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STABILIZATION OF EMULSIONS BY HETEROCOAGULATION OF CLAY MINERALS USING A MICROFLUIDIC DEVICE

Azarmidokht Gholamipour-Shirazi
Marcio Carvalho
Department of Mechanical Engineering, Pontificia Universidade Catolica do Rio de Janeiro - PUC-Rio, Rio de Janeiro, Brazil
e-mails: a_gholamipour@esp.puc-rio.br, msc@puc-rio.br

Jon Otto Fossum
Department of Physics, Norwegian University of Science and Technology - NTNU, Trondheim, Norway
jon.fossum@ntnu.no

Abstract. *The Research on emulsions is driven by their wide-spreading use in different industries, such as food, cosmetic, pharmaceutical and oil recovery. Emulsions are stabilized by suitable surfactants (electrostatic stabilization), polymers, solid particles (steric stabilization) or a combination of them. A microfluidic emulsification is the process of droplet formation out of two or more liquids under strictly controlled conditions, without pre-emulsification step. Microfluidic technology offers a powerful tool for investigating the properties of emulsions themselves. In this work stable O/W emulsions were formed with hydrophilic Laponite RD® nanoparticles adsorbed at the interface of the oil phase and water in a T junction microfluidic chip. In some conditions, emulsions were stable up to 40 days.*

Keywords: *Pickering emulsion, steric stabilization, microfluidics, emulsion stability*

1. INTRODUCTION

Emulsions are metastable dispersions of liquid droplets in another immiscible one in the presence of surface-active species. They have been the subject of considerable fundamental and applied investigations.(Bibette, Calderon, & Poulin, 1999) Research on emulsions is driven by their wide-spreading use in different industries, such as food, cosmetic, pharmaceutical and oil recovery.(Sjoblom, 2001)

Emulsions are stabilized by suitable surfactants (electrostatic stabilization) (Sjoblom, 2012), polymers, solid particles (steric stabilization)(Napper & Netschey, 1971) or a combination of them. There are several advantages in using solid particles as stabilizers; (i) the concentration of conventional emulsifying agents can be reduced and hazardous surfactants may be replaced by less harmful materials. It is of great importance particularly in the cosmetic and pharmaceutical fields.(Arditty, Whitby, Binks, Schmitt, & Leal-Calderon, 2003) (ii)Higher stability is obtained against changing chemical parameters such as pH, salt concentration, temperature and oil composition, (Abend, Bonnke, Gutschner, & Lagaly, 1998) (iii) Emulsion viscosity or flow type can be adjusted to required practical application just by modifying solid particles concentration or type (iv) Emulsion type (O/W or W/O) is ruled by solid particle hydrophobicity. (Abend et al., 1998)

Particles adsorb strongly to liquid-liquid interfaces and the energy of attachment depends on the contact angle, θ, which solid particles make with the oil-water interface. Thus, if θ (measured through the water phase) is <90°, particles are hydrophilic and stabilize O/W emulsions, whereas if θ > 90°, particles are hydrophobic and stabilize W/O emulsions. (Binks & Lumsdon, 2000) The strength with which a particle is held at an oil-water interface is related not only to θ but also to interfacial tension.(Binks & Lumsdon, 2000) In other words, the continuous phase of the preferred emulsion is normally the one in which the particles are preferentially dispersed.(Arditty et al., 2003; Leal-Calderon & Schmitt, 2008) Both O/W and W/O emulsions are maximally stable to coalescence when particles are partially wettable by both water and oil phases. (Arditty et al., 2003; Ashby & Binks, 2000; Leal-Calderon & Schmitt, 2008) However, the characteristic particle size and the interactions between particles are equally important in emulsion stabilization. It has been reported that the characteristic particle size must be considerably smaller than the size of the emulsion droplets and weakly flocculated dispersions are more efficient in stabilizing emulsions. (Arditty et al., 2003; Leal-Calderon & Schmitt, 2008)

Emulsion type varies also with the type of the oil (polar or non-polar) and the composition of the aqueous phase (with respect to pH).(Ashby & Binks, 2000) More polar oils preferentially give water-in-oil emulsions.(Binks & Clint, 2002) Also, the oil/water volume ratio also plays an important role in determining the emulsion type. For any particle type, it has been reported that the stability to sedimentation of W/O emulsions or to creaming of O/W emulsions increases toward inversion, induced by changes in water volume fraction.(Binks & Lumsdon, 2000)

Conventional emulsification methods are based on passing a pre-emulsion with large drops through a high shear region in such a way as to promote turbulence and/or cavitation and thereby to disrupt large drops into smaller ones.(Vladisavljević, Kobayashi, & Nakajima, 2012) Due to exposure of the drops to a variable shear and pressure field, the resulting is highly polydisperse. A microfluidic emulsification is the process of droplet formation out of two or more liquids under strictly controlled conditions, without pre-emulsification step.(Maan, Nazir, Khan, Boom, & Schroën, 2015; Vladisavljević et al., 2012) It has the potential to be an important strategy for fabricating colloidosomes for the controlled delivery of active ingredients (drugs, vaccines, hormones).(Priest, Reid, & Whitby, 2011) Microfluidic junctions and flow focusing devices can generate single, double, triple and multiple emulsion droplets in a single step.(Vladisavljević et al., 2012) While bulk emulsification methods offer limited insights, microfluidic emulsification provides a unique platform to uncover the early stages of emulsion formation.(Priest et al., 2011) Moreover microfluidic technology offers a powerful tool for investigating the properties of emulsions themselves.(Bremond & Bibette, 2012; Woodward, Cosgrove, Espidel, Jenkins, & Shaw, 2007). In this work stable O/W emulsions were formed with hydrophilic Laponite RD® nanoparticles adsorbed at the interface of the oil phase and water in T junction chip. Salt (NaCl or $CaCl_2$) was added to flocculate the Laponite particles and hence to increase the emulsion stability.(Ashby & Binks, 2000)

2. MATERIALS AND METHODS

Laponite RD® suspensions were prepared by dispersing Laponite in deionized water (0.16 µS/cm at 25°C) using using a IKA WERKE Ultra-Turrax® T25 basic homogeniser (rotor-stator) with an 1.8 cm head operating at 17 500 rpm for 30 min while cooling sample in an ice/water bath. Laponite-salt suspensions were prepared by dispersing salt to Laponite RD® dispersions using an ultrasonic bath (40 kHz for at least 40 min). All dispersions were transferred into stoppered glass vessels and were kept refrigerated prior to use.
The oil was Drakeol7®. In case of bioreagent grade (Sigma-Aldrich), its viscosity is 14.2-17.2 cSt at 40°C and its density is 0.84 g mL^{-1}. In order to simulate the real conditions, here, we used the industrial oil grade. To remove polar and amphiphilic impurities from the oil phase, it was washed several times with excess of deionized water, decanted and centrifuged.
The experimental set-up is shown schematically in Figure1.

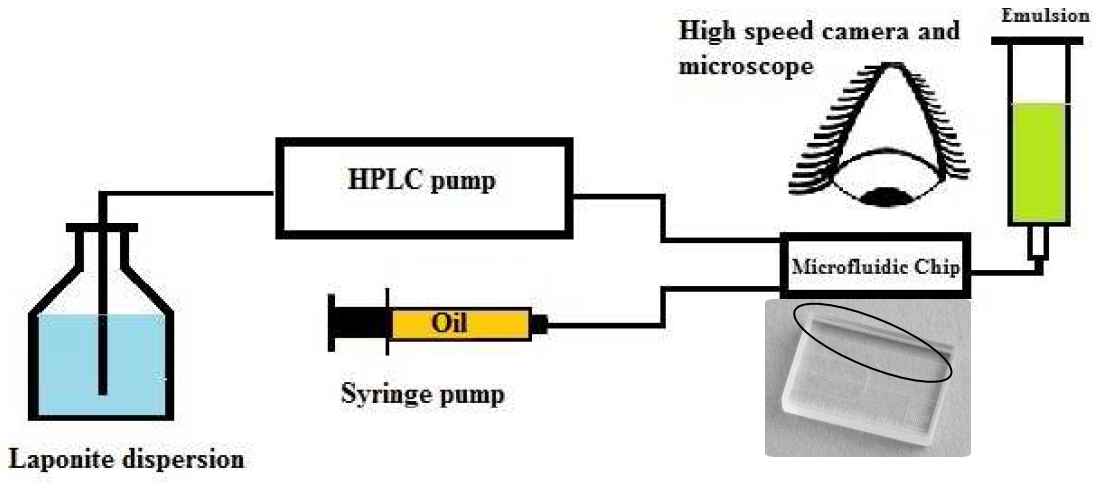


Figure 1. Experimental setup

The setup composed of two streams of Laponite dispersion,with or without salt and purified oil simultaneously delivered by an HPLC pump (Waters) and a syringe pump (NE-1000,New Era Pump Systems, Inc.,NY, USA) to a droplet T junction chip (Dolomite ®, Syrris do Brasil Ltda, Sao Paulo, Brasil) . The channel cross-section is 100µm × 300µm and the channel cross-section at junction is 100µm × 105µm. It typically forms droplets of around 20 – 150µm in diameter. The emulsion was collected in cylinders (made out of polyacryl amide) with the inner diameter of 1.0 cm. They were kept at room temperature in a vertical position and were observed for emulsion coalescence. The experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

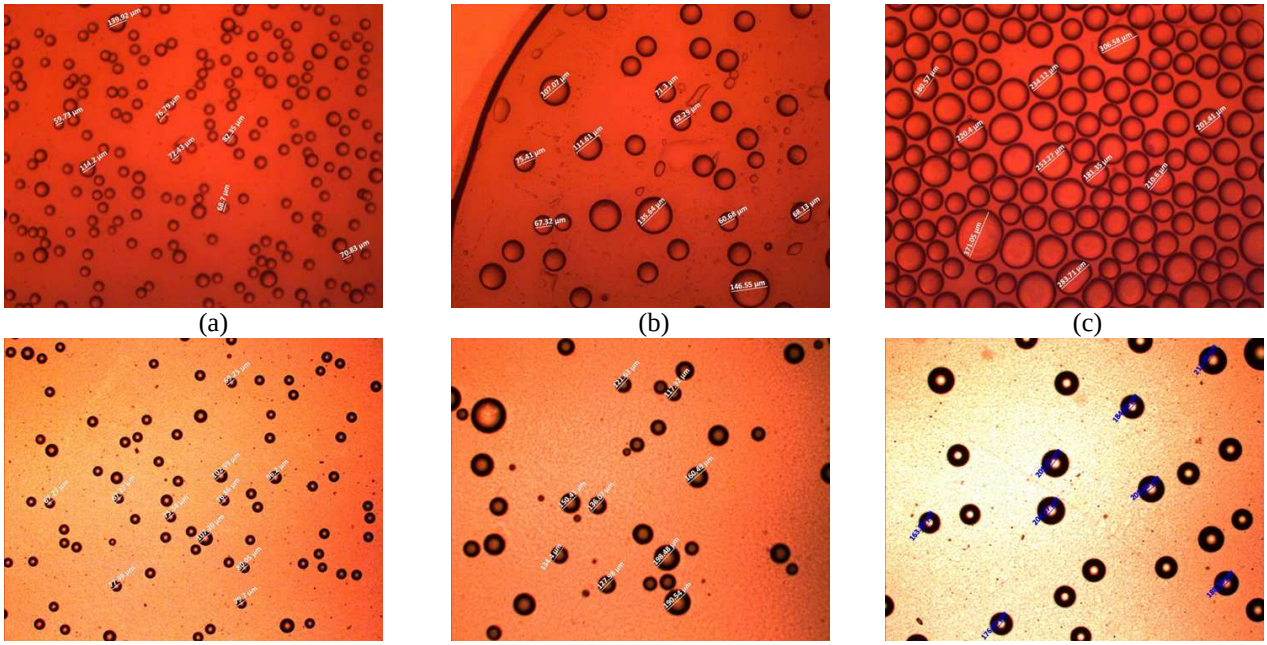
In this work stable O/W emulsions were formed with hydrophilic Laponite RD® nanoparticles adsorbed at the interface of Drakeol 7 ® as the oil phase and water in a Dolomite ® droplet T junction chip. Salt (NaCl or $CaCl_2$) was added to flocculate the Laponite particles and hence to increase the emulsion stability.(Ashby & Binks, 2000) The presence of particles did not influence drop formation dynamics and thus the size of the drops generated. Different flow rates and different Laponite concentrations were examined to determine their effect on the stability of the formed emulsions. The summary of experiments and their brief results are presented in Tab. 1. The Laponite and salt concentrations were taken from(Ashby & Binks, 2000).

Table 1. Summary of the conducted experiments and the brief results. In all cases, aqueous phase flowrate is 0.150 ml min^{-1} respectively.

Oil phase flowrate (ml hr^{-1})	Aqueous phase	Emulsion stability (during emulsion preparation)
0.5	Laponite 0.5 wt%	Creaming observed during emulsion preparation
0.5	Laponite 1.0 wt% and NaCl 0.1M	Creaming was observed during one hour after emulsion preparation
0.5	Laponite 1.5 wt% and NaCl 0.1M	No visible phase separation and coalescence was observed
0.5	Laponite 1.5 wt% and $CaCl_2$ 0.1M	No visible phase separation and coalescence was observed
0.5	Laponite 1.5 wt% and $CaCl_2$ 0.05M	No visible phase separation and coalescence was observed
1.5	Laponite 1.5 wt% and NaCl 0.1M	No visible phase separation and coalescence was observed
1.5	Laponite 1.5 wt% and $CaCl_2$ 0.1M	No visible phase separation and coalescence was observed
1.5	Laponite 1.5 wt% and $CaCl_2$ 0.05M	No visible phase separation and coalescence was observed
3.5	Laponite 1.5 wt% and NaCl 0.1M	No visible phase separation and coalescence was observed
3.5	Laponite 1.5 wt% and $CaCl_2$ 0.1M	No visible phase separation and coalescence was observed
3.5	Laponite 1.5 wt% and $CaCl_2$ 0.05M	No visible phase separation and coalescence was observed

Stable emulsions were obtained at Laponite concentration of 1.5% and salt concentrations of 0.1 and 0.05M. In all cases droplets were typically formed with a diameter between 80 - 220 µm. For relatively stable emulsion (Laponite 1.0 wt% and NaCl 0.1M) and despite coalescence the distinct droplets are observed even after 32 days.

A sample of each emulsion was observed under the microscope and all the emulsions show some degree of coalescence (Fig. 2). By increasing oil flowrate the coalescence is increased. Using hydrated calcium chloride gives rise to the more stable emulsion than using sodium chloride, which shows that divalent ions such as calcium produce a very important increase in Laponite adhesion in the oil-water interface. Further interfacial dilational rheology studies (unpublished results) showed a high mobility of Laponite particles and an elastic film at 1.5% wt and 0.1M concentration of Laponite and NaCl were observed. Moreover a crumpling was observed upon compression after an overnight aging time.



(a) (b) (c)

(d) (e) (f)

Figure 2. (a) Laponite 1.5 wt%, $CaCl_2$ 0.1M,Oil flowrate: 0.5 ml hr^{-1}, Aqueous phase flowrate: 0.150 ml min^{-1}, first day, (b) Laponite 1.5 wt%, $CaCl_2$ 0.1M, Oil flowrate: 1.5 ml hr^{-1}, Aqueous phase flowrate: 0.150 ml min^{-1}, first day, (c) Laponite 1.5 wt%, $CaCl_2$ 0.1M, Oil flowrate: 3.5 ml hr^{-1}, Aqueous phase flowrate: 0.150 ml min^{-1}, first day, (d) Emulsion in (a) on day 39^{th} , (e) Emulsion in (b) on day 39^{th} (f) Emulsion in (c) on day 39^{th}

4. ACKNOWLEDGEMENTS

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