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Phase behavior and SANS investigations of edible sugar–limonene microemulsions

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Abstract

We have studied the phase behavior and microstructure of edible microemulsions of d-limonene with concentrated aqueous sugar solutions (>65 wt%) using sucrose laurate and sucrose oleate as surfactants. The phase behavior of these mixtures was systematically studied as a function of temperature and surfactant composition, identifying the specific effects of sugar concentration, surfactant chain length, and oil loading on the formation of microemulsion and lamellar phases. Small-angle neutron scattering experiments confirm the presence of well-structured microemulsions with domain sizes ranging from ∼35 to 60 nm. With few exceptions, the patterns of microemulsion phase behavior with concentrated sugar solutions are very similar to that of aqueous systems.

Keywords: Microemulsion glass; Sugar surfactants; Limonene; Encapsulation

1. Introduction

Microemulsions, comprising of surfactant, oil, and water, have widespread utility in detergency, synthesis of nanoparticles, drug delivery, microreactors, and other applications that take advantage of their self-assembled microstructure and thermodynamic stability. Furthering this range of applications, our recent report of anhydrous microemulsion glasses demonstrated that sugar-rich microemulsions, containing equal masses of polymerizable liquid oils and sugars, can be completely dehydrated to the solid glassy state without phase separation [1].

The formation of microemulsion glasses starts from liquid precursor microemulsions wherein water in traditional microemulsions is replaced with concentrated (>65 wt%) aqueous sugar solutions. We report here the detailed phase behavior and structure of sugar-based microemulsion glass precursors prepared using edible surfactants (sucrose oleate/sucrose laurate) and d-limonene, the principal component of citrus oil. Using supersaturated, equimolar solutions of sucrose and trehalose as the "aqueous" phase, we studied the effects of varying sugar concentration, alkyl chain length of the surfactant, oil loading, and increasing surfactant concentration on the phase behavior. Neutron scattering spectra, as analyzed using the Teubner–Strey model, was used to probe the domain size and correlation lengths of the microemulsion structure. The wide temperature stability of these concentrated sugar microemulsions (∼20–65 °C) achievable with as little as ∼7 wt% surfactant, is an important characteristic that make them useful not only for the preparation of solid microemulsion glasses by spray drying, but also in various surface cleaning applications.

2. Experimental methods

2.1. Materials

Food grade sucrose laurate (80% monolaurate, 20% higher substitution) and sucrose oleate (74% sucrose monooleate, 23% sucrose dioleate, 3% higher substitution) surfactants were supplied by Mitsubishi Kagaku-Foods Corporation, Japan and used as received. D-limonene (97%) with 0.1 wt% butylated hydroxytoluene (BHT) added as an antioxidant was purchased from Aldrich Chemical and used as received. Sucrose and trehalose dihydrate (99%) were purchased from Acros Organics and

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used as received. Deionized water with a specific resistance of 18.2 MΩ cm was used in preparing all samples.

2.2. Phase diagram determination

Following the nomenclature of Kahlweit et al. [2,3], composition variables used in determining the phase diagrams are defined as follows:

Mass ratio of oil to sugars in the mixture (α),

$$\alpha = \frac{\text{oil}}{(\text{oil} + \text{sugars})} \times 100 \quad \text{in wt\%} \tag{1}$$

mass ratio of long chain surfactant to long + short chain surfactants (ε),

$$\varepsilon = \frac{\text{sucrose oleate}}{(\text{sucrose oleate} + \text{sucrose laurate})} \times 100 \quad \text{in wt\%} \tag{2}$$

and mass fraction of surfactant in the overall mixture (γ),

Stock solutions, 25 wt% sucrose oleate in 65 wt% aqueous sugar solution and 40 wt% sucrose laurate in water, were prepared to facilitate the phase behavior studies. Sucrose oleate is insoluble in water, but highly soluble in concentrated sugar solutions. One gram samples were prepared by gently heating mixtures of sugar, surfactant solutions, and water in flat bottom screw-cap tubes, evaporating excess water when necessary by passing argon over the sample, then adding d-limonene. Mixtures of sugar, surfactant, and water were prepared by combining appropriate amounts of sucrose oleate and sucrose laurate stock solutions with additional sugar and water as necessary. In preparing 80 wt% concentrated sugar solutions, excess water is added initially to facilitate mixing, and subsequently removed by passing dry argon and re-weighing periodically. Complete dissolution of the sugars is important to avoid crystallization. The sample tubes were immersed in isothermal water baths (±0.02 °C), stirred vigorously with gold-coated NdFeB magnetic stir-bars, and then allowed to phase separate for up to 12 h to locate accurately boundaries between one and two phase regions. The presence of multiple phases was determined by visual inspection in both transmitted and scattered light, using crossed polarizers to determine the presence of liquid crystalline phases. Although optical rotation arising from the optically pure sugars can be observed, this is weak and noticeably distinct from that arising due to liquid crystalline phases.

2.3. Neutron scattering

Neutron scattering experiments were performed using the 30-m small angle neutron scattering (NG-3 SANS) instrument at the National Institute of Standards and Technology (NIST), Gaithersburg, MD. Neutrons of wavelength λ = 6 Å were collimated and focused on samples held in 1 mm quartz cells. The coherent scattering, arising principally from the difference in mass density between the sugar and oil, was sufficient compared to the incoherent scattering background even without deuteration. Three sample-to-detector distances (1.33, 4.5 and 13.17 m) were used to cover a scattering vector $q = 4\pi \sin(\theta/2)/\lambda$, ranging from 0.015 to 6 nm^{-1}. Additional neutron scattering experiments were performed using the small angle neutron diffractometer (SAND) instrument at the Argonne National Laboratory (ANL), Argonne, IL. Data were corrected for background, circularly averaged, then set to an absolute intensity scale using software provided by NIST and ANL.

SANS and SAND data were fitted using the Teubner and Strey model [4] for the static scattering indensity distribution $I(q)$ of microemulsions:

$$I(q) = \frac{(8\pi/\xi_{\mathrm{TS}})\phi_1\phi_2\Delta\rho^2 c_2}{a_2 + c_1 q^2 + c_2 q^4} + b \tag{3}$$

where a_2, c_1 and c_2 are variables related to the Landau free energy expansion. ϕ_1 and ϕ_2 represent the volume fraction of the oil and water phase, respectively and $\Delta\rho$ corresponds to the scattering length difference. ξ_{TS} is the correlation length and b accounts for the incoherent background, which results due to the scattering from hydrogen. In practice, the factor $(8\pi/\xi_{\mathrm{TS}})\phi_1\phi_2\Delta\rho^2 c_2$ is incorporated into the parameters a_2, c_1 and c_2 [5–7] and scattering data is least-squares fitted to

$$I(q) = \frac{1}{a_2 + c_1 q^2 + c_2 q^4} + b \tag{4}$$

This scattering intensity equation is equivalent to the real-space density correlation function:

$$G(r) = \frac{d_{\mathrm{TS}}}{2\pi r} \mathrm{e}^{-r/\xi_{\mathrm{TS}}} \sin\left[\frac{2\pi r}{d_{\mathrm{TS}}}\right] \tag{5}$$

representing a periodic structure modulated by an exponential decay. The parameters d_{TS} and ξ_{TS}, representing the domain size (periodicity) and correlation length, respectively are related to the scattering parameters via

$$d_{\mathrm{TS}} = 2\pi\left[\frac{1}{2}\left(\frac{a_2}{c_2}\right)^{1/2} - \frac{1}{4}\frac{c_1}{c_2}\right]^{-1/2} \tag{6}$$

$$\xi_{\mathrm{TS}} = \left[\frac{1}{2}\left(\frac{a_2}{c_2}\right)^{1/2} + \frac{1}{4}\frac{c_1}{c_2}\right]^{-1/2} \tag{7}$$

3. Results

3.1. Effects of increasing sugar concentration

Figs. 1 and 2 show the phase diagram of sugar-based-microemulsions containing equal masses of sugar and d-limonene (α = 50%). Water used in traditional microemulsions is replaced with supersaturated 65, 75 and 80 wt% aqueous solutions of sugar. Phase boundaries delineate two phase emulsion, one phase microemulsion, and one phase liquid crystalline regions. With increasing sugar concentration in the aqueous phase, the one phase regions shifts progressively downward. With the sucrose oleate:sucrose laurate ratio (ε) fixed at 70:30, increasing the sugar concentration from 65 to 75%, causes the upper phase boundary to shift 30 °C downwards (Fig. 1). The lamellar phase and the lower bound, which presumably also exist for 75% sugar, are shifted to below room temperature. However,

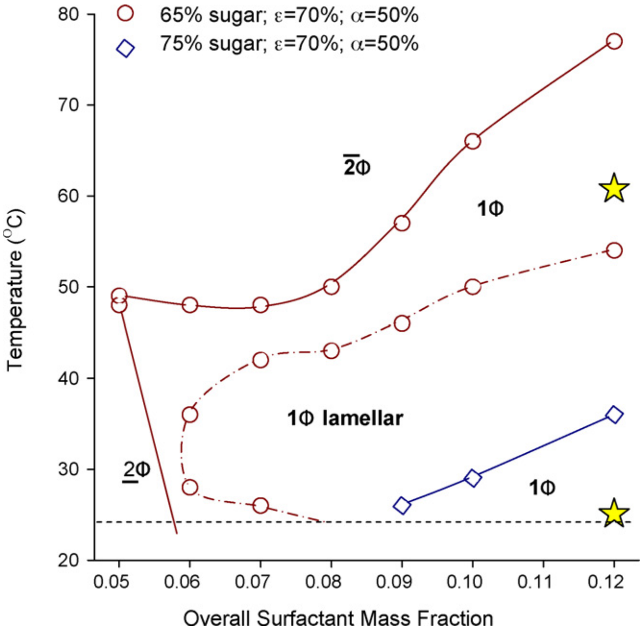

Fig. 1. Phase diagram of aqueous mixtures of sugar, limonene, sugar ester surfactants showing the progression of phase behavior with increasing sugar concentration. Markings identify temperature and composition of microemulsion and liquid crystalline samples probed with SANS (Fig. 3).

the samples phase separate very slowly at room temperature, precluding accurate determination of phase boundaries below room temperature. Dashed line at 23 °C (Fig. 1) delineates the below room temperature region.

The same phenomena are observed for sucrose oleate:sucrose laurate ratio (ε) fixed at 50:50 (Fig. 2). Both the upper and lower boundaries shift downwards in temperature as the sugar concentration increased from 75 to 80%. Microemulsions with 80% sugar in their aqueous phase are viscous and require several hours to phase separate.

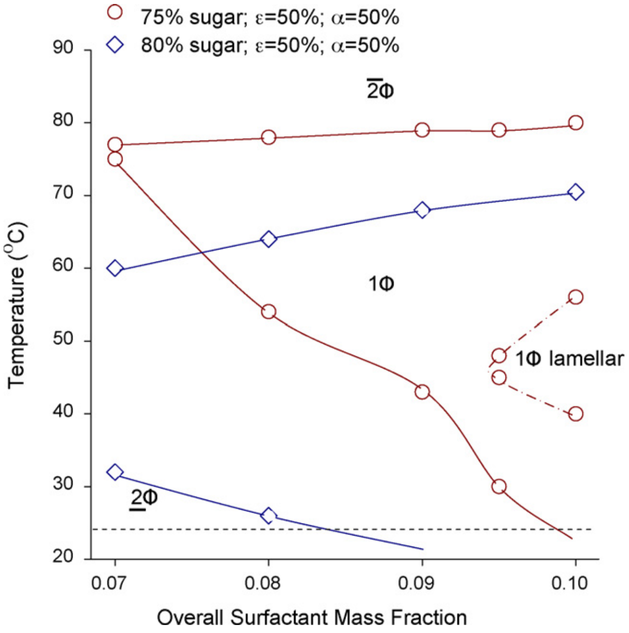

Fig. 2. Phase diagram of aqueous mixtures of sugar, limonene, sugar ester surfactants showing the progression of phase behavior with further increase in sugar concentration. Not shown is a small one phase lamellar region present above 9% surfactant for 80% sugar.

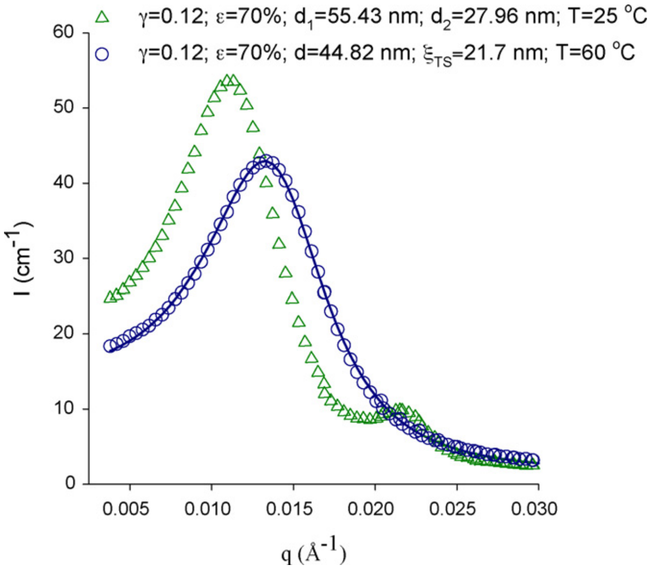

Fig. 3. SANS spectra of microemulsion and lamellar phase samples marked in Fig. 1. Solid line fitted to the microemulsion SANS spectra is calculated from the Teubner–Strey model. SANS measurements performed at NIST.

Representative microstructures of the microemulsion and lamellar regions were determined using SANS for the 65% sugar sample at temperatures and surfactant loading indicated in Fig. 1. SANS spectra of the microemulsion (Fig. 3) with composition corresponding to that marked by the star at 60 °C in Fig. 1, is dominated by a single peak, analysis of which yields Teubner–Strey domain size and correlation length of 44.8 and 21.7 nm, respectively. SANS spectra of the liquid crystalline phase (Fig. 3) with composition corresponding to that marked by the star at 25 °C show two peaks that correspond to a lamellar structure with repeat spacing of ∼28 nm.

3.2. *Effects of surfactant alkyl chain length*

Fixing the mass ratio of sugar to d-limonene at 50:50 and concentration of sugar in the aqueous phase at 75%, increasing the fraction of the longer chain sucrose oleate surfactant from $\varepsilon = 50$ to 70% shifts the one phase region downwards (Fig. 4). The upper phase boundary shifts downwards by ∼25 °C, for every 10% increase in the sucrose oleate fraction. Accompanying this downwards shift with increasing size of the effective surfactant alkyl chain length is an enlargement of the liquid crystalline phase, consistent with interfacial curvature arguments [8,9] and the general patterns of microemulsion phase behavior observed for alkyl glucoside surfactants [10,11].

3.3. *Compensatory effects of sugar concentration and surfactant alkyl chain length*

The opposing effects of increasing sugar concentration and sucrose laurate fraction on temperature of the one phase microemulsion window (Figs. 1, 2 and 4) can be used to advan-

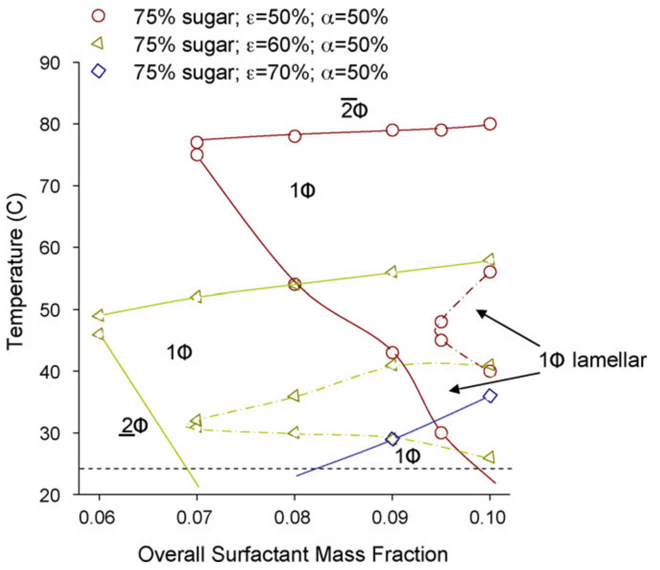

Fig. 4. Phase diagram of aqueous mixtures of sugar, limonene, sugar ester surfactants showing the progression of phase behavior with varying ratio of sucrose oleate and sucrose laurate surfactants.

tage in forming one phase microemulsions at specific temperatures for arbitrary sugar concentrations. Should it be desirable to have a one phase microemulsions containing equal masses of sugar and d-limonene at ∼50 °C, Fig. 5 shows how the sucrose oleate:sucrose laurate ratio can be varied to compensate for varying sugar concentrations and maintain one phase conditions.

3.4. Effects of varying oil loading

Fig. 6 shows the effects of reducing oil loading from 50:50 limonene:sugar to 30:70 limonene:sugar, while the sucrose oleate:sucrose laurate ratio is fixed at 50:50 with 75% sugar in the aqueous phase. Reducing the oil loading from $\alpha = 50$ to 30% shifts the one phase region downwards and causes significant expansion of the liquid crystalline region to lower surfactant concentration. Again, the high viscosity of the samples precluded determination of the lower liquid crystalline and microemulsion boundaries. These boundaries are nonetheless evident when the phase behavior is shifted upwards by reducing the sucrose oleate:sucrose laurate ratio to 40:60 (Fig. 7). Reducing the oil loading also reduces the minimum amount of surfactant necessary to form one phase microemulsions from ∼7 wt% to less than 5 wt%.

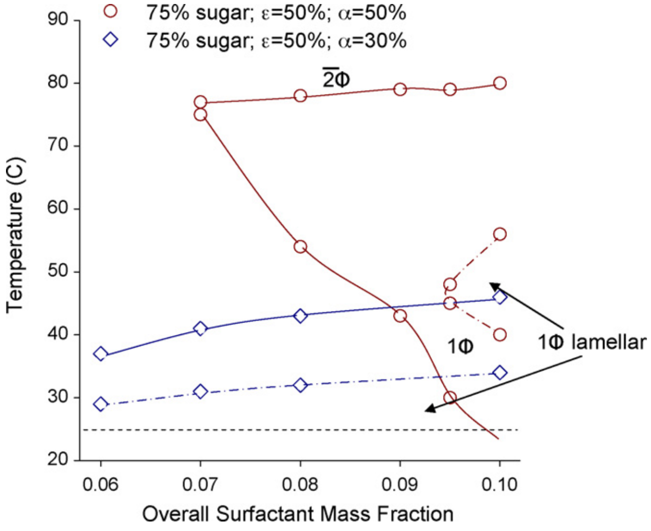

Fig. 6. Phase diagram of aqueous mixtures of sugar, limonene, sugar ester surfactants showing the progression of phase behavior with varying oil loading. Very slow phase separation precluded precise determination of lower boundaries for the lamellar and microemulsion phases at 30% oil loading.

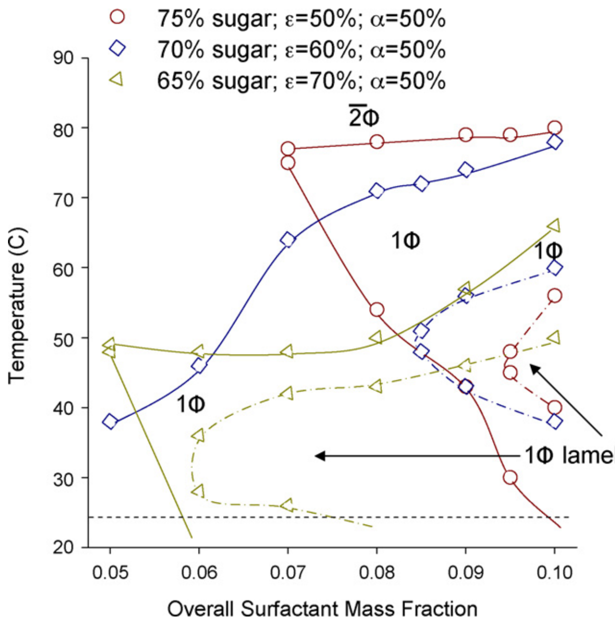

Fig. 5. Phase diagram of aqueous mixtures of sugar, limonene, sugar ester surfactants showing the compensatory adjustment of long to short chain surfactant ratio to accommodate different sugar concentrations.

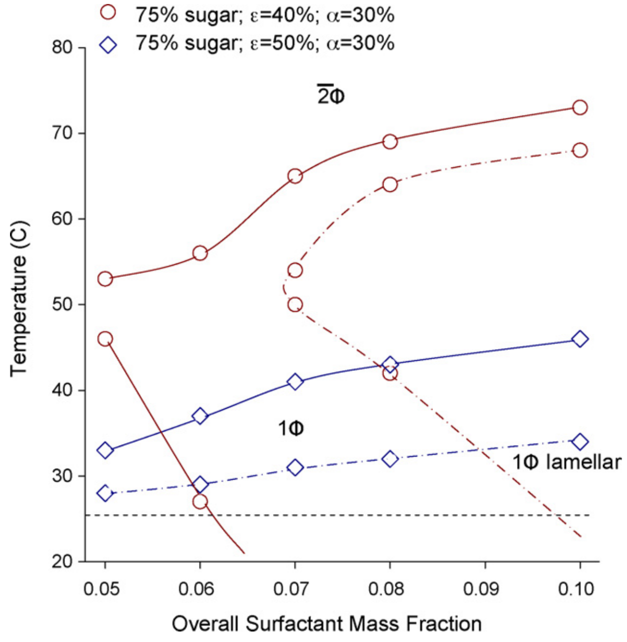

Fig. 7. Adjusting the sucrose oleate:sucrose laurate ratio for 30% oil loading from 50:50 to 40:60 shifts the microemulsion and lamellar regions upwards, allowing for precise determination of lower phase boundaries.

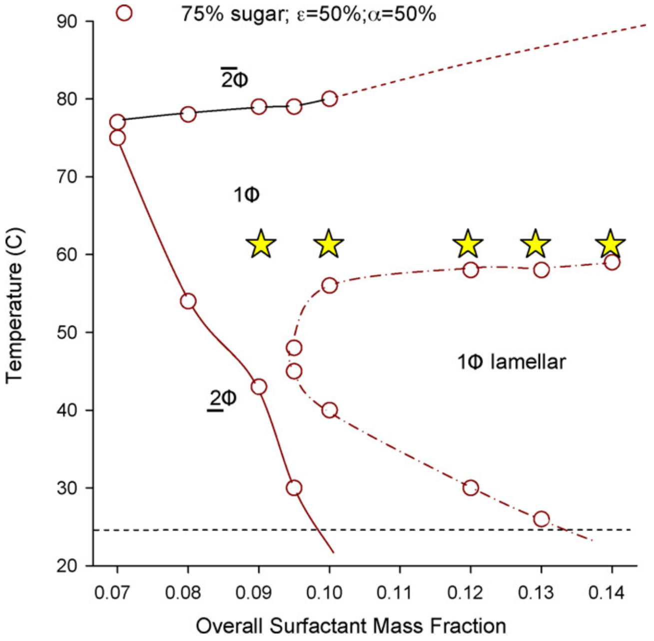

Fig. 8. Phase diagram and composition-temperature of microemulsions samples probed with SANS (Fig. 9).

3.5. *Effects of increasing surfactant concentration on microemulsion structure*

Fixing the mass ratios of sucrose oleate:sucrose laurate and sugar:oil at 50%, we studied the structure of microemulsions with increasing surfactant concentrations, marked in Fig. 8, using SANS. The SANS spectra and model lines from Teubner–Strey analysis is shown in Fig. 9. With increasing concentration of surfactant, the domain size shrinks monotonically with increasing surfactant concentration (Fig. 10) consistent with the packing of a larger interfacial area in a fixed volume.

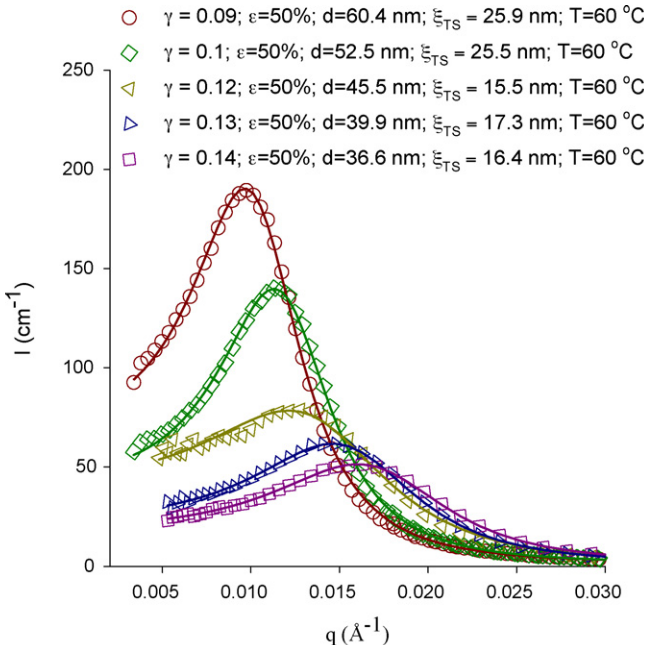

Fig. 9. SANS spectra of concentrated sugars, d-limonene and surfactant mixtures (Fig. 8) showing the effect of increasing surfactant concentration. Symbols and lines represent measured and model calculated intensities, respectively.

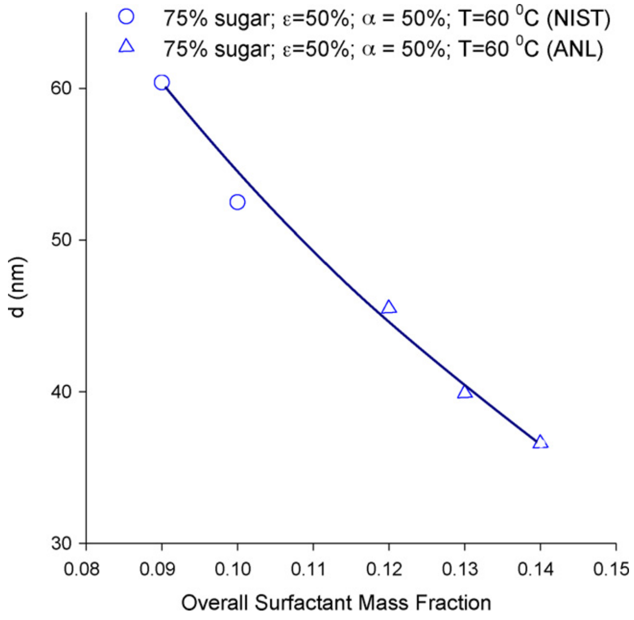

Fig. 10. Variation of domain size with increasing surfactant concentration.

4. Discussion

A striking observation from this study is the large one phase microemulsion and one phase lamellar regions present in the phase diagram of sugar-rich d-limonene microemulsions of sucrose oleate and sucrose laurate. In all the phase diagrams, a two-phase coexistence region between the one phase microemulsion and one phase liquid crystalline regions is expected because of differences in their internal symmetry [12] and order parameter. However, despite a concerted effort to locate these two phase regions, none were observed. These two phase regions likely span only a very small temperature window (<0.2 °C) and/or the refractive index difference between the microemulsion and lamellar phases is too small to observe the two phases. Consistent with earlier observations in predominantly aqueous systems with alkyl glucoside surfactants [10,11,13–18], the one phase region of these sugar-based microemulsions also spans a much larger temperature window than that typically observed for non-ionic oligoethyleneglycol surfactants [19–21]. Fig. 8 shows, for example, mixtures containing equal amounts of sugar and d-limonene with only 10 wt% surfactant that can be heated from room temperature to 80 °C with no phase separation. For samples containing more surfactant, no visible change in optical transparency can be observed upon heating from the one phase microemulsion state at room temperature, across the one phase lamellar region, and up to the upper phase boundary at >80 °C.

In practical spray drying processes, the complex interplay of water and oil evaporation during drying of these liquid microemulsion glass precursors lead to compositional gradients that become trapped in the sample. Controlled dehydration of these microemulsions in thermostated desiccant filled chambers whose vapor phase is saturated with limonene oil does lead to solid transparent microemulsion glasses. However, gradients set into the samples during desiccation lead to inconsistent compositional, physical, and microstructural analysis. To minimize compositional gradients and other drying derived artifacts, we are developing techniques for handling and studying the phase behavior of "ultra-viscous" microemulsion that form at much higher sugar concentrations (>95%).

5. Conclusions

We have mapped out the phase diagrams of edible microemulsions of concentrated sugar solutions with d-limonene. The surfactants used, sucrose laurate and sucrose laurate, are very efficient and allow the preparation of microemulsions containing equal masses of limonene and sugar at overall surfactants concentrations less than 10 wt%. Increasing concentration of sugar in the supersaturated aqueous phases, simulating the effect of dehydration, e.g., in a spray-dryer, shifts the one phase region downwards. Nonetheless, the temperature range of one phase microemulsions can be tuned effectively by variation of the ratio of long and short chain sucrose ester surfactants. Reduction of oil loading shifts the temperature of the microemulsion region downwards. This is accompanied by a reduction in the minimum amount of surfactant necessary to form single phase microemulsions and an enlargement of an adjacent single phase lamellar phase. Two phase regions, which typically separate single phase microemulsion and lamellar regions were very small and never observed. Small angle neutron scattering confirms the presence of microstructure with domain sizes that decrease in size with increasing surfactant loading.

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