

## DROP SIZE IN CONCENTRATED EMULSIONS, OBTAINED BY ROTOR-STATOR HOMOGENIZATION

Abstract No 53

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### Abstract (english) (1458 characters)

Systematic emulsification experiments were performed to determine the mean volume surface diameter,  $d_{32}$ , and maximal drop diameter,  $dV_{95}$ , as functions of (a) oil volume fraction,  $10\% < F_i < 90\%$ ; (b) Interfacial tension; (c) Viscosities of the continuous phase (between 1 and 50 mPa.s) and dispersed phase (between 3 and 10000 mPa.s); and (d) Rotor speed in the homogenizer. The rheological properties of the formed emulsions were measured to analyze the relation between shear stress during emulsification and size of the formed drops. The experimental results showed that: (1) For viscous oils ( $\eta_{aD} > 20$  mPa.s),  $d_{32}$ ,  $dV_{95}$ , and drop polydispersity decrease significantly upon increase of  $F_i$  above 40%; for less viscous oil ( $\eta_{aD} = 3$  mPa.s),  $d_{32}$  and  $dV_{95}$  remain almost constant in the entire studied range of  $F_i$ . (2) At  $F_i < 50\%$ ,  $d_{32}$  and  $dV_{95}$  significantly increase with the increase of  $\eta_{aD}$ , whereas at  $F_i = 85\%$ ,  $d_{32}$  and  $dV_{95}$  are almost unaffected by oil viscosity (for  $\eta_{aD}$  between 3 and 10000 mPa.s). The interfacial tension and speed of rotation affect significantly the final drop sizes, for all oil volume fractions studied. The obtained results are explained theoretically by considering two different regimes of emulsification, corresponding to low and high  $F_i$ , respectively. New theoretical expression for the mean drop size after emulsification of concentrated emulsions (with  $F_i > 80\%$ ) is proposed and verified experimentally.

## DROP SIZE IN CONCENTRATED EMULSIONS, OBTAINED BY ROTOR-STATOR HOMOGENIZATION

### 1/ Introduction.

In a series of recent studies (1-3) we investigated the effects of several factors (viscosity of the phases, interfacial tension, hydrodynamic conditions, etc.) on the mean drop size and polydispersity of emulsions formed in turbulent flow. An important and non-trivial observation was that the drop size and polydispersity could be strongly reduced (at appropriate conditions) by increasing the viscosity of the external phase,  $\eta_c$ , and/or the drop volume fraction above ca.  $\Phi > 50\%$ . The latter two effects were explained with the transition from inertial regime of emulsification (at low  $\eta_c$  and  $\Phi$ ) to viscous regime of emulsification (at high  $\eta_c$  and/or high  $\Phi$ ), due to increase of the size of the smallest turbulent eddies in the turbulent flow (1). The latter explanation gave a conceptual and theoretical framework for analysis of the drop breakup process in concentrated emulsions, subject to turbulent flow.

The focus of the current study is to analyze deeper the effect of oil volume fraction on the process of drop breakup, especially in the range of semi-concentrated ( $50 \text{ vol. } \% < \Phi < 75 \text{ vol. } \%$ ) and highly concentrated emulsions ( $\Phi > 75 \text{ vol. } \%$ ).

### 2/ Materials and methods.

**2/1. Materials.** Two nonionic surfactants were used to ensure different oil-water interfacial tensions: polyoxyethylene-8 tridecyl ether (Lutensol A8) and polyoxyethylene-20 tridecyl ether (Lutensol TO20), products of BASF. The emulsifier concentration in the aqueous solutions (10 wt %) was chosen sufficiently high to suppress drop-drop coalescence during emulsification. As dispersed phase we used several oils of different viscosities: hexadecane with  $\eta_D = 3.0 \text{ mPa}\cdot\text{s}$  (Merck); mineral oils with  $\eta_D = 25$  and  $130 \text{ mPa}\cdot\text{s}$  (Sigma-Aldrich; called below "Light" and "Heavy" oil, respectively); and four silicone oils with  $\eta_D = 95, 194, 1024,$  and  $10000 \text{ mPa}\cdot\text{s}$  (denoted for clarity as SilXX, where XX expresses oil viscosity). All quoted viscosities are measured at  $25^\circ\text{C}$ . The mineral oils and hexadecane were purified from surface-active contaminations by passing them through a glass column, filled with Florisil adsorbent (4). The silicone oils were used as received.

**2/2. Emulsification by Ultra Turrax.** This equipment was used in the experiments, aimed to study the effect of oil viscosity in wide range (between 3 and  $10,000 \text{ mPa}\cdot\text{s}$ ), in which both mineral and silicone oils were included. The following procedure was used: (1) The necessary amount of oil was added to the aqueous phase, under continuous stirring to form coarse oil-in-water emulsion. (2) This emulsion was further homogenized by Ultra Turrax for 5 min, at a specified rotation speed. (3) Samples for measuring the mean drop size and for characterization of the rheological properties of the formed emulsions were taken. Water bath was used for keeping the temperature during emulsification at  $T = 25 \pm 3^\circ\text{C}$ .

**2/3. Emulsification by magic Lab (IKA).** This rotor-stator mixer was used in the experiments with mineral oils only. The emulsions were obtained in a two-step process: The first step is the formation of oil-water premix (200 ml coarse emulsion). In the second step, this coarse emulsion is poured into the inlet funnel of the magic Lab mixer. Rotor Module 6F was used, at rotation speeds of 5,000; 10,200 or 20,000 rpm. The emulsion passes several times through the homogenization unit, as a result of pumping the emulsion in a closed circulation loop. During this step, the emulsion in the funnel is constantly stirred to make sure that the entire emulsion passes through the homogenizer. This emulsification stage continues for 15 min. To maintain the temperature constant during emulsification, we used cryo-thermostat (F31-C, Julabo LaborTechnik GmbH), connected to the magic Lab mixer.

**2/4. Determination of drop size distribution.** The drop size distribution in the obtained emulsions was determined by video-enhanced optical microscopy (5,6). For each sample, the

diameters of at least 1000 drops were measured. The accuracy of the optical measurements was estimated to be  $\approx 0.3 \mu\text{m}$  (5). Two characteristic drop sizes were determined from the measured drop diameters: (1) The mean volume-surface diameter,  $d_{32}$  and (2) The volume-95 diameter,  $d_{V95}$ , which is defined as the diameter for which 95 % by volume of the dispersed oil is contained in drops with  $d < d_{V95}$  and presents an experimentally accessible measure of the maximum drop size (1).

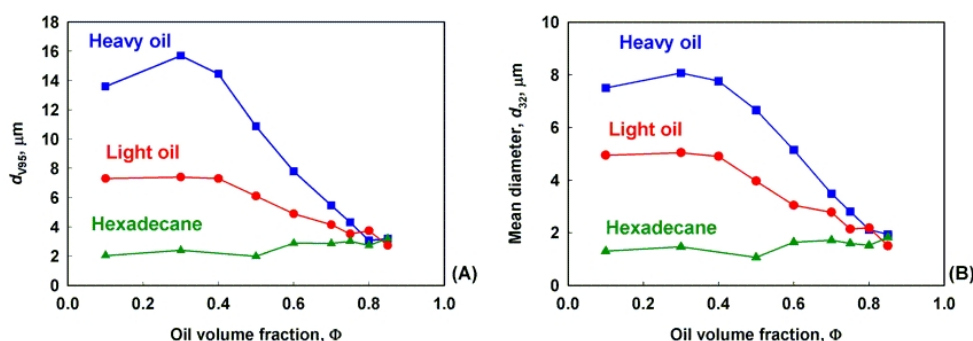
**2/5. Measurement of the viscosities.** The viscosities of the used surfactant solutions were measured by capillary viscometer (when the viscosity was below 5 mPa.s) and with Brookfield rotational viscometer when the viscosity was above 5 mPa.s. The viscosity of the used oils was measured by Brookfield rotational viscometer

**2/6. Measurement of interfacial tension.** The equilibrium oil-water interfacial tension was measured by a drop-shape-analysis of pendant oil drops, immersed in the surfactant solutions. The measurements were performed on commercial Drop Shape Analysis system DSA 10 (Krüss GmbH, Hamburg, Germany).

### 3/ Main experimental results from the emulsification experiments.

**3/1. Effect of oil volume fraction for mineral oil emulsions.** The effect of oil volume fraction on the mean drop size, maximal drop size, and polydispersity of the formed emulsions was studied with mineral oils having different viscosities: 3 mPa.s (hexadecane), 25 mPa.s (light oil) and 130 mPa.s (heavy oil). The obtained experimental results are shown in Figure 1. It is seen that for heavy and light oil emulsions (blue squares and red circles in the figure), both  $d_{32}$  and  $d_{V95}$  remain almost constant at  $\Phi < 0.5$  and decreased significantly with the increase of  $\Phi$  from 0.5 to 0.8. The further increase of  $\Phi$  from 0.8 to 0.85 does not change noticeably the mean and maximum drop diameters. This significant change in the mean and maximal drop diameters at intermediate volume fractions is accompanied by a significant decrease of the polydispersity of these emulsions from 1.9 to 1.4 (here the polydispersity is defined as the ratio  $d_{V95}/d_{32}$ ). In contrast, the mean and maximum drop diameters in the hexadecane emulsions remained almost constant in the entire range of studied volume fractions,  $\Phi$ , see the green triangles in Figure 1.

From this series of experiments we can conclude that the drop size decreases significantly with increasing of  $\Phi$  for emulsions of mineral oils with  $\eta_D > 25 \text{ mPa.s}$ . For emulsions with  $\Phi < 0.8$ , the mean and maximum drop sizes increase with  $\eta_D$ , whereas at  $\Phi = 0.8$  and 0.85 the emulsions have  $d_{V95} \approx 3 \mu\text{m}$  and  $d_{32} \approx 1.8 \mu\text{m}$ , irrespectively of oil viscosity.



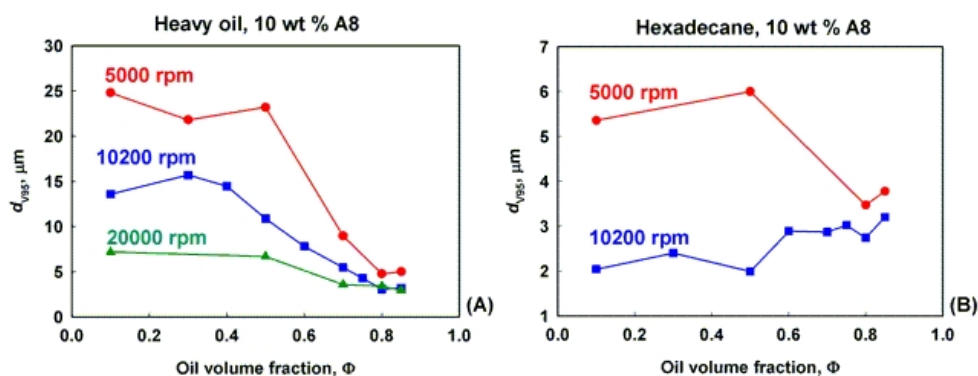
**Figure 1.** Dependence of (A) maximal diameter by volume,  $d_{V95}$ , and (B) mean volume-surface diameter,  $d_{32}$ , on the oil volume fraction,  $\Phi$ , for emulsions stabilized by 10 wt % A8 of hexadecane (green triangles); light oil (red circles), and heavy oil (blue squares). These emulsions were prepared by magic Lab mixer, operated at 10,200 rpm.

Similar series of experiments was performed with Ultra Turrax homogenizer. The emulsions were prepared at 20500 rpm for 5 min. The comparison of the results obtained with the two rotor-stator homogenizers showed that the mean and maximum drop diameters were slightly smaller for the emulsions prepared by magic Lab, as compared to those prepared with Ultra Turrax. This difference is easily explained by the higher rate of energy dissipation in the magic Lab. On the other hand, the effects of all factors studied were very similar for the emulsions prepared by these two homogenizers. In particular, the mean and maximum drop diameters for hexadecane and heavy oil emulsions were almost the same at high drop volume fraction,  $\Phi = 0.85$ , which evidences that for viscous oils, the drop breakup process is much more efficient at high  $\Phi$ .

### 3/2. Effect of rotational speed on $d(\Phi)$ dependence for mineral oil emulsions.

Experiments at three rotational speeds 5000; 10200 and 20000 rpm were performed with heavy oil emulsions, at different oil volume fractions, see Figure 2A. The results showed that the dependences  $d(\Phi)$  are similar for all rotation speeds studied: At  $\Phi < 0.4$ ,  $d_{V95}$  does not depend on  $\Phi$ , but depends significantly on the rotation speed (smaller drops are formed at higher rpm). At  $0.4 < \Phi < 0.80$ ,  $d_{V95}$  and  $d_{32}$  decrease rapidly with the increase of  $\Phi$  and again depend significantly on the rotation speed. In contrast, the relative difference in the sizes of emulsions, formed at different rotation speeds, is much smaller at  $\Phi > 0.75$ , as compared to the range of low  $\Phi$ . In general, the higher rotation speed leads to smaller drops, as expected, but this effect is much less pronounced at high drop volume fraction.

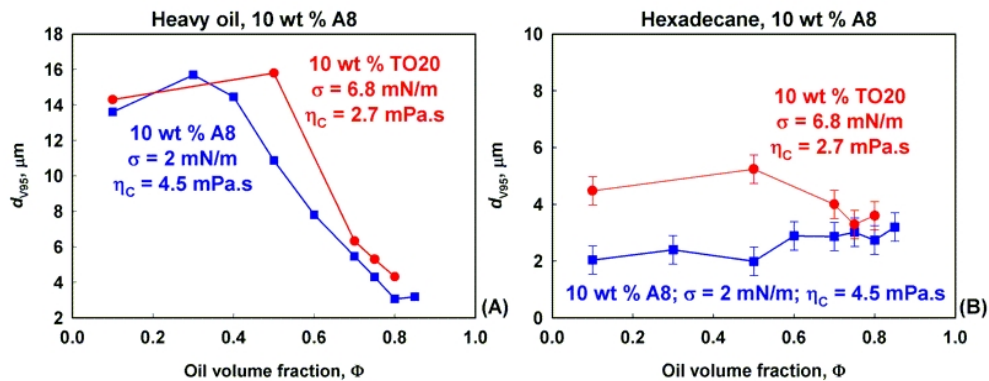
Similar series of experiments was performed with hexadecane emulsions, at two rotation speeds, see Figure 2B. One sees that at the lower rotation speed, 5000 rpm, there is a transitional drop volume fraction, after which  $d_{V95}$  and  $d_{32}$  decrease with the increase of  $\Phi$ , similarly to the case of heavy oil emulsions. At the higher rotation speed, 10200 rpm, the drop size slightly increases with the oil volume fractions.



**Figure 2.** Dependence of maximum diameter by volume,  $d_{V95}$ , on the oil volume fraction,  $\Phi$ , for (A) heavy oil and (B) hexadecane in water emulsions, stabilized by 10 wt % A8, prepared by stirring with magic Lab at 5000 rpm (red circles), 10200 rpm (blue squares), or 20000 rpm (green triangles).

**3/3. Effect of interfacial tension on the dependence  $d(\Phi)$ .** To check how the interfacial tension affects the mean and maximum drop sizes of the formed emulsions, we performed two series of experiments, by using as emulsifiers A8 ( $\sigma = 2$  mN/m and  $\eta_C = 4.5$  mPa.s) and TO20 ( $\sigma = 6.8$  mN/m and  $\eta_C = 2.7$  mPa.s). These emulsions were prepared by magic Lab at 10200 rpm. As oily phase we used heavy oil (Figure 3A) or hexadecane (Figure 3B). For Heavy oil, the dependences of  $d(\Phi)$  are very similar for both surfactants, but the mean and the maximum drop diameters are only slightly larger for the emulsions stabilized by TO20, despite the fact that the interfacial tensions are rather different for these two emulsifiers. The explanation of this non-trivial result is that, at low  $\Phi$ , the emulsification is in the inertial turbulent regime and, for this viscous oil, the energy dissipation

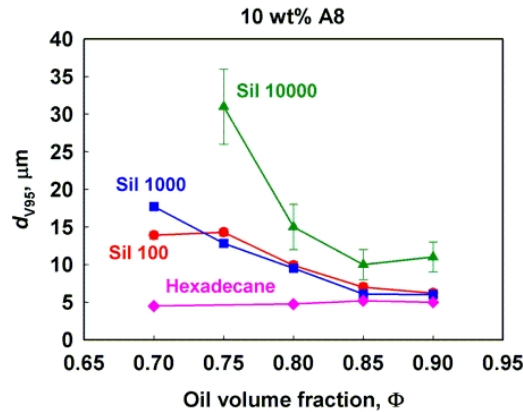
inside the breaking drops dominates the interfacial forces (1). On the other hand, at high  $\Phi$ , where the drop breakup is in the viscous turbulent regime of emulsification, the mean drop size does not depend on the interfacial tension, because a capillary instability and drop breakup occur well before reaching the longest stable threads, for which the interfacial tension is decisive. For hexadecane, one sees from Figure 3B that  $\sigma$  affects significantly the drop size at low  $\Phi$  (in the inertial turbulent regime of emulsification), because the interfacial forces are important for this low-viscosity oil (1). At  $\Phi > 0.5$ , the transition to viscous regime of emulsification leads to much smaller effect of  $\sigma$  on the size of the formed drops (similarly to the case of heavy oil).



**Figure 3.** Dependence of maximum diameter by volume,  $d_{v95}$ , on the oil volume fraction,  $\Phi$ , for (A) heavy oil and (B) hexadecane in water emulsions, prepared in magic Lab mixer and stabilized by two different emulsifiers, A8 and TO20.

Therefore, we can conclude that, at low  $\Phi$ , the effect of interfacial tension on the mean and maximum drop sizes is significant in emulsions of low-viscosity oils (hexadecane), whereas this effect is relatively small at high  $\Phi$  for both viscous and low-viscosity oils.

**3/4. Emulsification of viscous silicone oils.** The emulsification in turbulent flow of viscous oils with  $\eta_D > 10 \text{ mPa.s}$  is rather difficult (1). To check whether viscous oils could be emulsified in the rotor-stator homogenizer, we performed experiments with highly viscous silicone oils ( $\eta_D$  between 100 and 10000  $\text{mPa.s}$ ), by using 10 wt % A8 solution as aqueous phase. The obtained experimental results are shown in Figure 4. The most important result from this series of experiments was that the mean and maximum drop sizes depended slightly on the viscosity of the oily phase for emulsions with  $\Phi \geq 0.85$ . Remarkably, even the silicone oil with viscosity 10,000  $\text{mPa.s}$  was successfully emulsified at high  $\Phi$  and emulsions with relatively small polydispersity were obtained. Note that this viscous oil could not be emulsified at  $\Phi < 0.7$  - bulk layer of non-emulsified oil remained after the homogenization procedure.

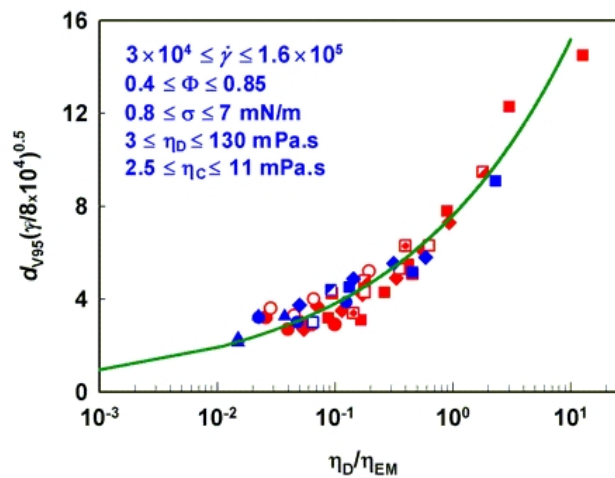


**Figure 4.** Dependence of maximum diameter by volume,  $d_{v95}$ , on oil volume fraction,  $\Phi$ , for emulsions of silicone oils with viscosity of 100 mPa.s (red circles); 1000 mPa.s (blue squares) and 10,000 mPa.s (green triangles). These emulsions were stabilized by 10 wt % A8 and prepared by stirring for 5 min with Ultra Turrax, at 20500 rpm.

**3/5. Formula describing the mean and maximum drop diameters.** The obtained experimental results show that the emulsification at high drop volume fractions is rather interesting, because very viscous oils could be emulsified and the mean drop size depends slightly on the particular emulsification conditions. We found that all experimental results for the mean and maximum drop diameters, obtained at intermediate and high drop volume fraction,  $0.4 \leq \Phi \leq 0.85$ , could be described by a simple scaling law:

$$d = A\dot{\gamma}^{-0.5} \left( \frac{\eta_D}{\eta_{EM}} \right)^{0.3} \quad (1)$$

where  $A = 0.0018$  for  $d_{32}$  and  $A = 0.0027$  for  $d_{v95}$ , and the emulsion viscosity  $\eta_{EM}$  was calculated by the cell model of Yaron and Gal-Or (7), see Figure 5. The physico-chemical basis for this scaling law is currently analysed.



**Figure 5.** Description by Eq. 1 of the maximum drop diameter,  $d_{v95}$ , for emulsions obtained under various conditions (as shown in the figure). These emulsions are obtained by magic Lab with different oils, oil volume fractions, emulsifiers, and rotation speeds.

#### 4/ Conclusions

The main results from this study could be summarized as follows:

- (1) The mean and maximum drop diameters decrease with the increase of  $\Phi > 40\%$ , for oils with  $\eta_D \geq 25$  mPa.s.
- (2) The drop size and polydispersity increase with  $\eta_D$  at  $\Phi < 0.8$ , and do not depend on  $\eta_D$  at  $\Phi = 0.8$  and  $0.85$ .
- (3) The drop size and polydispersity decrease with the increase of rotation speed, however, this effect is much smaller at high  $\Phi$ .
- (4) Interfacial tension has minor effect on the drop size distribution for concentrated emulsions, whereas the viscosity of the continuous phase,  $\eta_C$  affects significantly the size of the formed drops.
- (5) Simple scaling can describe all results obtained at moderate and high drop volume fractions,  $0.4 < \Phi < 0.9$  see Eq. (1) and Figure 5.

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