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Effect of the properties of oil, particles, and water on the production of Pickering emulsions

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ABSTRACT

Oil-in-water Pickering emulsions were prepared using a standard mixing configuration. Emulsification experiments were performed in an unbaffled tank using an off-centered pitched-blade turbine. Regular and modified glass beads were used as a stabilizer, and their size, concentration, and wettability effects were investigated as were oil viscosity and the properties of the aqueous phase (pH and salinity). Our findings highlighted the importance of the stabilization mechanism in the emulsification process, which is different from that of surfactant-based systems. The stabilization mechanism can be divided into four steps: (1) droplet formation by breakage, (2) particle/droplet approach and collision, (3) particle adsorption, and (4) formation of the particle network. Emulsification efficiency was mainly quantified by size distribution measurements using a Mastersizer 3000 (Malvern). Our results showed that droplet stabilization is closely related to particle/droplet approach, collision, and initial adsorption and that it is highly sensitive to oil viscosity and particle size and wettability, while the properties of the aqueous phase influence stabilization mainly through their effect on particle interactions (flocculation). The smallest droplets with the narrowest distribution were obtained with small particles, low oil viscosities, and good oil/particle affinity. It was possible to modulate the effects of particle size and oil viscosity by increasing oil/particle affinity. We also showed that stabilization efficiency is dependent on the particle fraction.

1. Introduction

Fine particles have been used as emulsifiers since the beginning of the 20th century when solid-stabilized emulsions were first described by Ramsden (1903) and Pickering (1907). Following in the footsteps of this pioneering work, it was later shown that particles display much greater potential for producing highly stable emulsions than surfactants (Binks, 2002). Other studies showed that highly stable emulsions result from the formation of a steric particle barrier around the droplets that prevents coalescence. It has also been shown that the most stable emulsions are obtained when particles form a close-packed network due to capillary forces and to particle interactions at the interface (Levine and Bowen, 1991, 1992, 1993). This led to the realization that stability at the interface must be taken into consideration in order to analyze the stability of emulsions. Based on this realization, two approaches were developed (Binks and Horozov, 2006). The first is a thermodynamic approach based on a free energy analysis that considers that stability is achieved when the system reaches its minimal free energy. The second is a mechanical approach based on a force analysis that considers that stability is reached when the sum of the forces is zero.

Based on the first approach, the energy of particle detachment from the interface can be calculated using the following formula (Levine et al., 1989a,b):

$$E = \pi R^2 \gamma_{ow} (1 \pm \cos\theta)^2 \qquad (1)$$

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A similar approach has been used to define particle adsorption energy in order to analyze the stability of Pickering emulsions based on the line tension effect (Arditty et al., 2003; Sacanna et al., 2007), to deduce the equilibrium position of the particles at the interface (Komura et al., 2006; Hey and Kingston, 2006), and to deduce the equilibrium particle concentration at the interface (Hirose et al., 2008).

The force analysis approach was also used by Princen (1969) and Rapacchietta and Neumann (1977) and, more recently, by Joseph et al. (2003) and Singh and Joseph (2005). Based on the results reported in the literature and standard emulsification operation mechanisms (breakage and coalescence), the stabilization of emulsions by particles in a non-coalescent system occurs in four steps:

1. Droplet formation by breakage
2. Particle/droplet approach and collision
3. Particle adsorption
4. Network formation and droplet stabilization

Process-scale studies of emulsion stability have shown that less stable emulsions are obtained when highly hydrophobic or hydrophilic particles are used and that the most stable emulsions are obtained when particles with intermediate wettability are used (Yan and Masliyah, 1995a, 1997; Binks and Lumsdon, 2000; Yan et al., 2001; Stiller et al., 2004; Ding et al., 2005). Emulsion stability can also be improved by increasing particle concentrations (Yan and Masliyah, 1995a,b, 1997, 1994, 1996a; Yan et al., 1997), reducing particle size (Binks and Lumsdon, 2001; Tambe and Sharma, 1994), using monodispersed particles (Tarimala and Dai, 2004), using ellipsoidal particles (Madivala et al., 2009), and slightly increasing water salinity, all of which mainly act on particle flocculation through their impact on the repulsive electrical double layer force (Binks and Lumsdon, 1999; Binks and Whitby, 2005; Binks et al., 2006; Yang et al., 2007; Horozov et al., 2007; Golemanov et al., 2006). Increasing oil viscosity prevents stabilization by hindering particle adsorption and/or by hampering emulsion formation (Golemanov et al., 2006; Fournier et al., 2009).

In addition to emulsion stability, studies on emulsion size have shown that droplet size can be reduced by decreasing particle size (Binks and Lumsdon, 2001; Tambe and Sharma, 1994) or by increasing particle concentrations (Binks and Rodrigues, 2003; Binks and Whitby, 2004; Binks et al., 2005). The effect of particle concentration on droplet size was notably studied by Arditty et al. (2003), who defined the so-called "limited coalescence phenomenon," which assumes that the droplets generated will coalesce until the reach the coverage limit, which in turn is defined by the particles available in the system. This makes it possible to predict droplet size based on particle concentration.

On the other hand, many other studies have investigated emulsion types, and the authors have concluded that this aspect is mainly controlled by particle affinity with the two phases. For example, hydrophilic particles produce oil/water emulsions while hydrophobic particles produce water/oil emulsions (Binks and Lumsdon, 2000; Yan et al., 2001; Stiller et al., 2004; Binks et al., 2005). This behavior is observed when the dispersed phase fraction is smaller or equal to the continuous phase fraction and when the particles are initially dispersed in the phase with which they have most affinity, which then becomes the continuous phase (Bancroft rule). Emulsion type can also be affected by oil polarity (Binks and Lumsdon, 2000; Binks and Whitby, 2005; Golemanov et al., 2006; Binks and Clint, 2002; Frelichowska et al., 2009; Zhou et al., 2011) and water pH (Yan and Masliyah, 1996a,b; Yan et al., 1997; Gu et al., 2003) due to the effect of these two parameters on particle wettability.

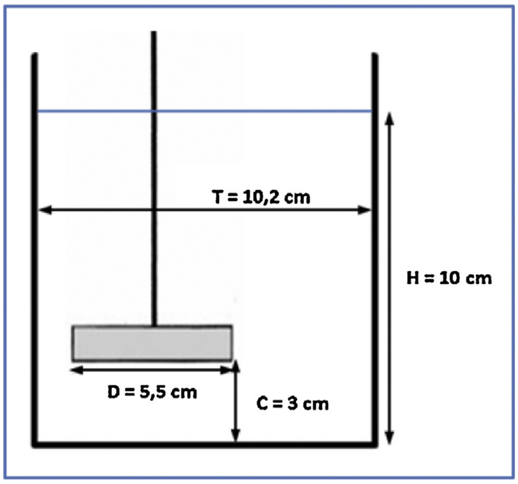

Fig. 1 – Emulsification setup.

In summary, the effects of the formulation on the final properties of Pickering emulsions (Table 1 presents the parameters affecting the properties of Pickering emulsions) have received much attention while the emulsification process itself has been largely neglected. The goals of the present study were to analyze the emulsification process in order to determine the parameters with the most impact on the properties of the final emulsion and to understand the effect these parameters have on the various stabilization steps.

We produced Pickering emulsions using a system that mimics industrial conditions in order to study the effects of particle size and wettability, oil viscosity, and continuous phase pH and salinity on the properties of emulsions. Emulsions were notably characterized by determining the droplet size distribution using a Mastersizer 3000 (Malvern) to make accurate size measurements.

2. Materials and methods

2.1. *Materials*

Glass beads (Potters Industry and Cospheric) were used as solid particles (Table 2). Deionized water (72.6 mJ/m^2 at 20 °C) was used as the continuous phase. Silicone oils (CLEARCO Inc.) were used as dispersed phases (Table 3). The salinity and pH of the continuous phase were controlled using NaCl (commercial grade, Fisher Scientific) and NaOH/HCl (analytical grade, Fisher Scientific), respectively.

2.2. *Experimental methods*

2.2.1. *Emulsification setup*

Emulsification experiments were performed with a standard configuration using an unbaffled 1 L beaker to ensure a simple flow field and to generate controlled turbulence. An off-centered pitched-blade turbine was used to minimize vortex formation (Fig. 1). In terms of mixing performances, this system is equivalent to a centered impeller with baffles for the considered regimes (Nishikawa et al., 1979; Novak et al., 1982; King and Muskett, 1985; Karcz and Szoplik, 2004; Karcz et al., 2005; Montante et al., 2005). The oil-to-water volume ratio was