Modelling W/O/W double emulsions preparation in static mixers with shear-thinning dispersed phase

Noureddine Lebaz[1], Kristy Touma[1], Ranim Chakleh[1], Fouad Azizi[2], Nida Sheibat-Othman[1]*

1 Univesite Claude Bernard Lyon 1, LAGEPP, UMR 5007, CNRS, Villeurbanne, Lyon

2 American University of Beirut, Riyad El-Solh, Beirut, Lebanon

nida.othman@univ-lyon1.fr

Highlights

- A continuous process for the preparation of double emulsions is developed
- The droplet breakage kernel is adapted to account for the shear-thinning behavior of droplets
- Validation over a wide range of conditions (viscosity, inner fraction, turbulence intensity)

1. Introduction

Most reported DEs are prepared in batch mixing processes using impellers or rotor-stator devices. At the industrial scale, developing continuous emulsification processes would be beneficial. This study aims to investigate a novel double emulsification process based on the use of static mixers. Static mixers are motionless porous structures inserted into cylindrical pipes. They are largely employed at the industrial scale for mixing miscible fluids, to enhance mass and heat transfer and for the preparation of single emulsions (see review [1]). A population balance model is developed to describe droplet breakage within the static mixers and validated over a wide range of operating conditions. While modelling simple emulsification in static mixers was already addressed in the literature, the preparation of double emulsions fundamentally differs and requires particular treatment. First, the inner droplets are themselves constituted of emulsions, so the evolution of their viscosity (which greatly influences the breakage rate) depends not only on the oil phase but also on the encapsulated fraction of inner droplets, and possibly their size. Moreover, some leakage of inner droplets might occur, so affecting the volume of the outer droplets. Finally, salt is generally used to overcome the Laplace pressure of droplets, thus increasing the encapsulation efficiency, but this might affect the surface tension. In this work, we focus on the shear thinning behavior of the dispersed phase and propose a methodology to account for this effect in the population balance equation.

2. Methods

The inner W/O emulsion is prepared by mixing silicone oil (in which a lipophilic surfactant (Abil EM97S) is previously dissolved), with water (in which NaCl is previously dissolved at a concentration of 0.1 M) using a high shear device (Ultra-Turrax) at 12 000 rpm for 4 min. The selected silicone oils have several viscosities, between 5 mPa.s and 350 mPa.s. The aqueous dispersed phase fraction was varied from 10 to 40 wt.%.

To prepare the W/O/W double emulsions, the inner emulsion is mixed with an aqueous phase (constituted of water, plus glycerol which acts as viscosity enhancer, and the hydrophilic surfactant Tween20) by pumping them through 20 SMX+ static mixing elements in series. The pressure drop in the system is monitored using a pressure gauge (Keller LEO1: 0-3 bar, ± 3 mbar).

A population balance model was developed to describe the breakage of the outer droplets in the static mixers. Coalescence could be neglected because of the low external dispersed phase fraction (1 wt.%) and the use of a surfactant [2]. Ostwald ripening could also be neglected due to the very low solubility of silicone oil in water. Assuming spatial variation of shear in the mixers leads to the following breakage population balance equation [3]:

$$\frac{\partial \bar{n}(v,t)}{\partial t} = \int_v^{\infty} b(v,v')\bar{n}(v',t)\frac{1}{V}\int_{\boldsymbol{x}} g(\boldsymbol{x},v')\mathrm{d}\boldsymbol{x}\,\mathrm{d}v' - \bar{n}(v,t)\frac{1}{V}\int_{\boldsymbol{x}} g(\boldsymbol{x},v)\mathrm{d}\boldsymbol{x} \quad (1)$$

where $n(v,t)$ is the number-based DSD density, v the outer droplet volume, $g(v)$ the breakage kernel for a droplet of size v, $b(v, v')$ is the daughter size distribution function giving the distribution of daughter droplets generated by the breakage of a droplet of volume v' and $\boldsymbol{x}$ is the space vector. The breakage kernel is based on the Coulaloglou and Tavlarides (1977) framework [4] extended first to consider droplets breakage within the inertial and dissipation subranges of turbulence and second to account for both surface and viscosity forces to the cohesion of the dispersed phase[2]. Besides, the dispersed phase is a shear-thinning pseudo-single-phase system, so the apparent viscosity was modelled using the power law, $\mu_{\mathrm{d}} = K\dot{\gamma}^{m-1}$, where $\dot{\gamma}$ is the shear-rate [5]. Computational fluid dynamic simulations were carried out to evaluate the probability density function (pdf) of shear within the mixers $f(\dot{\gamma})$ [6], which was inserted in the kernel as follows:

$$\bar{g}(v) = \frac{1}{V}\int_V g(\boldsymbol{x}, v)\mathrm{d}\boldsymbol{x} = \int_0^\infty g(\dot{\gamma}, v) f(\dot{\gamma})\mathrm{d}\dot{\gamma} \quad (2)$$

3. Results and discussion

The parameters of the modified Coulaloglou and Tavlarides breakage kernel were identified over the total available experimental data. A global optimization method was adopted by starting from various points to avoid convergence toward local minima. To give a global picture of the model prediction capabilities, Figure 1 compares the predicted volume-based mean diameter (d_{43}) with that obtained experimentally. The variation of the operating conditions are attested by the wide variation of d_{43} in the experiments, from 30 μm to 190 μm. The predictions of the model are with a satisfactory limit.

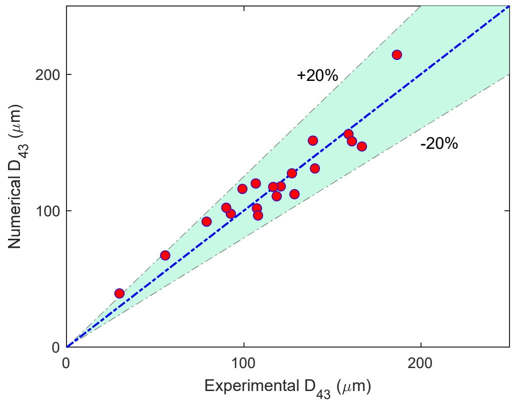

Figure 1. Overall comparison of the predicted volume-based mean diameter (D_{43}) against that obtained experimentally.

4. Conclusions

A new breakage kernel is proposed to describe the breakage of non-Newtonian shear-thinning droplets. It is applied to double emulsion preparation in static mixers. The feasibility of continuous preparation of double emulsions, with high encapsulation ratio, and the validity of the model are both demonstrated.

References

[1] J.P. Valdés, L. Kahouadji, O.K. Matar, Current advances in liquid–liquid mixing in static mixers: A review, Chemical Engineering Research and Design 177 (2022) 694–731. https://doi.org/10.1016/j.cherd.2021.11.016.

[2] N. Lebaz, F. Azizi, N. Sheibat-Othman, Modeling Droplet Breakage in Continuous Emulsification Using Static Mixers in the Framework of the Entire Spectrum of Turbulent Energy, Ind. Eng. Chem. Res. 61 (2022) 541–553. https://doi.org/10.1021/acs.iecr.1c03529.

[3] A. Buffo, J. De Bona, M. Vanni, D.L. Marchisio, Simplified volume-averaged models for liquid–liquid dispersions: Correct derivation and comparison with other approaches, Chemical Engineering Science 153 (2016) 382–393. https://doi.org/10.1016/j.ces.2016.07.032.

[4] C.A. Coulaloglou, L.L. Tavlarides, Description of interaction processes in agitated liquid-liquid dispersions, Chemical Engineering Science 32 (1977) 1289–1297.

[5] N. Lebaz, K. Touma, N. Sheibat-Othman, An original continuous process for double emulsions preparation using static mixers: Focus on the viscosity, Colloids and Surfaces A: Physicochemical and Engineering Aspects 674 (2023) 131984. https://doi.org/10.1016/j.colsurfa.2023.131984.

[6] F. Azizi, W. Abou-Hweij, N. Lebaz, N. Sheibat-Othman, A numerical evaluation of flows through an SMX-Plus mixer, Chemical Engineering Research and Design 178 (2022) 382–394. https://doi.org/10.1016/j.cherd.2021.12.030.

Keywords

Population balance modeling, droplet breakage, double emulsions, static mixers.