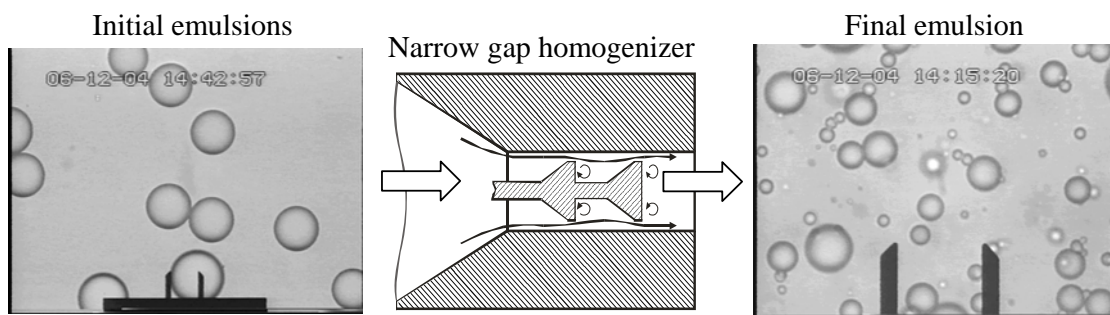


## Kinetics of drop breakup during emulsification in turbulent flow

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**Abstract.** Systematic set of emulsification experiments is performed to elucidate the role of several factors, which control the process of drop breakup during emulsification in turbulent flow. As starting oil-water premixes we use emulsions containing monodisperse oil drops, which are generated by the method of membrane emulsification. By passing these premixes through a narrow-gap homogenizer working in turbulent regime, we study the evolution of the number concentration of drops with given diameter, as a function of emulsification time. The experiments are performed at high surfactant concentration and low oil volume fraction to eliminate the process of drop-drop coalescence. The experimental data are analyzed by using a kinetic scheme, which takes into account the generation of drops of a given size (as a result of breakup of larger drops) and their disappearance (as a result of their own breakup process). The analysis allowed us to determine the rate constant of the process of drop breakup, as a function of drop diameter, hydrodynamic conditions during emulsification, interfacial tension and viscosity of the drop phase. The breakup rate constants, determined in this way, are compared with available theoretical expressions in the literature and their modifications. An explicit expression is designed to describe the experimental data, which accounts for: (a) the frequency of collisions between drops and turbulent eddies, and (b) the efficiency of drop breakup, which is related to the energy required for drop deformation and breakup into smaller drops. The energy for drop deformation contains two contributions, originating from the drop surface extension and from the viscous dissipation inside the drop, respectively.

## 1/ Introduction.

The emulsification process can be considered as consisting of two “elementary reactions”: (a) drop breakup and (b) drop-drop coalescence. At high emulsifier concentrations, the coalescence process can be neglected and the evolution of drop-size distribution during emulsification could be described by considering the drop breakup only. The classical studies by Kolmogorov (1) and Hinze (2) on the emulsification in turbulent flow showed that the maximal diameter of the so-called “stable drops”,  $d_K$ , is determined by the balance of the fluctuations in the hydrodynamic pressure of the continuous phase, which induces drop deformation, and the drop capillary pressure opposing this deformation. Such stable drops are able to survive the disruptive forces of the pressure fluctuations, even after a relatively long period of emulsification, when a steady-state drop size distribution is established. Subsequent studies (3-5) showed that, in the case of viscous oils, one should consider also the viscous dissipation inside the breaking drops to determine the maximal diameter,  $d_K$ .

In the real systems, the steady-state drop-size distribution is established after a breakup of the large drops with diameter  $d > d_K$ , which are initially present in the original emulsion. The description of the kinetics of this breakup process is a challenging scientific problem, with important practical implications, which has not been solved completely. One of the main difficulties in the investigation of the drop breakup process and in the prediction of the resulting steady-state drop-size distribution, is the lack of reliable information about the number and size of the smaller “daughter drops”, which are formed after the breakup of the large drops.

Narsimhan et al. (6,7) studied experimentally and theoretically the kinetics of drop breakup in stirred tanks. From the experimental data, these authors determined the dependence of the rate constant of drop breakup,  $k_{BR}$ , as a function of drop diameter,  $d$ . To interpret the experimental data, Narsimhan et al. (6,7) used the so-called “self-similarity” assumption, which implies a certain functional relation between the probability for formation of daughter drops of a given size and the dependence  $k_{BR}(d)$ .

In our studies (8,9), we use a somewhat different approach to determine  $k_{BR}$ . First, we performed a series of emulsification experiments, in which we varied the oil viscosity, interfacial tension, and rate of energy dissipation (8). Direct checks showed (8) that we could not describe the experimental data for many of the systems studied, by using the self-similarity assumption, as originally formulated in Refs. (6,7). Therefore, we analyzed the probability for formation of daughter drops by detailed investigation of the evolution of the drop-size distribution, observed during the emulsification process. Second, to interpret the data, we formulated a new kinetic scheme of the drop-breakup process, in which we considered the drops as having diameters, which belong to a discrete set of values (8). Following this approach, we were able to quantify the dependence of the rate constant of drop breakup,  $k_{BR}$ , on all factors studied – drop size, oil viscosity, interfacial tension, and energy of power dissipation. Non-trivial information about the dependence of the probability for formation of daughter drops on these factors was obtained (9). Third, the experimentally determined dependence of  $k_{BR}$  on the factors studied was described by

suggesting a new semi-empirical formula, which was designed by combining ideas from the original papers by Prince and Blanch (10), and by Calabrese et al. (4), see Figure 4 below.

In the current paper we summarize our main results about the dependence of  $k_{BR}$  on the factors studied. A detailed description of the used approach and the complete set of results, including those for the probability of daughter drop formation, are presented elsewhere (8,9).

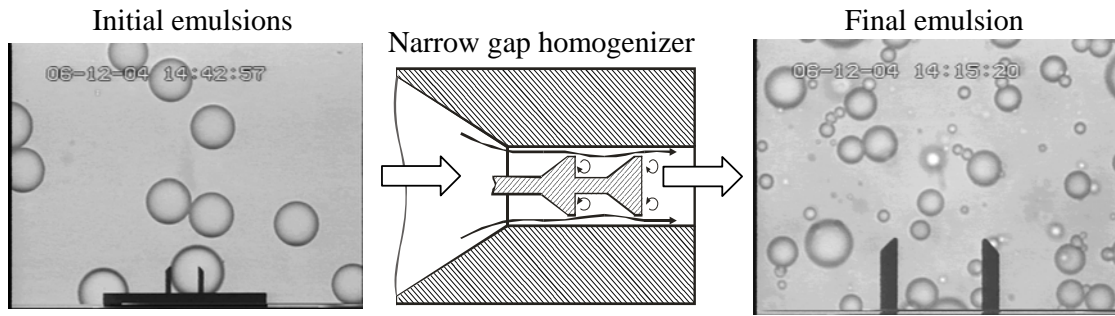
## **2/ Materials and Methods.**

*2.1. Materials.* As emulsifiers we used the nonionic surfactant polyoxyethylene-20 hexadecyl ether (Brij 58, product of Sigma) and the protein derivative sodium caseinate (Na caseinate; commercial name Alanate 180; product of NXMP). The emulsifier concentrations, 1 wt % for Brij 58 and 0.5 wt % for Na caseinate, were chosen sufficiently high to suppress the drop-drop coalescence during emulsification. All emulsifier solutions were prepared with deionized water, purified by a Milli-Q Organex system (Millipore) and contained 0.15 M NaCl (Merck, analytical grade). Series of oils with different viscosities,  $\eta_D$ , were used: hexadecane with  $\eta_D = 3.0$  mPa.s (HxD, product of Merck), soybean oil with  $\eta_D = 50$  mPa.s (SBO, commercial product), and four silicone oils with  $\eta_D = 50; 95; 194$  and  $491$  mPa.s. Hexadecane and SBO were purified from surface-active contaminations by passing the oils through a glass column filled with Florisil adsorbent. The silicone oils (products of BASF and Rhodia) were used as received.

*2.2. Emulsion preparation.* All emulsions were obtained by applying a two-stage protocol: First, a monodisperse initial emulsion (oil-in-water premix) was prepared by using the method of membrane emulsification (11), which was realized on a laboratory micro-kit module, equipped with tubular Shirasu porous glass membranes (SPG Technology, Miyazaki, Japan). Three membranes, with average pore diameters of  $1.1 \mu\text{m}$ ,  $10.7 \mu\text{m}$  and  $19.3 \mu\text{m}$ , were used to obtain monodisperse emulsions with different drop diameters. The second emulsification step was accomplished by passing the initial monodisperse emulsion, in a series of consecutive passes, through a narrow-gap homogenizer, working in turbulent regime (Figure 1). The homogenizer head contained two consecutive annular slits (annular gaps) with an external diameter of  $6.54$  mm and width of  $395 \mu\text{m}$ . Each of these slits had a length of  $1$  mm (8). For studying the evolution of the drop size distribution, as a function of the emulsification time, samples were taken from the emulsion passed through the homogenizer, after each of the first 10 passes and, afterwards, after every fifth pass.

*2.3. Determination of drop size distribution in the emulsions.* The drop size distribution was determined by optical microscopy. The oil drops were observed by microscope Axioplan (Zeiss, Germany), equipped with objective Epiplan  $\times 50$ , and connected to a CCD camera and video-recorder. The diameters of the recorded drops were measured one by one, with custom-made image analysis software, and the mean volume-surface diameter,  $d_{32}$ , was afterward calculated (8).

*2.4. Measurements of oil viscosity and interfacial tension.* The oil viscosity was measured on a Gemini rheometer (Bohlin, UK). The oil-water interfacial tension was measured on instrument DSA10 (Krüss, Germany) by drop-shape-analysis of pendant oil drops, immersed in the surfactant solution.



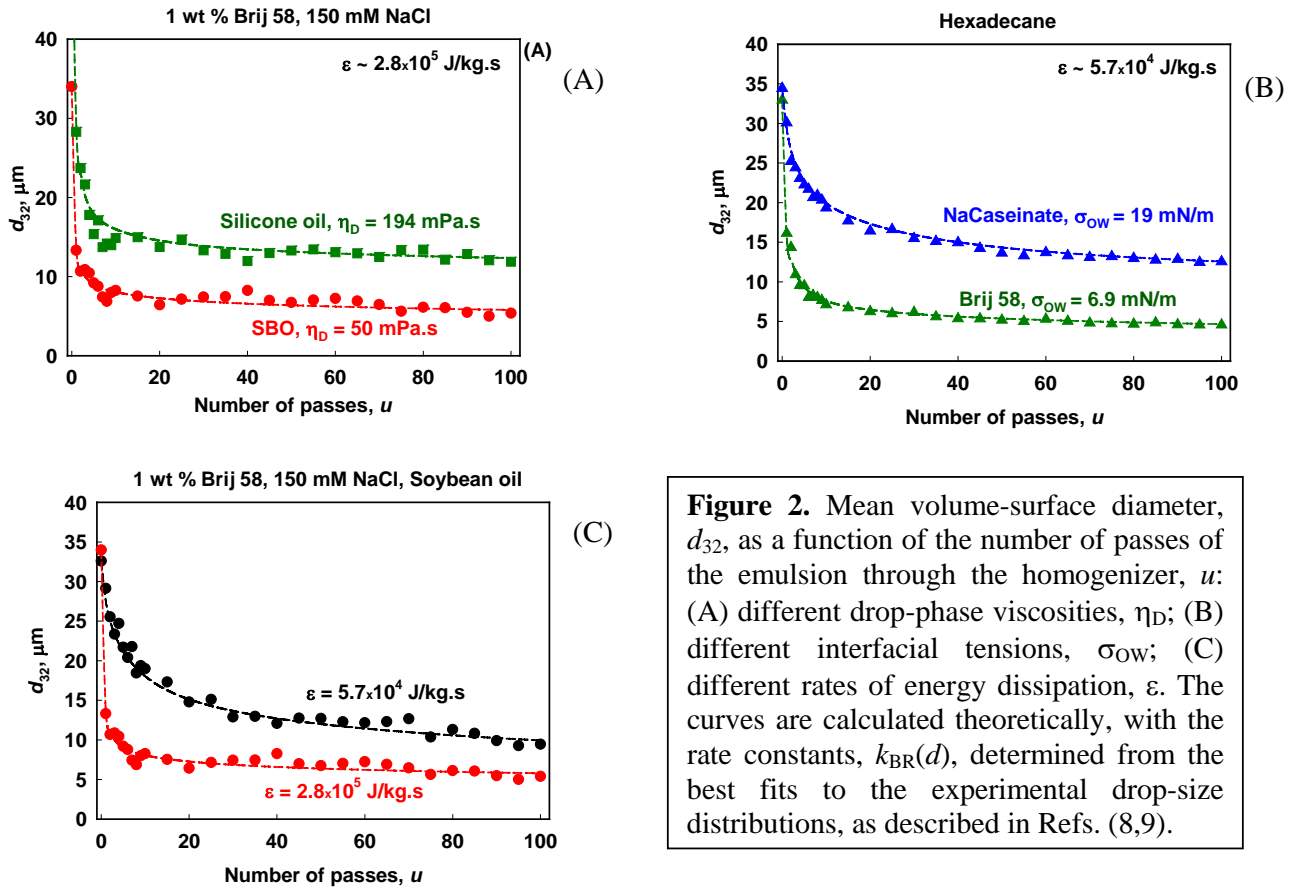
**Figure 1.** Optical microscopy images of an initial emulsion prepared by membrane emulsification and of the final emulsion, obtained after 100 passes ( $u = 100$ ) through the narrow-gap homogenizer. The distance between the vertical marks is 20  $\mu\text{m}$ .

### 3/ Results and Discussion.

*3.1. Mean volume-surface diameter, as a function of the emulsification time.* The experiments showed that the mean volume-surface diameter,  $d_{32}$ , decreased with the number of passes,  $u$ , of the emulsion drops through the homogenizer. The decrease of  $d_{32}$  was rather steep during the first several passes, while during the subsequent passes it occurred more gradually, until an approximately “steady-state” value was reached. The experiments revealed that the evolution of  $d_{32}$  with the emulsification time depended strongly on oil viscosity, interfacial tension, and hydrodynamic conditions.

The effect of the oil viscosity,  $\eta_D$ , was studied in the range between 3 and 500 mPa.s, for emulsions of HxD, SBO and four silicone oils (SO), all of them stabilized by 1 wt % Brij 58. The role of the interfacial tension,  $\sigma_{OW}$ , was studied in the range between 6.9 and 28 mN/m, with emulsions of SBO and HxD, stabilized by 1 wt % Brij 58 or 0.5 wt % Na caseinate. The effect of the hydrodynamic conditions was explored by using two different flow rates of the emulsion through the homogenizer, which corresponded to two values of the rate of energy dissipation,  $\varepsilon = 0.57 \times 10^5 \text{ J}/(\text{kg}\cdot\text{s})$  and  $\varepsilon = 2.8 \times 10^5 \text{ J}/(\text{kg}\cdot\text{s})$ . Emulsions of SBO and hexadecane, stabilized by 1 wt % Brij 58 or 0.5 wt % Na caseinate, were used in this last series of experiments.

The main results for the dependence  $d_{32}(u)$  could be summarized as follows: When the emulsification was performed at higher rate of energy dissipation, and/or at lower oil viscosity and interfacial tension, a rapid decrease of  $d_{32}$  was observed after passing the premix only once through the homogenizer, see Figure 2. In contrast, at the lower value  $\varepsilon = 0.57 \times 10^5 \text{ J}/(\text{kg}\cdot\text{s})$ , or at higher  $\eta_D$  (100-500 mPa.s) and  $\sigma_{OW}$  (19 mN/m), the decrease of  $d_{32}$  was more gradual, see Figures 2A and 2B for examples. As expected, the “steady-state” drop diameter, reached at the end of the emulsification procedure (after 100 passes), was smaller in the emulsions prepared at higher values of  $\varepsilon$ , and at lower values of  $\eta_D$  and  $\sigma_{OW}$ .



**Figure 2.** Mean volume-surface diameter,  $d_{32}$ , as a function of the number of passes of the emulsion through the homogenizer,  $u$ : (A) different drop-phase viscosities,  $\eta_D$ ; (B) different interfacial tensions,  $\sigma_{OW}$ ; (C) different rates of energy dissipation,  $\epsilon$ . The curves are calculated theoretically, with the rate constants,  $k_{BR}(d)$ , determined from the best fits to the experimental drop-size distributions, as described in Refs. (8,9).

*3.2. Kinetic model used for data analysis.* A detailed description of the kinetic scheme, used for determination of the rate constant of drop breakup,  $k_{BR}$ , is presented in Ref. (8). Due to lack of space, here we explain briefly only the basic assumptions in the model: (a) The process of drop-drop coalescence is neglected; (b) The process of drop breakup is considered as irreversible reaction of first order; (c) The emulsion droplets are classified by size in a discrete set of intervals - all drops falling in a given interval are considered as having uniform size, corresponding to the average diameter of the respective interval. The average volumes of the drops, falling into two neighboring intervals, differ by a factor of two,  $v_S = 2v_{S-1}$ . Thus, the average diameters,  $d_S$ , of the intervals are defined through the relation  $d_S = \sqrt[3]{2^S} d_0$ , where  $d_0 = 0.25 \mu\text{m}$  has the meaning of the average diameter of the smallest drops in the system. (d) Set of differential equations is formulated to describe the evolution of the number concentrations of the drops,  $n_S$  (having a diameter  $d_S$ ), as a function of the number of passes of the emulsion through the homogenizer,  $u$ . For this purpose, the homogenizer head is considered as a “chemical” reactor with ideal displacement, in which the changes in the concentration of the drops along the reactor axes is described by the following kinetic equation:

$$V_1 \frac{dn_S(x)}{dx} = -k_S n_S(x) + \sum_{q=S+1}^N 2^{q-S} p_{q,S} k_q n_q(x) \quad 0 \leq x \leq L \quad (1)$$

Here  $V_1$  is the linear velocity of the emulsion along the reactor (viz. the narrow slit of the homogenizer),  $x$  is the distance from the beginning of the reactor,  $L$  is the reactor length, and  $n_S(x)$  is the number concentration of drops with diameter  $d_S$ . Note that, if the time for emulsion passage through the homogenizer is  $\theta = L/V_1$ , the total emulsification time after  $u$  passes of the emulsion through the homogenizer is  $t_E = u\theta$ . The first term in the right-hand side of Eq. (1) expresses the rate of breakup of the drops with size  $d_S$ , while  $k_S$  is the corresponding rate constant. The second term in Eq. (1) accounts for the rate of formation of these drops, as a result of the breakup of larger drops with size  $d_q > d_S$ . The parameter  $p_{q,S}$  expresses the probability for the generation of “daughter” drops of size  $d_S$  from the drops with size  $d_q$ . The probability  $p_{q,S}$  is normalized by the total mass of the breaking drop with diameter  $d_q$ , i.e.  $\sum_S p_{q,S} = 1$ . The procedure for determination of  $p_{q,S}$  from the experimentally determined size-distribution histograms is explained in Ref. (9).

Note that the largest drops in the emulsion, with diameter  $d_N$ , can only break to smaller droplets, so that the respective kinetic equation includes the breakup term only. On the other side of the size spectrum, the kinetic equations for the drops with diameter smaller or equal to the Kolmogorov size,  $d_S \leq d_K$ , include only terms related to drop generation as a result of the breakup of larger drops.

The kinetic equations for all drops in the emulsion were solved, with  $n_S(u=1, x=0) = n_S^0$  used as initial condition ( $0 \leq S \leq N$ ), where  $n_S^0$  was the number concentration of drops with diameter  $d_S$  before starting the emulsification with the narrow-gap homogenizer. The values of  $n_S^0$  were determined from the drop-size distribution in the initial emulsion, which was produced by membrane emulsification (see Section 2.2). The entire set of equations (1) for all drops in the system, and for all passes of the respective emulsion through the homogenizer ( $1 \leq u \leq 100$ ) was solved, and a comparison between the predicted and the experimentally determined drop-size distributions was made to determine the breakup rate constant  $k_{BR}(d_S)$ . The respective elaborated procedure, including the determination of the probabilities  $p_{q,S}$ , is presented in Refs. (8,9).

### 3.3. Breakup rate constants, as determined from the experiments - effects of $d$ , $\varepsilon$ , $\eta_D$ and $\sigma_{ow}$ .

Following the procedure outlined above, we determined the values of  $k_{BR}(d)$  for eleven emulsions, prepared under different experimental conditions. For all systems studied, the values of  $k_{BR}$  rapidly decreased with the increase of oil viscosity and interfacial tension, and with the decrease of the rate of energy dissipation. Further, the values of  $k_{BR}$  rapidly decreased with the decrease of drop diameter,  $d$ , and became virtually zero when  $d \rightarrow d_K$  (Figure 3).

The effect of oil viscosity on  $k_{BR}$  was studied at  $\varepsilon = 2.8 \times 10^5$  J/kg.s, with Brij 58-stabilized emulsions of hexadecane, SBO and two silicone oils. As seen from Figure 3A,  $k_{BR}$  decreased rapidly with the increase of  $\eta_D$ . As an example, the increase of  $\eta_D$  from 194 to 495 mPa.s for the silicone oils, led to decrease of  $k_{BR}$  from 108 to  $2 \text{ s}^{-1}$  for the drops with  $d \approx 40 \text{ }\mu\text{m}$ , and from 16 to

$0.02 \text{ s}^{-1}$  for the drops with  $d \approx 32 \text{ }\mu\text{m}$ . The interfacial tensions of the silicone oils were similar ( $\approx 10.5 \text{ mN/m}$ ), so that the observed decrease in  $k_{BR}$  was due exclusively to the difference in their viscosities.

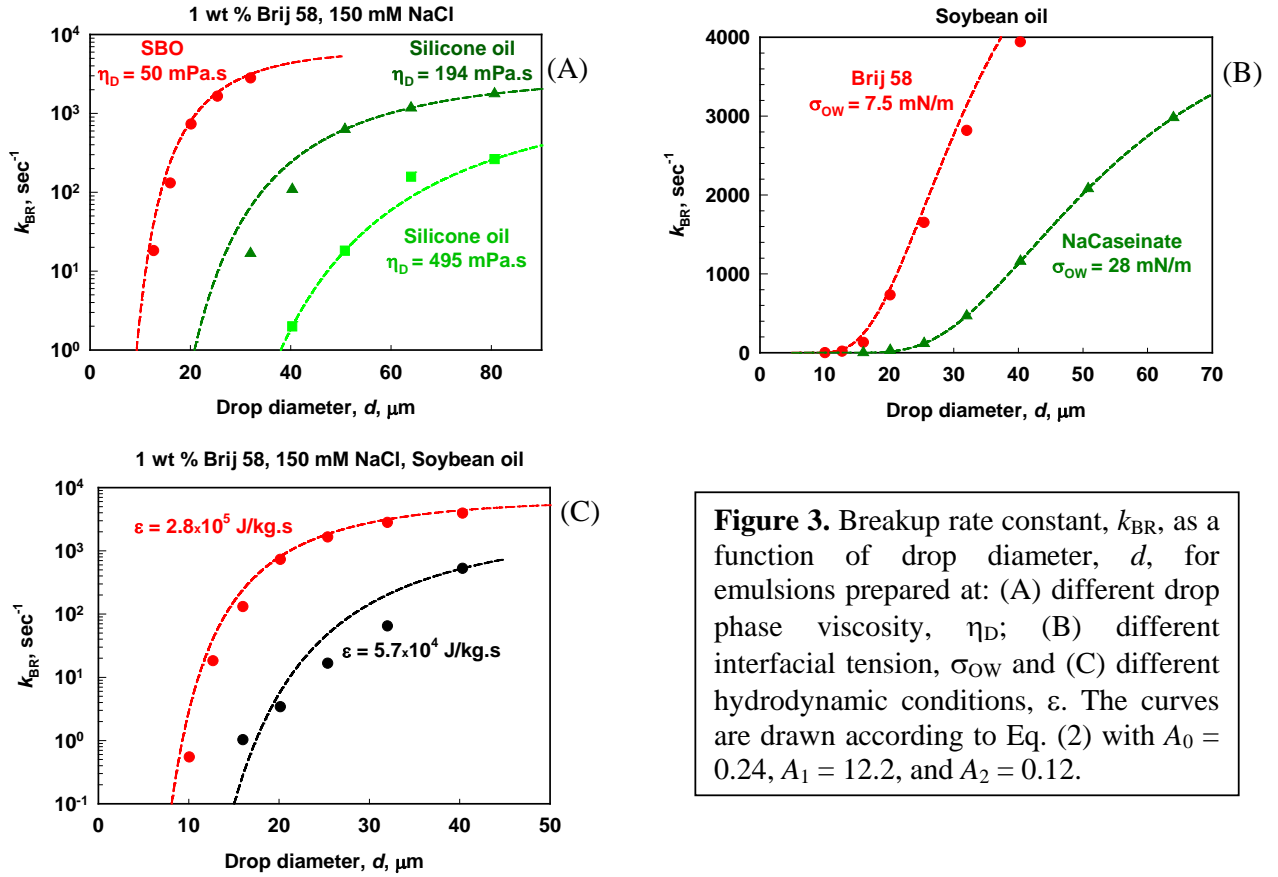
The effect of interfacial tension on  $k_{BR}$  was studied with soybean oil emulsions, stabilized by Brij 58 or Na caseinate. As seen from Figure 3B,  $k_{BR}$  for the emulsion stabilized by Na caseinate ( $\sigma_{OW} = 28 \text{ mN/m}$ ) was much smaller than that for the Brij 58-stabilized emulsion ( $\sigma_{OW} = 7.5 \text{ mN/m}$ ) for all drops with  $d > d_K$ .

The effect of  $\varepsilon$  on  $k_{BR}$  is illustrated in Figure 3C for two SBO-emulsions ( $\eta_D = 50 \text{ mPa.s}$ ), stabilized by Brij 58 ( $\sigma_{OW} = 7.5 \text{ mN/m}$ ), obtained at two different flow rates (i.e., two different values of  $\varepsilon$ ). One sees that  $k_{BR}$  for drops of given diameter increases by one-two orders of magnitude, when  $\varepsilon$  is increased by 5 times (from  $0.57 \times 10^5$  to  $2.8 \times 10^5 \text{ J/kg.s}$ ).

*3.4. Comparison of the experimental results for  $k_{BR}$  with theoretical models for breakup rate.* We compared the observed dependencies  $k_{BR}$  on the various factors with theoretical models published in the literature (10,12). Neither of the available models was able to describe the complete set of results obtained in our experiments. Therefore, combining ideas from the previous studies by Prince and Blanch (10) and Calabrese et al. (4), we constructed a new theoretical expression, assuming that  $k_{BR}$  is a product of (a) the frequency of drop-eddy collisions and (b) the drop breakup efficiency upon such collisions:

$$k_{BR} = A_0 \frac{\varepsilon^{1/3}}{d^{2/3}} \exp \left[ -\frac{(E_\sigma + E_{DIS})}{\bar{E}} \right] = A_0 \frac{\varepsilon^{1/3}}{d^{2/3}} \exp \left[ -\frac{A_1 (\sigma_{OW} + A_2 \varepsilon^{1/3} d^{1/3} \eta_D)}{\rho_C \varepsilon^{2/3} d^{5/3}} \right] \quad (2)$$

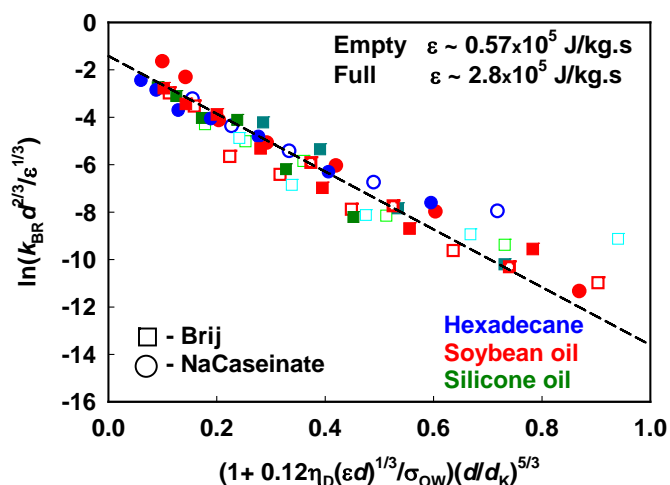
The pre-exponential term in Eq. (2) accounts for the frequency of collisions between drops with diameter  $d$  and eddies of similar size (10). The exponential factor accounts for the efficiency of drop breakup, which is presented in Ref. (12) as a ratio of the surface extension energy,  $E_\sigma$ , required for drop deformation, and the mean turbulent energy,  $\bar{E}$ , of the turbulent eddies with size  $d$ . This exponential term is introduced by analogy with the activation energy, used in chemical kinetics to account for the reactive collisions in the molecular theory of gases. Following the idea of Calabrese et al. (4) (originally proposed to explain the steady-state drop size in emulsions of viscous oils), we included in the ‘‘activation energy’’ suggested in Ref. (10) an additional term accounting for the energy dissipated inside the drops during their deformation,  $E_{DIS}$ . Thus we account for the effect of drop-phase viscosity on the breakup process. The constants  $A_0$ ,  $A_1$  and  $A_2$  in Eq. (2) were found by a non-linear regression to the experimental data, whereas all other parameters were known from the experiment.



**Figure 3.** Breakup rate constant,  $k_{BR}$ , as a function of drop diameter,  $d$ , for emulsions prepared at: (A) different drop phase viscosity,  $\eta_D$ ; (B) different interfacial tension,  $\sigma_{OW}$  and (C) different hydrodynamic conditions,  $\varepsilon$ . The curves are drawn according to Eq. (2) with  $A_0 = 0.24$ ,  $A_1 = 12.2$ , and  $A_2 = 0.12$ .

Figure 4 shows a comparison of the experimental data for  $k_{BR}$  and the theoretical expression, Eq. (2), which predicts a linear dependence, when the data are plotted in appropriate scale. One sees that all data follow the predicted linear dependence down to drop sizes  $d \approx d_K$  (the last points on the right-hand side of Figure 4). Furthermore, the data for all systems converge around a master line, which indicates that Eq. 2 adequately represents the dependence of  $k_{BR}$  on all factors studied:  $d$ ,  $\varepsilon$ ,  $\eta_D$  and  $\sigma_{OW}$ . The values of  $A_0$ ,  $A_1$  and  $A_2$ , determined from the fit to the data, are all rather reasonable from physical viewpoint.  $A_0$  plays the role of the “steric factor” in the collision theory of chemical kinetics. The obtained value  $A_0 \approx 0.24$  indicates that, in average, about 1 in 4 active drop-eddy collisions leads to drop breakup.  $A_1 \approx 12.2$  is close to the value  $A_1 \approx 9.0$ , which is theoretically predicted in Ref. (10).  $A_2$  accounts for the relative contribution of the viscous dissipation energy to the surface extension energy in the process of drop breakup. The obtained value,  $A_2 \approx 0.12$ , falls in the range of values proposed by Davis (3) and Calabrese et al. (4) to describe the experimental results for the mean and maximal drop diameters at steady-state. Further discussion of these results is presented in Refs. (8,9).





**Figure 4.** Logarithm of the normalized breakup rate constants,  $k_{BR} d^{2/3} / \epsilon^{1/3}$ , as a function of the normalized diameter of the drops in the studied systems, as determined by Eq. (2) with  $A_0 = 0.24$ ,  $A_1 = 12.2$  and  $A_2 = 0.12$ .

#### 4/ Conclusions.

- Systematic set of experiments with oil-in-water emulsions was performed to determine the rate of drop breakup in turbulent flow. The effects of drop diameter,  $d$ , oil viscosity,  $\eta_D$ , interfacial tension,  $\sigma_{OW}$ , and rate of energy dissipation,  $\epsilon$ , on the kinetics of the drop breakup process were quantified.
- A kinetic scheme for data analysis is formulated, based on the assumption that the drop breakup is an irreversible reaction of first order and that daughter drops of various sizes are formed in the breakup event. This scheme allowed us to determine the breakup rate constant,  $k_{BR}$ .
- The results show that  $k_{BR}$  decreases with the decrease of  $d$  and tends to zero, when  $d$  approaches the Kolmogorov size,  $d_K$ . At given drop diameter,  $k_{BR}$  depends strongly on the values of all other factors studied:  $\eta_D$ ,  $\sigma_{OW}$ , and  $\epsilon$ .
- A semi-empirical formula for the dependence  $k_{BR}$  on the factors studied was constructed and verified by the experimental results. The formula represents  $k_{BR}$  as a product of (a) the drop-eddy collision frequency and (b) the drop breakup efficiency. The latter includes contributions of the energy for surface extension and the viscous energy dissipated inside the drops, in the process of drop deformation and breakup.

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