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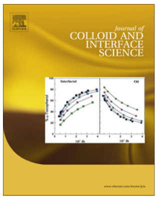

Dilute nanoemulsions via separation of satellite droplets

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ABSTRACT

A facile method is suggested for fabrication of dilute nanoemulsions. In a typical emulsification process, drops are usually accompanied by off-grade satellite droplets. The size of these satellite droplets ranges from hundreds of nanometers to above microns. Experiments were carried out to assess the possibility of separation of nanodrops from macroemulsions made via a conventional method in order to produce nanoemulsions. A low-power homogenizer was used to produce parent emulsions which were then injected from the bottom to a glass column containing water and allowed to cream. By monitoring drops remaining in the bottom of the column, it is clearly shown how progressively smaller they become with time yielding eventually dilute nanoemulsions. The average diameter of drops reduced to 100 nm when oil with high viscosity was used. The concentration of resulting nanoemulsions increased with increasing viscosity and ratio of the disperse phase of parent emulsions.

1. Introduction

Emulsions with drop sizes below 1 μm are often termed 'nano' [1], 'mini' or 'submicron' [2] emulsions. Emulsions are generally thermodynamically unstable and encounter physical instabilities such as creaming, aggregation, flocculation and coalescence. Nanoemulsions are visually more transparent and considered kinetically stable with regard to creaming [3], but can exhibit Ostwald ripening for dispersed phases even with limited solubility in the continuous phase. With many applications in the cosmetic, pharmaceutical, and food industries, the study of nanoemulsions has become of increasing interest [4]. In particular, conversion of nanodrops into nanoparticles by chemical reactions such as polymerization has been the focus of many studies [5].

Nanoemulsions are usually produced either by energy-intensive methods like ultrasonication and high-pressure homogenization [6–8] or low-energy methods such as phase inversion and spontaneous emulsifications [9–12]. These methods, however, suffer from application of too much energy, surfactant or solvent.

In many conventional emulsification methods to produce macroemulsions, large drops are accompanied by small droplets whose average size could be as small as one micron. These droplets, called satellite or daughter droplets, are a result of the rupture mechanisms occurring in emulsification processes [13–16]. Formation of satellite droplets have long been recognized as an undesirable side effect in emulsification processes. These satellite droplets, however, have been always observed and analyzed in combination with parent drops [17–19]. Although the preparation of nanoemulsions by separation of satellite droplets has conceptually been realized [20], it has not been explicitly and experimentally verified. In this research, we aim to separate the submicronic satellite droplets from ruptured emulsions in order to produce nanoemulsions by only utilizing the process of creaming. Creaming is a phenomenon by which dispersed droplets rise due to their lower density until eventually the two phases completely separate. Creaming is in particular well suited to macro-nanodroplet separation as macrodrops cream more quickly than their nanoscale counterparts which move randomly according to their Brownian motion.

In the process of creaming, individual drops with similar sizes will rise together at a similar velocity. This suggests that gravity-induced creaming can theoretically be used to obtain uniform macroemulsions. Surprisingly and to the best of authors' knowledge, there is no report in the literature that has investigated such a possibility. Therefore, the separation of emulsions into a series of uniform emulsions ranging from macro to nano was also considered in this study. Uniform emulsions have progressively become of great interest due to their unique properties, such as efficient, controllable delivery of active ingredients [21] and stability with regards to the rate of Ostwald Ripening. Monodisperse emulsions have a well-defined drop size which enables accurate characterization of their rheological properties, from which experimental results can be compared to theory [22]. Methods for creation of monodisperse drops can be divided into two categories. The first comprises of rather sophisticated and expensive techniques that directly produce uniform emulsions [23–25]. Recent developments have presented methods such as micro-channel and membrane

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emulsification to produce emulsions with high monodispersity [26,27]. The second route consists of two stages; initially to create a polydisperse emulsion by conventional methods including homogenization and mechanical mixers; then finally to screen the resulting emulsion to produce fine emulsions. Methods include centrifugal fractionation [28], and surfactant-assisted flocculation described by Bibette [29]. The latter method involves the periodic addition of excess surfactant to the mixture, whereby a depletion mechanism promotes the flocculation of larger drops, until all that remains is a fine emulsion [30,31]. Micelle-induced flocculation arises when concentration of surfactant is above the critical micelle concentration (CMC), and drops are separated by a distance less than the diameter of a micelle. The exclusion of micelles in the area between the drops results in a lowering of osmotic pressure, which induces attractive interaction between the drops, eventually causing (reversible) flocculation [32–34]. As surfactant is added between intervals, flocculation is induced for drops with a size that is decreasing each time, and the newly formed creamed layers are removed. Surfactant-assisted flocculation has been implemented in another work to obtain relatively dilute monodisperse emulsions with drop sizes in the submicron range [35]. The origin of submicron droplets, however, has not been discussed.

The aim of this research is threefold; first to show that nanodroplets are also formed as a part of drop rupture mechanisms, second to take advantage of this phenomenon to produce dilute nanoemulsions for applications where small volume is sufficient, and third to study the possibility of producing drops with narrow size distribution using creaming. The methods discussed here for producing nanoemulsions, as well as uniform drops, require a high amount of energy or consumption of resources such as surfactants and expensive materials. This article will present a method for obtaining dilute nanoemulsions from an initially polydisperse emulsion without the need for excess energy and resources. The method is based on the creaming phenomena, but without adding excess surfactant, and is limited to low phase ratio. This limitation, however, is shared by many other well-established emulsification processes such as spontaneous emulsification [10,36] and microemulsion dilution [37]. Dilute nanoemulsions have found their own applications in several industries, such as in food industry for encapsulation of flavors in fizzy drinks, which are only required in small amount [38]. Note that some emulsification methods that are used within research laboratories are not suitable for scale-up to industrial production or require large investment. A possible advantage of the suggested methodology is that it utilizes existing emulsion manufacturing lines for production of dilute nanoemulsions therefore reducing the cost and increasing production flexibility.

2. Experimental section

2.1. Materials

n-Hexadecane (purity ⩾99%) was supplied by Alfa Aesar and had density of 773 kg/m^3 and viscosity of 4.5 cSt. Two grades of Polydimethylpolysiloxane (PDMS) oil with viscosity and density of 5 cSt and 965 kg/m^3, and 100 cSt and 960 kg/m^3 were used. Sodium dodecyl sulphate (SDS, purity ⩾98.5%) was supplied by Sigma Aldrich. Deionized water was obtained from an ELGA PURELAB Option water purification system.

2.2. Preparation of emulsions

Parent oil-in-water emulsions were prepared by shearing oil and deionized water with 0.5 wt.% SDS with an Ultra-Turrax T25 Basic low-power homogenizer (500 W with 6500–24,000 rpm) for 2.5 min. The concentration of surfactant used was almost twice that of CMC of SDS (0.24 wt.%), but because of small to medium concentration of oil phase used, it is unlikely that formation of flocs is significantly assisted by micelle-depletion mechanism. A speed setting of 6500 rpm was used. All experiments were carried out at room temperature (22 °C).

2.3. Characterisation

Experiments were carried out in a 0.55 m tall, 0.035 m diameter glass column with a syringe port located at the top. The column was attached to the outlet of a PVC-U ball valve purchased from RS-Components, with an internal diameter of 0.04 m. A glass cell with a syringe port located underneath was connected to the inlet of the valve. The column was filled with a 0.5 wt.% SDS/deionized water solution. Precautions were taken to ensure that the empty space inside the ball valve was also filled with water and then locked. The emulsions were then injected into the bottom cell and the ball valve was released, allowing them to cream. This marks time *zero*. A lamp was placed behind the upper region of the column to increase visibility of the creaming emulsion as it approached the surface, enabling samples of the first drops to reach the surface to be taken. Samples were taken at different time intervals from the bottom and the top (within the creamed layer). The average size and size distribution of nanoemulsions were measured using dynamic light scattering (DLS; Malvern Nanosizer). Drop size and size distribution for macroemulsions were measured using an optical microscope (Kyowa Unilux-12). For making the drop size distribution curves, at least 1000 drops were measured and their frequencies were drawn against drop diameter for bin intervals of 1 μm. The phase ratio of emulsions was found by conductivity measurements.

3. Results and discussion

3.1. Analysis of top (creamed) layer

Fig. 1a shows the time variations in the drop size distribution (DSD) of samples taken within the creamed layer for an oil phase ratio of $\varphi = 0.05$, which was not uniform at all, and covered the whole range of drop sizes within the original emulsion. One might have expected to see drops of larger size to rise faster, leading to accumulation of larger drops at the surface (representing the higher end of DSD of the original emulsion), followed by gradual transformation of the DSD to that of the initial emulsion as smaller drops reach the surface.

The sluggish changes of DSD with time suggest that flocculation plays an important role in the creaming rate of the emulsion. For a basic system where a single oil droplet rises through the continuous phase, the rising velocity of drops (U_s) can be represented by the Stokes' velocity [39]:

$$U_s = \frac{2}{9}\frac{(\rho_d - \rho_c)}{\mu} g r^2 \tag{1}$$

where ρ_c is the density of the medium (continuous phase); ρ_d, the density of the drop; g, gravitational acceleration; r, radius of the drop; and μ the viscosity of the medium.

A preliminary experiment was performed to ensure that the design of the column did not hinder the motion of the rising droplets. Using a syringe pump, n-hexadecane was injected into the column (filled with an aqueous solution of 0.5 wt.% SDS), and the time taken for individual drops to reach the surface was recorded. Results showed that actual velocities of the drops were overestimated by their corresponding Stokes velocities. For the $\varphi = 0.05$ emulsion, the time taken for the first drops to reach 0.55 m was 5.0 min, which gave an actual velocity of 1.80×10^{-3} m/s. The sample