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Scale-up model obtained from the rheological analysis of highly concentrated emulsions prepared at three scales

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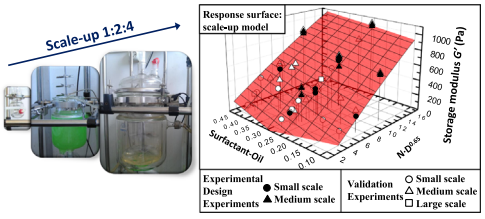
HIGHLIGHTS

- Highly concentrated w/o emulsions are prepared at three scales with geometric similarity.
- A full rheological characterization of the emulsions prepared is performed.
- The effect of the process variables and scale on the rheological parameters is studied.
- Empirical models for the rheological parameters are derived, which yield a reasonable prediction of experimental data.
- The scaling is consistent with power input per unit volume constant.

GRAPHICAL ABSTRACT



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ABSTRACT

We examine the scale invariants in the preparation of highly concentrated w/o emulsions at different scales and in varying conditions. The emulsions are characterized using rheological parameters, owing to their highly elastic behavior. We first construct and validate empirical models to describe the rheological properties. These models yield a reasonable prediction of experimental data. We then build an empirical scale-up model, to predict the preparation and composition conditions that have to be kept constant at each scale to prepare the same emulsion. For this purpose, three preparation scales with geometric similarity are used. The parameter ND^{α}, as a function of the stirring rate N, the scale (D, impeller diameter) and the exponent α (calculated empirically from the regression of all the experiments in the three scales), is defined as the scale invariant that needs to be optimized, once the dispersed phase of the emulsion, the surfactant concentration, and the dispersed phase addition time are set. As far as we know, no other study has obtained a scale invariant factor ND^{α} for the preparation of highly concentrated emulsions prepared at three different scales, which covers all three scales, different addition times and surfactant concentrations. The power law exponent obtained seems to indicate that the scale-up criterion for this system is the power input per unit volume (P/V).

1. Introduction

Emulsions are prepared and used currently in many applications. They are used as templates for the synthesis of porous materials (Blin et al., 2006; Zhang and Cooper, 2005; Binks, 2002; Du et al., 2010; Menner et al., 2006; Imhof and Pine, 1997). A specific, monodisperse and known pore size is usually desired. It is thus essential to monitor and predict the emulsion properties such as droplet size and size distribution, as they determine the pore or particle size and specific surface area of the product. Emulsion preparation is delicate, since a small variation in the procedure can change the final result. In this study, we work with highly concentrated water-in-oil (w/o)

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emulsions – used as a template for preparing hollow silica spheres – to determine how the process variables and, more importantly, the preparation scale, influence the final product. We performed a scale-up study using three scales with geometric similarity, and a scale ratio of 1:2:4. The largest tank we used has a capacity of 6 L.

Emulsions are characterized, once the dispersed phase is set, by their droplet size and droplet size distribution. In a previous study (May-Masnou et al., 2013), we examined the influence of the process variables on these parameters. We concluded that they were mainly influenced by the stirring rate and the surfactant concentration. We also studied the scale-up effect, but using only two different scales (1:2). Droplet size was measured by optical microscopy.

Another interesting feature of these emulsions is their rheological behavior. Many studies deal with the rheological properties of highly concentrated emulsions (Welch et al., 2006; Pal, 2006; Jager-Lézer et al., 1998; Masalova et al., 2011; May-Masnou et al., 2011; Alam et al., 2010; Derkach, 2009), also called gel-emulsions (Pons et al., 1993; Matsumoto et al., 2009; Kunieda et al., 1996), since they possess distinct flow behavior: they have a high yield stress τ_0, are highly elastic ($G' \gg G''$) and they have high viscosity η, which decreases with shear rate (shear-thinning). Regarding the large amplitude oscillatory shear (LAOS) behavior, these emulsions behave as type III fluids, or weak strain overshoot, in which only G'' shows strain overshoot (Hyun et al., 2002, 2003), whereas G' is constant in the linear viscoelastic region (LVR) and then decays. The critical stress (τ_c) at which the loss modulus is maximum (G''_{max}) in the oscillatory shear test is assimilated to a yield stress by Jager-Lézer et al. (1998), since it confirms the transition from the elastic to the viscous region.

In the study by May-Masnou et al. (2013) we obtained some empirical models that described the emulsion droplet size and polydispersity as a function of the process variables at two different scales. Here we derive empirical models and perform the scale-up study with the rheological parameters of the emulsions (viscosity, yield stress, viscoelastic parameters…), which are acquired using a rheometer.

The experimental design pursues the scale-up criteria for systems of this kind, particularly the scale-up invariant related to the stirring rate and the preparation scale.

2. Experimental section

2.1. Materials

Dodecane (99.5%), which constitutes the emulsion continuous phase, and Span80®, which is the surfactant (HLB=4.3), were both purchased from Sigma-Aldrich. Deionized Milli-Q water constitutes the dispersed phase, which is 90% of the emulsion weight (88% vol/vol).

2.2. Preparation of highly concentrated emulsions

Emulsions were prepared in three geometrically similar glass jacketed vessels (Fig. 1a), agitated with a three-level P-4 pitched blade impeller (Fig. 1b). The installation is the same as the one described in May-Masnou et al. (2013).

The w/o emulsions were prepared following a two-step batch method: addition of dispersed phase and droplet breakup, followed by emulsion homogenization. The continuous phase is prepared beforehand by weighing, mixing and introducing into the vessel, which is already at the desired temperature, a certain amount of surfactant and oil. The impeller is placed slightly above the continuous phase in order to start the emulsification as soon as the dispersed phase is transferred to the vessel. While the dispersed phase is being added, the stirrer produces enough shear stress to break up the droplets and form the emulsion. Once all the dispersed phase has been added, the emulsion is stirred at the same rate for a further 5 min in order to homogenize the emulsion and ensure the incorporation of all the dispersed phase. The dispersed phase is added through a peristaltic pump (ISMATEC Reglo used in small scale and ISMATEC MCP used in both medium and large scales) to regulate the flow rate. A thermostatic bath (HAAKE F6-C35 used in both small and large scale; HUBER Ministat 230, in medium scale) regulates the temperature of the refrigeration fluid (mixture of Milli-Q water and ethylene glycol) at 25 °C. The digital laboratory stirrer IKA Eurostar power control-visc sets the stirring rate.

The characteristic dimensions of the three scales are shown in Table 1. The linear geometric relation between the three scales is 1:2:4 for both the vessel diameter (B) and height (H). However, for the impeller diameter (D), the impeller blades of the larger scale had to be shortened to prevent the friction of the metallic blades on the vessel glass walls, caused by the increased vibration of the system when working at high stirring rates. Although we do not believe that this change significantly alters the results or conclusions, this change should be taken into consideration in the assessment of possible errors and deviations, since variations in the impeller design or diameter can cause significant differences in power consumption or flow patterns (Aubin and Xuereb, 2006; Kumaresan and Joshi, 2006).

The stirring rate N (rpm) and the addition flow rate Q (mL/min) are fixed according to the experimentation plan. The torque T supplied by the agitator was measured along all the process duration. The data were collected in LabWorldSoft (IKA) software.

2.3. Characterization of the emulsions

2.3.1. Rheological parameters

The rheological tests were performed in a HAAKE Mars III Rheometer (Thermo Fisher Scientifics) and data were collected in HAAKE RheoWin Job Manager and were visualized and saved in

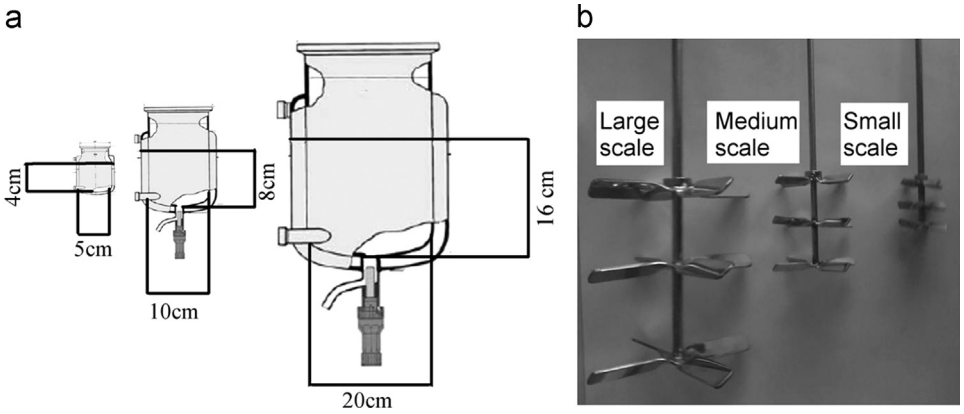

Fig. 1. (a) Liquid height and vessel diameter of the three scales. (b) Impellers used at the three scales.