The effect of dissolved gas on coalescence of oil drops studied with microfluidics

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GRAPHICAL ABSTRACT
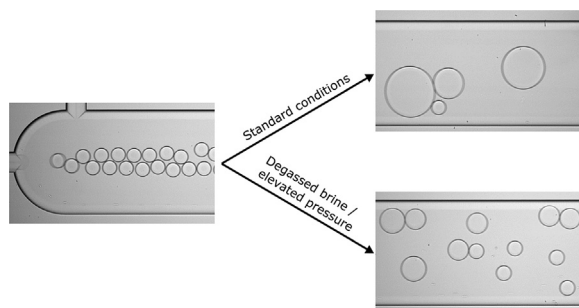
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ABSTRACT

Hypothesis: In literature it is stated that the stability of oil-in-water emulsions could be enhanced by decreasing the so-called "hydrophobic interactions" between surfaces through removal of dissolved atmospheric gases. Since the effect of the dissolved gases depends on the hydrophobicity of the oil phase, as well as the system pressure, we vary this effect systematically and monitor droplet coalescence in a tailor-made microfluidic device.

Experiments: The coalescence of oil drops in standard and degassed conditions was studied by direct observation using a microfluidic setup. Two model oils (heptane and xylene) were used to represent different hydrophobicity of the dispersed phases, together with an oil with dynamic interfacial behaviour (diluted crude oil). In addition, the effect of the volume fraction, droplet size and degassing method was studied.

Findings: At ambient pressure, the degassing of the continuous phase reduced the extent of coalescence for the model oils, which is in agreement with other reports. No effect of the dissolved gases was found on the drop formation process. At elevated pressures, the dissolved gases influenced only the most hydrophobic oil (heptane), while causing no effect in the other systems. The coalescence frequencies decreased upon the reduction of the drop sizes, which was justified with the theory for two interacting spheres.

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1. Introduction

Emulsions are kinetically stabilized systems of dispersed drops that, given sufficient time, will phase-separate. Coalescence is one

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of the main processes that governs emulsion stability, and is important in various applications, including petroleum, pharmaceutical and food industry. Liao and Lucas [1] presented a literature review of coalescence theories, and most widely used is probably the film drainage model proposed by Shinnar and Church [2]. In this model, the coalescence process is divided into three steps: (1) approach of droplets leading to thin film formation, (2) film drainage and (3) film rupture, leading to coalescence. The film thickness and drainage process are governed by droplet features, fluid characteristics, interfacial properties and flow aspects [3]. These factors will give rise to interaction forces acting across the thin film between droplets, of which the attractive interactions are generally considered to be the result of van der Waals forces, whereas the repulsive interactions originate from overlapping electrical double layers or steric (often polymer-induced) repulsion.

However, additional attractive interactions that cannot be explained by van der Waals interactions, have long been observed between hydrophobic surfaces in aqueous solutions [4,5]. In an early review, Christenson and Claesson [6] put these 'hydrophobic interactions' into the following categories:

(1) Strong, short-range attractive interactions between stable surfaces. These interactions were found between very hydrophobic surfaces and occur in a similar range as the van der Waal attraction (i.e. up to 20 nm), but are stronger.
(2) Attractive interactions of variable strength and range in the presence of bubbles. These ranged from 25 to 250 nm and originated from the presence of nanobubbles near the vicinity of hydrophobic surfaces.
(3) Very long-ranged attractive interactions that decay exponentially. These interactions are most elusive and difficult to explain, in regard to both the origin and magnitude of the attraction, but are commonly observed in systems with mobile hydrophobic groups.

More recently, it has been suggested that the 'hydrophobic interactions' may be a combination of long-ranged attraction (likely originating from bridging bubbles) that are not directly related to the hydrophobicity of the surfaces, and truly hydrophobic interactions at short range (separation distances <10–20 nm) [7,8].

It is clear that the origin of these interactions is not well understood, although interesting results were reported. The presence of dissolved atmospheric gases (typically 1 mM at standard conditions) affects the hydrophobic interactions considerably [7,9,10], and numerous papers have demonstrated the importance of dissolved gas for particle aggregation [11,12], emulsion stability [9,13,14] and surface tension [15]. Conversely, degassing improved removal of hydrophobic contaminants from water [16]. The effect of dissolved gases was also studied in reverse osmosis desalination process at laboratory [17] and pilot scale [18], and in both cases degassing improved process performance. The influence of dissolved gas on formation and stability of emulsion droplets has only been studied at ambient pressure.

Recently, microfluidics have become popular tools to investigate emulsions [19–21], including coalescence of drops in both oil-in-water [22,23] and water-in-oil systems [24,25]. Krebs et al. used it to quantify coalescence of oil droplets, leading to coalescence time distributions as function of the droplet velocity and size [26], and surfactant concentration [27]. Microfluidic tools are well fitted to study emulsion stability in more extreme conditions, i.e. high temperature [28–30], g-force [31], but also elevated pressure. Still, emulsion behaviour in microfluidics at pressurized conditions has scarcely been reported [32], while, to the best of our knowledge, no one has studied the effect of dissolved gas on emulsion stability at elevated pressures.

The objective of this work was to study the effect of dissolved gas on the droplet coalescence at elevated pressure. Microfluidic methods were developed to provide insight into the stability of oil-in-water emulsions through direct observations at high frame rates. The influence of droplet size and dispersed phase volume fraction were investigated using two pure model oils, heptane and xylene. Furthermore, diluted crude oil with dynamic interfacial behaviour was used. The results of triplicate measurements (>1000 droplets each) were reported as coalescence frequency values, in combination with drop size distributions.

2. Experimental

2.1. Materials

Heptane (Chromasolv for HPLC, Sigma-Aldrich, USA) and xylene (isomeric mixture for analysis, Merck, Germany) were used as received. The crude oil was produced at the Norwegian Continental Shelf, and diluted to 25 wt.% in a mixture of heptane and xylene (later referred to as HX) with mass ratio 71.5:28.5, which corresponded to a saturated to aromatic ratio in the crude oil (characteristics were reported elsewhere: crude oil D in [33]). The basic physical parameters of the oil phases used here are listed in Table 1.

Densities of oil phases were measured with a DMA 5000 laboratory density meter (Anton Paar, Austria). Viscosity was obtained by using a MCR 301 laboratory rheometer (Anton Paar, Austria) with cylindrical geometry (CC-27). The interfacial tension (IFT) between model oil and water phases were measured with Du Noüy ring tensiometer (Sigma 70, KSV, Finland), while the IFT of brine and diluted crude oil was measured with a pendant drop tensiometer (PAT-1M, Sinterface Technologies, Germany).

3.5 wt.% sodium chloride (for analysis, Merck Millipore, USA) was dissolved in deionized water (resistivity > 18.2 MΩ cm, Millipore Simplicity Systems, Germany) to make standard brine solutions, referred to as Std-Brine. For degassing of brine, an ultrasonic bath (Bransonic CPXH2800-E, Emerson, USA) was used for 15 min (further referred to as Deg-Brine). To compare the efficiency of degassing by ultrasonication, a series of experiments was also performed with conventionally degassed brines (vacuum < 25 mmHg).

The dissolved gas from the brine and one of the model oils (xylene) was also removed through repeated freezing and thawing procedure. The samples were put in Schlenk tubes and sealed in nitrogen atmosphere to avoid condensation of oxygen. Next, they were frozen by immersing the tubes into liquid nitrogen. Once frozen, the samples were put under vacuum (ca. 10^{-4} bar) for 15 min. Afterwards, the sealed tubes were warmed under tepid water in order to thaw the liquid inside. The procedure was repeated until the bubbles stopped appearing in the solution (min. 3 times).

3. Methods

3.1. Microfluidic chips

Custom-designed glass microfluidic chips, Fig. 1, were provided by Micronit Microtechnologies B.V. (The Netherlands) and their design was similar to those used by Krebs et al. [27]. The inlet channels, leading to a *T*-junction where the droplets were created, were 100 μm wide. After passing a meandering channel, the droplets entered a coalescence chamber with a width of 500 μm, where they could undergo coalescence. The length of the coalescence chamber was approximately 33 mm and led to the outlet of the chip. The chips had an additional inlet for the continuous phase, located at the beginning of the coalescence channel. This