Journal of Colloid and Interface Science 336 (2009) 329–334

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Effect of molecular weight of triglycerides on the formation and rheological behavior of cubic and hexagonal phase based gel emulsions

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ARTICLE INFO

Article history:
Received 25 December 2008
Accepted 26 March 2009
Available online 5 April 2009

Keywords:
Triglycerides
Rheology
Liquid crystal based gel emulsion
Phase behavior
Cubic phase
Hexagonal phase

ABSTRACT

The effect of triglyceride molecular weight on the formation and rheology of cubic (O/I_1) and hexagonal (O/H_1) phase based gel emulsions has been studied in water/$C_{12}EO_8$ systems. It was found that the addition of TDG (1,2,3-tridecanoyl glycerol) in the micellar solution leads to the formation of the I_1 phase, which can solubilize some added oil. From SAXS data, it is revealed that the interlayer spacing (d) and the length of hydrophobic part (r_l) increase with increasing TDG concentration in the I_1 phase, whereas the effective cross-sectional area (a_s) decreases. After the oil solubilization limit, the d value remains nearly constant, indicating the I_1+O phase appears. The high viscosity of the I_1 phase facilitates the formation of the O/I_1 gel emulsion. It has been observed that the formation and stability of the O/I_1 and O/H_1 gel emulsion is highly dependent on the molecular weight of triglycerides, namely, the high molecular weight triglycerides show better performance (formation and stability) compared to the low molecular weight triglycerides. The rheological behavior of the I_1 phase was found to change from viscoelastic to elastic nature with TDG content. The values of the complex viscosity, $|\eta^*|$ show different trends at different fixed frequencies within the I_1 phase, whereas it decrease monotonically in the O/I_1 gel emulsions. The increasing values of the $|\eta^*|$ (at lower frequency) could be due to the neighboring micellar interaction and decreasing values of the $|\eta^*|$ in the O/I_1 gel emulsion could relate to the volume fraction of the I_1 phase in the system. It is also figured out that the rheological parameters (elastic modulus, viscous modulus, and $|\eta^*|$) of the O/I_1 the gel emulsion do not depend on the oil nature, whereas the O/H_1 gel emulsion shows oil nature dependency.

1. Introduction

Highly concentrated or high internal phase ratio emulsions (HIPREs) have been the objects of many studies for several years [1–8]. It is known that HIPREs can form in the water (O/W) and oil (W/O) rich region under certain conditions [2,9–11]. Due to their characteristic features such as high volume fraction of the internal phase, high viscosity, and transparency, they are also referred to as gel emulsions [1,3,12,13]. Rheological properties of HIPREs were also studied and found that range from viscoelastic to elastic nature depending on the system composition and temperature [6,14,15]. HIPREs have been used for practical applications such as aviation fuels, emulsion explosives, and cosmetics [16–19].

Another kind of gel emulsion that is lyotropic liquid crystal based gel emulsion has been taken attention. In contrast with HIPREs, LC based gel emulsion shows high viscosity even at low volume fraction of internal phase and prolonged stability [20–23]. Among the liquid crystals, cubic phase (I_1) is the most viscous phase and, thus commonly used to prepare O/I_1 gel emulsion [20,21,24]. Generally, the I_1 phase is formed in aqueous system with very hydrophilic nonionic surfactant such as poly(oxyehtylene) alkyl ether [25], poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) triblock copolymer [26,27], polyglycerol fatty acid ester [28], and sucrose fatty acid ester [29]. Besides, the solubilization of oil in the micellar (W_m) or hexagonal phase (H_1) often induces the I_1 phase [21,30]. The I_1 phase is normally formed between the micellar and the hexagonal phase as a function of surfactant concentration. Several authors studied the rheological behavior of the I_1 phase [31,32] and O/I_1 gel emulsion [22,24].

On the other hand, hexagonal phase (H_1) is also highly viscous and is very common in aqueous surfactant solution, e.g., poly(oxyethylene) alkyl ether [25], sodium dodecyl sulfate [33], poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) triblock copolymer [34], and poly(oxyethylene)-poly(oxypropylene) diblock copolymer [26], sucrose monododecanoate [35]. Recently, we have found that the H_1 phase could form O/H_1 gel emulsion similarly to the O/I_1 gel emulsion [36]. We have extensively studied the formation, stability, and rheological behavior of the H_1 phase and O/H_1 gel emulsion, which was compared to the O/I_1 gel emulsion. In our study, we mainly concentrated on hydrocarbon oils. To our knowledge, there are few studies counted, in which triglyceride is used to study the gel emulsion instead of hydrocarbon oil as a dispersed phase [37].

Triglycerides or triacylglycerols are a simple class of lipids consisting of glycerol esterifies with three fatty acid moieties. Moreover, natural fats and oils including all vegetable oils, such

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doi:10.1016/j.jcis.2009.03.054

as palm oil or sunflower oil and animal fats, consist almost exclusively of triglyceride. These are commonly used for cosmetics, foods, and so on. Although triglyceride is an important class of food oil, detail rheological study of triglyceride-containing gel emulsion is still missing. Aramaki and Yanagimachi [37] reported the phase behavior and rheological properties of the I_1 phase and the O/I_1 gel emulsion as a function of triglyceride concentrations (mainly 1,2,3-trioctanoylglycerol, TOG) in water/$C_{12}EO_{25}$ system. However, they did not show the effect of the molecular weight of triglycerides on the formation and stability of O/I_1 gel emulsion containing triglycerides as a dispersed phase.

The present paper is the supposed to guide for the gel emulsion with triglycerides in the same way as previous detailed investigation of hydrocarbon oils [36]. In this contribution, we have mainly studied the formation, stability, and rheology of the O/I_1 and O/H_1 gel emulsions with different molecular weight triglycerides. The changes of the microstructural parameters (d, r_I, and a_s) of the I_1 phase with the addition of TDG were also evaluated.

2. Experimental

2.1. Materials

Monodisperse octa(oxyethylene) dodecyl ether ($C_{12}EO_8$) was purchased from Nikko Chemicals, Japan. 1,2,3-Trihexanoylglycerol (tricaproin, THG) and 1,2,3-tridecanoylglycerol (tricaprin, TDG) were purchased from Tokyo Chemical Industry. 1,2,3-Trioctanoylglycerol (tricaplyrin, TOG) was purchased from Sigma–Aldrich Chemicals. Olive oil (average carbon number 17) was purchased from Wako Chemical Industries Ltd. Structure of triglyceride was presented elsewhere [30]. All these chemicals were highly pure and were used as received. Millipore-filtered water was used to prepare all the samples.

2.2. Methods

2.2.1. Preparation (formation) of gel emulsion

All components were added together at a final composition, melted at 80 °C, and then instantly mixed with a vortex mixer for around 2 min at 2500 rpm in open air-cooling. Around room temperature, we observed a highly viscous emulsion that did not flow when the glass tube was turned upside down.

2.2.2. Small-angle X-ray scattering measurements

The interlayer spacing of liquid crystals was measured using small-angle X-ray scattering, performed on a small-angle X-ray scattering camera equipped with rotating anode and a CCD detector (Rigaku, Nanoviewer). The samples of liquid crystals were filled in a hole of an iron plate and covered by plastic films for the measurement (Mylar seal method). The type of liquid crystal was determined by the SAXS peak position [38]. According to the geometry of liquid crystals, the effective cross-sectional area per surfactant molecule, a_s, is calculated by the following equations using the interlayer spacing, d, obtained from the SAXS measurement.

For the I_1 phase [30,38],

$$r_I = d\left\{\frac{3}{4\pi n_c}(\phi_L + \phi_O)\right\}^{1/3} C, \tag{1}$$

$$a_s = \frac{3v_L}{r_I}\left(\frac{\phi_L + \phi_O}{\phi_L}\right), \tag{2}$$

where, r_I is the radius of lipophilic core of spherical micelle in the I_1 phase, n_c is the number of micelles in a unit cell of cubic phase, and C is a constant ($C = (h^2 + k^2 + l^2)^{1/2}$), where h, k, and l are miller indices. The values of the constants (n_c,C) are (1,1) for simple cubic, (2,$\sqrt{2}$) for body-centered cubic, and (4,$\sqrt{3}$) for face centered cubic structures. v_L is the volume of the lipophilic part of one surfactant molecule. ϕ_O and ϕ_L are the volume fraction of oil and lipophilic part of surfactant in the system, respectively.

2.2.3. Rheological measurements

Rheological measurements (oscillatory) on a ternary mixture of water/surfactant/triglycerides in the samples were carried out as a function of oil concentrations. All samples for rheological measurements were homogenized with repeated centrifugation and kept in a water bath at 25 °C for 24 h before measurements to ensure equilibration. Rheology of the gel emulsion was done within 24 h after preparation. The rheological measurements were performed in ARES rheometer (Rheometric Scientific) using cone plate geometry (ϕ = 25 mm, cone angle = 0.1 rad) in the linear viscoelastic regime, as determined previously by dynamic strain sweep measurements. A sample cover provided with the instrument was used to minimize the change in sample composition by evaporation during measurements.

3. Results and discussion

3.1. Effect of TDG on the structural parameters of the I_1 phase

The partial ternary phase diagram of the water/$C_{12}EO_8$/TDG is already reported [39], here we would examine the change of interlayer spacing, d, length of the hydrophobic part r_I, and the effective cross-sectional area per surfactant molecule, a_s, of the I_1 phase with the addition of TDG. It should be noticed that the d value could give us information regarding the phase boundary between the I_1 phase and the I_1+O region and also to determine r_1 and a_s. To evaluate the structural changes (d,r_I,a_s) in the I_1 phase, we have performed SAXS measurement at a constant water/$C_{12}EO_8$ ratio (60/40). We have calculated the structural parameters by using Eqs. (1) and (2) and presented in Fig. 1.

It is inferred in Fig. 1 that the values of the interlayer spacing (d) increase with the TDG content and after a certain concentration, it show nearly constant. Intersection of these two lines is considered as phase boundary between the I_1 phase and the I_1+O region. Visual inspection could also ascertain phase boundary that changes from transparent (I_1 phase) to turbid (I_1+O). Simultaneously, the length of the hydrophobic part (r_I) of the aggregates increases with the oil content but the effective cross-sectional area per surfactant molecule (a_s) decreases. It is already pointed out that the a_s decreases in the I_1 phase if oil is solubilized in the aggregate cores

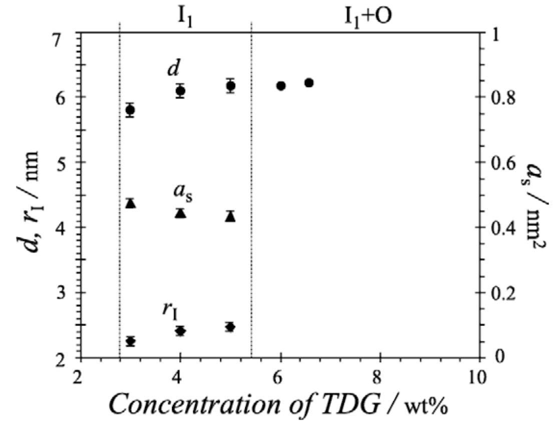

Fig. 1. Change in the interlayer spacings (d), effective cross-sectional area (a_s), and the length of hydrophobic part (r_I), of the I_1 phase are plotted as a function of TDG (wt.%) in a fixed water/$C_{12}EO_8$ ratio = 60/40.