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Physicochemical investigation of mixed surfactant reverse micelles: Water solubilization and conductometric studies

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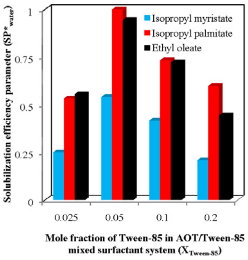
HIGHLIGHTS

- Mixed ionic/nonionic reverse micelles exhibit synergism in solubilization capacity.
- Hydrophobic moiety and head group of nonionic's affect the solubilization phenomena.
- Solubilization of water in oil(s) is more stabilized in isopropyl palmitate.
- Solubilization efficiency parameter has been evaluated to underline efficacy of the oils.
- Structure of polar lipophilic oils influences water solubilization and related phenomena.

GRAPHICAL ABSTRACT



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ABSTRACT

Solubilization of water in mixed reverse micelles (RMs) comprising sodium bis(2-ethylhexyl) sulfosuccinate (AOT), and polyoxyethylene (20) sorbitan trioleate (Tween-85) or polyoxyethylene (20) sorbitan monooleate (Tween-80) or sorbitan trioleate (Span-85) has been studied at different compositions ($X_{\text{nonionic}} = 0$–1.0) at a total surfactant concentration, $S_T = 0.1\ \text{mol dm}^{-3}$ in polar lipophilic oils of different chemical structures: viz., ethyl oleate (EO), isopropyl myristate (IPM) and isopropyl palmitate (IPP) at 303 K. The enhancement in water solubilization (i.e., synergism) has been evidenced by the addition of nonionic surfactant to AOT/oil(s)/water systems. The maximum water solubilization capacity ($\omega_{0,\text{max}}$) and $X_{\text{nonionic,max}}$ (mole fraction at which synergism occurs) have been influenced by polar head group and hydrophobic moiety of nonionic surfactant. The standard free energy change of dissolution of water (ΔG_s^0) of these systems depends on water content, $X_{\text{Tween-85}}$ and oil. Solubilization efficiency parameter ($\text{SP}^*_{\text{water}}$) has been evaluated to underline the efficacy of oils in obtaining maximum water solubilization capacity in mixed RMs. Conductance behavior of these systems in absence and presence of additives (bile salts and hydrotrope) has also been investigated under varied water content (ω) at 303 K. Volume-induced percolation threshold (ω_p) depends on $X_{\text{Tween-85}}$, oil type, and additives. An attempt has been made to give an insight to the mechanism of solubilization phenomena, standard free energy change of dissolution of water, percolation in conductance and microstructures of these systems by dynamic light scattering (DLS) measurements, wherein the chemical structures of both nonionic surfactants and polar lipophilic oils played significant role.

1. Introduction

Reverse micelles (RMs) are macroscopically homogeneous mixtures of oil, water (or, sodium chloride) and surfactant(s), which in the microscopic level individual domains of oil and water separated

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by a monolayer of surfactant(s). They possess some unique characteristics such as thermodynamic stability (imparting long shell life), compartmentalized polar and non-polar dispersed nano-domains, ease of formation, ultralow surface tension, low viscosity, large surface area and optical transparency. One of the most important features of RMs is the presence of highly structured yet heterogeneous water molecules present in biological systems such as membranes. These properties qualify them to be prospective drug delivery systems provided they are composed of nontoxic excipients [1,2]. These applications depend crucially on the water solubilization capacity, which changes in response to the environmental variables, such as surfactant properties, composition, type of oil, temperature, valence of counter ions, and salt concentration [3,4].

An important aspect of RM/microemulsion design is its ability to solubilize a maximum amount of dispersed phase (i.e. water) into the continuous phase. Single surfactant does not necessarily produce the best RMs. Method which has been suggested to enhance water solubilization capacity in RMs is using surfactant mixtures. Stabilizing the RM with a mixture of surfactants is very common. In commercial applications, blending of surfactants is the rule rather than the exception. This is for many reasons, but mainly because the surfactant mixtures may improve the product performance. Minimizing the amount of surfactant added to any product or processes gives obvious economic and environmental benefits, and an effective means of doing this is with synergistic mixtures [5]. The investigation on the solubilization capacity of anionic or cationic surfactant with nonionic surfactant mixtures in non polar solvents showed that the solubilization of water (or, sodium chloride) increased significantly with the incorporation of nonionic surfactant [6–8].

The structure and properties of RMs have been investigated extensively by employing a variety of physicochemical techniques, for example, Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), fluorescence spectroscopy, scattering techniques, calorimetry, dynamic light scattering (DLS), and conductivity [9–19]. Among these, electrical conductivity provides a convenient, useful, and accessible tool for probing the microstructure of RMs. Of the different physical properties of RMs, percolation of conductance is striking; where many fold (100–1000 times) increase in conductance can take place after a threshold volume fraction of the dispersant (water) at a constant temperature or after a threshold temperature at a constant composition [20–22]. The basic understanding of percolation process and related aspects in water-in-oil (w/o) microemulsions/RMs has been reported by a number of research workers [22–25]. Understanding the percolation process is also important for performing enzymatic reactions in w/o microemulsion or RMs [26]. Other technique which can contribute significantly in understanding the inter-micellar interaction in RMs is dynamic light scattering (DLS) [27]. Coupling the conductance study with DLS technique can give better insight into the percolation mechanism vis-à-vis droplet dimension and the polydispersity index (PDI) of mixed RMs [3].

Till now, most of the studies regarding the solubilization phenomenon and conducting properties coupling with droplet dimensions in RMs stabilized by both single and mixed surfactant systems have been carried out using linear hydrocarbons as solvent. However, polar lipophilic oils, which possess different chemical structures and physicochemical properties compared to the hydrocarbon oils, are widely used in biologically resembling systems, pharmaceuticals and drug delivery. Such studies using these oils are seldom reported in literature [6,7]. Very recently, Mehta et al. [28] reported the fully characterization of polyoxyethylene (10) oleyl ether (Brij-96)/cosurfactant ($C_2OH{-}C_6OH$)/ethyl oleate (EO) or isopropyl palmitate (IPP) or isopropyl myristate (IPM)/water microemulsion systems using conductivity, optical microscopy, dilution method, absorption, and FTIR spectroscopy. Also, Wang et al. [29] formulated self-nanoemulsifying drug delivery systems (SNEDDS) using polyoxyethylene sorbitan fatty acid esters (Tweens) and sorbitan fatty acid esters (Spans) as surfactants and IPM or EO or methyl oleate (MO) or methyl decanoate (MD) as oils to improve the dissolution rate of ibuprofen (a model poorly water soluble drug). Their studies also suggested possibility for controlling the droplet size yielded by SNEDDS. In the present report, we contemplate to undertake studies on the solubilization and thermodynamics of dissolution of water (ΔG_s^0), and conductance behavior of AOT RMs in the presence of non-ionic surfactants with different chemical structures that is, with similar or dissimilar polar head group and hydrophobic moieties [viz., polyoxyethylene (20) sorbitan trioleate (Tween-85) or polyoxyethylene (20) sorbitan monooleate (Tween-80) or sorbitan trioleate (Span-85)] in polar lipophilic oils of different chemical structures [consisting of long fatty acid chain and short alkyl chain (linear or branch) on either side of hydrophilic ester moiety, viz. EO, IPM, IPP] at different physicochemical conditions. Further, droplet size has been measured of these systems by dynamic light scattering (DLS) technique by changing compositions and oil types. Also, the effect of additives [viz. sodium cholate (NaC), sodium deoxycholate (NaDC), sodium taurodeoxycholate (NaTDC) and sodium salicylate (NaSl)] on the percolation of conductance in mixed RMs has also been taken up, as such studies in mixed RMs are rarely reported [19]. These studies would be of much importance and significance to underline the solubilization of water, microstructure and droplet dimensions of these novel systems in absence and presence of additives. Solubilization efficiency parameter (SP^*_{water}) has been evaluated to underline the efficacy of a particular oil in obtaining maximum water solubilization capacity at the corresponding composition in mixed RMs on the basis of a relative increase in solubilization of the dispersed phase (herein, water) in the oil compared to single AOT-based RM. Further, an attempt has been made to decipher the physicochemical concept of SP^*_{water} in the light of standard free energy change of dissolution of water in these systems. Polar lipophilic oils are noteworthy to investigate because of their structural resemblance to the lipids in living systems and they are expected to be environment friendly [30]. AOT or nonionic surfactants (Brijs, Tweens, and Spans) stabilized in IPM, IPP, and EO find applications in biologically relevant microemulsion systems [30–34]. Further, bile salts play vital roles in a number of physiological processes such as lipid digestion, drug adsorption, and cholesterol solubilization [35]. Finally, an attempt has been made to improve the understanding of the synergism in solubilization of water due to the addition of nonionic surfactant(s) to ionic surfactant in these oils, wherein variation in their chemical structures has been taken into account. And, also appearance of maximum in solubilization capacity has been examined to correlate microstructural variation due to the curvature effect and attractive interaction of the surfactant aggregates from conductance, DLS measurements and thermodynamic approach. Such a comprehensive study in mixed RMs is not reported in literature.

2. Experimental

2.1. Materials

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 99%), polyoxyethylene (20) sorbitan trioleate (Tween-85), polyoxyethylene (20) sorbitan monooleate (Tween-80) are purchased from Sigma, USA. Sorbitan trioleate (Span-85) is a product of Fluka (Switzerland). The surfactants were used without further purification. Ethyl oleate (EO, ≥98%), isopropyl myristate (IPM, ≥98%), isopropyl palmitate (IPP, 99%), sodium cholate (NaC, ≥99%), sodium