Properties of microemulsions with mixed nonionic surfactants and citrus oil

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ABSTRACT

Water/propylene glycol/sucrose laurate/ethoxylated mono-di-glyceride/citrus oil microemulsion systems were formulated and characterized using electrical conductivity, dynamic light scattering, and small angle X-ray scattering. The solubilization capacity of water in the oil is dependent on the surfactants mixing ratio (w/w). The free energy of solubilization (ΔG_s^o) for water-in-oil microemulsions were calculated and found to decrease with water content in the water-in-oil microemulsions region and increase in the oil-in-water region, ΔG_s^o decreased with increasing ethoxylated mono-di-glyceride content in the mixed surfactants. Static percolation phenomena were observed in these systems, and the water volume fraction percolation threshold was determined. The activation energy of conductive flow depends on the surfactants mixing ratio. The hydrodynamic diameter of the diluted microemulsions decreases with the increase in temperature. The periodicity and the correlation length those are characteristic lengths for the domain size of the microemulsions increase with the increase in the aqueous phase content.

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1. Introduction

Microemulsions are transparent self assemblies having polar and nonpolar micro domains. They consist either of water droplets in oil or oil droplets in water surrounded by surfactant film, or they have a bicontinuous microstructure, i.e. continuous channels of oil and water separated by the surfactant. Due to their unique properties that include thermodynamic stability, large surface area, low viscosity, and ultralow surface tension and their enormous potential application these systems were extensively investigated [1–4]. Microemulsions formulated with cyclic oils were extensively studied [1,5–8]. Among these cyclic oils; flavors and perfumes were extensively used for the preparation of biocompatible microemulsions [8]. The incorporation of the cyclic mono-terpenes as oil component on microemulsion formation both in water and propylene glycol containing systems was reported [7–10]. It should be noted here that much more complex structures such as liquid crystalline phases, lamellar phases, and phases with chaotic structure have been identified in the literature in the presence of terpenes [11,12]. Alcohol free microemulsions based on the citrus oil R(+)-limonene were previously reported [13–15]. The addition of glycols to surfactant systems is frequently used [16–19]. The presence of glycol influences the extent of the microemulsions regions and their internal structure. The role of glycols in microemulsions is similar to that of alcohols [16–19]. Microemulsions based on

terpenes were applied for topical drug delivery [20–22]. These systems showed a good solubilizing capacity and excellent skin permeation rate of drugs. R(+)-limonene based microemulsions resulted in enhanced solubilization of nutraceuticals (i.e. cholesterol and phytosterols, lycopene, lutein, and lutein esters) [23–25]. Microemulsion catalysis was used in the furfural-cysteine model reaction studied in oil/water microemulsions based on nonionic surfactants and R(+)-limonene for selective flavor formation. The chemical reaction was found to occur preferably at the interfacial film [25–28]. Microemulsion formulated using R(+)-limonene was used for aquifer washing [29,30]. In this study we report for the first time on the formulation and characterization of biocompatible microemulsions based on safe mixed nonionic surfactants and the citrus oil R(+)-limonene.

2. Experimental

2.1. Materials

Sucrose laurate (L1695) was obtained from Mitsubishi-Kasei Food Corp., (Mie, Japan). The purity of combined lauric acid equals 95%, the esters compositions are 80% monoester and 20% di, tri and polyester, hydrophilic–lipophilic balance (HLB) equals 16. Ethoxylated mono-di-glyceride (EMDG) (MAZOL 80 MG KOSHER), HLB equals 13.5. Ethoxylated mono-di-glyceride was obtained from BASF Corporation (Gurnee, Illinois, USA). R(+)-limonene (98%) (LIM) was purchased from Sigma Chemicals Co. (St. Louis, USA). 1,2-Propanediol (Propylene glycol, PG) (≥99.5%) was purchased from BDH (Poole, UK). Sodium chloride (NaCl) of analytical grade was

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purchased from J.T. Baker Inc. (Phillipsburg, USA). All of the components were used as supplied without further purification. Triple distilled water was used.

2.2. Methods

2.2.1. Pseudoternary phase behavior at constant temperature

The phase behavior of a system consisting of water, oil, mixture of surfactants, cosurfactant may be described in a phase tetrahedron which apexes represent the pure components. Mixtures at fixed weight ratios of oil, and mixed surfactants were prepared in culture tubes sealed with Viton lined screw caps. Water and propylene glycol at the weight ratio of 2/1 were then added dropwise until its solubilization limit which is the threshold of phase separation was reached. Vigorous stirring followed all of the aqueous phase additions on a vortex mixer. The time for equilibration between additions in successive aliquots was typically from a few minutes up to 24 h. Phase transitions were detected visually by the appearance of cloudiness or sharply defined separated phases. The completion of this process was hastened by centrifuging the samples. The phase behavior was determined at 25, 37, and 45 ± 0.1 °C.

2.2.2. Electrical conductivity measurements

A conductivity meter with a Tetra Con® 325 conductivity cell (graphite electrodes, cell constant: 0.475 cm^{-1} ± 1.5%) was used to measure the conductivity of samples the compositions of which lie along the one phase channel with a temperature precision of ±0.1 °C. In the case of nonionic microemulsions, a small amount of an aqueous electrolyte must be added for electrical conduction [31]. Thus, a 0.01 M sodium chloride aqueous solution was used in the preparation of the microemulsion samples in place of pure water. The 0.01 was not picked randomly but this the minimum salt concentration that can be added to the system without affecting the phase boundaries. The electrode was dipped in the microemulsion sample until equilibrium was reached and reading became stable. Reproducibility was checked for certain samples and no significant differences were observed. The constant of the conductivity cell was calibrated using standard KCl solutions and checked a minimum of three times during the course of the working experiment.

2.2.3. Dynamic light scattering

Particle size measurements were performed using Zetasizer Nano S (ZEN 1600) for the measurement of size and molecular weight of dispersed particles and molecules in solution by Malvern Instruments Ltd. (Worcestershire, United Kingdom). The equipment includes 4 mW, 633 nm He–Ne laser. Size measurement range between 0.6 nm and 6 μ, size measurement angle equals 173°, concentration range for size measurement is between 0.1 ppm (0.00001 vol%)–40 wt%, molecular weight range is between 10^3 and 10^7 Da and temperature measurement range is between 2 and 90 °C. 1.5 ml microemulsion sample is introduced in a disposable polystyrene cuvettes and measured at temperatures range between 20 and 50 °C by steps of 5 °C. The particle hydrodynamic diameter is calculated from the translational diffusion coefficient, D, (m^2/s) using the Stokes–Einstein relationship:

$$d_H = k_B T / 6\pi\eta D \tag{1}$$

where d_H is the hydrodynamic diameter (nm), k_B is Boltzmann's constant, T is the absolute temperature (K) and η is the solvent viscosity (Pa s). The results are averages of 3 experiments.

2.2.4. Small angle X-ray SCATTERING (SAXS)

Scattering experiments were performed using Ni-filtered Cu Kα radiation (0.154 nm) from an Eliott GX6 rotating X-ray generator that operated at a power rating up to 1.2 kW. X-radiation was further monochromated and collimated by a single Franks mirror and
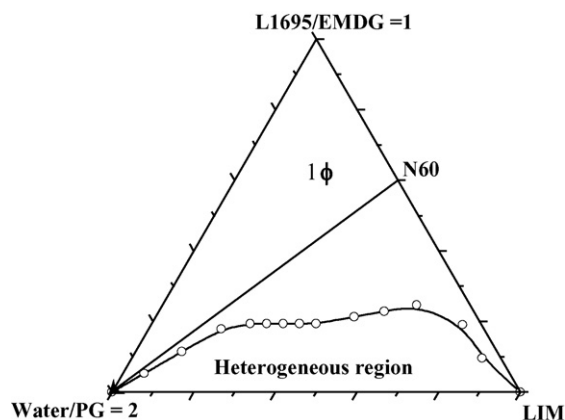

Fig. 1. Pseudoternary phase diagram of the water + propylene glycol/sucrose laurate/ethoxylated mono-di-glyceride/R(+)-limonene system at 25 °C. The mixing ratio (w/w) of sucrose laurate/ethoxylated mono-di-glyceride equals unity and that of water/propylene glycol equals 2/1. The one phase region is designated by 1φ, and the multiphase region is designated by heterogeneous region. Along the dilution line N60 the weight ratio of sucrose laurate/ethoxylated mono-di-glyceride/R(+)-limonene equals 3/3/2.

a series of slits and height limits and measured by a linear position-sensitive detector. The sample was inserted into 1–1.5 mm quartz or lithium glass capillaries, which were then flame-sealed. Each sample was checked before and after the experiment to verify that no fluid had been lost during the time of exposure, approximately 3 h. The temperature was maintained at 25 ± 1 °C. The sample-to-detector distance was 0.46 m, and the scattering patterns were measured using the Lake procedure [32].

2.2.5. X-ray data analysis

In this case, the scattering patterns after background subtraction were fit to the expression due to Teubner and Strey [33]:

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

with the constants a_2, c_1, c_2 and b obtained by using the Levenburg–Marquardt procedure [34]. Such a functional form is simple and convenient for the fitting of spectra. Eq. (2) corresponds to a real space correlation function of the form

$$\gamma(r) = (\sin k r / k r)e^{-r/\xi} \tag{3}$$

The correlation function describes a structure with periodicity $d = (2\pi/k)$ (nm) damped as a function of correlation length ξ (nm). This formalism also predicts the surface to volume ratio, but because this ratio is inversely related to the correlation length and therefore must go to zero for a perfectly ordered system, calculated values are frequently found to be too low [35]. The characteristic lengths of the domain size d and ξ are related to the constants in Eq. (2) by [33]:

$$d = 2\pi[(1/2)(a_2/c_2)^{1/2} - (c_1/4c_2)]^{-1/2} \tag{4}$$

$$\xi = [(1/2)(a_2/c_2)^{1/2} + (c_1/4c_2)]^{-1/2} \tag{5}$$

3. Results and discussion

3.1. Phase behavior

The pseudoternary phase diagram of the water/propylene glycol/sucrose laurate/ethoxylated mono-di-glyceride/R(+)-limonene (W/PG/L1695/EMDG/LIM) at 25 °C is presented in Fig. 1. The mixing ratio (w/w) of sucrose laurate/ethoxylated mono-di-glyceride equals unity and that of water/propylene glycol equals 2/1. The phase behavior indicates the presence of an isotropic and low