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Regular Article

Interactions between micro-scale oil droplets in aqueous surfactant solution determined using optical tweezers

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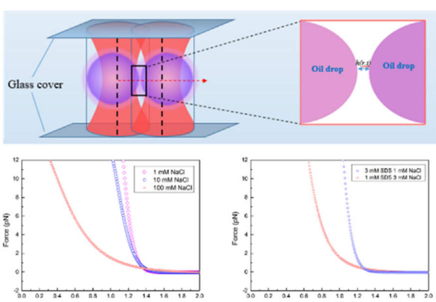
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: The stability of the emulsions is crucial, which relies on a well-developed understanding of dynamic interaction forces between single dispersed droplets. In the previous studies, many interests focus on the oil droplets of size range of 20–200 μm. However, emulsion droplets with diameter below 10 μm are rarely mentioned, which is the size scale of real emulsion droplets in various applications, such as toners, spacers for liquid crystal displays, and materials in biomedical and biochemical analysis. The micro-scale droplets have many differences on the deformation, internal pressure and hydrodynamic effects. It is necessary to understand the interaction mechanisms between two real size scales of oil droplets for guiding practical production and application.

Experiments: In this work, tetradecane was chosen as the model oil phase in all experiments. The interaction forces of two tetradecane droplets with the diameter of 5.0 μm in water in the presence of surfactant and salt solution were directly measured using optical tweezers. The force-distance curves were established, and the zeta potential of tetradecane droplets was studied using Zetasizer Nano ZSP.

Findings: The absolute value of zeta potential of tetradecane droplets was found to decrease with the increase of salt concentration and increase with the increase of surfactant concentration. The repulsive force between two tetradecane droplets was found to decrease with the increase of salt concentration because the electrostatic double-layer force was suppressed gradually with the increase of salt concentration. The "hydrodynamic suction" effect during the process of retraction becomes more pronounced due to the corresponding increase in the hydrodynamic force with the increase of the approaching velocity between the tetradecane droplets. Furthermore, we found the existing model for the measurement of large droplets by atomic force microscope (AFM) is invalid for the measurement of micro-scale droplets by optical tweezers. The deformation of colliding micro-scale droplets can be safely ignored, which is

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quite different from the large droplets. Our results provide a useful method to study the interaction forces between micro-scale emulsion droplets with pN force resolution, and gives a deep insight of the stabilization mechanism of real size scale of O/W emulsions. These findings have significant implications on the stability of emulsions in many food, cosmetics, medicine, and advanced materials.

1. Introduction

The stability of emulsions plays a crucial role in the production of many food [1], cosmetics [2], medicine [3,4], advanced materials [5–7]. Emulsions can be stabilized by various stabilizers, such as surfactants [8], polymer [9], nano-particles [10], etc. These stabilizers readily adsorb onto the oil-water interfaces, which leads to an electrostatic double-layer repulsive force or a steric barrier that prevents the coalescence of emulsion droplets. The stability of the emulsions relies on a well-developed understanding of interaction forces between single dispersed droplets [11]. It is crucial to understand and measure the hydrodynamic interaction force and surface forces, such as van der Waals (VDW), electrostatic double layer (EDL), hydrophobic, steric interaction and so on.

Recently, some experiment tools involving surface force apparatus (SFA) [12–15] and atomic force microscope(AFM) [16–21], have been developed to make such stability measurement by directly measuring the interaction forces between two oil droplets under the various solution conditions, such as single ionic surfactant systems [11,22,23], polymers [24], polyelectrolytes [25], proteins [1,23], and salt solutions [26,27]. The emulsion systems usually are chosen in the size range of 20–200 μm in these studies and the force measured between droplets is usually in the scale of tens of nano-Newton. The theoretical model of equilibrium and dynamic forces between droplets is also well established in the literature. However, the measurement and theoretical model of emulsion droplets with diameter below 10 μm are rarely mentioned, which is the size scale of real emulsion droplets widely used in various applications [28–30], involving toners, spacers for liquid crystal displays, and materials in biomedical and biochemical analysis. Furthermore, we will prove in Section 4.2 that the existing model is not valid for micro-scale droplets. We will also show that the equilibrium force between micro-scale droplets is dominated by mechanisms different from that of large droplets. It is vital to summary the interaction mechanisms between two micro-scale oil droplets. Therefore, we focus on the oil droplets diameter below 10 μm in the ionic surfactant and salt solution by optical tweezers in this work.

It is easy for ionic surfactants to dissociate in the aqueous solution and adsorb onto the oil-water interface, which leads to the electrostatic repulsive force that provides stability against coalescence. According to Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [31–34], higher surfactant concentrations bring out higher ion adsorption capacity. Therefore, droplets with more surfactants will cause higher repulsive effect. The concentration of salt solution makes a significant influence on the Debye length, while salt solution and surfactant have a common effect on the electrostatic double-layer force. Therefore, salt solution and surfactant have a profound influence on the measured force during approach and separation process. In addition, the hydrodynamic pressure in the thin film of the continuous phase between two oil droplets can also make a major contribution to interfacial deformations and determine magnitude of the measured force at different velocities.

In this work, optical tweezers (NanoTracker™ 2) were used to measure the dynamic interaction forces between two tetradecane droplets with the diameter of 5.0 μm in different concentration of SDS (sodium dodecylsulfate) and NaCl (sodium chloride) solutions. The magnitude of the interaction forces determined using optical tweezers was in the order of pN (10^{-12} N), providing higher force resolution and more stable and precise force curve in the order of pN compared with other experiment tools. Optical tweezers have a unique advantage in deeper perspective of the dynamic interaction mechanism between tiny oil droplets. The magnitude of the measured force (pN) opened a new size scale of the measurement of interactions between emulsion droplets in the work. Optical tweezers can achieve accurately observing the dynamics of individual droplets by controlling the movement of particles precisely. This work provides a fresh approach to study the interaction behaviors of emulsified oil droplets with SDS adsorbed at the oil/water interface in the different salt concentrations, and the results give clear insights into the stabilization mechanisms of micron-sized O/W emulsion droplets.

2. Experiments

2.1. Materials and methods

Tetradecane with high purity was obtained from Aladdin and used as the oil phase for all emulsions. SDS (sodium dodecylsulfate) was supplied by Aladdin and used as ionic surfactant. All aqueous solutions were prepared using Milli-Q water (Millipore deionized) with a resistance of ≥18.2 MΩ·cm. Interfacial tensions between tetradecane and aqueous solution with different salt concentrations in the presence of SDS were measured by using the pendent drop tensiometry (OCAH200, Data Physics Instruments GmbH, Germany), as listed in Table 1. The measurements of zeta potentials of tetradecane oil droplets under different aqueous conditions were conducted by using Zetasizer Nano ZSP (Malvern Instruments, UK), as listed in Table 1. All the experiments were carried out at room temperature (25 °C).

2.2. Optical tweezers measurement

Optical tweezers are capable of capturing colloidal particles in optical traps of highly focused laser beams, which is based on the principle of photon momentum changes when photons pass through two different refractive index interfaces [35]. It is necessary that the refractive index of the dispersed phase to be trapped is higher than that of aqueous phase [36]. More details can refer to

Table 1
Experimentally measured Zeta potential, Interfacial tension, pH of tetradecane emulsion droplets in the water solution with SDS and NaCl.

SDS Concentration (mM)	Solution condition	Zeta potential (mV)	Interfacial tension (mN/m)	pH
3.0	1 mM NaCl	−91.3 ± 1.1	6.03 ± 0.50	6.99 ± 0.04
3.0	10 mM NaCl	−87.9 ± 1.9	5.21 ± 0.30	7.17 ± 0.01
3.0	100 mM NaCl	−58.8 ± 3.0	3.43 ± 0.30	7.03 ± 0.02
1.0	3 mM NaCl	−88.9 ± 0.7	10.52 ± 0.30	6.95 ± 0.03