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Properties of microemulsions based on mixed nonionic surfactants and mixed oils

Monzer Fanun *

Colloids and Surfaces Research Laboratory, Faculty of Science and Technology, Al-Quds University, P.O. Box 51000 East Jerusalem, Palestine

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ABSTRACT

The systems studied were water/sucrose laurate/ethoxylated mono-di-glyceride/isopropylmyristate/peppermint oil. The solubilization capacity of water in the oils is dependent on the surfactants and oils mixing ratios (w/w). The transport properties (electrical conductivity and dynamic viscosity) were studied as function of water volume fraction. Electric percolation phenomenon was observed in these systems and the water volume fraction percolation thresholds were determined. The diffusion properties investigated by nuclear magnetic resonance confirm a progressive transformation of the water-in-oil to bicontinuous and inversion to oil-in-water microemulsions that occur upon dilution with water. The diffusion coefficients of surfactants increase with the increase in the water volume fraction. The structural parameters studied by small angle X-ray scattering that include the periodicity and correlation length were estimated. The periodicity increases linearly with the increase in the water volume fraction whereas the correlation length increases with the increase in the water volume fraction to a certain value then decreases. Cryogenic transmission electron microscopy images for diluted microemulsions revealed the presence of spheroidal droplets of up to 10 nm diameter.

1. Introduction

Microemulsions are optically isotropic and thermodynamically stable colloidal assemblies having polar and nonpolar micro domains. Microemulsions are scientifically seeing a renaissance and applications are rising rapidly [1]. In many of these applications, the oils are mixtures of various components, and it is interesting to know how oil mixtures, rather than single component oils, are solubilized in microemulsions. It has been shown that different types of oil molecules can be solubilized at diverse places in the microemulsions [1–11]. Weakly hydrophobic or polar molecules can be located in the palisade layer or close to the surfactant headgroup while strongly hydrophobic molecules (e.g., saturated alkanes and alicyclic hydrocarbons) are solubilized preferentially in the hydrophobic core. It has been also suggested [1–11] that hydrophobicity is not the only factor affecting the placement of a particular solute in the surfactant aggregate. Other factors such as molecular size and shape, the free energy associated with molecular conformational constraints experienced by the solute in different solubilization placements, the surface activity of the solubilizate have also been thought to influence the placement. Accordingly, if oil mixtures are solubilized, it is possible that the division of the individual oil components between the different solubilization locations is not the same. A two-state solubilization model was postulated [6–9] for polar solubilizates involving a distribution of solute molecules between the adsorbed state close to the micelle/water interface and the dissolved state in the hydrocarbon core. Solubilization in the adsorbed state is supposed to take place owing to the surface-active behavior of the solute at the interface. Based on the two-state solubilization theory, we assume that the total solubilization can be divided into two contributions: the interfacial and the core contributions. The two oil components have different core/interfacial site distributions characteristic because of their different molecular structures. Consequently, one component becomes enriched in the interfacial location. In this study, we aim to investigate for the first time the effect of adding peppermint oil to isopropylmyristate on the formation and properties of biocompatible microemulsions based on the mixed sucrose laurate and ethoxylated mono-di-glyceride. These microemulsions are intended for the use in cosmetic and pharmaceutical applications.

2. Experimental

2.1. Materials

The sucrose monolaurate (L1695) was obtained from Mitsubishi-Kasei Food Corp., (Mie, Japan). The purity of combined Lauric acid equals 95%, the ester compositions are 80% monoester and 20% di, tri and polyester, and HLB equals 16. Ethoxylated mono-di-glyceride (EMDG) (MAZOL 80 MG KOSHER), ethoxylated mono-di-glyceride was obtained from BASF Corporation (Gurnee, Illinois, USA). Ethoxylated mono-di-glyceride is a nonionic surfactant composed of a mixture of stearate and palmitate partial esters of glycerin ethoxylated with approximately 20 mol of ethylene oxide per mole of alpha-mono-glyceride reaction mixture, and HLB equals 13.5. Peppermint

* Tel.: +970 22 79 97 53; fax: +970 22 79 69 60.
E-mail addresses: Fanunm@gmail.com, mfanun@science.alquds.edu.

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oil (MNT), (98%) and isopropylmyristate (98%) (IPM) were purchased from Sigma Chemicals Co. (St. Louis, USA). Sodium chloride (NaCl) of analytical grade was 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 diagrams at constant temperature

The phase behavior of a system consisting of water, mixed oil, surfactant (or a mixture of surfactants) may be described on a phase tetrahedron whose apexes respectively represent the pure components. However, it is more convenient to describe the phase behavior on a pseudo-ternary phase triangles. Obviously, a fixed (weight, volume or mole) ratio must be chosen for any two of the components and one of the triangle vertices represents 100% of this binary mixture. Mixtures at fixed weight ratios of mixed oil, surfactant (or mixed surfactants) were prepared in culture tubes sealed with Viton lined screw caps. Water was then added dropwise until its solubilization limit was reached. Vigorous stirring followed all of the aqueous phase additions on a vortex mixer. The time for equilibration between additions of 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 diagrams were determined at 25 ± 0.1 °C.

2.2.2. Electrical conductivity measurements

Conductivity measurements were performed at temperatures ±0.1 °C on samples the compositions of which lie along the one-phase channel, using a conductimeter, the conductivity cell used is Tetra Con® 325, the electrode material is graphite and the cell constant is 0.475 cm^{-1} ± 1.5%. The range of application is between 1 μS/cm to 2 S/cm with an accuracy of ±0.5%, and the temperature range is from −5 to 100 °C. In the case of nonionic microemulsions, a small amount of an aqueous electrolyte must be added for electrical conduction [12]. Thus, a 0.01 M sodium chloride aqueous solution was used in the preparation of the microemulsion samples in place of pure water. The electrode was dipped in the microemulsion sample until equilibrium was reached and reading becomes 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 shift.

2.2.3. Viscosity measurements

Viscosity was measured using a rotational viscometer, model DV-1PL spindle from Anton Paar GmbH (Graz, Austria). "Double cylinder" geometry was used. Viscosities at 200 s^{-1} shear rate were obtained at 25 ± 0.1 °C. Reproducibility (triplicate) was checked for the samples and no significant differences (±SD) where observed.

2.2.4. Pulsed gradient spin echo-nuclear magnetic resonance (PGSE-NMR)

NMR measurements was performed on Bruker DRX-400 spectrometer with a BGU II [13,14] gradient amplifier unit and a 5-mm BBI probe equipped with a *z*-gradient coil, providing a *z*-gradient strength (G) of up to 55 G cm^{-1}. The self-diffusion coefficients were determined using bipolar-pulsed field gradient stimulated spin echo (BPFG-SSE). In this work, we used bipolar gradient pulses as described by Wu et al. [13] to reduce the eddy-current effects. Experiments were carried out by varying the gradient strength and keeping all other timing parameters constant. The self-diffusion coefficient (D) is given by

$$I = I_o \exp\left[\gamma^2 G^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right) D\right] \quad (1)$$

Where I is the measured signal intensity, I_o is the signal intensity for $G = 0$, γ is the gyro magnetic ratio for the ^1H nucleus, δ is the gradient pulse length, Δ is the time between the two gradients in the pulse sequence (and hence defines the diffusion time). Typically, we use $\Delta = 100$ ms, $\delta = 8$ ms, and vary G from 1.7 to 32.3 G cm^{-1} in 32 steps.

2.2.5. Small angle X-ray scattering (SAXS)

Scattering experiments were performed using Ni-filtered CuKα ×6 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 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 [15].

2.2.6. X-ray data analysis

In this case, the scattering patterns after background subtraction were fit to the expression due to Teubner and Strey [16]:

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

with the constants a_2, c_1, c_2 and b obtained by using the Levenburg–Marquardt procedure [17]. Such a functional form is simple and convenient for the fitting of spectra. Eq. (3) corresponds to a real space correlation function of the form

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

The correlation function describes a structure with periodicity $d = (2\pi/k)$ damped as a function of correlation length ξ. 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 [18]. d and ξ are related to the constants in Eq. (2) by [16]:

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

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

2.2.7. Cryo-transmission electron microscopy (Cryo-TEM)

Samples were prepared in a controlled environment vitrification chamber (CEVS) [19], at 25 °C and controlled humidity (>95% relative humidity), by placing a ~5 μl drop of the microemulsion on a holey polymer film supported on a TEM grid. The drop was blotted by a filter paper creating a thin film of the liquid over the grid, which was then immediately vitrified in liquid ethane at its freezing temperature. The grid was transferred under liquid nitrogen to a cold-stage (Model 626, Gatan, Inc., Warrendle, PA) which was introduced into the electron microscope JEOL 200FX or a Philips CM12, operated at 100 kV in the conventional TEM mode with a nominal under focus of about 4 μm. The working temperature was below −168 °C, and the images were recorded on Kodak SO-163 film, developed for maximum electron speed.