CONTROLLED MICROFLUIDIC EMULSIFICATION OF OIL IN A CLAY NANOFLUID: ROLE OF SALT FOR PICKERING STABILIZATION

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Abstract. 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. 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 oil in water emulsions were formed with hydrophilic Laponite RD® nanoparticles adsorbed at the interface of the oil phase and aqueous clay nanofluid in a T junction microfluidic chip. Emulsions stability up to at least 40 days could be observed.

INTRODUCTION

Emulsions are metastable dispersions of droplets in an immiscible liquid in the presence of surface-active species. They have been the subject of considerable fundamental and applied investigations.[1] Research on emulsions is driven by their wide-spread use in different industries, such as food, cosmetic, pharmaceutical and oil recovery.[2]

Emulsions are stabilized by suitable surfactants[3], polymers, solid particles[4] or a combination of them. There are several advantages in using solid particles as stabilizers (i.e. Pickering emulsions[5]); (i) the concentration of conventional emulsifying agents can be reduced and hazardous surfactants may be replaced by less harmful materials. This is of great importance particularly in the cosmetic and pharmaceutical fields.[6] (ii) Higher stability is obtained by changing chemical parameters such as pH, salt concentration, temperature and oil composition,[7] (iii) Emulsion viscosity or flow type can be adjusted to required practical application just by modifying solid particles concentration or type (iv) Emulsion type: Oil/Water (O/W) or Water/Oil (W/O) may be controlled by solid particle hydrophobicity.[7]

Particles adsorb strongly to liquid-liquid interfaces and the energy of attachment depends on the contact angle θ that the solid particles make with the oil and water phase. Thus, if θ (measured through the water phase) is $< 90°$, particles are hydrophilic and stabilize O/W

emulsions, whereas if $\theta > 90°$, particles are hydrophobic and stabilize W/O emulsions.[8] The strength at which a particle is held at an oil-water interface is related not only to the contact angle but also to interfacial tension.[8] In other words, the continuous phase of the preferred emulsion is normally the one in which the particles are preferentially dispersed.[6], [9] Both O/W and W/O emulsions are maximally stable to coalescence when particles are partially wetted by both water and oil phases.[6], [9], [10] 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 that weakly flocculated dispersions are more efficient in stabilizing emulsions.[6], [9]. This makes nanofluids particularly interesting as continuous phase, since both nanoparticles and also their flocculates can be considerable smaller than typical emulsion drop sizes.

Emulsion type also varies with the type of oil (polar or non-polar) and composition of the aqueous phase (with respect to pH).[10] More polar oils preferentially give rise to water-in-oil emulsions.[11] Also, the O/W 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 O/W volume fraction.[8]

Conventional emulsification methods are based on flowing an oil and water mixture with large drops through a high shear region to promote breaking large drops into smaller ones. Due to exposure of the drops to a non-uniform flow, the resulting emulsion is highly polydisperse. In addition, the drop size distribution is a function of the viscosity of each individual phase. Therefore, changing particle and salt concentration of an aqueous dispersion may affect the emulsion formation process, not only its stability.[10] Microfluidic emulsification is the process of droplet formation out of two or more liquids under strictly controlled conditions, without pre-emulsification step.[12], [13] It has the potential to be an important strategy for fabricating colloidosomes for the controlled delivery of active ingredients (drugs, vaccines, hormones).[14] Microfluidic junctions and flow focusing devices can generate almost monodispersed single, double, triple and multiple emulsion droplets in a single step.[12] Moreover, microfluidic technology offers a powerful tool for investigating the properties of emulsions themselves.[15], [16]

In this work, particle-stabilized oil in water emulsions were formed in a T-junction microfluidic device. The stability of the emulsions as a function of concentration of salt (NaCl) and hydrophilic Laponite RD nanoparticles in the aqueous phase was studied to determine the conditions necessary to form stable systems. Because a microfluidic system was used to produce the emulsions, the initial drop size distribution for all systems analyzed were the same.

MATERIALS AND METHODS

Laponite RD® nano fluid suspensions were prepared by dispersing Laponite in deionized water ($\nu = 0.16$ μS/cm at 25°C) using an IKA WERKE Ultra-Turrax® T25 basic homogeniser (rotor-stator) with a 1.8 cm head operating at 17 500 rpm for 30 min while cooling sample in an ice/water bath. All dispersions were filtered (Whatman ® Grade 1 Qualitative Filtration Paper), transferred into stoppered glass vessels and were kept refrigerated prior to use. Laponite-salt nano fluid suspensions were prepared by dispersing salt to Laponite RD® dispersions using an ultrasonic bath (40 kHz for at least 40 min). The pH of Laponite suspensions was in the range of 8-9.
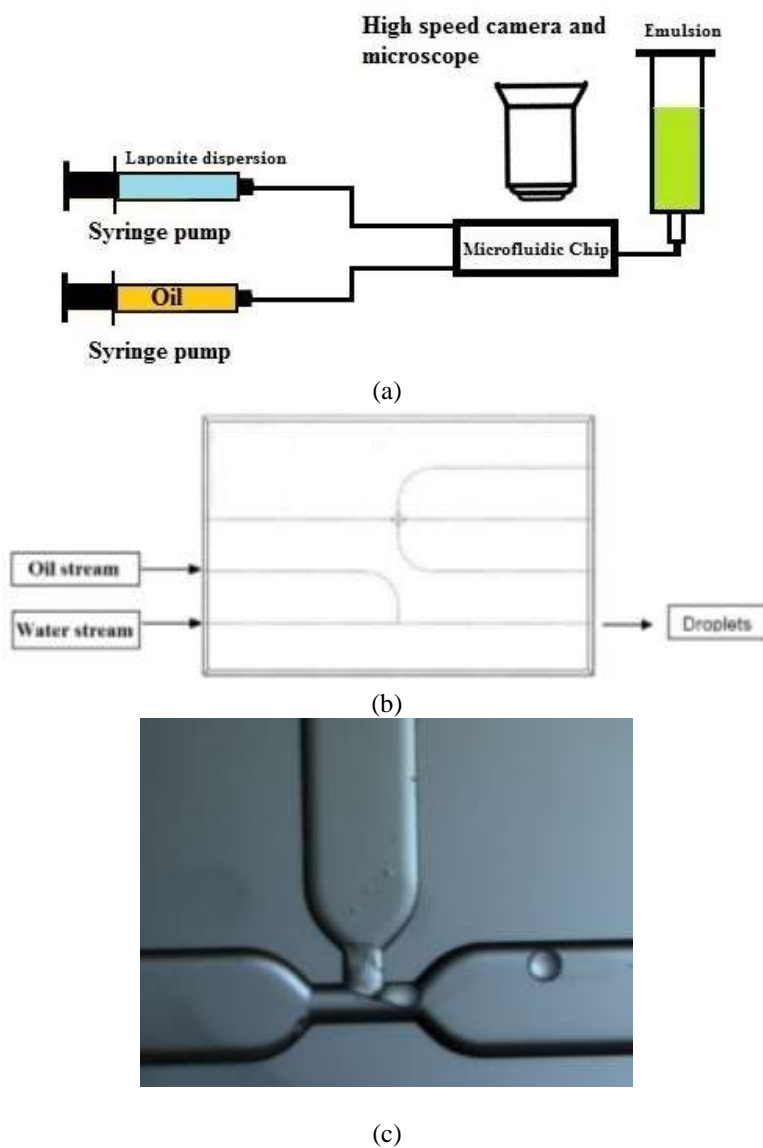

(a)

(b)

(c)

Figure 1(a)Experimental setup (b) chip design (c)drop formation at the T-junction

The oil phase used was the paraffinic mineral oil Drakeol7® ($\rho = 0.81$ g.cm^{-3}, $\nu = 21.7$ mm^2.s^{-1}). To remove polar and amphiphilic impurities from the oil phase, it was washed several times with excess of deionized water, decanted and centrifuged.

The setup (Fig 1a) was composed of two streams, one with Laponite dispersion, with or without salt, and the other with purified oil, simultaneously delivered by syringe pumps (Harvard Apparatus 11 Plus Syringe Pump) to a droplet T junction chip (Fig 1b) (Dolomite ®, Syrris do Brasil Ltda, Sao Paulo, Brazil) . The channels of the microfluidic device has a rounded cross-section with dimensions of 100µm × 300µm. At the T-junction, the dimensions are reduced to 100µm × 105µm. Oil phase flowrate was set at 0.5 ml.h^{-1} and the aqueous phase flowrate was set at 0.150 ml. min^{-1}. At these flow rates, the emulsion concentration was 5.5% oil in water and the drop size distribution was approximately monodispersed with diameter in the range of 80 - 120 µm. The emulsions were 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 at different time intervals to analyze droplet coalescence. The experiments were carried out at room temperature. At least three samples were analyzed from a particular emulsion.

Different Laponite and salt concentrations in the nano fluids were used to determine their effect on the stability of the formed emulsions. The presence of particles did not influence drop formation dynamics and thus the size of the drops generated did not vary with particle and salt concentration.

RESULTS AND DISCUSSIONS

To study the emulsion stability, a sample of approximately 200 µL of emulsion was spread over a hemocytometer. Samples were taken for different conditions (salt and particle concentration) and resting time to determine the evolution of drop size distribution with time.

Due to limited view field under the microscope, multiple photos were taken for each slide to cover the entire sample. These photos were then assembled as a mosaic picture for each slide using Image J (ver.1.50d). A typical image is shown in Fig. 2, just after preparation (resting time = 0) and an aqueous phase with 1.5wt% Laponite and 0.1 M NaCl.
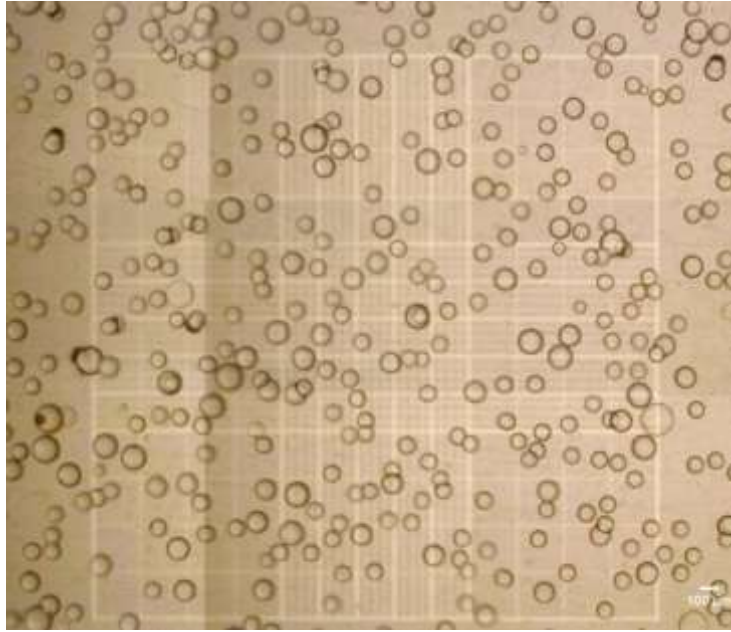
Figure 2 Image of O/W emulsion just after preparation, aqueous phase is Laponite 1.5 wt. %, NaCl 0.1M. Oil phase flowrate is 0.5 ml.h^{-1}; aqueous phase flowrate is 0.150 ml. min^{-1}

Effect of salt concentration

The effect of salt concentration was analyzed by studying the evolution of drop size distribution with time for an aqueous phase with 1.5 wt.% of Laponite and different NaCl concentrations: 0.05, 0.1 and 0.5M. At none of these concentrations Laponite dispersion can be considered as a physical gel.[17]

Ashby and Binks [10] deduced that stable O/W emulsions are only formed under conditions where the colloidal particles in the nano fluid are slightly flocculated. The salt, here, plays the role of the electrolyte and flocculating agent for Laponite.[18] Therefore, the stability of the corresponding O/W emulsions is very dependent on salt concentration. Among these three emulsions, the one with the lowest salt concentration is not stable. Large drops are observed under the microscope (Fig 3a) just after preparation. The drop diameter distribution for resting time 0, 1 and 4 days is shown in Fig.4a. For the longest resting time, several drops larger than 300 µm could be observed. After 5 days of resting time, very large drops could be observed in the collecting cylinder (Fig. 3b) but there was no phase separation, i.e. an oil film could not be observed over the water continuous phase. At the low salt concentration, e.g. 0.05 M NaCl, Laponite particles are not flocculated[21] and coalescence is rapid.

By increasing NaCl concentration, small nano fluidic flocs are formed and they may get absorbed to the O/W interfaces, delaying or completely preventing coalescence. Ashby and Binks [10] have shown that the O/W emulsions in Laponite 1.5 wt.% and NaCl 0.1M are stable

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for at least 6 months. Our results confirm the enhanced emulsion stability at these conditions. Figure 4b shows that at 0.1 M NaCl, the drop diameter distribution only changes after 30 days. At the highest salt concentration, e.g. 0.5M, the extensive flocculation leads to larger floc size and the adsorption at to the drop interfaces is reduced.[19] Hence, flocculated solids are far less likely to form a continuous barrier between the water droplets, and, coalescence occur, as it is clear from Figs. 3c and 3d, which show images of the 0.5 M NaCl emulsion at 0 and 12 days of resting time.
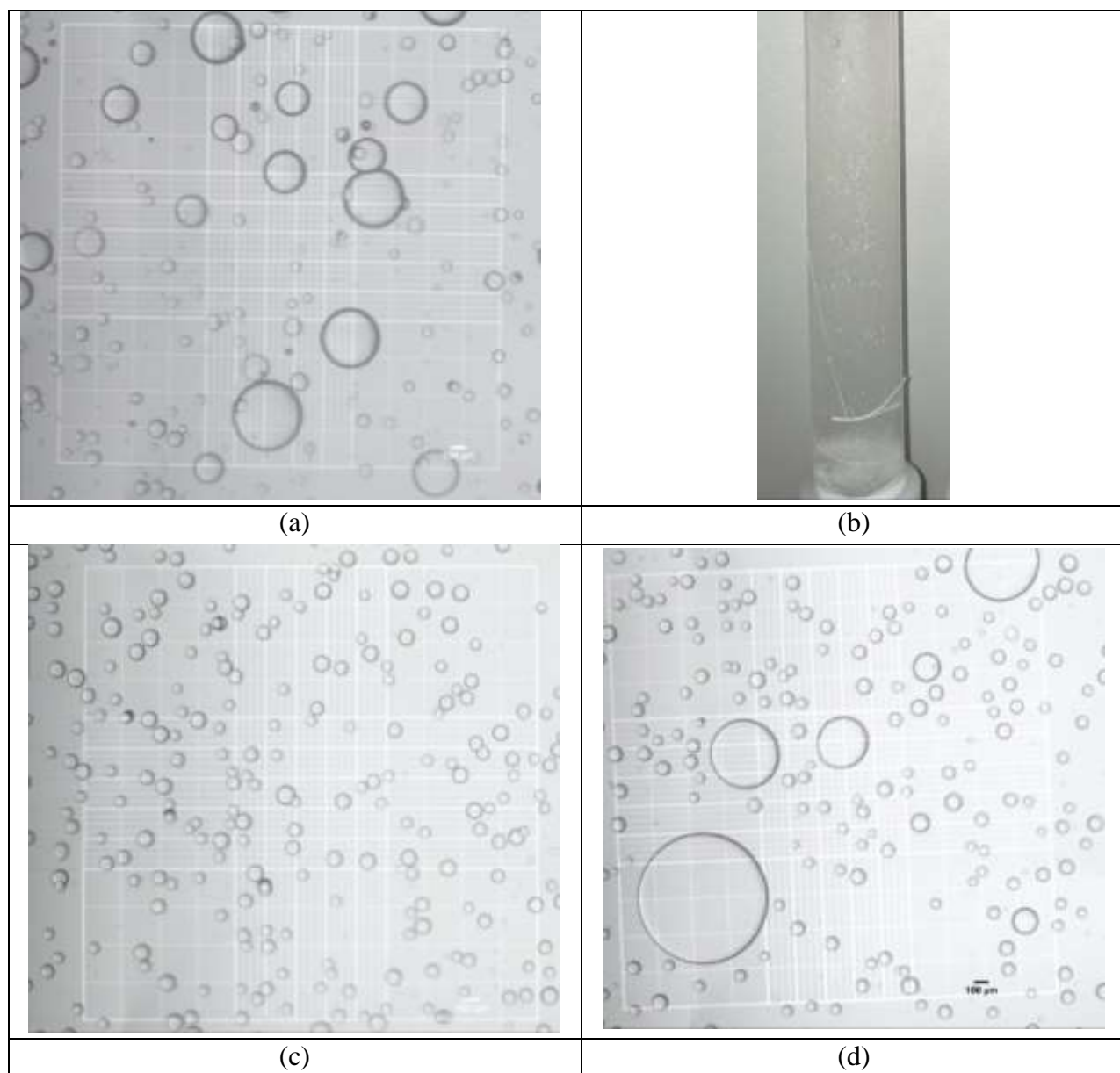

| (a) | (b) |
| (c) | (d) |

Figure 3 O/W emulsions stabilized by Laponite 1.5 wt.% at different NaCl concentrations. (a) NaCl 0.05M on the preparation day (b) NaCl 0.05M, five days after preparation (c) NaCl 0.5M on the preparation day (d) NaCl 0. 5M, 12 days after preparation
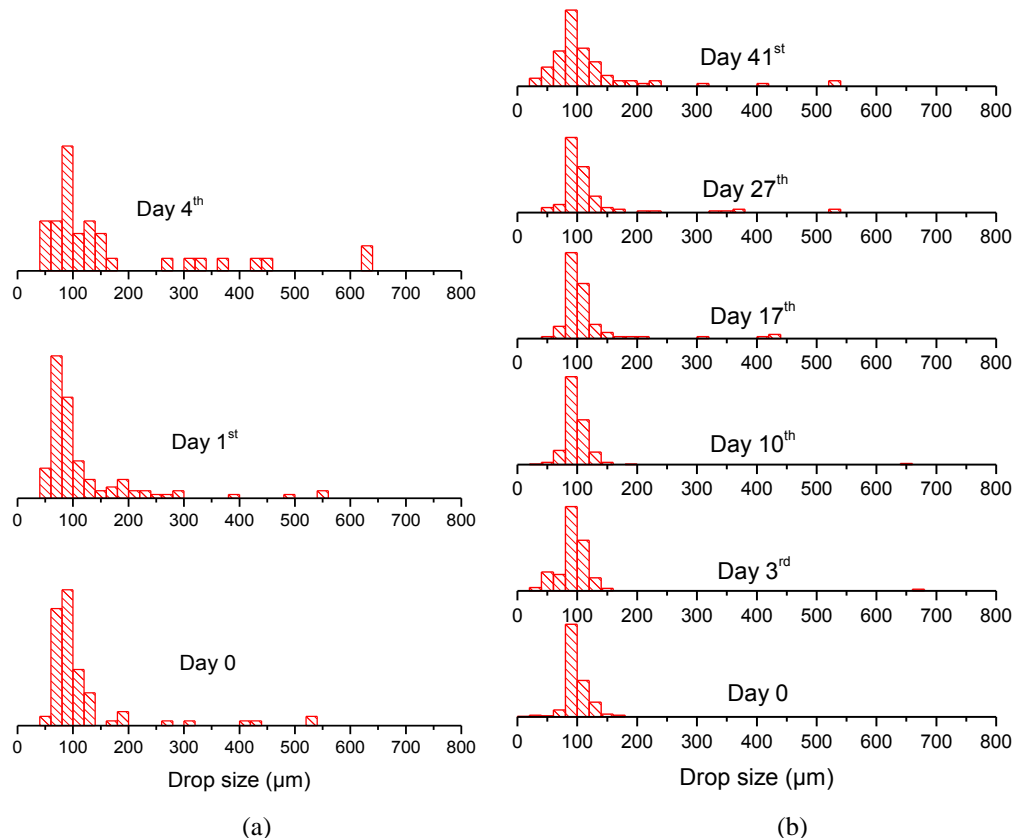
Figure 4 Evolution of size distribution of O/W emulsion stabilized by Laponite: (a) 1.5% Laponite and NaCl 0.05M and (b) 1.5% Laponite and NaCl 0.1M.

Effect of Laponite concentration

Three different emulsions formed using Laponite dispersions with concentrations equal to 0.5, 1 and 1.5 wt. % at the presence of NaCl 0.1M, were also studied to analyze the effect of particle concentration. Again, at none of these concentrations Laponite dispersion can be considered as a physical gel.[17]

Frelichowska et al.[20] while investigating stability of oil-in-water Pickering emulsions stabilized by hydrophobized fumed silica reported two crucial factors that affect the emulsion droplet size during O/W Pickering emulsion preparation process: (i) the concentration of nanoparticles in the aqueous phase; (ii) the amount of oil phase. In their findings, which can easily be generalized to clay nanoparticles, they identified three regimes as the silica-to-oil ratio increased: poor stability at low silica-to-oil ratio, stable emulsions with droplet size control by the silica-to-oil ratio, and lastly stable fine emulsions coexisting with excess silica at high silica-to-oil ratio.

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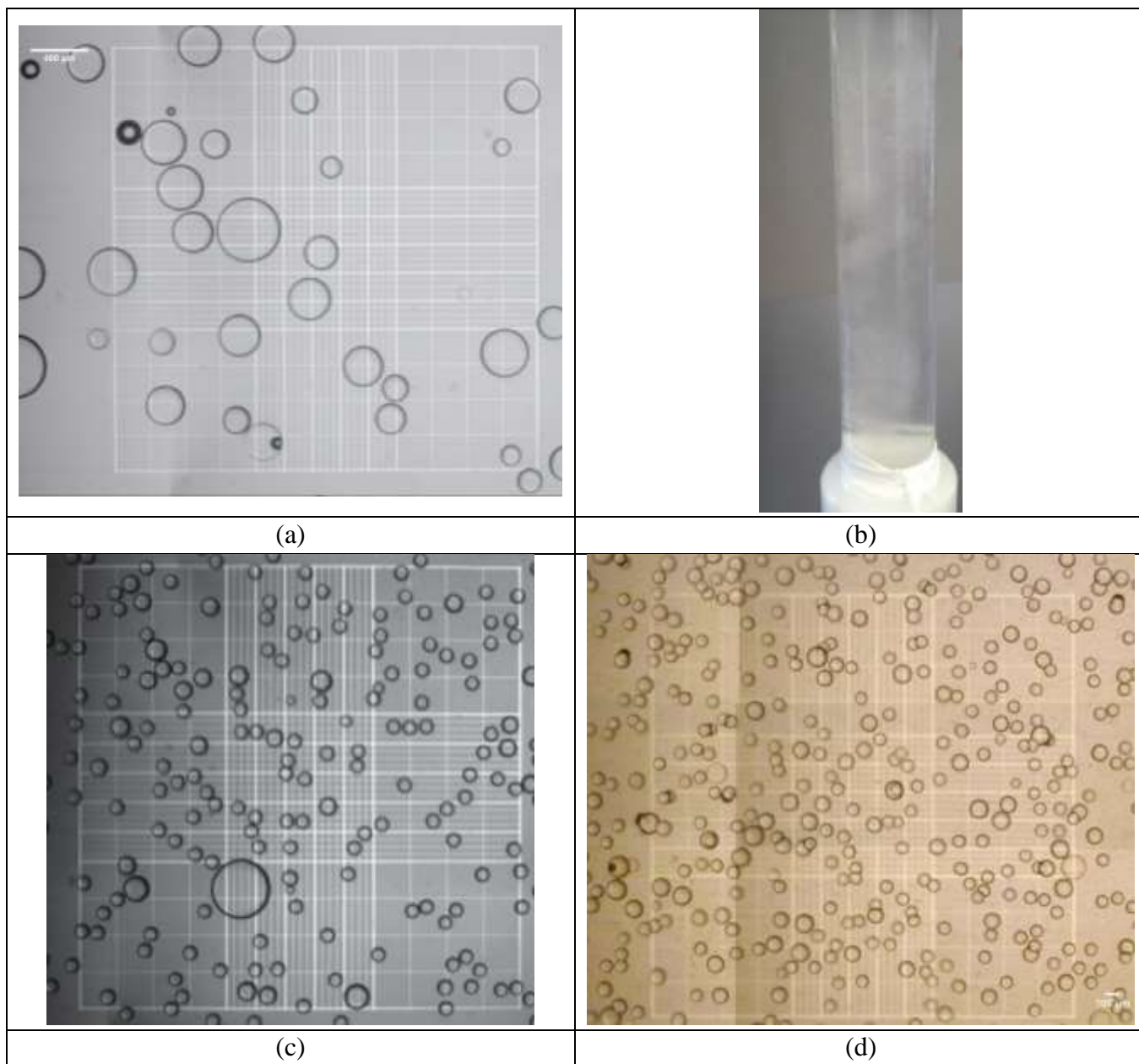|	
(a)	(b)
(c)	(d)

Figure 5 O/W emulsions stabilized by different Laponite concentrations at NaCl 0.1M. (a) Laponite 0.5 wt.%, on the preparation day (b) Laponite 0.5 wt.%, on the preparation day, the collecting cylinder (c) Laponite 1.0 wt.%, on the preparation day (d) Laponite 1.5 wt.%, on the preparation day

At low Laponite concentration (0.5 wt.%), emulsion is not stable even on its preparation day. Large drops are observed, as shown in Figs. 5a and 5b. At Laponite concentration of 1 and 1.5 wt %, the prepared emulsions were stable after preparation, as shown in Figs. 5c and 5d. Figures 6a and 6b presents the evolution of the drop size distribution for 1.5 and 1.0 wt.%, respectively. Both emulsions remain stable up to 17 days. Figures 6c and 6d show the images of the emulsion state at the largest resting time for both cases.
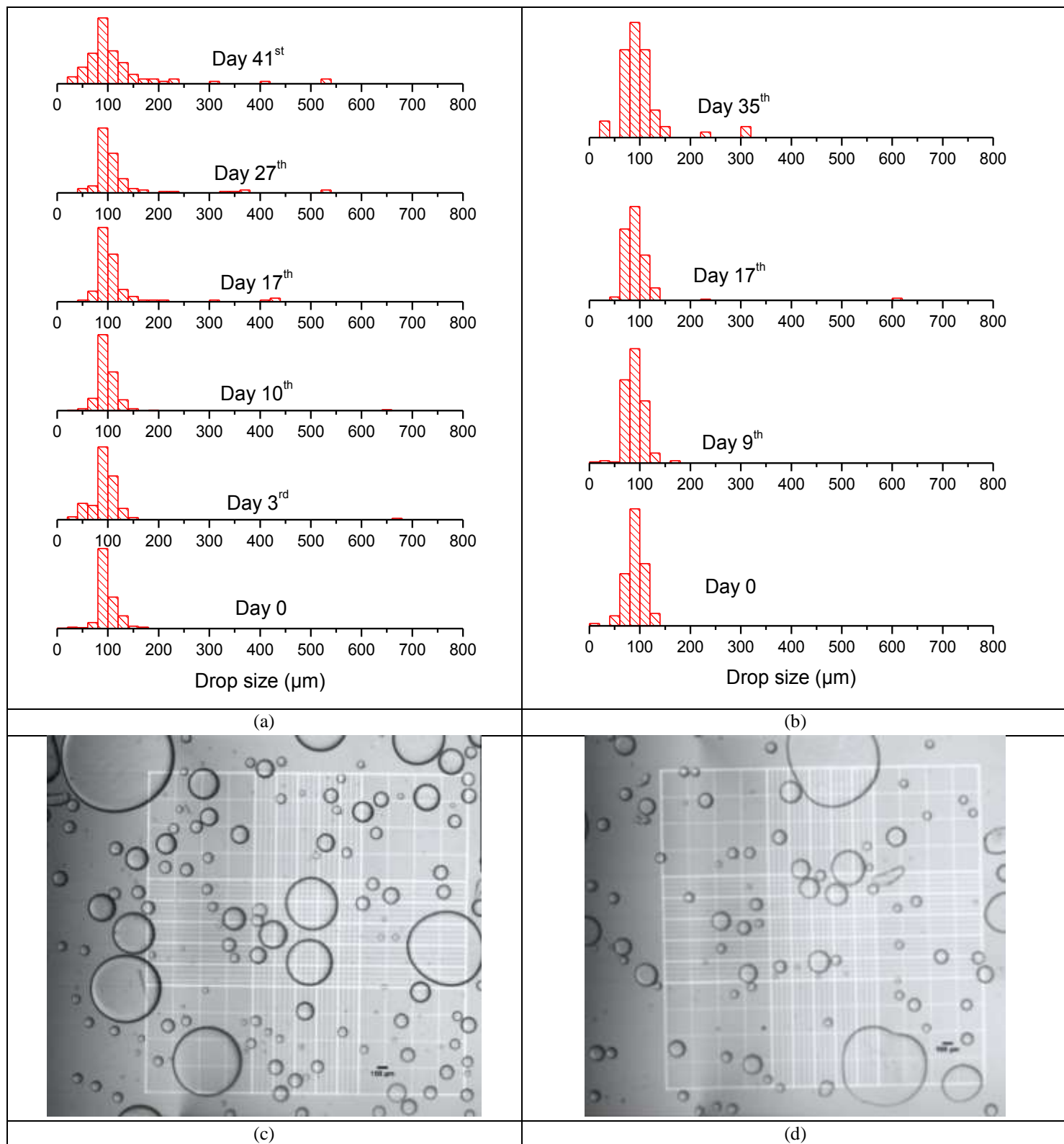
Figure 6 Evolution of Particle size distribution by time for (a) emulsion prepared with Laponite 1.5 wt.%, NaCl 0.1M. (b) emulsion prepared with Laponite 1.0 wt.%, NaCl 0.1M. Respective images at the highest resting time are shown in (c) and (d).

A possible explanation for the coalescence after 17 days observed in both systems is the change in the structure of the clay particles layer at the interface. This phenomenon has already been observed in other studies with Langmuir monolayers at the oil/water interface.[21], [22] Although very large drops appear later, but the particle size distribution is less monodisperse since the preparation day. The time-lapse video of the least stable emulsion (0.5 wt% of Laponite) shows the destabilizing process in the emulsion (Supplementary information, Movie 1).

The delay in drop coalescence reported here can be directly associated with the nano particle structure formation at the oil-water interface. Interface rheological characterization [23] of these systems has shown that the elastic modulus of the interface, associated with the structure formation, becomes very high at the conditions that produced the most stable emulsion, e.g. 1.5 wt % Laponite and 0.1 M NaCl.

FINAL REMARKS

Emulsions consisting of oil drops dispersed in hydrophilic Laponite RD nanoparticle suspension were formed in a T-junction microfluidic device. The stability of the emulsions as a function of nano particle and salt (NaCl) concentration was studied to find the conditions that led to stable systems. Since the dynamics of drop formation in the microfluidic junction was not affected by the aqueous phase formulation, the initial drop diameter distribution was the same for all system analyzed.

The results show that drop coalescence can be avoided or delayed if a nano particle network is formed at the oil-water interface. This occurs if the force between the colloidal Laponite particles is made attractive by the addition of salt in the aqueous nanofluidic phase, inducing the clay particles to flocculate. Therefore, the stability of the emulsion is a strong function of the salt content. The drop size distribution was kept the same for more than 30 days with a salt (NaCl) concentration of 0.1 M and nano particle concentration of 1%. It is important to note that at these conditions, the Laponite suspension was not in a percolating gel phase and thus the observed delayed coalescence is related to interfacial phenomena, and not by the bulk properties of the emulsion continuous phase. The optimum condition for emulsion stability matches the conditions at which the elastic modulus of the interface is highest.

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