CHEMICAL ENGINEERING RESEARCH AND DESIGN 95 (2015) 162–172

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

The application of a multi-scale approach to the manufacture of concentrated and highly concentrated emulsions

*Diego Pradilla, Watson Vargas, Oscar Alvarez**

Grupo de Diseño de Producto y de Proceso (GDPP), Departamento de Ingeniería Química, Universidad de los Andes, Carrera 1 N 18A-12, Edificio Mario Laserna, Piso 7, Bogotá, Colombia

ABSTRACT

In this work, a multi-scale approach is applied to the emulsification process of concentrated emulsions. Whereas a vast number of studies have focused on either formulation or processing (Mason et al., 1997; Pal, 1999; Dimitrova and Leal-Calderon, 2004; Derkach, 2009; Capdevila et al., 2010), we propose a transversal study that includes those variables and also covers aspects of the rheological behavior, the droplet size and the near infra-red spectra (NIRS).

The analysis on oil-in-water (O/W) and water-in-oil (W/O) emulsions yielded results that depend on the energy incorporated during the emulsification process. First, depending on the tip velocity and pumping capacity of the impeller, a certain amount of energy can be incorporated to a given formulation (i.e., concentration of the dispersed phase). Second, as a consequence, the properties (rheology and droplet size) (Zölzer and Eicke, 1993; Ewoldt and McKinley, 2007; Evans et al., 2009) of the resulting emulsion are set and mathematical relationships are established. Finally, it is possible to visualize via NIRS not only the changes in concentration (Aske et al., 2002; Sjöblom et al., 2003; Araujo et al., 2008) but also the influence of the changes in droplet size and couple all three aspects.

The novelty of these results rests on the treatment of the energy as a transversal variable to the scales studied instead of handling only the formulation variables.

Keywords: Emulsions; Mixing; Rheology

1. Introduction

Emulsions are a type of colloidal system in which droplets of a liquid are dispersed in a second immiscible liquid. Emulsions are widely used in a variety of industrial applications: cosmetics, food, pharmacy, coatings, oil recovery and the so-called liquid explosives (Jager-Lézer et al., 1998; Clausse et al., 1999; Dimitrova and Leal-Calderon, 2001,2004; Sjoblom, 2001; Tadros, 2004; Pal, 2006; Masalova and Malkin, 2008; Capdevila et al., 2010; Bouyer et al., 2011; Masalova et al., 2011). These products are non-equilibrium systems, which means that they are thermodynamically unstable and consequently two variables must be considered for their formation: energy (which must be incorporated through the emulsification process) and a surfactant that stabilizes the droplets by ensuring a short range repulsive interaction at the interface (Dimitrova and Leal-Calderon, 1999; Datta et al., 2011). Highly concentrated emulsions also known as high internal phase ratio emulsions (Pal, 1996,1998a,b,1999,2006; Clausse et al., 2007) and concentrated emulsions are of special interest because of the complexity of their rheological behavior resulting from the increasing relevance of the interactions between the droplets as they come closer to one another. In most cases, this proximity causes the spherical droplets to change in shape and take the shape of polyhedrons.

A multi-scale approach could be defined as a way of creating a link between what happens within a system (in this case, an emulsion) and its performance as a finished product. The

* *Corresponding author*. Tel.: +57 1 3394949x3935; fax: +57 1 3324334.
E-mail addresses: d-pradil@uniandes.edu.co (D. Pradilla), wvargas@uniandes.edu.co (W. Vargas), oalvarez@uniandes.edu.co (O. Alvarez).

Received 28 February 2014; Received in revised form 6 October 2014; Accepted 23 October 2014
Available online 1 November 2014
http://dx.doi.org/10.1016/j.cherd.2014.10.016
0263-8762/

practical use of such link (or links) has been acknowledged by some authors using several field specific examples (Jager-Lézer et al., 1998; Sagis, 2011; Charton et al., 2013).

Recently, Sagis (2011) pointed out that the dynamic behavior of the interfaces of high surface to volume ratio systems, such as emulsions (also dispersions of vesicles, dispersion of nanocapsules, etc.) is responsible for the macroscopic dynamics. Therefore, a study solely focused on the molecular scale (i.e., surface active material adsorption, desorption kinetics, diffusion mechanisms, surface rheology, etc.) would not suffice if the goal of the study was to evaluate overall performance of a product in different scenarios. In fact, interactions at the molecular scale are only a part of what defines the behavior of emulsions.

Analogously, at the macroscopic level, as highlighted by Dimitrova and Leal-Calderon (2004), Babak et al. (2001) and more recently by Derkach (2009), several factors affect the behavior of emulsions: the volume fraction of the dispersed phase, the droplet size, the polydispersity of the droplets, the temperature and the emulsification process. This behavior is usually studied using rheological measurements such as steady-state flow experiments to determine the viscosity as a function of the shear rate and thus observing both the shear thinning behavior and the yield stress (Pal, 1999) -and oscillatory experiments in which the elastic and viscous moduli (G' and G'') are obtained (Mason et al., 1997; Fa et al., 2004). Also, the droplet size and droplet size distribution are usually obtained through optical microscopy or light diffraction techniques.

The overall goal of this work is to use a novel multi-scale approach, which analyzes the coupled effects between, first, the formulation and the composition variables of a product (i.e., an emulsion), second, the process through which the product is made and third, the properties that the product exhibits. These properties can be studied using a multi-level method, meaning that the responses at different levels can be analyzed. In this sense, the product will have properties at the macroscopic level, described in this case by the rheology of the system, the microscopic level, related to the average droplet size, and the molecular level, represented in this case by the combinations and overtones in a near infrared spectrum. This novel approach allows the simultaneous study of aspects at the three mentioned levels, covering the main variables that influence emulsion preparation.

The first part of this work establishes the relationships between the energy incorporated through the emulsification process, the concentration of the dispersed phase and the properties at the three levels, using three different types of impellers to prepare oil-in-water (O/W) emulsions with concentrations ranging from 80 to 90 (wt%). Using a similar approach, Alvarez et al. (2010) established a relationship between the energy incorporated through the emulsification process and the macroscopic properties (the rheology) of water-in-oil (W/O) emulsions. They also established a second relationship that relates the energy incorporated to the microscopic structure of the system (the average droplet size). The relationships are shown in the following equations:

$$G' \propto E_v^{0.6} \quad (1)$$

$$R_m \propto E_v^{-0.3} \quad (2)$$

In these equations, E_v corresponds to the energy incorporated through the emulsification process, R_m is the average droplet size and G' is the value of the elastic modulus in the linear viscoelastic region. Eqs. (1) and (2) indicate how the elasticity and the average droplet size change with respect to the incorporated energy for W/O emulsions when the concentration of the dispersed phase is between 92 and 96 (wt%).

The second part of this work, studies how average droplet size affects the near infrared spectra (NIR) of O/W emulsions. Similarly, the effect of the concentration of the dispersed phase on the different trends will also be studied for concentrations of 30–80 (wt%).

According to Sjøblom (Aske et al., 2002; Sjöblom et al., 2003), when the near infrared spectra (NIR) spectra of a water-in-oil emulsion is obtained, the water droplets within the emulsion will scatter portions of the incoming light with an intensity that follows Eq. (3):

$$\frac{I_d}{I_0} \propto \frac{r^6}{x^2 \lambda^4} \quad (3)$$

where r is the droplet radius, x is the sample thickness, λ is the wavelength and I_d/I_0 is a measurement of the extinction of light. This means that for two water-in-oil emulsions that have the same formulation but differ in their droplet size distributions, the emulsion with bigger droplets will scatter light with a greater total intensity than the emulsion with smaller droplets. This will shift the spectra toward areas of higher absorbance for the emulsion with greater average droplet size. Araujo et al. (2008) observed similar changes in the NIR spectra of water-in-crude oil emulsions due to changes in the average droplet size and concentration of water. However, the trends of the different spectra were opposite to those reported previously (Aske et al., 2002; Sjöblom et al., 2003).

Finally, the third part of this work will use creep tests to study concentrated and highly concentrated W/O emulsions and analyze the behavior of the compliance modulus, $J(t)$, when the concentrations of the dispersed phase and the applied stress within the linear viscoelastic region are changed.

Creep testing has been commonly used to determine the yield stress at which some materials may fracture or to determine the viscosity of soft materials at low shear rates (Tadros, 2004). Typically, oscillatory measurements are used to obtain reliable results in the short-time/high frequency domain and creep measurements are used to obtain information in the long-time/low-frequency domain. However, creep testing can also be used to obtain information about the viscoelastic nature of concentrated and highly concentrated emulsions (Zölzer and Eicke, 1993; Baravian and Quemada, 1998; Jager-Lézer et al., 1998; Ewoldt and McKinley, 2007). Therefore, the information obtained through a creep experiment contains essentially the same information as oscillatory measurements, and accordingly, changes in the morphology of the droplets can also be observed using a different technique.

2. Materials and methods

2.1. Materials

Highly concentrated oil-in-water (O/W) and water-in-oil (W/O) emulsions were prepared with mineral oil (USP-grade), mili-Q de-ionized water and two non-ionic surfactants provided by Croda: Span 80® (Sorbitan Monooleate), oil soluble, HLB 4.3, and Tween 20® (polisorbate 20), water soluble, HLB 16.7.