



## Effects of water content and oil on physicochemical and microenvironmental properties of mixed surfactant microemulsions



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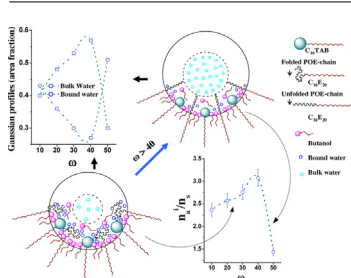
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### HIGHLIGHTS

- Oil dependent phase characteristics were studied for mixed microemulsions.
- Appearance of conductance percolation supports well with the droplet dimension.
- Relative changes in anisotropy values upon hydration of non-ionic's corroborate synergism.
- Synergism in interfacial composition was observed at a specific water content mixed system.
- Relative abundance of water correlates with interfacial alkanol population.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 3 December 2013

Received in revised form 26 February 2014

Accepted 1 March 2014

Available online 12 March 2014

#### Keywords:

Dynamic light scattering

Conductance

Fluorescence measurement

Fourier transform infrared spectroscopy

State of water

Dilution method

### ABSTRACT

In this report, phase behavior, conductivity, viscosity, dynamic light scattering, fluorescence lifetime, steady state fluorescence anisotropy and Fourier transform infrared spectroscopy (FTIR) techniques were employed for understanding of the physicochemical properties and microenvironment of water-in-oil microemulsion comprising equimolar (1:1) cetyltrimethylammonium bromide ( $C_{16}TAB$ ) and polyoxyethylene (20) cetyl ether ( $C_{16}E_{20}$ )/1-butanol/heptane or decane, with varying water content ( $\omega$ ) at 303 K. Both conductivity and viscosity of these systems were increased with increase in  $\omega$  in both oils. Droplet size was also increased with increase in  $\omega$  and corroborated well with the conductance and viscosity measurements, and depends on oil chain length. The physicochemical changes in the microenvironment with increase in  $\omega$  were presented by measuring the changes in decay time using a fluoroprobe (7-hydroxycoumarin). The effect of hydration on the microstructure of these systems was studied by polarized fluorescence measurements. FTIR measurements reveal three states of water molecules, viz. trapped, bound and bulk water, in water pool of these systems. Further, the interfacial composition and free energy of transfer of 1-butanol from oil to the interface were evaluated by the dilution method. Changes in interfacial composition as a function of  $\omega$  corroborate well with FTIR results indicating bound and bulk water.

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## 1. Introduction

Microemulsions are ternary or pseudo-ternary dispersed systems comprising mixtures of oil, water and surfactant or (surfactant + cosurfactant). They possess some unique characteristics, such as thermodynamic stability (imparting long shelf-life), compartmentalized polar and non-polar dispersed nano-domains, ease of preparation, low viscosity, ultralow interfacial tension, isotropic and optical transparency (infrequently faint translucency) [1,2]. Due to the existence of both polar and non-polar microdomains, both hydrophilic and lipophilic drug molecules could be solubilized, encapsulated and stabilized in these microscopically heterogeneous and macroscopically homogeneous systems [3]. Typical water-in-oil (w/o) microemulsions or reverse micelles (RMs) consist of nanoscopic water pools dispersed in a nonpolar solvent separated by surfactant monolayer [4]. The physicochemical properties of water molecules localized in the interior of the microemulsions or RMs i.e., confined water is different from those of bulk water, and has been found to be strongly dependent on the chemical nature of the dispersant phase (oil), surfactant, cosurfactant and also on the hydration level of the w/o microemulsions [5,8]. The change in the structural properties, such as the size, shape, and interfacial rigidity of the microemulsions play an important role in controlling the chemical reactivity of the reactants, morphology of the nano-materials, and the release of the drug molecules from the microemulsion droplets [9–11]. The droplet sizes of the microemulsions are usually controlled by a parameter,  $\omega$  (which is equal to molar ratio of water and surfactant). Extensive studies have been performed to understand the interaction and dynamics of the microemulsion droplets using various techniques, such as small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), transmission electron microscopy, dynamic light scattering (DLS), nuclear magnetic resonance (NMR), fluorescence spectroscopy, conductance, and viscosity measurements [12,13]. Further, reports on the interaction of dye molecules within confined environment of RMs to elucidate the properties of these organized systems [14,15]. Dye molecules can be accommodated in a RM in three different locations: (a) external organic solvent, (b) micellar interface formed by surfactant monolayer, and (c) internal polar core depending upon nature of the dye and the medium. Hence, nature and size of RMs can be deciphered by monitoring spectral behavior of dye molecules.

Surfactant mixtures often give rise to enhanced performance over the individual components or exhibit synergism in their physicochemical properties. Because of this property, such mixtures are of theoretical interest as well as could potentially be employed in a wide range of applications. Reports on the use of the blends of ionic/nonionic surfactant microemulsions as templates for enzymatic activity, nanoparticle synthesis, and chemical reactivity are available in literature [16–18]. Further, characterization of water-in oil (w/o) mixed surfactant microemulsions using conductivity [19–21], viscosity [20–22], SANS [23], solubilization [24,25], interfacial composition [20,21,26], Fourier transform infrared (FTIR) spectroscopy [20,21,27], and NMR [28] reveals a significant modification of physicochemical properties of the oil/water interface as well as the state of the confined water inside the pool compared to the corresponding single surfactant systems. These findings summarized that the influence of surfactant mixing on overall formation and stability of microemulsions are a direct consequence of molecular interactions of the constituents at the oil/water interface.

Very recently, we have reported the interfacial composition, thermodynamics of alkanol transfer process, solubilization behavior, transport and microstructural properties, and the dynamics of confined water of mixed surfactant (ionic and nonionic) w/o microemulsions under different physicochemical conditions,

by employing the dilution method (Schulman's method of cosurfactant titration of the oil/water interface), conductivity, viscosity, DLS and FTIR measurements [20,21,25,26,29]. In view of these studies, the present report aims at a precise characterization on the basis of molecular interactions among the constituents and explicate the formation vis-à-vis the nature of the oil/water interface of equimolar (1:1) mixed surfactant w/o microemulsions [water/cetyltrimethylammonium bromide ( $C_{16}TAB$ ) + polyoxyethylene (20) cetyl ether ( $C_{16}E_{20}$ )]/1-butanol (Bu)/heptane (Hp) or decane (Dc)] as a function of molar ratio of water and surfactant ( $\omega = 10 \rightarrow 50$ ) at 303 K. Both of these surfactants ( $C_{16}TAB$  and  $C_{16}E_{20}$ ) are chosen in such a way that they possess similar hydrocarbon tail (constituting 16 carbon atoms in the linear hydrocarbon chain), but they differ in charge type and size of the polar head groups, so that the possible interaction between the hydrocarbon chains of both surfactants gets minimized [23,30]. Bu is used as structure making cosurfactant for w/o microemulsion formulation due to its potential industrial as well as biological applications [31,32]. Formation, microstructure, internal dynamics (interface dynamics of the droplets and dynamics of confined water) and composition of the mixed interfacial film of these systems have been characterized by means of the phase study, conductivity, viscosity, DLS, fluorescence lifetime, steady state fluorescence anisotropy, FTIR measurements and dilution method as a function of water content. Finally, the correlation of the results in terms of the evaluated physicochemical parameters has been made, which is expected to improve the basic understanding of the formation and characterization of the interface that imparts stability to mixed surfactant w/o microemulsions.

## 2. Experimental

### 2.1. Materials

Cetyltrimethylammonium bromide ( $C_{16}TAB$ , >99%), polyoxyethylene (20) cetyl ether ( $C_{16}E_{20}$ , >98.5%) were the products of Sigma Aldrich, USA and Fluka, Switzerland, respectively. The cosurfactant [1-butanol (Bu, >98%)] and oils [heptane (Hp, >98%) and decane (Dc, >98%)] were products of Fluka, Switzerland, Lancaster, England and E. Merck, Germany, respectively. The dye, 7-hydroxycoumarin (HCM, >99%) and 2-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl) benzoate (Eosin Y, >99%) were the products of Chem Service, West Chester, USA and E. Merck, Germany, respectively. Colloidal dispersion of silica (Ludox AM-30 colloidal silica, 30 wt% suspensions in water) was the product of Sigma Aldrich, USA. All these chemicals were used without further purification. Doubly distilled water of conductivity less than  $3 \mu S cm^{-1}$  was used in the experiments.

### 2.2. Methods

#### 2.2.1. Preparation of microemulsion

Microemulsions were prepared using the blends of  $C_{16}TAB$  and  $C_{16}E_{20}$  at a fixed composition of the surfactant(s) (1:1) in Hp or Dc oil and then adding calculated amount of the de-ionized water or aqueous solution of dye or fluoroprobe (depending upon their solubility's in water) at different concentration levels to obtain the desired  $\omega$  ( $= [water] / [surfactant(s)]$ ). The resulting solution was vortexed for about at least 60 s. All the samples were single phase and optically transparent under the experimental conditions of the conductance, viscosity, DLS, fluorescence and FTIR spectroscopic measurements reported herein. The addition of the de-ionized water or aqueous dye or fluoroprobe was controlled by using a micro-syringe. For different instrumental measurements, the composition of the microemulsions was kept constant at mass ratio of surfactant(s) and cosurfactant equals to 1:2.

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