Kinetics of Drop Breakage and Drop-Drop Coalescence in Turbulent Flow

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Emulsions are disperse systems in which one liquid is dispersed in the form of small droplets within another (immiscible) liquid. These droplets are with typical size range between several hundred nanometers and several millimetres. Many everyday consumer products are emulsions, such as many foods, pharmaceutical drugs and paints. Emulsions play also an important role in various technological processes, such as extraction and water purification from organic contaminants. The size of the dispersed drops in these systems is of crucial importance for their properties and for their efficiency upon application.

The disruption of big droplets in smaller ones usually occurs in so-called turbulent flow. The latter flow is generated by passing the two immiscible liquids through a device with special geometry, called "homogenizer", with a high linear speed. Usually, the liquids are forced to make multiple passes through the homogenizer, as smaller and smaller drops are formed after each pass.

The size of the droplets after emulsification depends on two opposite processes: drop breakup leading to formation of several smaller drops from a larger one, and drop-drop coalescence leading to formation of a larger drop from two smaller drops. In the general case, the

evolution of the drop-size distribution during emulsification is governed by the competition of these two opposite processes [1-6]. To characterize the kinetics of drop breakage there are three main types of theoretical models used in the literature. In the first type of models, the breakage rate constant, k_{BR}, is considered as a product of the reciprocal time of drop deformation and the efficiency of drop breakage [1,7]. In the second type of models, k_{BR} is described as a product of the eddy-drop collision frequency and the efficiency of drop breakage [8-10]. In both cases, the efficiency of drop breakage is expressed as an exponential term, including the ratio of the surface energy for drop deformation and the kinetic energy of the turbulent eddies. In the third type of models, k_{BR} is assumed equal to the inverse drop breakage time, which in turn is determined from the balance of stresses acting on the breaking drop [11-14].

The coalescence rate constant is usually described as a product of the probability for drop-drop encounter and the coalescence efficiency, which depends on the ratio between the drainage time and contact time between two drops upon collision [1]. In most theoretical considerations so far it is assumed that the breakage and coalescence occur simultaneously in the same part of the equipment [1-6].

In the last years our group has performed several related studies [15-20] about the detailed mechanisms of emulsification in turbulent flow. One major line in our studies was to clarify experimentally and describe theoretically the role of the main factors on: (1) Drop-breakage rate constants, k_{BR} (2) Drop-drop coalescence rate constants, k_C, and (3) Size distribution and number of the daughter drops, which are formed as a result of drop breakage in turbulent flow. These factors include: (i) Rate of energy dissipation in the active zone of the homogenizer, ε; (ii) Interfacial tension, σ; (iii) Viscosity of the oil phase, η_D; (iv) Viscosity of the aqueous phase, η_C; (v) Oil volume fraction, Φ, and (vi) Surfactant concentration. The studied emulsions were prepared using either a "narrow-gap" homogenizer or "rotor-stator" homogenizer.

To describe the evolution of the drop size distribution after a certain number of passes through the homogenizer we assumed that the

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processes of breakage and coalescence of the drops are spatially divided, i.e. they happen at different places in the homogenizer. The model presumes that the breakage of the droplets happens in the processing element of the device, in the so called "active zone", where the rate of energy dissipation is much higher, while the coalescence happens in the tubes of the homogenizer where the energy dissipation is significantly lower and insufficient to break the drops. Therefore, the homogenizer is modelled as consisting of two consequent plug flow reactors with ideal displacement, one of which is the processing element, where the breakage of the drops takes place, and the other one represents the tubes, where drops coalesce – see Figure 1.
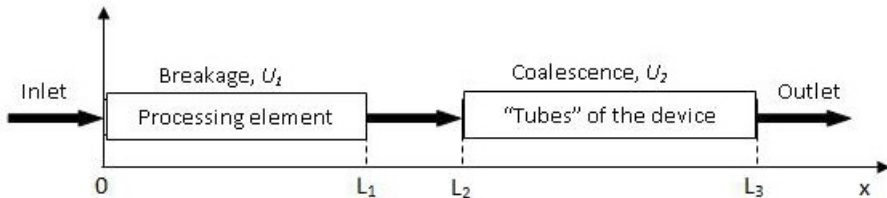

Figure 1: Schematic representation of the homogenizer as two consequent flow reactors with ideal displacement, corresponding to the processing element where the drops breakage takes place and tubes in which the coalescence between drops happens. The distribution by number of drops with mean diameter d_S depends on the distance from the inlet of the homogenizer, x, and on the number of passes of the emulsion through the device, u.

According to our model, the only process that happens in the area of the processing element is the drop breakage (fragmentation into smaller droplets) but not coalescence. In such a case, the simplest differential equation is the one that describes the decrease of the concentration of the biggest drops with size d_N in the emulsion, because this concentration changes only as a result of their own breakage:

$$U_1 \frac{dn_N(x)}{dx} = -k_N^{BR} n_N(x). \tag{1}$$

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Here U_1 is the mean linear velocity of the fluid in the processing element, $n_N(x)$ is the concentration of the biggest drops in the emulsion at a distance x from the starting point of the processing element, and k_N^{BR} is the rate constant of breakage of these drops.

The differential equation which describes the change of concentration, n_S, of drops with diameter d_S, which could both break and form during emulsification is:

$$U_1 \frac{dn_S(x)}{dx} = -k_S^{BR} n_S(x) + \sum_{M=S+1}^{N} 2^{M-S} p_{S,M} \, k_M^{BR} \, n_M(x) \text{ for } D < S < N \quad (2)$$

The first term on the right side of Eq. (2) stands for the rate of breakage of these drops, while the second term stands for the rate of their formation as a result of the breakage of bigger drops. The factor $(2^{M-S} p_{S,M})$ represents the average number of drops with diameter d_S which form while a drop of a size d_M breaks, where $N \geq M \geq S$.

For drops with diameters $d_S \leq d_D$, which could only be formed after breakage of bigger drops, the first term in Eq. (2) is zero and the kinetic equation is simplified to:

$$U_1 \frac{dn_S(x)}{dx} = \sum_{M=S+1}^{N} 2^{M-S} p_{S,M} \, k_M^{BR} \, n_M(x) \text{ for } 0 < S < D. \quad (3)$$

The initial concentrations for the process of breakage of the drops are the concentrations of these drops in the initial emulsion.

To describe the process of drop-drop coalescence we start with a differential equation describing the change of the concentration of the smallest droplets with diameter d_0 of the initial emulsion, because their concentration could decrease as a result of their coalescence only (in the part of the device, where no drop breakage occurs):

$$U_1 \frac{dn_0(x)}{dx} = -k_0^C [n_0(x)]^2. \quad (4)$$

Here, $n_0(x)$ is the concentration of the smallest droplets in the emulsion that are at a distance x from the inlet of the tubes, and k_0^C is the rate constant of coalescence of these drops.

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The concentration of the next in size drops with diameter d_1 along the tubes would depend on their disappearance because of their own coalescence, and also because of their formation as a result of the coalescence of the smallest droplets with size d_0:

$$U_1 \frac{dn_1(x)}{dx} = -k_1^C [n_1(x)]^2 + k_0^C [n_0(x)]^2, \tag{5}$$

where $n_1(x)$ is the concentration of the drops with size d_1 at a distance x from the inlet of the homogenizer, and k_1^C is the rate constant of coalescence of these drops.

Similarly the concentration of drops with size $d_s > d_0$ depends on the difference between the rate of formation as a result of coalescence of the drops with size d_s and on the rate of the process of their own coalescence that leads to formation of drops with size d_{s+1}. Respectively, the kinetic equation for the change of the particle concentration of the biggest drops looks as follows:

$$U_1 \frac{dn_N(x)}{dx} = -k_N^C [n_N(x)]^2 + k_{N-1}^C [n_{N-1}(x)]^2, \tag{6}$$

where $n_N(x)$ and $n_{N-1}(x)$ are the concentrations of the biggest drops with size d_N and the second in size drops with size d_{N-1}, respectively, and k_N^C and k_{N-1}^C are the corresponding constants of coalescence.

The comparison of the theoretical predictions with the experimental results allowed us to reveal that the results for all studied systems at high surfactant concentration can be described reasonably well by an explicit expression, which considers k_{BR} as a product of the drop-turbulent eddy collision frequency and the breakage efficiency. The breakage efficiency term includes the relative contributions of the surface extension energy and the energy dissipated inside the breaking drop, as compared to the mean kinetic energy of the turbulent eddies with size similar to the diameter of the breaking drop. The following expression for k_{BR} was derived:

$$k_{BR}(d) = B_1 \frac{\varepsilon^{1/3}}{d^{2/3}} \exp\left[-B_2 \left(\frac{d_{KI}}{d} \right)^{5/3} \left(1 + B_3 \frac{\eta_D \varepsilon^{1/3} d^{1/3}}{\sigma} \right) \right] \tag{7}$$

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Here ε is the rate of energy dissipation in the processing element, d is the diameter of the drop that breaks, η_D is the viscosity of the drop phase, σ is the interfacial tension, and d_{KI} is defined as $d_{KI} = \sigma^{3/5}\varepsilon^{-2/5}\rho_C^{-3/5}$, with ρ_C being the mass density of the continuous phase. The constant B_3 accounts for the relative contribution from the viscous dissipation in the drop that breaks (compared to the contribution from the capillary pressure), and the value is determined so that the results for the steady size and for the kinetic studies to be described in a self-consistent way, $B_3 = 0.37$ (see Vankova et al. [17] for details). From the best interpolation of the experimental data the constants $B_1 = 0.086$ and $B_2 = 5.12$ were determined [17]. The proposed expression for k_{BR}, Eq. (7), is found to describe reasonably well the respective experimental results for a wide range of oil viscosities ($3 \leq \eta_D \leq 500 \, mPa.s$), interfacial tensions ($7 \leq \sigma \leq 28 \, mN/m$), and energy dissipation rates ($6.4 \times 10^4 \leq \varepsilon \leq 3.4 \times 10^5 \, J/kg.s$), see Figure 2.
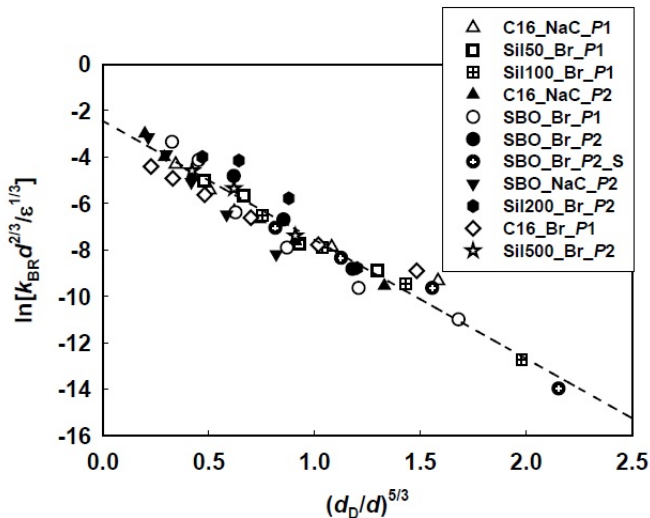

Figure 2: Comparison of the experimental data for k_{BR} for all emulsions studied (the symbols) with the predictions of Eq. (7) (the dashed line).

To describe our experimental data at low surfactant concentrations

where the coalescence is also important, we derived the following expressions for the coalescence rate constants. For small non-deformed spherical drops we have showed that the coalescence rate constant k_C could be presented as:

$$k_C(d) = C_1 \frac{\pi}{2} d^3 \left(\frac{\varepsilon_P \rho}{\eta_C} \right)^{1/2} \left[\frac{4^3 A_H}{24\pi\sigma d^2} \right]^{C_2/12} \tag{8}$$

Here C_1 and C_2 are numerical unknown constants, d is the diameter of the drops which coalesce, ε_P is the rate of energy dissipation in the pipes of the equipment, ρ is the mass density of the continuous phase, η_C is the viscosity of the continuous phase, A_H is the Hamaker constant, which characterizes the van der Waals interactions between the drops across the continuous phase, and σ is the interfacial tension. The coalescence rate constant for the larger drops, between which a plane parallel film is formed before their coalescence, is given by:

$$
\begin{aligned}
k_C(d) & = & C_1 \frac{\pi}{2} d^3 \left(\frac{\varepsilon_P \rho}{\eta_C} \right)^{1/2} \left(\frac{4 h_{INV}}{d} \right)^{C_2/4} \\
& & \times \exp \left(-\frac{9 C_2}{128} \frac{(\eta_C \varepsilon_P \rho)^2 d^4}{\sigma_{OW}^2} \left(\frac{1}{h_{CR}^2} - \frac{1}{h_{INV}^2} \right) \right)
\end{aligned}
\tag{9}
$$

Here h_{INV} is the film thickness at which the flat film is formed between the drops and h_{CR} is the critical film thickness at which the drop-drop coalescence occurs, which can be determined by the following expression:

$$h_{INV} = \frac{F_d}{2\pi\sigma} = \frac{3}{4} \frac{\eta_C \dot{\gamma} d^2}{\sigma} = \frac{3}{4} \frac{(\varepsilon_P \rho \eta_C)^{1/2} d^2}{\sigma} \tag{10}$$

The critical film thickness is given by:

$$h_{CR} = 0.21 \left(\frac{3 A_H^2 (\varepsilon_P \rho \eta_C)^{1/2} d^4}{8 \sigma_{OW}^3} \right)^{1/7}. \tag{11}$$

The threshold drop diameter above which the drops deform and a planar film is formed between them before they coalesce, and the

drop-drop coalescence is described by Eq. (9), is given by:

$$d_{INV} = 0.372 \left[\frac{\sigma^2 A_H}{(\eta_C \varepsilon_P \rho_C)^{3/2}} \right]^{1/5}.$$ (12)

Therefore for $d < d_{INV}$ we used Eq. (8), whereas for $d > d_{INV}$ we used Eq. (10) for the coalescence rate constants.

The description of the experimental results with the proposed theoretical model is shown in Figure 3. One sees that for both type of emulsions oil-in-water and water-in-oil the theoretical framework describes very well the experimental results.
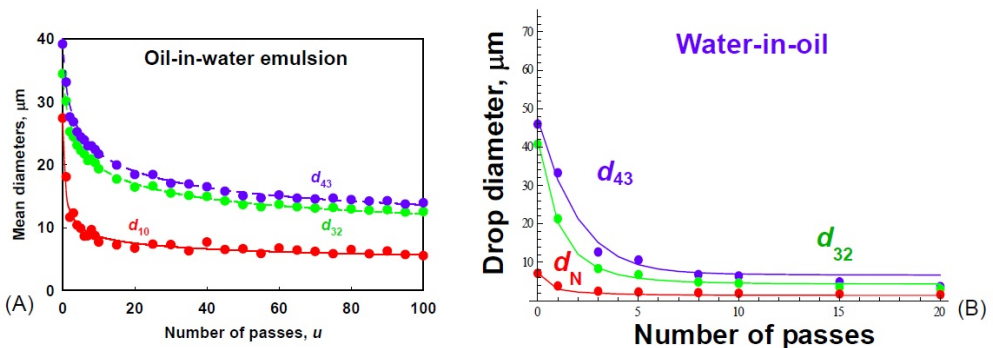

Figure 3: Comparison between the theoretically calculated (the curves) and the experimentally obtained (the points) dependence of the drop diameter on the number of passes through the homogenizer of (A) oil-water and (B) water-in-oil emulsions. Data for d_{43} (the blue symbols), d_{32} (the green symbols) and d_N (the red symbols) are presented.

Concluding, we have built a complete set of equations to describe the processes of drop breakage and drop-drop coalescence in turbulent flow which is applicable to both oil-in-water and water-in-oil emulsions.

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