4; Θ_1 = 0.8, and L = 24) for various values of γ. The extremal behavior of the curves as μ increases is explained by the fact that an increase in the particle concentration (optical thickness) first leads to an increase in the heat transfer by radiation, since the cold layers adjacent to the channel walls of the moving medium absorb the radiation of the core of the flow weakly due to the optical thickness. Upon a further increase in the particle concentration the boundary layers shield the radiation of the flow core more and more strongly, and the heat exchange, having reached a maximum, decreases.

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EFFECT OF INHOMOGENEITY OF THE DISPERSE PHASE ON COALESCENCE AND MASS-TRANSFER PROCESSES IN LIQUID EMULSIONS

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The coalescence of drops of a disperse phase serves as the basis for the separation of immiscible liquids in the absence of extraction and mass-transfer processes, in the chemical, pharmaceutical, food, and many other branches of industry [1]. In recent years great progress has been made in the use of highly effective demulsifiers to break up petroleum emulsions in industrial plants and oil refineries [2, 3]. However, interaction between drops, which has an exceptionally great effect on mass transfer and chemical reactions in the disperse phase, has been insufficiently studied [4].

The coalescence of drops under the action of agitation, in particular with the motion of an emulsion under turbulent conditions, is bound up with an increase in the rate of a broad range of technological processes and with an increase in the quality of mass-transfer and coagulation processes in pipelines and apparatus. An analysis of the interaction between finely dispersed drops with the break-up of emulsions by chemical methods using demulsifiers also makes it possible to solve the problem of two-phase flows in pipelines; these methods

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are bound up with a determination of the true content of the phases, and of the limits of the existence of different structural forms of the flow.

In accordance with the real conditions of the breakdown of stable emulsions, a study was made of the coalescence of an inhomogeneous disperse phase, part of whose drops is stabilized by adsorption shells, breaking down with an interaction with drops of a solution of reagent. The difference in the frequency of the effective collisions makes it possible to model the mass transfer and coalescence of the drops, accompanied by a distribution of the demulsifier in the disperse phase of stable systems of immiscible liquids. The results of numerical computer experiments make it possible to draw important practical conclusions, to calculate the attainable degree of completion of the real mass-transfer processes in the design stage, and can serve as a basis for the optimization and control of processes connected with coalescence of the disperse phase of emulsions.

1. Description of Homogeneous Coalescence

Let us consider a coagulation process in homogeneous unstable emulsions, where none of the drops of the disperse phase have adsorbed shells. For definiteness in the description of the coalescence of finely dispersed drops in an emulsion formed by two immiscible liquids, the mixing conditions are limited to turbulent flow in a horizontal pipeline. We use the equations of the material balance of the number of drops and the volume of the disperse phase in differential form, in accordance with [5, 6]

$$\frac{d\delta}{dl} = -\frac{\delta}{3n}\frac{dn}{dl}, \quad \frac{dn}{dl} = -\frac{\theta}{2}\frac{n}{v_0}, \tag{1.1}$$

where δ is the diameter; n is the number of drops in unit volume of the continuous medium; v_0 is the mean mass rate of flow in a pipeline of length l.

The coalescence model is constructed taking account of the following simplifying assumptions. The turbulent flow in the pipeline is locally isotropic; the drops of the disperse phase do not exceed the microscale of the turbulence λ_0, and are completely entrained by pulsations of the velocity of the continuous medium. The emulsion is assumed to be monodisperse and dilute. The latter makes it possible to disregard the effect of the concentration of drops on the viscosity and the characteristics of the turbulence of a two-phase flow.

The frequency of the coalescence of drops under the action of the averaged gradient of the pulsational velocities of a locally isotropic flow has the form [7, 8]

$$\theta = K_\Gamma \frac{4}{3} nR^3\Gamma, \tag{1.2}$$

where R is the effective coalescence radius of the drops, in monodisperse emulsions equal to their diameter δ; K_Γ is the constant of the collision efficiency, defined as the ratio of the number of coalescences of the drops to the total number of their collisions. In the case of locally isotropic turbulence, the averaged gradient $\Gamma = (2\varepsilon/15\nu)^{0.5}$ [9]. The dissipation energy per unit mass of the turbulent flow per unit time $\varepsilon = \lambda v_0^3/2D$ [10]. The coefficient of the hydraulic resistance is expressed in terms of the Reynolds number $Re = v_0 D/\nu$ using the Blasius formula $\lambda = 0.3164/Re^{0.25}$ (D is the diameter of the pipeline, ν is the kinetic viscosity of the continuous medium).

Taking account of the expression for the concentration of the disperse phase $W = n\pi\delta^3/6$ and the boundary condition $\delta|_{l=0} = \delta_0$, after substitution of the expression for the frequency of the coalescences (1.2), the solution of the system of equations (1.1) with respect to the diameter is written in the form

$$\frac{\delta}{\delta_0} = \exp\left(\frac{K_\Gamma W\,Re^{\frac{3}{8}}}{16.22D}\, l\right). \tag{1.3}$$

2. Model of Inhomogeneous Coalescence

The coalescence of a homogeneous disperse phase is generalized for an emulsion, the drops in which are divided into two classes, mainly due to the difference in the constants of the collision efficiency; this is done in the following way. We denote the number of such drops by n_1 and n_2, and their diameters by δ_1 and δ_2. We write the constants of the collision efficiency of identical drops in terms of K_{11} and K_{22}, and of different drops in terms of K_{12}. The expression for the frequency of coalescence (1.2), for the i-th drops with an effective coalescence radius $((\delta_i + \delta_j)/2)^3$, is taken in the following form:

$$\theta_{ij} = K_{ij}\frac{4}{3}n_i\left(\frac{\delta_i+\delta_j}{2}\right)^3\Gamma, \quad i, j = 1, 2.$$

The equation for calculation of the diameters of coalescing drops is the condition for conservation of the volume of the inhomogeneous disperse phase, which is written in the form

$$n_1\pi\delta_1/6 + n_2\pi\delta_2/6 = W. \tag{2.1}$$

In view of the fact that W = const, differentiation of the left-hand part of expression (2.1) gives, for the diameters δ_1 and δ_2, a dependence similar to the first equation of system (1.1).

In the general case, the number of drops of each class, with coalescence frequency θ_{ij}, is described by the differential equations

$$\frac{dn_1}{dl} = -\frac{\theta_{11}}{2}\frac{n_1}{v_0} - \theta_{12}\frac{n_2}{v_0}, \quad \frac{dn_2}{dl} = -\theta_{21}\frac{n_1}{v_0} - \frac{\theta_{22}}{2}\frac{n_2}{v_0},$$

with the boundary conditions

$$n_i|_{l=0} = n_i^0, \quad i = 1, 2.$$

We assume that drops with a diameter δ_1 have adsorbed shells, preventing their coalescence, i.e., $K_{11} = 0$. Drops with the diameter δ_2 contain a highly effective emulsifier, which promotes the coalescence of these drops with drops having a dimension δ_1, and the breakdown of the protective shells at the surface of the newly formed drops, bringing them into the class of drops n_2. Therefore, the diameter of the stabilized drops δ_1 = const, and their number n_1 decreases only due to coalescence with drops n_2. The number of drops n_2 can change only due to coalescence between themselves; their diameter is determined by relationship (2.1) and increases from its initial dimension of δ_2^0 to the value $\delta \leqslant \lambda_0 = D/Re^{0.75}$, which is the upper limit of the region of application of the gradient mechanism of coalescence [8].

On the basis of the assumptions adopted, the system of equations describing coalescence in an inhomogeneous disperse phase is brought to the form

$$\frac{dn_1}{dl} = -\frac{4}{3}K_{12}n_1n_2\left(\frac{\delta_1+\delta_2}{2}\right)^3\frac{\Gamma}{v_0},$$
$$\frac{dn_2}{dl} = -\frac{2}{3}K_{22}n_2^2\delta_2^3\frac{\Gamma}{v_0}, \quad n_1\frac{\pi\delta_1^3}{6} + n_2\frac{\pi\delta_2^3}{6} = W. \tag{2.2}$$

3. Evaluation of Results of Numerical Analysis

We introduce the parameters α and α_0, characterizing the relative fraction of the total concentration of the disperse phase W, represented by drops without stabilized shells:

$$\alpha = \frac{n_2\pi\delta_2^3}{6W}, \quad \alpha_0 = \frac{n_2^0\pi(\delta_2^0)^3}{6W}.$$

We bring system (2.2) into dimensionless form

$$\frac{dN_1}{dl} = -\frac{K_{12}\alpha_0 W\Gamma}{\pi\beta^3 v_0}(1+\delta_*)^3 N_1N_2, \tag{3.1}$$

$$\frac{dN_2}{dl} = -\frac{4K_{22}\alpha_0 W\Gamma}{\pi\beta^3 v_0}\delta_*^3 N_2^2, \quad N_1(1-\alpha_0) + \frac{\alpha_0}{\beta^3}\delta_*^3 N_2 = 1$$

with the boundary conditions

$$N_1|_{l=0} = 1,\ N_2|_{l=0} = 1,\ \delta_*|_{l=0} = \beta, \tag{3.2}$$

where $N_1 = \frac{n_1}{n_1^0}$; $N_2 = \frac{n_2}{n_2^0}$; $\delta_* = \frac{\delta_2}{\delta_1}$; $\beta = \frac{\delta_2^0}{\delta_1}$.

With $\alpha_0 = 1$, $N_1 = 0$, and the system (3.1) reduces to the starting equations for a homogeneous disperse phase (1.1). The system of dimensionless equations (3.1) with the boundary conditions (3.2) was solved in a computer, using a Runge–Kutta method of the fourth order of exactness [11, 12]. The absence of any special characteristics in the behavior of the system permitted the use of a finite-difference scheme with a constant spacing of the integration.

Numerical calculations were used to study the coalescence of drops of a solution of a highly effective demulsifier, under conditions where part of the disperse phase is stabilized by adsorbed shells. The turbulence of the flow was characterized by Re = 20,000; the diameter of the pipeline was taken equal to 0.2 m. A monodisperse dilute emulsion with a relative volumetric concentration of drops W = 0.01 was investigated.

It is well known that, with an increase in the concentration of drops, the damping of turbulent pulsations [13] leads, generally speaking, to a lowering of the frequency of their collisions. However, a large number of experimental investigations has shown that [14] the role of an increase in the concentration of drops increases their negative action on the collision frequency, and the efficiency of the coalescence rises. In addition, the assumption of the monodispersity of the drops lowers the total number of their collisions with respect to a polydisperse system which is equivalent in number of drops [15]. The results of the calculations describe the most favorable conditions for the breakdown of an emulsion.

Figures 1 and 2 give the results of numerical modelling of coalescence in the inhomogeneous phase of an emulsion with the parameters $K_{12} = K_{22} = 0.5$; $\beta = 1$; curves 1) $\delta_2^0 = 25$; 2) 15; 3) 10; 4) 5 µm. The value of L_0 denotes the length of the pipeline, required for the aggregation of the drops up to the value λ_0 in a homogeneous emulsion with $\alpha_0 = 1$ (according to formula (1.3)), while L reflects the effect of the stable part of the disperse phase on the aggregation of drops without adsorbed shells. Along with the aggregation of drops without adsorbed shells, there is a reduction in the number of drops with a dimension δ_1 = const, entrained into coalescence. An analysis of curves 1-4 shows that, with a decrease in α_0, the rate of coalescence drops by more than twice. This contradicts the experimental data on the breakdown of stable emulsions [1, 3]. Therefore, the modelling of coalescence allows of the conclusion that, under real conditions, K_{12} cannot be assumed equal to K_{22}.

As an illustration of the character of coalescence with different collision-efficiency constants, Fig. 3 gives curves characterizing the effect of the value of α_0 on the aggregation of drops with the parameters $\delta_2^0 = \delta_1 = 10$ µm; $K_{22} = 0.5$; curve 1) $K_{12}/K_{22} = 1$; 2) 0.75; 3) 0.5; 4) 0.25; 5) 0.1; 6) 0.01. Thus, for curves 5, 6, in the region of small values of α_0, the aggregation process practically stops, which attests to the good correspondence of the model of the coalescence of an inhomogeneous disperse phase to real processes of the breakdown of stable emulsions.

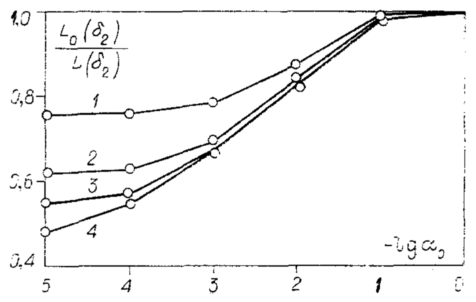

Fig. 1

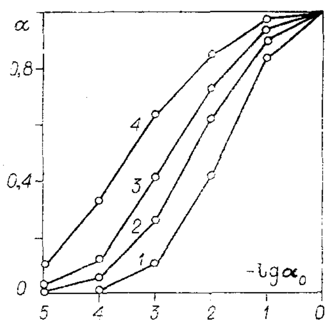

Fig. 2

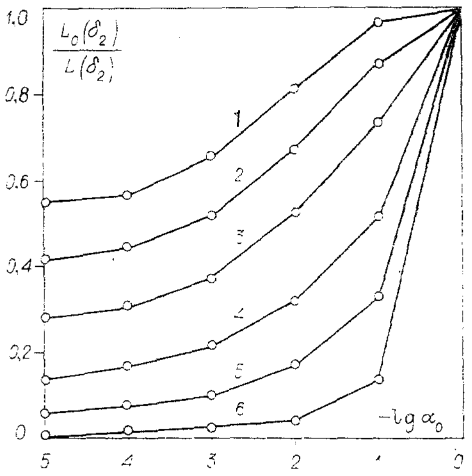

Fig. 3

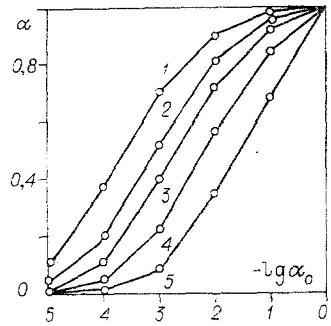

Fig. 4

It is obvious that agreement between the model and real emulsion systems is attained by the choice of appropriate collision-efficiency constants, reflecting the effect of the composition and physicochemical properties of the phases of the emulsion, of stabilizing components, and of emulsifiers of various type, on coalescence. It is practically impossible to take analytical account of the effect of these factors without bringing in experimental data on real liquid systems [16]. Only a comparison of calculated data and the results of a study of the aggregation of an actual emulsion system in model units makes it possible to take account of its individual special characteristics [17].

An investigation was also made of the effect of the ratio of the initial sizes of drops of the two classes δ_1 and δ_2^0 on the rate of mass transfer and coalescence. Figure 4 shows the results of a numerical calculation of the coalescence of a disperse phase α with the parameters δ_1 = 10 μm; $K_{12} = K_{22} = 0.5$; curve 1) $\delta_2^0/\delta_1 = 0.5$; 2) 0.75; 3) 1; 4) 1.5; 5) 2.5. It was found that, if drops with a solution of demulsifier are smaller than stabilized drops, then, other conditions being equal, the coalescence process promotes more efficient mass transfer in the disperse phase. Therefore, the drop sizes of the solution of demulsifier, along with their initial number, can serve as an effective means for acting on the process of the breakdown of stable emulsions.

It must be noted that, along with a size increase in part of the flow, finely dispersed drops with a size of δ_1 remain in the flow (in Figs. 2-4 their number is characterized by the value of $1 - \alpha$). The qualitative completion of mass-transfer and aggregation processes in the disperse phase of emulsions of immiscible liquids occurs with $\alpha \approx 1$. Therefore, the data of Figs. 1-4 can be regarded as modelling of the process of aggregation of a homogeneous disperse phase under conditions differing from those adopted in the calculations (the ideal model (1.1)-(1.3)). Then, the appearance of inhomogeneity of the disperse phase with respect to the composition, numer, and sizes of the drops can be interpreted as an actual reflection of a deviation of the real process from some calculated indices. Starting from this, a model of inhomogeneous coalescence (3.1) can be used for optimization and control of coalescence in the homogeneous disperse phase of liquid emulsions.

To take account of the effect of the residual content of drops n_1, not participating in the coalescence, on the efficiency of the aggregation of the disperse phase as a whole, the mean-volumetric drop diameter is introduced

$$\langle\delta\rangle = \delta_1 \Big/ \left(1 - \alpha + \frac{\alpha}{\beta^3}\right)^{1/3}.$$

Here, coalescence in an inhomogeneous disperse phase is limited by a size $\delta_2 = \lambda_0$ and a length of the pipeline $L(\lambda_0)$, which reflects the effect on the efficiency of the aggregation of drops with a diameter δ_1 = const, compared with the homogeneous coalescence of an equivalent number of drops with a mean size of $\langle\delta\rangle$, characterized in accordance with (1.3) by a length of the pipeline $L_0(\langle\delta\rangle)$. Figure 5 shows the character of the weakening of the coalescence in a stabilized emulsion with the parameters δ_1 = 10 μm; $K_{12} = K_{22} = 0.5$; curve 1)

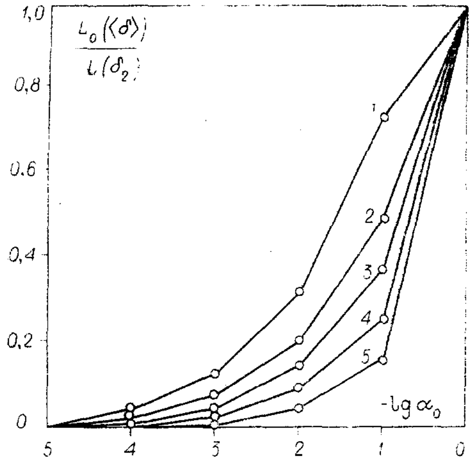

Fig. 5

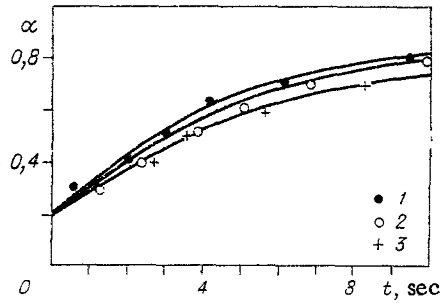

Fig. 6

δ_2^0/δ_1 = 0.5; 2) 0.75; 3) 1.0; 4) 1.5; 5) 2.5. The character of these curves attests to a considerable effect of drops with adsorbed shells on the aggregation of the disperse phase, even with the most favorable ratio of the collision-efficiency constants.

4. Determination of Constants K_{12} and K_{22}

To be able to evaluate the validity of the proposed coalescence model (3.1) from experimental data, we must know the collision-efficiency constants of dispersed drops of liquid between themselves K_{22}, as well as with drops stabilized by protective shells K_{12}.

Evaluation of K_{22}. A large number of pieces of experimental work [4] have been devoted to a study of the rate of interaction in the homogeneous disperse phase of agitated binary liquid systems, not containing emulsion stabilizers. However, in these pieces of work, the determination of the coalescence frequency is bound up with such indirect methods as investigation of the rate of distribution of a dye, the change in the concentration of the indicator, or the course of a chemical reaction. Only [18] gives the results of direct measurement using an optical pickup made of glass fiber, and high-speed cinephotography of the number of collisions of the drops ending in coalescence. It was established by visual observations that, under the conditions of the experiment, the drop size is far less than the scale of the turbulent eddies. This latter fact offers the possibility of comparing the theoretical collision frequency, calculated using formula (1.2), with measurement results given in Table 3 of [18].

The calculated value of the frequency of collisions in a mixing apparatus, taking account of the averaged value of the dissipation energy with W = 0.5%, was 1.9 sec^{-1}, while, at two points of the apparatus sufficiently far removed from the turbine, it corresponded to values of 1.3 and 3.1 sec^{-1}. Thus, the mechanism of homogeneous coalescence, the simplest form of the model (3.1) with $n_1 = n_1^0 = 0$, is rather well confirmed by the experimental data. In accordance with the well-known procedure for evaluation of the parameters of differential equations [19], this makes it possible to determine the collision-efficiency constant for drops without adsorbed shells K_{22} from the data of Table 3 of [18]. To assure the reliability of practical calculations, we take the constant as equal to its minimal experimental value $K_{22} = 0.02$.

Evaluation of K_{12}. It is obvious that, with a lowering of the strength of the interphase films, the value of the constant K_{12} approaches the upper limit of the region of possible values, corresponding to the value of K_{22}. On the other hand, the strengthening of the adsorbed films, associated with the rheological and physicochemical special characteristics of disperse systems [1-3], in the limiting case makes it possible to regard the drops as similar to solid particles. Therefore, the lower boundary of possible values of the constant K_{12} corresponds to coalescence of the drops of liquid with solid particles.

The results of an experimental investigation in a three-phase emulsion system, whose disperse phase consists of drops of pure liquid and drops containing a different number of solid crystals, are given in [20]. Depending on the content of solid particles in the drops, the efficiency of their collisions with drops of pure liquids and, consequently, the constant K_{12}, take on different values. A comparison of the experimental data and the results of calculations, together with a verification of the model of inhomogeneous coalescence, makes it possible, at the same time, to evaluate the values of K_{12} under the conditions in question. The points in Fig. 6 represent the results of an experimental study of coalescence [20] using a dye, with the reaction of components contained in drops of different sorts; the curves represent numerical calculations (1 corresponds to K_{12} = 0.0065; 2 to 0.006; 3 to 0.005). Curves 1-3 are plotted for a volumetric fraction of solid particles of 0.52, 0.65, and 0.71; the value of the parameter α_0 is taken equal to 0.2; β = 0.5; K_{22} = 0.02. The agreement was found to be very good; the values of K_{22} are in agreement with a ratio $K_{22}/K_{12} \approx 3$, obtained experimentally.

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