition $d_{32} \sim \lambda_0$ corresponding to the gradient mechanism for coalescence of drops [13], also agrees with the theoretical representations. In this case, the concentration dependence of the rate of coalescence of drops takes the form

$$F_g(W) = W / (1 + 5.4\, W)^{0.375}. \tag{8}$$

The agreement between curve IV and data 4 of a similar calculation based on the viscous concentration dependence, used in [13] with $K_R = 2.0$ for specific calculations

$$F_g(W) = W / \exp\left[0.375\left(\frac{2.0\, W}{1 - W}\right)\right], \tag{9}$$

reflects the decrease, characteristic of this mechanism, in the averaged gradient of the velocity pulsations with constant energy dissipation in the self-similar viscosity regime $Re_M > 10{,}000$. The discrepancy of the interpretation of the gradient regime of coalescence based on the pulsation mechanism [5] leads, in addition, to erroneous conclusions concerning the decrease in the rate of coalescence of drops with increasing agitation rate instead of the natural increase in the rate of coagulation of the dispersed phase [3, 6, 11, 16-19]. Everything said above is reflected in Fig. 1 by an approximation using curve IV and the coefficient 1.86 of the empirical dependence III and calculations 3.

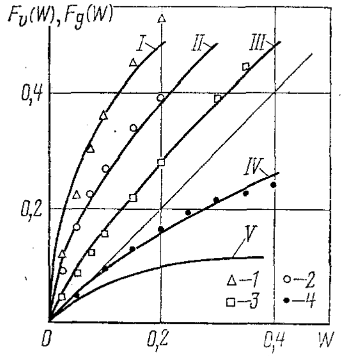

Fig. 1. Functional relation between the coalescence rate and the concentration of the dispersed phase from data on direct measurements (I — $W^{0.45}$, II — $W^{0.6}$, III — $W^{0.8}$) and based on calculations (IV from Eq. (8) and V from (7)), as well as the model approximation of the experimental data with the help of the following equations: 1, 2) Eq. (7); 3) Eq. (8); 4) Eq. (9).

In conclusion, using the data in [6, 17], we shall estimate the magnitude of the constants reflecting the efficiency of collisions of drops induced by velocity pulsations in concentrated emulsions. The relative number of theoretically possible collisions ending in coalescence is determined by the relation $\theta = K_v\bar{\theta}$. This important parameter takes into account the effect of such important factors, on the process of coagulation and not reflected in the theoretical analysis, as the properties of the boundary separating the phases, the presence of surface active substances, stabilizing additives, and other physicochemical properties of real liquid systems [20]. The quantity $\bar{\theta}$ was calculated from the dependence tested under conditions of homogeneous turbulent flow [19], written for concentrated emulsions in the form

$$\bar{\theta} = 4\sqrt{2/3\,\pi}\,\bar{v}(W)\,W/d_{32}(W). \tag{10}$$

The results of a direct measurement of $\theta$ are presented in Table 1. It turned out that under real conditions 1-10 of 100,000 collisions between drops induced by turbulent pulsations end up in coalescence. In their turn, the very low values of $K_v$ in the concentrated two-phase systems examined are also explained by a decrease inthe magnitude of the pulsations relative to the critical velocity, leading to the coalescence of colliding drops [21].

Thus, the available experimental data and Eqs. (2), (4), (5), and (10) taking into account the quantity $K_v$, which is obtained by measuring $\theta$ under model conditions or identifying real technological processes, are shown to agree quite well [20]. The dependences obtained permit calculating the coalescence in coarsely dispersed emulsions and can serve as a basis for optimizing and controlling processes that involve turbulent mixing in concentrated emulsions in a nonequilibrium dispersed phase.

## NOTATION

n, number of drops per unit volume of emulsion; t, time; $\lambda_0$ and L, micro- and macroscales of turbulence; $\rho_e$, $\rho_c$, and $\rho_d$, densities of the emulsion, the continuous, and the disperse phases, respectively; $\sigma$, interphase tension; W, concentration of the dispersed phase; $D_T$, diameter of the agitating turbine; N, rate of rotation of the turbine; D and H, diameter and height of the mixing volume; $d_{32}$, averaged volume-surface diameter of the drops; $d_m$, maximum size of drops that are stable with respect to fragmentation; f(W), concentration dependence; $\bar{v}$ and $\bar{v}(W)$, averaged magnitudes of the pulsation velocity in finely dispersed and coarsely dispersed emulsions; $\bar{\theta}$ and $\theta$, rates of collisions and coalescence of drops; $t_c$ and $\theta_c$, time and rate of circulation; $Re_M$, Reynolds number of mixer; $\mu_e$, effective viscosity of the emulsion; $K_v$, constant describing the efficiency of collisions drops induced by velocity pulsations; $F_v(W)$ and $F_g(W)$, functional relations between the rate of coalescence and concentration of drops in the inertial and gradient regimes.

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