

**INFLUENCE OF THE DISPERSED PHASE VISCOSITY ON THE  
MIXING OF CONCENTRATED OIL-IN-WATER EMULSIONS  
IN THE TRANSITION FLOW REGIME**

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**Abstract.** We have evaluated the emulsification of oil of varying viscosities for concentrated dispersions (> 60 %). Rushton type impellers and baffled mixing vessels were used. The emulsions were prepared in the transition regime ( $80 < Re < 200$ ). It was found that, as the concentration increases, it is the emulsion viscosity that controls droplet size, regardless of the dispersed phase viscosity and the hydrodynamics. We have follow an experimental procedure that allows for the full scale-up of the results.

**Résumé.** Nous avons évalué l'émulsification d'émulsions concentrées (> 60 %) huile-dans-eau. Des cuves chicanées et des agitateurs du type Rushton on été utilisés pour le mélange des émulsions. L'agitation a été menée en régime de transition ( $80 < Re < 200$ ). On a trouvé que la viscosité de l'émulsion contrôle la taille de gouttelette à mesure que la concentration augmente, malgré la viscosité de l'huile et l'hydrodynamique. Notre méthode expérimentale permet l'extrapolation des résultats.

**Key-words.** mixing, concentrated emulsions, dispersed phase viscosity

There is hardly a process plant that does not include the blending or mixing of fluids of different phases, either miscible or immiscible. The emulsification of two, or more immiscible liquids, is a common operation in the food, cosmetic and pharmaceutical industries. Although a good deal is known about the mixing of low concentration liquid-liquid systems, the dynamic of formation of concentrated emulsions which necessarily contain a surfactant, is still not well understood. This is due to the high number of parameters involved that include the hydrodynamic phenomena, frequently of the turbulent type, and the physicochemical effects due to the nature and composition of the many phases implicated.

There has been two main approaches to deal with this complex problem. On the one hand, there is the exclusive hydrodynamic approximation in which the turbulent mixing of very dilute ( $< 2$  %) or low concentration ( $< 40$  %) dispersions is evaluated, no surfactants added (e.g., Refs. 1-8). However, it is the concentrated range (> 50 %) of surfactant stabilized emulsions that is usually of practical importance. On the other hand, there are many works that have tackled the physicochemical intricacies of the problem (e.g., Ref.9). Unfortunately, little attention, if any, is paid to the dynamic aspect of the emulsion formation, i.e., the physical and rheological properties of the fluid, the geometry of the mixing device, the flow regime ( $Re$ ) and the power consumption ( $P_M$ ). As a consequence, it is difficult if not impossible to reproduce and scale-up these works.

It cannot be denied that both approaches have been extremely useful to untangle the complexities of liquid-liquid mixing. However, none have fully addressed the industrial issues. To our knowledge, only a few investigators have attempted to combine both approaches (10-16), but their results are still difficult to scale-up. In this work, we combine the dynamic and the physicochemical approaches, by means of well-known scale-up procedures. In this sense, the standard mixing geometry as well as Rushton type turbines (17) were used and both the  $Re$  number and the  $P_M$  were computed for each experiment.

Most of the experimental test were carried out in a way that ensured a similar macroscopic flow pattern, i.e. matching  $Re$  number (80 to 200). In order to maintain similar  $Re$  numbers, the size of the impeller (and hence, of the mixing vessel) for constant mixing speed was increased as the emulsion concentration increased. In some cases, both impeller size and mixing speed were varied in order to maintain a similar  $Re$ .

Previous to the mixing experiments, a rheological evaluation was carried out. Several emulsions of varying dispersed phase content (40 to 80 %) and mean droplet diameter (2 to 40  $\mu\text{m}$ ) were evaluated in order to obtain the emulsions viscosities in the shear rate range expected during mixing. The viscosity obtained in this fashion was used to predict the mixing conditions (impeller size and mixing conditions) for a given Re.

The physicochemical variables can be combined into a single dimensionless parameter, the SAD/RT, described elsewhere (9). In our work, the SAD/RT was virtually the same for all the systems evaluated and, as a result, the equilibrium interfacial tension was also similar. One composition variable, or  $\phi$ , was scanned throughout this work, and the viscosity of the oil phase was also varied (10, 100 and 1000 mPa.s).

The droplet size evolution with mixing provides an insight of the phenomena occurring on the microscopic level. Therefore, the experimental tests consisted of mixing for a maximum period of two hours, during which samples of emulsions were withdrawn from the vessel and the droplet size distribution was measured. In this manner, the Sauter mean diameter,  $d_{32}$ , was monitored as a function of mixing time.

## EXPERIMENTAL PROCEDURE

One of the first requirements of this work was that the emulsions should be sufficiently stable in order to be able to measure the droplet size distribution. Consequently, the static stability of the emulsions was assessed and it was verified that the droplet size distribution experienced negligible changes over extended periods of time (several days) for the less concentrated systems (50 %) and no perceptible changes for the more concentrated (> 60 %). These emulsions were formulated with 2 % w/w of an anionic surfactant, sodium dodecyl sulphate (SDS). The 2 % surfactant concentration was calculated based on the dispersed phase in order to maintain a constant surfactant/oil mass ratio for all the  $\phi$  values scanned.

The viscosity of the dispersed phase,  $\mu_D$ , was changed by blending kerosene (1 mPa.s) and a commercial lube oil (3 Pa.s) in different proportions in order to obtain  $\mu_D$  values of 10, 100 and 1000 mPa.s. The equilibrium interfacial tension of every system was measured by means of the spinning drop method. The experimental value was about 1 to 3 mN/m, regardless of the oil phase viscosity and  $\phi$ .

A laser diffraction based optical instrument was used to measure the droplet size distribution of the emulsion samples. The samples were withdrawn by means of a pipette placed in a fixed position (r: T/4, z: H/3), in the neighbourhood of the impeller region. At the beginning of this work, two samples were taken simultaneously at two different places, one in the impeller region and the other in the circulation region, in order to verify that the surfactant would inhibit droplet coalesce, as expected. Since no coalesce was found, sampling in the circulation region was discontinued.

Conventional mixers, able to maintain a constant mixing speed, were used to perform the mixing tests. Depending on the expected emulsion viscosity, the mixing speed was varied from 800 to 1200 rpm. We used baffled, flat bottomed vessels and Rushton impellers whose geometric proportions complied with the so-called standard configuration (H=T, D = 2/5 T, C = 1/3 H, B = 1/10 T). Four impeller sizes were necessary to scale the Re number (3, 4.5, 6 and 12 cm). The volume of the vessels varied accordingly.

A rotational viscometer was used to carry out the simple shear evaluation of the emulsions and the kerosene/lube oil blends viscosity measurement. Concentric cylinders sensors were utilised with this purpose.

## CALCULATION OF Re AND $\varepsilon_M$

As aforementioned, the simple shear rheological behavior of concentrated emulsions (> 40 %) and various droplet sizes was carried out. A typical shear-thinning rheological behavior was obtained for the more concentrated samples (> 50 %). As shown in Fig. 1, which depicts the apparent viscosity as a function of shear rate of a 2  $\mu\text{m}$  emulsion, the flow curve tends to an asymptotic viscosity value at high shear rate, or  $\eta_{\infty}$  (18). The  $\eta_{\infty}$  value was used to obtain empirical correlations of the type

$$\eta_r = 1 + 2.5 \frac{\eta_{\infty}}{\eta_c} a^2 + b \exp(c \dot{\gamma}) \quad (1)$$

in which  $\eta_r$  is the relative viscosity ( $\eta/\eta_c$ ) and a, b and c are adjustable coefficients. Three different correlations were obtained for  $d_{43}$  values of 2, 20 and 40  $\mu\text{m}$ . This size range encompasses most of the experimental results. The shape of Eq. 1 was inspired on the Thomas semi-empirical correlation (19), in which coefficients a, b and c are equal to 10.05, 0.00273 and 16.06, respectively.

With the rheological information at hand, the necessary impeller size and mixing speed to obtain a minimum Re number of 100, were estimated by means of the expression

$$\text{Re} = \frac{ND^2}{\eta_{\infty}} \quad (2)$$

We purposely underestimated the Re number by using the viscosity corresponding to the more viscous emulsion, this is, the 2 μm emulsion. Once the mixing test was carried out, the Re number was corrected by computing the emulsion viscosity according to the resultant droplet size and value, using the corresponding empirical correlation (Eq. 1). In this manner, the corrected Re was always equal or larger than the first estimate.

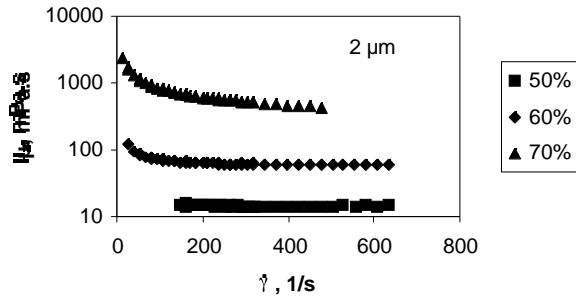


Fig.1. Apparent viscosity as a function of shear rate for 2 μm size emulsions of varying dispersed phase content. μ<sub>D</sub>: 3 Pa.s.

It has to be noted that the restriction of minimum Re number equal to 100 was imposed in order to ensure whole fluid circulation in the mixing vessel and, hence, a homogeneous emulsion. The 100 value is the minimum value for yield stress, non-Newtonian fluids, according to Solomon et al and Hirata and Aoshima (20,21). We expected the more concentrated emulsions to show a viscoplastic behavior (22) and, in fact, the 80 %, 2 μm emulsion, was viscoelastic (G'/G'': 40 for a stress sweep) and, hence, viscoplastic. Due to the high viscosity of this emulsion, the larger Re number that could be reached was 80, but we considered this value good enough for our purposes.

An additional constraint was imposed on the experimental conditions, this is, a minimum impeller shear rate of 100 s<sup>-1</sup>. The purpose of this condition was to assure that the viscosity near the impeller was close to the high shear rate asymptotic value ( ) and, then, the Re estimate be as accurate as possible. The impeller shear rate was computed by means of the Robertson y Ulbrecht correlation (23), which was developed for Rushton turbines in the 100 < Re < 2.9.10<sup>4</sup> range,

$$\dot{\gamma} = 3,3 \frac{ND^2}{N}^{0,5} \quad (3)$$

In Eq. 3, is the kinematic viscosity calculated with the zero-shear viscosity,  $\nu_0$ . Eq. 3 yielded that a minimum mixing speed of 600 rpm was necessary to ensure shear rates larger than 100 s<sup>-1</sup>.

As aforementioned, it was found that the emulsions were quite homogeneous in the mixing vessel, indicating that negligible coalescence was occurring outside the impeller region. This is an interesting result since it is in the impeller region that the “essence” of the process takes place, given that, away from this zone, the fluid just recirculates. In fact, it is in the impeller region that most of the energy is dissipated (24,25). Therefore, it is necessary to compute the  $\epsilon_M$  parameter, not only for scale-up purposes but to assess the microscopic mean energy dissipation rate,  $\langle \epsilon \rangle$ , given that  $\epsilon_M$  is 95 to 105 % of  $\langle \epsilon \rangle$  (26).

The specific power,  $P_M$ , was calculated as follows. Once the Re number was corrected, the power number was obtained making use curves of  $Po$  as a function of Re available in the literature (27). Then, the power input could be calculated as shown in Eq. 4,

$$P = N_p N^3 D^5 \quad (4)$$

Finally,  $\epsilon_M$  was obtained by dividing P by V, where V is the liquid volume in the mixing vessel. It is worth to note that, for the Re range used in this work,  $Po$  hardly varies with it (3 to 4).

## RESULTS

As expected the droplet size diminished with mixing time. Fig. 2 shows the typical behavior obtained in this work of Sauter diameter as a function of specific energy,  $\hat{E}$  ( $\mu_D$  multiplied by the mixing time). It can be observed that, on a log-log plot,  $d_{32}$  is a linear function of  $\hat{E}$  (mean slope of  $-0.20$ ), indicating that alike mechanisms are involved in the size reduction process. We considered that this result is a good proof of the validity of our experimental method since we are comparing really similar systems.

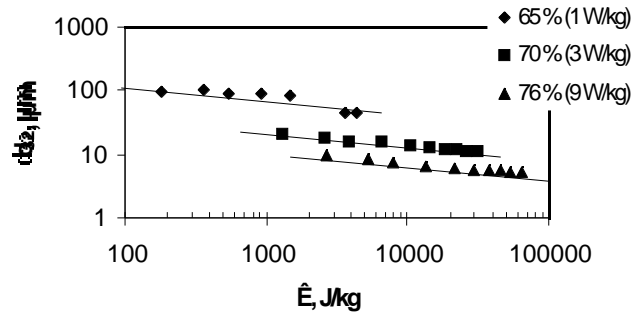


Fig. 2. Sauter diameter as a function of specific energy for values of 65, 71 and 76 %.  $\mu_D$ : 100 mPa.s

As expected, as the oil phase viscosity increased, the droplet size also increased. This can be seen in Fig. 3 which depicts the Sauter diameter as a function of  $\mu_D$ , on a log-log plot, for an equal  $\hat{E}$  value. The relationship between these two parameters is approximately linear and the mean slope for the whole experimental data is about 0.38 (0.33 to 0.40). Interestingly, this result is in good agreement with the 3/8 slope obtained by Calabrese et al (5,6), also reported by Walstra (28), which corresponds to the mixing of low concentration dispersions in turbulent conditions.

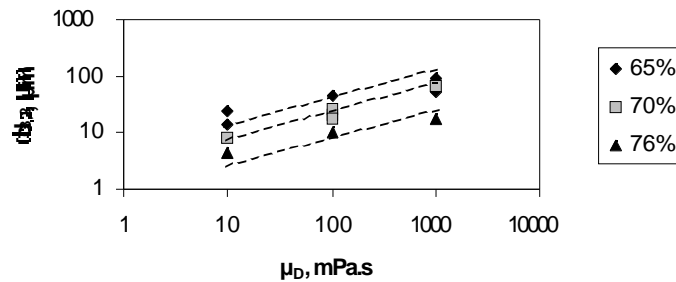


Fig. 3. Sauter diameter as a function of  $\mu_D$  for values of 65 to 76 %. Re: 100 to 200.  $\mu_M$ : 1 to 9 W/kg.

Both Figs. 2 and 3 show that the droplet size diminishes as  $\mu_D$  increases. This reduction may be first attributed to the increase of  $\mu_M$  that is required to maintain matching Re numbers. However, a similar trend is obtained for emulsions that were prepared at the same  $\mu_M$  but different Re. This can be observed in Fig. 4; the droplet size still tends to decrease with increasing  $\mu_D$ , despite the fact Re diminishes.

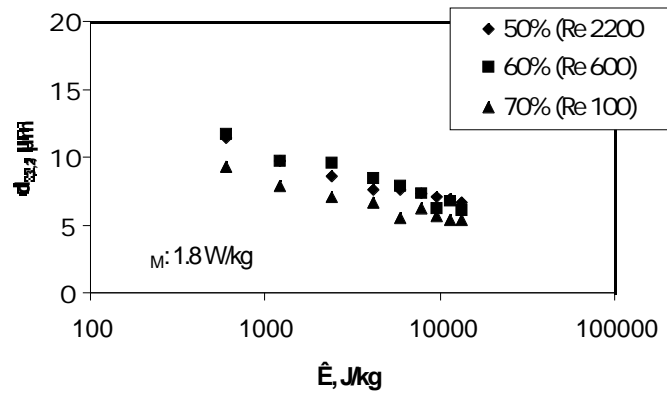


Fig. 4. Sauter diameter as a function of specific energy for emulsions prepared at the same specific power and decreasing Re.  $\mu_D$ : 10 mPa.s.

Finally, we have prepared Fig. 5 that shows the Sauter diameter as a function of  $\phi$  for an equal  $\dot{E}$  value and  $\mu_D$  as the parameter. For the sake of clarity, no distinction of Re or  $M$  has been made in this figure, although the arrows points in the direction in which both variables increase. It can be seen in the aforementioned figure that the less concentrated emulsions are highly dependent on the dynamic conditions and  $\mu_D$ . However, as  $\phi$  increases, the droplet size seems to converge to an asymptotic value, becoming more independent of the dynamic conditions and  $\mu_D$ .

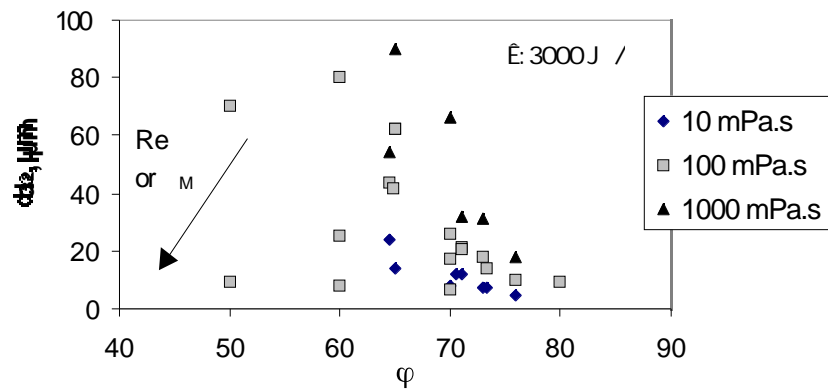


Fig. 5. Sauter diameter as a function of dispersed phase content for a constant  $\dot{E}$  value.  $\mu_D$ : 10 to 1000 mPa.s. Arrow points in the direction Re and  $M$  increase.

Therefore, it can be said that the dynamic conditions determine the droplet size for the less concentrated emulsions while the dispersed phase content, or composition, determines the droplet size for the high dispersed phase contents. However, the last affirmation is not enough to explain the underlying mechanisms that promote smaller droplet sizes. There has to be other properties that evolve with  $\phi$  and that are responsible for this phenomenon. There are two candidates that can be accounted for and these are the interfacial tension and the emulsion viscosity. Regarding the first property, we obtained that the equilibrium interfacial tension is about the same (1 to 3 mN/m) for the  $\phi$  scan, regardless of the oil viscosity. It is clear that equal equilibrium interfacial tension does not guarantee that the dynamic interfacial tension is comparable since the last contains the convective contribution due to the mixing. However, given that most of the cases evaluated in this work involved similar Re, and that the physicochemical nature of the phases does not vary with  $\phi$ , it can be reasonably expected that the dynamic interfacial tension be also similar. Regarding the viscosity of the emulsion, it is seen that this property experiences a strong change as  $\phi$  increases, from 10 mPa.s for a 50 % emulsion, to about 10 Pa.s for an 80 % emulsion.

Therefore, the emulsion viscosity appears to be responsible for the phenomenon in discussion. Whatever the underlying mechanism that is responsible for the droplet rupturing, either elongation, viscous stresses, pressure fluctuations or drop-vortex collisions (29), the transfer of momentum seems to improve with the emulsion viscosity, resulting in an enhanced process efficiency in the sense of the droplet size reduction. In any case, these result are in agreement with several authors that have found consistently that highly concentrated emulsions, or HIPR, seem to be "easier" to make and to yield very small droplet sizes (30-32), as a contrast with less concentrated dispersions.

## CONCLUSIONS

We have evaluated the mixing of concentrated, stable emulsions, in the transition regime. It has been found that, as dispersed phase content increases, it is the viscosity of the emulsion that commands the droplet reduction phenomenon. From a practical point of view, this implies that the efficiency of the mixing process can be strongly improved by increasing the internal phase content, and no penalty of increased power input is involved by doing this. In fact, the results point to the fact that less power input is necessary for a more efficient droplet rupturing process.

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