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Formulation and characterization of microemulsions based on mixed nonionic surfactants and peppermint oil

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

Water/sucrose laurate/ethoxylated mono-di-glyceride/ethanol/peppermint oil microemulsion systems were formulated and characterized using electrical conductivity, dynamic viscosity, nuclear magnetic resonance, dynamic light scattering, small angle X-ray scattering and cryogenic transmission electron microscopy. The solubilization capacity of water in the oil is dependent on the surfactants and ethanol/oil mixing ratios (w/w). Static percolation phenomena were observed in these systems, and the water volume fraction percolation threshold was determined. A progressive transformation of the water-in-oil to bicontinuous and inversion to oil-in-water microemulsions occurs upon dilution with water, which was revealed by the determination of the diffusion coefficients of both oil and water inside the microemulsions. The diffusion coefficients of the surfactants at the interface of the microemulsions increase with increasing water volume fraction. The periodicity of the microemulsions increases linearly with increasing water volume fraction. In addition, the correlation length increases with water volume fraction to a certain value then decreases. Cryo-TEM images of the oil-in-water microemulsions revealed the presence of spheroidal droplets of up to 12 nm diameter.

1. Introduction

Microemulsions are clear, thermodynamically stable mixtures of two immiscible liquids brought together by the means of surfactant or a mixture of surfactants forming a film separating the immiscible phases. The unique properties of microemulsions that include ultralow interfacial tension, large interfacial area, low viscosity, and high solubilization capacity attracted researchers [1–4]. In the majority of industrial applications a mixture of surfactants is used for the formation of microemulsions. Mixtures of nonionic surfactants are more effective than other class of surfactants due to their efficacy at lowering the monomer concentration and their insusceptibility to precipitate. The incorporation of another surfactant into the mixture of water, oil and surfactant provides an additional degree of freedom, which enables the adjustment of phase behavior [1,5–7]. Microemulsions formulated with cyclic oils were extensively studied [8–11].The placement of the oil in the surfactant aggregates highly affects the change in surfactant layer curvature [12,13]. It is known that cyclic hydrocarbons tend to penetrate in the surfactant layer and widen the effective cross-sectional area per surfactant. As a result, the surfactant layer curvature becomes less positive or negative. Peppermint oil is cyclic edible oil that was not explored for the formation of microemulsions. The fact that the peppermint oil is a natural, the preparation of microemulsions using it and with emulsifiers allowed for human use may open the way for the formation of new pharmaceutical, cosmetic and food items. The study of the properties of these microemulsions may have a large impact on the determination of the most appropriate application possible and to also to establish a relationship between the property and the intended application. In this study, we report for the first time on the formation and characterization of microemulsions based on safe nonionic surfactants and peppermint oil.

2. Experimental

2.1. Materials

Ethoxylated mono-di-glyceride (EMDG) (MAZOL 80 MG KOSHER) was obtained from BASF Corporation (Gurnee, Illinois, USA). It 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, hydrophilic lipophilic balance (HLB) equals 13.5 (see chemical structure in Supplementary Material SM Fig. 1A). Sucrose monolaurate (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, HLB equals 16 (see chemical structure in

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* Fax: +970 22 79 69 60.
E-mail addresses: Fanunm@gmail.com, mfanun@science.alquds.edu

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Supplementary Material SM Fig. 1B). Peppermint oil (MNT), (98%) was purchased from Sigma Chemicals Co. (St. Louis, USA). Ethanol (EtOH) (minimum 99.8%) was 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. Pseudo-ternary phase diagrams at constant temperature

The phase behavior of a system consisting of water, oil, surfactant (or a mixture of surfactants), cosurfactant 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 oil, surfactant (or mixed surfactants) and cosurfactant were prepared in culture tubes sealed with Viton lined screw caps. Water was then added drop wise 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 separations 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 [14]. 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 [15,16] 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 $G\,\text{cm}^{-1}$. 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. [15] 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

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

where I is the measured signal intensity, I_o is the signal intensity for $G = 0$, γ is the gyro magnetic ratio for the ^{1}H 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 $G\,\text{cm}^{-1}$ in 32 steps.

2.2.5. Dynamic light scattering

Each liquid sample was inserted into a 10 mm diameter borosilicate test tube and centrifuged for 15 min at 3000 rpm in order to remove dust. The test tube was then placed in a temperature-controlled vat of toluene as the index matching fluid. The light source was an argon ion laser (Spectra Physics – Lexel; $\lambda = 514.5$ nm). Photons scattered by the sample were collected by an ITT PW130 photomultiplier tube mounted at 90° to the incident laser beam. The photoelectron count-time autocorrelation function was calculated with a BI 2030 AT (Brookhaven Instruments) digital autocorrelator and was analyzed using the constrained regularization algorithm, CONTIN [17,18] to give an intensity weighted distribution of the translational diffusion coefficients D_z. Particle hydrodynamic radius was calculated from the translational diffusion coefficient using the Stokes–Einstein relationship:

$$D_\text{H} = k_\text{B}T/6\pi\eta D_\text{z} \tag{2}$$

where D_H is the hydrodynamic diameter, k_B is Boltzmann's constant, T is the absolute temperature and η is the solvent viscosity. The results are averages of 3 or 4 experiments. D_H is obtained from the positions of the peaks of the intensity weighted size distribution function.

2.2.6. 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 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 [19].

2.2.7. X-ray data analysis

In this case, the scattering patterns after background subtraction were fit to the expression due to Teubner and Strey [20]:

$$I(q) = (1/a_2 + c_1 q^2 + c_2 q^4) + b \tag{3}$$

with the constants a_2, c_1, c_2 and b obtained by using the Levenburg–Marquardt procedure [21]. 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

$$\gamma(r) = (\sin kr/kr)e^{-r/\xi} \tag{4}$$

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 fre-