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Influences of addition of hydrophilic surfactants on the W/O emulsions stabilized by lipophilic surfactants

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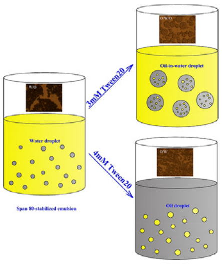
HIGHLIGHTS

- O/W/O multiple emulsions were formed in the emulsion system.
- Absorption changes of 1640 cm^{-1} and 3380 cm^{-1} indicate the morphologies changes.
- Micelles transport contributes to the inversion of W/O to O/W.

GRAPHICAL ABSTRACT



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ABSTRACT

Lipophilic surfactants were used in the oil/water system to form W/O emulsions, and the consequences of addition of hydrophilic surfactants to the emulsions were examined. The process was monitored by visual and microscopic observations and the droplet size as well as emulsion conductivity were determined. Multiple oil-in-water-in-oil (O/W/O) emulsions were observed when the hydrophilic surfactants concentrations were low. Surprisingly, the emulsion inverted to oil-in-water (O/W) when the concentrations of the hydrophilic surfactants were increased. The infrared (IR) spectrometer was also used to investigate the interesting phenomenon and the results demonstrated that the absorption changes of the hydroxyl groups and alkyl groups in IR spectra could effectively explain the morphologies changes. Morphological evolution of the emulsion with stirring time was applied to analyze the mechanism of the inversion of W/O to O/W.

1. Introduction

Emulsions are kind of dispersions composed of two immiscible liquids (usually water and organic solvent) that form two phases: the dispersed phase as liquid droplets and the surrounding continuous phase. Depending on the state of their components, emulsions can be classified into simple emulsions and multiple emulsions [1,2]. Multiple emulsions are complex structured fluids that the droplets of the dispersed phase contain one or several finer droplets of the continuous phase. Thus, they have also been termed “emulsions of emulsions”. There exist at least two types of multiple emulsions, namely oil-in-water-in-oil (O/W/O) emulsion, where oil droplets are located within water droplets that are dispersed within a continuous oil, and water-in-oil-in-water (W/O/W) emulsion, where water droplets are dispersed in oil droplets, which in turn are dispersed in a continuous aqueous phase. The multiphase, compartmentalized structure of multiple emulsions makes them useful in systems requiring controlled release or uptake capabilities. Research in multiple emulsions has experienced a continuous increase in the last years, as evidenced by the numerous publications [3–6]. This enormous interest is triggered by the widespread

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applications, for example, food [7], cosmetic [8], polymer synthesis [9] and pharmacy [10,11].

Multiple emulsions are typically more difficult to prepare and control than simple emulsions, in large part given the presence of two thermodynamically unstable interfaces, i.e. the W/O interface and the O/W interface. Consequently, a systematic study of the effects of composition parameters and different processes such as (i) type of the oil phase, (ii) phase volume fraction, (iii) type of emulsifying agents, (iv) hydrophilic/lipophilic surfactant ratio, and (v) process variables (agitation speed and emulsification temperature) on emulsion formation and stability is necessary if multiple emulsion formation is considered. Moreover, such a systematic investigation will contribute not only to our understanding of multiple emulsions, but also emulsion systems in general, from both a practical and theoretical view [12].

In the case of O/W/O emulsions, a two-step method [13,14] is generally adopted where an O/W emulsion is formed, and then dispersed in a secondary oil phase. The primary emulsion (O/W) is typically made using a hydrophilic surfactant with a high HLB whereas in the second step, the primary emulsion is gently emulsified within an external phase that contains a lipophilic surfactant with a low HLB to produce the O/W/O emulsions. Moreover, the primary O/W emulsion is carried out under high-shear conditions to obtain small droplets while the secondary emulsification step is prepared with less shear force to avoid rupture of the internal droplets. The composition of the multiple emulsion is of significant importance to the stability and release properties. Much work has been carried out on optimizing the nature of the surfactants, the nature of the oils, and the volume fractions of the water and the oil [15]. Besides, the microcapillary device [16] and membranes [17] were utilized to the O/W/O multiple emulsion formation.

In this study, the W/O emulsions stabilized by lipophilic surfactants were prepared at room temperature. Then appropriate amount of hydrophilic surfactants were added into the system and the consequences of addition of hydrophilic surfactants were systematically studied. The obtained emulsions were characterized by visual and microscopic observations and the droplet size as well as emulsion conductivity were determined.

2. Materials and methods

2.1. Materials

Liquid paraffin ($d = 0.86–0.89\ \mathrm{g/cm^3}$, C.P.) is used as the oil phase and its purity is greater than 99%. The components of the liquid paraffin are mainly isoalkane, and the carbon number ranges from 16 to 26. The water phase is deionized water containing 0.2% (w/w) potassium chloride (99.5%, C.P.) to set the electrical conductivity. The lipophilic surfactants are Sorbitan monopalmitate (Span 40, HLB = 6.7, C.P.), sorbitan monoctadecanoate (Span 60, HLB = 4.7, C.P.) and sorbitan monooleate (Span 80, HLB = 4.3, C.P.). The hydrophilic surfactants are polyoxyethylene sorbitan monolaurate (Tween 20, HLB = 16.7, C.P.), polyoxyethylene sorbitan monopalmitate (Tween 40, HLB = 16.0, C.P.), polyoxyethylene sorbitan monooleate (Tween 80, HLB = 15.0, C.P.), polyoxyethylene (10) nonylphenol (OP-10, HLB = 14.8, C.P.) and sodium dodecyl sulfate (SDS, HLB = 40.0, C.P.). All reagents are purchased from Shanghai Civi Chemical Technology Co., China and used as received without further purification.

The concentrations of water (oil) are expressed as percent (v/v) based on the volume of the water (oil) present in the systems as 100 vol%; the hydrophilic surfactants concentrations are expressed as millimole (mM).

2.2. Preparation of emulsions

The primary W/O emulsions were prepared first and then hydrophilic surfactants were added into the W/O emulsion in order to investigate the influences. The primary W/O emulsions were prepared by adding the aqueous phase (50%) containing 0.2% (w/w) KCl solution to the oil phase with 2 wt% lipophilic surfactants included. After adding the water phase to the oil phase, the emulsions were homogenized using a homogenizer (AD200l-P, Shanghai Angni Instruments & Meters Co., Ltd.) for 30 min at 4000 rpm. Then the hydrophilic surfactants were added into the emulsions and the experimental parameters were maintained constant at a stirring rate of 4000 rpm for 20 min. After the emulsification, the conductivities and IR spectra of the samples were immediately determined, and then the samples were poured into glass tubes and carefully sealed.

The emulsion conductivity was immediately observed by a DDS-307 conductometer (Shanghai Precision & Scientific Instrument Co., Ltd.) after stirring with a Pt/platinized electrode at 25 °C. Large conductivity values indicate O/W emulsions, whereas low values indicate W/O emulsions. At the same time, IR spectra were monitored by a Fourier transform infrared (FTIR) spectroscopy (TENSOR27, Germany Brooke Fourier Infrared Spectrometer Co., Ltd.). Software collected spectra in absorbance mode (wavenumbers from 4000 to 400 $\mathrm{cm^{-1}}$) and this spectral range provided obvious changes of hydroxyl groups and alkyl groups. A high speed CCD camera (AOS X-PRI) was used to observe emulsion morphologies. For sample preparation, a small amount of the emulsion was placed on the microscope glass slide and then quickly covered by the cover slip and the covered sample was finger pressed to make it as thin as possible. The droplet sizes were determined by Photon correlation spectroscopy (PCS) using Malvern Mastersizer 3000. An argon laser with variable intensity was used to cover the size range involved. Measurement was carried out at 25 °C with a scattering angle of 90 °. Intensity averaged radius were computed from the intensity autocorrelation data with the cumulants method. And the intensity-intensity time correlation functions were analyzed by the CONTIN method. Before the measurement, the O/W samples were diluted with water which O/W/O samples were diluted with octane. Note that for kinetically stabilized emulsions, dilution does not alter the original emulsion drop size.

3. Results and discussion

3.1. Development of the primary W/O emulsions

The instability of multiple emulsions can be increased by the use of unsaturated oils in the oil phase, which prevents a close packed, condensed interfacial film [18,19]. Schmidts et al. [20] reported that paraffin oils, particularly the heavy paraffin, formed more stable formulations. Thus, heavy paraffin and three lipophilic surfactants with HLB values ranging from 4.3 to 6.7 were chosen for the preparation of primary W/O emulsions. The surfactants are of the same surfactant class (sorbitan ester) with different side chains resulting in various HLB values. It was found that the most stable emulsion was obtained using heavy paraffin stabilized with Sorbitan monooleate. Fig. 1 shows an optical micrograph of water-in-oil (50%, v/v water) emulsion. The conductivity of the emulsion is relative low ($\leq 1\ \mu\mathrm{S/cm}$), indicating the continuous oil phase. The viscosity of this primary emulsion was 1.5 Pa s and the average water droplet size was approximately 0.5 μm. Moreover, the emulsion remained stable for at least 2 days with no measurable change in droplet size distribution. The rHLB of paraffin oil is about 4 [21] and consequently emulsifiers with an HLB of approximately 4 will create the most stable formulations.