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# KINETICS OF BREAK-UP AND COALESCENCE OF DROPS IN MIXING VESSELS

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Processes dependent on drop sizes or specific interfacial area are usually carried out in turbulent flows, and often - in mixing equipment. Theoretical studies of drop formation due to turbulence are in most cases based on the well known work of Kolmogorov and its applications to mixing, described by several authors (Piterskich and Valashek, Calderbank, etc.). The essence of the approach consists in describing the mean size of drops formed in different flow conditions as a function of the turbulent energy dissipation rate, estimated as specific power consumption per unit of mass of agitated media:

$$\varepsilon_m = P / (\rho V)$$

This approach resulted in accumulation of important scientific and practical data. Currently used methods for the analysis of experimental and pilot-plant data and technical calculations are based on these results. On the other hand, these studies, as well as recently published theoretical results, have shown that the possibilities of an approach based on the average energy dissipation are limited to qualitative evaluations only. It became clear that further progress could only be achieved by analyzing the kinetics of breaking and coalescence of droplets in turbulent flows, and the dependence of these phenomena on local hydrodynamic conditions. Some steps in this direction have recently been made [1-3], dealing with the kinetics of drop breaking and with the distribution of the local values of turbulent dissipation as a function of mixing conditions. Synthesis of these results with an approximate analysis of coalescence is the subject of this presentation.

At the current stage of the research, the task is limited to simplified modeling of kinetics of simultaneous breaking and coalescence of droplets in the range of diameters corresponding to Kolmogorov's (non-viscous) range of linear micro-scales of turbulence. Furthermore, the mixing was assumed to be "perfect", i.e. all positions of a drop in the tank were assumed to be equally probable, and distributions of drop sizes and concentration of the disperse phase were considered uniform. The system was assumed to be monodisperse. In such conditions, the number of drops in a liquid-liquid system with defined physical properties and constant volume fraction of the disperse phase may be considered as a function of mixing intensity and process time. Its change, starting from some initial size, in a volume with non-uniform distribution of turbulence may be described by equation:

$$\frac{dd}{d\tau} = \frac{d}{3V} \int_v (N_c - N_b) dV \quad (1)$$

To use this equation, three functions should be known. The two of them, frequencies of coalescence and breaking,  $N_c$  and  $N_b$ , depend on the drop size, physical properties of the phases and local rate of turbulent dissipation of energy, while the third - distribution of turbulent dissipation by volume - depends on the macro-scale flow pattern in the mixing tank.

## THE FREQUENCY OF BREAKING

According to the results of recent studies in the kinetics of drop break-up in mixing vessels in the absence of coalescence [1-3], a quantitative description of drops break-up may be based on the universally known Kolmogorov's stability condition for a drop in a turbulent flow. An individual act of deformation and breaking must be assumed to occur under action of an instant velocity pulsation in the vicinity of the drop on the condition that the amplitude of the pulsation exceeds a certain minimum value  $v^*$ . The relation between this "critical" value and the mean square root velocity was estimated as

$$U^* = \frac{v^*}{v} = \frac{0.775}{\varepsilon^{1/3} d^{1/3}} \left( M/d + \sqrt{\left( (M/d)^2 + \frac{10\sigma}{\rho_c d} \right)} \right) \quad (2)$$

where

$$M = \left| 1.2 \frac{\rho_d}{\rho_c} v_d - 3v_c \right| \quad (3)$$

The linear scale of the "destroying" pulsations was estimated as  $l = 2.17 d$  - the minimum length of the deformed droplet, corresponding to the loss of stability. Within the framework of this model, the mean frequency of drops breaking in an area with the local turbulent dissipation  $\varepsilon$  may be estimated as

$$N_b = \text{mean frequency of pulsations of the scale } l \times \text{relative frequency of pulsations } l \text{ with amplitudes } v' \geq v^* \times \text{probability of one or more droplets residing in an area of the scale } l,$$

or

$$N_b = f_1 P(v' \geq v^*) (1 - P(0)) \quad (4)$$

where  $f_1 = \frac{1}{l^3} \frac{\varepsilon^{1/3}}{l^{2/3}}$  (5)

$$P(v' \geq v^*) \cong \sqrt{2/\pi} \int_{U^*}^{\infty} \exp(-U^2/2) dU \quad (6)$$

and  $P(0) \cong 1 - \exp(-19.6\varphi)$  (7)

## THE FREQUENCY OF COALESCENCE

The act of coalescence is usually assumed to occur (see for instance [4]) if (1) two droplets approach each other and collide and (2) the collision happens to be "efficient", i.e. the amplitude of the fluctuation is high enough to overcome the resistance of a liquid film separating the drops:

$$N_c = \text{frequency of collisions} \times \text{efficiency of collisions}$$

It seems, however, that the individual acts of collision and junction of the drops must not necessarily occur due to the same random turbulent fluctuation. The necessary condition of coalescence of two droplets may thus be assumed to consist in their being in contact as the fluctuation occurs. The term "in contact" here means that the distance between the drops' centers is practically equal to the drop diameter,  $d$ , and their surfaces are separated by a thin layer of ions existing on the water-oil boundary, water side. According to the postulates of the DLFO-theory [5], the interfacial boundary is surrounded with a "double layer" of ionized liquid. Due to interaction of these layers, the neighboring surfaces are kept from junction by electrostatic repulsive pressure,  $p$ . The value of this pressure depends on the chemical composition of substances. For "pure" oil - distilled water couple, the theoretically estimated value is about 20 Newtons per sq. m; it increases in emulsions stabilized with detergents, and decreases in solutions of flocculants and multivalent electrolytes. The coalescence only happens if the squeezing pulsational pressure is high enough to overcome the repulsive pressure. The condition for a random turbulent pulsation to be "efficient" may thus be formulated as

$$v'_n \geq v_c^* = \sqrt{(2p / \rho_c)} \quad (8)$$

where  $v'_n$  is the constituent of the pulsational velocity  $v'_\lambda$ , normal to the contact surface, and  $\lambda \equiv d$  is the linear scale of the "coalescing" pulsations.

According to this model, mean frequency of coalescence may be defined as

$$N_c = \text{mean frequency of pulsations of the scale } \lambda \times \text{relative frequency of pulsations with amplitudes satisfying the condition } v'_n \geq v_c^* \times \text{probability of the presence of two or more drops in an area of the scale } \lambda,$$

or

$$N_c = f_\lambda P(v'_n \geq v_c^*) (1 - P_\lambda(0) - P_\lambda(1)), \quad (9)$$

$$\text{where } f_\lambda = \frac{1}{\lambda^3} \frac{\varepsilon^{1/3}}{\lambda^{2/3}} \quad (10)$$

$$P(v'_n \geq v_c^*) = \frac{1}{\sqrt{2\pi}} \int_{v_c^*}^{\infty} \left(1 - \frac{V'}{V^*}\right) \exp(-V'^2/2) dV' \quad (11)$$

$$V^* = \frac{v_c^*}{v} = \frac{\sqrt{(2p / \rho_c)}}{\varepsilon^{1/3} \lambda^{1/3}} \quad (12)$$

$$\text{and } V' = v'_\lambda / \bar{v}_\lambda \quad (13)$$

The term  $(1 - \frac{V'}{V^*})$  in Eq. 11 accounts for the fact that  $v_n$  is a component of pulsation velocity normal to the contact surface.

The probability for the centers of the two drops to be in the area of the scale  $\lambda$  was estimated approximately as

$$1 - P_\lambda(0) - P_\lambda(1) \cong 1 - (1 + \varphi) \exp(-\varphi) \quad (14)$$

## DISTRIBUTION OF LOCAL RATES OF TURBULENT DISSIPATION

Distribution of local values of turbulent dissipation in mixing vessels is highly non-uniform, and the degree of non-uniformity and the features of the distribution are known to depend on the type and dimensions of vessels and agitators. An approximate description of this dependence has been recently developed. According to the results of these studies, we may consider the volume of agitated liquid as a combination of three areas with different levels of turbulence:

1. The area of vortices formed behind the agitator blades. The volume of this area is estimated [1] as:

$$V_m \cong Z_B L_B h_B^2 / 2 \quad (15a)$$

The value of turbulent dissipation rate in this area is extremely high (30-1000 times higher than the average value), and it depends on the difference between the tip velocity of the agitator and the tangential velocity of media:

$$\varepsilon_m \cong [(\omega_0 R_{\text{agt}} - v_m) \sin \alpha]^3 / L_B \quad (15b)$$

2. A jet formed around the agitator. The height of the jet is about  $1.5 h_B$ . Local values of turbulent dissipation in the jet are usually about  $(0.5-30) \varepsilon_{av}$ . They depend on the radius and may be estimated in the range of  $r_m \leq r \leq R$  using a numerical or approximate analytic solution of equation:

$$q (dE / dr) - d [2\pi r h_j v_E (dE / dr)] / dr + 2\pi r h_j \varepsilon = 0, \quad (16)$$

where  $v_E \cong \bar{v} l_m$ .

This equation is integrated under the boundary conditions of continuity of kinetic energy flow through the boundary  $r = r_m$ , account taken of Eq. 15b, and  $E$  approaching zero at  $r \rightarrow \infty$ ,

3. The main part of the volume, the jet and agitator excluded. The rate of turbulent dissipation in this area is about 0.05 - 0.3 of the average dissipation value,  $\varepsilon_{av}$  which for the main volume is calculated as:

$$\varepsilon_0 \cong \varepsilon_{av} \frac{V}{V - 1.5\pi R^2 h_B} \frac{v_m}{\omega R_m} \quad (17)$$

The tangential velocity,  $v_m$  can be calculated using the existing methods [6,7].

## EXPERIMENTAL RESEARCH AND DISCUSSION

All three groups of equations given above were checked separately. The equations of distribution of turbulent dissipation (Figs 15-17) were correlated [8] with published results of experimental measurements. Some of the results are shown in Fig. 1.

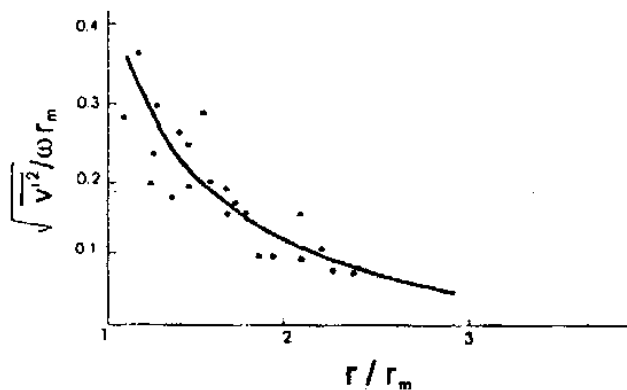


Fig. 1. Mean square root velocity fluctuation along the radius in the agitator plane. Points correspond to published data for 6-blade turbine.

The model and mathematical description of break-up kinetics (Eqs 3-8) underwent a thorough experimental verification. Studies of breaking in non-coalescing systems (in the presence of corresponding emulsifiers) were carried out [1,2] in vessels of three different volumes (up to 250 l) with 17 different agitators and 6 liquid couples. Relation of viscosities of phases varied by more than 600 times. Some of the results are shown in Figs. 2-4.

The values of drop sizes in Figs 3 and 4 are "final" values corresponding to the results of measurements for emulsifying times of over 1 hour.

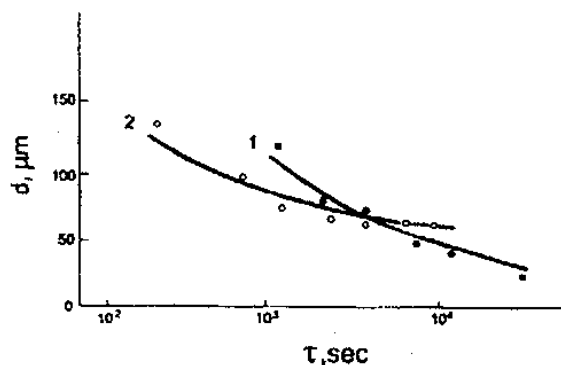


Fig. 2. Kinetics of drop breaking in the absence of coalescence. 1 - 6-blade turbine,  $\epsilon_m = 150$  W/Kg, 2 - disk agitator,  $\epsilon_m = 650$  W/Kg. Solid lines correspond to calculations by equations 1-7.

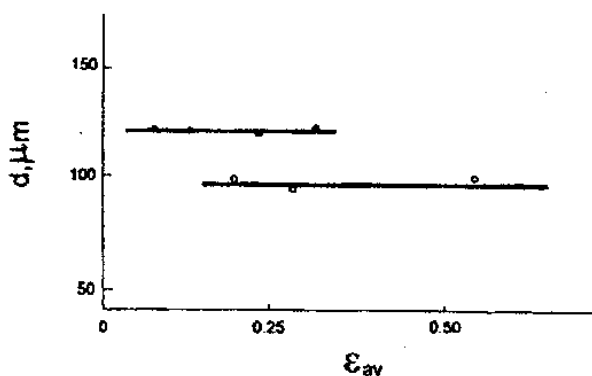


Fig. 3. Break-up in the absence of coalescence. Mean drop size ("final" values) vs. specific power for different agitators. 1 -  $\epsilon_m = 30$  W/Kg, 2 -  $\epsilon_m = 60$  W/Kg. Solid lines correspond to calculations by equations 1-7.

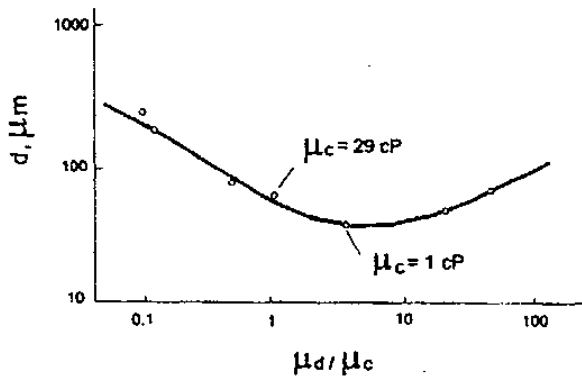


Fig. 4. Break-up in the absence of coalescence. Mean drop size vs. relation of viscosities.

Equations of frequency of coalescence were checked by measurements of the change in the mean drop size after reducing the stirrer's velocity [8]; the results of the measurements are illustrated in Fig. 5. Testing of the model in its complete form was performed by comparison of the calculated mean drop sizes with experimental data obtained with different agitators. Experiments were carried out in vessels of 2, 4.3 and 20 liters with standard baffles. Mixing was performed using 6-blade turbines and 4- and 2-blade paddle agitators, the agitator diameters being 55, 75, 100 and 125 mm, and  $h_B/r$  ratio - from 0.1 to 0.8.

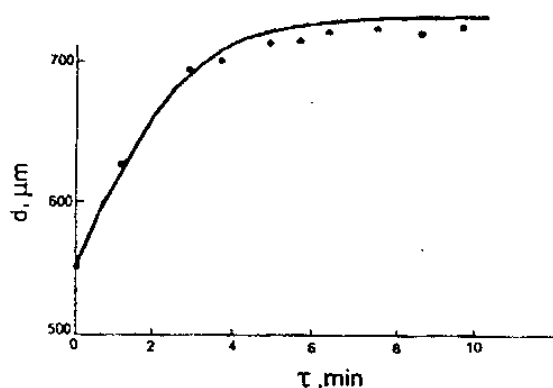


Fig. 5. Kinetics of coalescence.

Vessel - 4.3 l, agitator - 6-blade turbine, diameter 100 mm.  $\phi=0.19$ .  
Change from 240 to 160 RPM.  
Solid lines correspond to calculations by equations 1-7.

In all experiments presented in Figs 2, 3, 5 - 7, the carbon tetrachloride + kerosene solution (density 1.050 kg/cub. m, viscosity 3 cP) was used as a disperse phase. Distilled water and 0.2% solution of sulfuric acid were used as a continuous phase. Concentration of emulsions varied by 5 - 20 %. Measurements were performed using the well known light-scattering method with submerged glass fiber light conducting probe. The probe was calibrated using glass spheres of narrow size distributions. Some of the results of the measurements are presented in Figs 6 and 7. It was found that coalescence of droplets occurs not only in the most turbulized area behind the agitator's blades, but also in the radial jet around the agitator. The significance of this phenomenon increases with the increase of local dissipation; it results in a smaller slope of  $d$  vs.  $\epsilon_m$  curve as compared with the curves for non-coalescing conditions. This result, as well as the observed dependence of mean drop diameter on the concentration of emulsion and  $\epsilon_m$  values (i.e. on the mixing conditions), was found to agree with the predictions of the equations presented above.

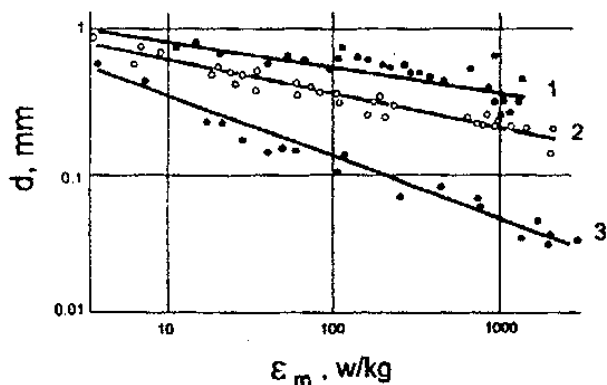


Fig. 6. Break-up and coalescence. Mean drop diameter ("final" value) vs.  $\epsilon_m$ .  
 1 -  $P = 20$  Pa; 2 -  $P = 7$  Pa; 3 -  $P \rightarrow \infty$  (stabilized)  
 Solid lines correspond to calculations by equations 1-7.

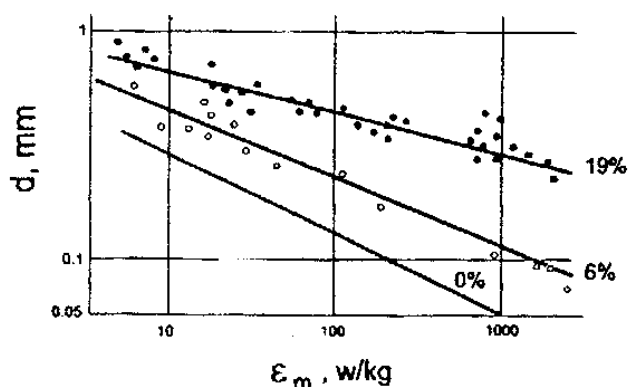


Fig. 7. Break-up and coalescence. Mean drop diameter vs.  $\epsilon_m$ . The effect of the concentration of the disperse phase. Solid lines correspond to calculations by equations 1-7.

## CONCLUSION

The system of equations presented above allows for describing the kinetics of drop breaking and coalescence as a function of tank and agitator geometry and properties of phases. In addition to viscosities and interfacial tension, these equations contain also an additional physical parameter - the restricting pressure of the electrostatic double layer. These equations may be applied without any additional experimental information on mixing, and they are used for mathematical simulation of mixing in Liquid-liquid systems implemented in the VisiMix software.

## NOMENCLATURE

- $h_B$  - width of blades
- $L_B$  - length of blades
- $N_b, N_c$  - frequencies of breaking and coalescence
- $q$  - flow rate in the jet
- $r_m$  - radius of agitator
- $v_m$  - tangential velocity of media at radius  $r_m$
- $\bar{v}$  - mean sq. root pulsational velocity
- $\phi$  - volume fraction of the disperse phase
- $\nu_c, \nu_d$  - kinematic viscosity of the continuous and disperse phases
- $\rho_c, \rho_d$  - density of the continuous and disperse phases



$\omega$  - angular velocity of agitator

$Z_b$  - number of blades

$\alpha$  - pitch angle of blades

## REFERENCES

1. Braginsky L.N. and Belevizkaya M.A., Break-up of Drops in Mixing Vessels in the Absence of Coalescence, Theor. Found. of Chem. Engng (USSR), 1990, v. 24, No. 4, (USA publication, 1991).
2. Braginsky L.N. and Belevizkaya M.A., Influence of Viscosity on Drop Size in Mixing Tanks, Theor. Found. of Chem. Engng. (USSR), 1991, v. 25, No. 6, (USA publication, 1992).
3. Braginsky L.N. and Kokotov Y.V., Influence of Turbulence and Viscosities on the Kinetics of drop breaking, J. Disp. Sci. Tech., 1993, No. 3.
4. Das P.K., Kumar R. and Ramkrishna D., Coalescence of Drops in Stirred Dispersion, Chem. Engng Sci., 1987, v. 42, No. 2, p.213-220.
5. Adamson A.A., Physical Chemistry of Surfaces, Wiley, N.Y., 1976.
6. Braginsky L.N., Begatchev V.I. and Barabash V.M., Mixing of Liquids, CHIMIA Publ. House, Leningrad, 1984.
7. Yaroshenko V.V., Braginsky L.N. and Barabash V.M., Meridional Circulation of Liquid during Mixing with Stirrers in Baffled Tanks, Theor. Found. of Chem. Engng. (USSR), 1988, v. 22, No. 6, (USA publication, 1989).
8. Braginsky L.N. and Kokotov Y.V., Kinetics of Break-up and Coalescence of Drops in Mixing Vessels, Report at CHISA-11, Prague, 1993.