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# Physicochemical studies of mixed surfactant microemulsions with isopropyl myristate as oil

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ABSTRACT

The present study is focused on evaluation of interfacial compositions and thermodynamic properties of w/o mixed surfactant [(sodium dodecylsulfate, SDS/polyoxyethylene (23) lauryl ether, Brij-35)/1-pentanol (Pn)/isopropyl myristate (IPM)] microemulsions under various physicochemical conditions by the *dilution method*. The number of moles of Pn at the interface ($n_a^i$) and bulk oil ($n_a^o$), and various thermodynamic parameters [viz. standard Gibbs free energy ($\Delta G^0_{o\to i}$), standard enthalpy ($\Delta H^0_{o\to i}$), and standard entropy ($\Delta S^0_{o\to i}$) of the transfer of Pn from bulk oil to the interface] have been found to be dependent on the molar ratio of water to surfactant ($\omega$), concentration of Brij-35 ($X_{\text{Brij-35}}$), and temperature. Temperature-insensitive microemulsions with zero specific heat capacity $(\Delta C^0_p)_{o\to i}$ have been formed at specific compositions. The intrinsic enthalpy change of the transfer process $(\Delta H^0)^*_{o\to i}$ has been evaluated from linear correlation between $\Delta H^0_{o\to i}$ and $\Delta S^0_{o\to i}$ at different experimental temperatures. The present report also aims at a precise characterization on the basis of molecular interactions between the constituents and provides insight into the nature of the oil/water interfaces of these systems by conductivity and dynamic light scattering studies as a function of $\omega$ and $X_{\text{Brij-35}}$. Conductivity studies reveal that incorporation of Brij-35 in non-percolating water/SDS/Pn/IPM systems makes them favorable for $\omega$-induced percolation behavior up to $X_{\text{Brij-35}} \leqslant 0.5$. But further addition of Brij-35 causes a decrease in conductivity with increasing $\omega$. Furthermore, the hydrodynamic diameters of the microemulsion droplets increase with increase in both $X_{\text{Brij-35}}$ and $\omega$. Correlations of the results in terms of the evaluated physicochemical parameters have been attempted.



## 1. Introduction

Microemulsions are clear, transparent or translucent, thermodynamically stable dispersions of oil and water, stabilized by an interfacial film of surfactant(s) frequently in combination with a cosurfactant and having diameter of the droplets in the range of 10–200 nm. Typical water-in-oil (w/o) microemulsion or reverse micelles (RMs) consist of nanoscopic pools of water dispersed in nonpolar solvent stabilized by surfactant monolayer [1,2]. The properties of confined water differ considerably from those of bulk water due to geometrical constraints of the environment and molecular interactions at the oil/water interface [3,4]. They have been used in various fields, such as pharmaceutics, nanoparticle synthesis, liquid–liquid extraction, cosmetic, detergency, and tertiary oil recovery, due to their very low interfacial tension, nanometer-sized droplets, high solubilization capacity, etc. [5–7]. The extensive research of microemulsions has focused on the understanding of their internal structure and dynamics. Various instrumental investigations reveal the microstructures of microemulsion systems, such as small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), dynamic light scattering (DLS), nuclear magnetic resonance (NMR), conductance, and viscosity [8–14].

The cosurfactant (short chain lipophilic n-alkyl alcohols) plays an important role by blending with surfactant(s) and partitions between the coexisting aqueous and oleic phases to control the bending elasticity of the interfacial layer offering stability to the dispersion and affecting the droplet dimensions of the microemulsion droplets [15]. So, to quantify the composition of the interfacial layer and the distribution of surfactant and cosurfactant between the interfacial layer and the water or oil phase, different phase diagrams were exploited, such as pseudo-ternary phase diagram, Winsor type, fishlike phase diagrams, and dilution phase diagram of water-in-oil (w/o) microemulsion [16,17]. The dilution phase diagram deals exclusively with the single phase of w/o microemulsion and is used to determine the compositions of the interfacial layer and the bulk phase, as well as the thermodynamic parameters. Understanding the thermodynamic properties and structural

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characteristics of microemulsions provides an important theoretical basis for applications. In view of the above, a simple turbidimetric titration (dilution method) has been used by a number of workers [9,18–25]. Earlier, Palazzo et al. showed that the composition of the interface determined by a "Schulman's cosurfactant titration" of water/cetyltrimethylammonium bromide (CTAB)/*n*-pentanol/*n*-hexane agreed well with the interfacial composition determined employing pulsed gradient spin-echo NMR (PSGE-NMR) data. The authors were also pointed out that the method has applications in scattering and diffusion studies because it provides extrapolation to single-particle properties by reducing inter-particle interactions of the microemulsion system without changing its composition [26]. Very recently, we have reported the characteristics role of cosurfactant (butanol or pentanol) on the formation and stabilization of the droplet surface, which relates to the evaluation of the interfacial composition, thermodynamic properties, and structural parameters of single (CPC or SDS or Brij-35) and mixed surfactant (CPC or CTAB or SDS blend with Brij-58 or Brij-78 at different proportions) w/o microemulsions stabilized in heptane or decane or dodecane under varying physicochemical environments, by employing the dilution method [27–30]. Mixed surfactants play a promising role in surface chemical applications. Mixed surfactant systems may be less expensive and often exhibit interfacial properties more pronounced than those of the individual surface-active components of the mixture [31,32]. The interactions between the constituent surfactants can lead to either synergism (attractive) or antagonism (repulsive) in terms of their physicochemical properties depending on the type and nature of the surfactants. The studies on mixed surfactant systems are therefore of considerable interest from fundamental as well as applied viewpoints.

In view of these studies, the present report aims at a precise determination of the molecular interactions among the constituents and enlighten the formation vis-à-vis nature of the oil/water interface of mixed surfactant blended w/o microemulsions [water/sodium dodecylsulfate (SDS)/polyoxyethylene (23) dodecyl ether (Brij-35)/cosurfactant (1-pentanol)/isopropyl myristate (IPM)] as function of water contents ($\omega$), content of nonionic ($X_{\text{non-ionic}}$), and temperature. Both of these surfactants (SDS and Brij-35) are chosen in such a way that they possess similar hydrocarbon tail (constituting 12 carbon atoms in the linear chain), but they differ in charge type and size of the polar head groups, so that the possible interactions between the hydrocarbon chains of two surfactants get minimized. In this work, 1-pentanol is used as structure forming cosurfactant due to its versatile biological as well as technological applications [33,34]. Also, IPM has been widely used in the formulation of biocompatible microemulsions for pharmaceutical, drug delivery, and biological applications [35,36]. However, studies on IPM (which is structurally and physicochemically different from conventional hydrocarbons [10,37]) derived w/o mixed surfactant microemulsion are not much reported in the literature using the dilution method [30]. Recently, Hait and Moulik [18] and Mohareb et al. [19] reported the formation characteristics of single surfactant CPC or CTAB or SDS using n-alkanol ($C_5$–$C_9$) as cosurfactant stabilized in IPM oil by dilution method. The present study sheds on the formation of w/o microemulsion, composition of mixed interfacial film, complete analysis of thermodynamic of the transfer process of cosurfactant from bulk oil to the interface, transport property and microstructure of these systems (to understand the possible interactions between the constituents of microemulsion droplets) by means of phase study, dilution method, conductivity, and dynamic light scattering (DLS) techniques. This study aims to improve the basic understanding of the formation and microstructure of mixed w/o microemulsions stabilized in polar lipophilic oil (IPM), which is not much reported in the literature [30].

## 2. Experimental

### 2.1. Materials

Sodium dodecylsulfate (SDS, ⩾99%) and polyoxyethylene (23) lauryl ether (Brij-35, ⩾99%) were purchased from Merck, Germany and Sigma Aldrich, USA, respectively. The oil, isopropyl myristate (IPM, ⩾98%), and the alkanol, 1-pentanol (Pn, ⩾98%) were the products of Fluka, Switzerland. All these chemicals were used without further purification. Doubly distilled water of conductivity less than 3 μS $cm^{-1}$ was used in the experiments.

### 2.2. Methods

#### 2.2.1. Sample preparation and phase behavior

The samples comprising mixed surfactants (SDS and Brij-35) at different proportions, cosurfactant (Pn), oil (IPM) and water with constant surfactant, and cosurfactant mass ratio (S:CS = 1:2) were formulated in a screw cap glass vials. The samples were monophasic, transparent, and stable. Phase behavior of chosen systems was constructed with at fixed temperature (303 K) using thermostated water bath (accuracy, ±0.1 K). The repeat experiments were found to be reproducible with an error limit of ±1%.

#### 2.2.2. Method of dilution

The Schulman's method of cosurfactant titration (dilution experiment) [38] was performed to investigate the interfacial composition of w/o mixed surfactant microemulsions, as described earlier [20,27], with necessary modification in assessment of microemulsion formation using spectrophotometric technique to measure the change in sample turbidity produced by alcohol (Pn) addition [39]. To a turbid solution comprising a blend of SDS and Brij-35 at various composition ($X_{\text{Brij-35}}$) and water in a given solvent (IPM) at 303 K, small aliquots of Pn was added. The point of single phase microemulsion formation was evidenced by a total loss of sample turbidity, cheeked by the sample absorbance measured at 320 nm [39]. The sharp decrease in absorbance observed in the sample titration with alkanol (Pn) allows precise determination of the amount cosurfactant needed to stabilize the microemulsion. The absorbance measurements were carried out at 320 nm in JASCO (V-530) UV-spectrophotometer employing thermostated cell. The amount of mixed surfactant(s) and oil(s) was taken as 0.5 mmol and 14.0 mmol, respectively, for each system.

#### 2.2.3. Conductance measurement

The electrical conductivity measurements were performed using Mettler Toledo (Switzerland) Conductivity Bridge. The instrument was calibrated with standard KCl solution. The temperature was kept constant (303 K) for conductivity measurement within ±0.01 °C by circulating thermostated water, through a jacketed vessel containing the solution.

#### 2.2.4. Dynamic light scattering (DLS) measurement

Diameter of the microemulsion droplets was determined using a Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd., UK). A He–Ne laser of 632.8 nm wavelength was used and the measurements were made at a scattering angle of 90°. Temperature was controlled by inbuilt Peltier heating–cooling device (±0.1 K). Refractive index of each solution was recorded with an ABBE type refractometer, as it was required as an input in determining the size of the microemulsion droplet by DLS technique. Viscosity data, as obtained from viscosity measurements, were used in processing DLS data. Samples were filtered thrice using Millipore(™) hydrophobic membrane filter of 0.25 μ pore size.