

Chapter II

Scope and Objectives

The self aggregation of amphiphilic (surfactant) molecules, either in the simplest form of monolayers or in the form of micelles, microemulsions and vesicles provides unique opportunity to bring the embedded molecules closer together, to orient them in a specific way and also, to alter their reactivity. The microstructure of self-organized assemblies of surfactant systems is of fundamental interest, and plays a substantial role in many important applications such as nanomaterial synthesis, drug delivery, separations, pharmaceutical formulation, and other dispersant technologies. Under the perspective of their potential technological and pharmaceutical applications, formulation and structural characterization of microemulsion systems have received much interest among other self-assembly systems, mainly due to the advantages of their physicochemical properties like ultralow interfacial tension, large interfacial area, low viscosity, and high solubilization capacity. The term “microemulsion” can be defined as homogenous, transparent, isotropic, thermodynamically stable dispersions of water and oil, which might be stabilized either by single surfactant, mixture of surfactants, or by surfactant/cosurfactant combination. However, microemulsion systems formed with mixed surfactants are known to offer properties superior than the pure components. Such studies using mixed surfactants and other ingredients (especially oils of low toxicity and polar lipophilic or biocompatible oil) are not much reported in literature. A typical feature of the adsorption of ionic (cationic/anionic)-nonionic surfactant mixtures shows the synergism or anti-synergism (antagonism) at the interfaces. Blend of surfactants often exhibits interfacial properties more pronounced than those of the individual surface-active components in the mixture. It is important to obtain quantitative information and elucidate the mechanism of assembly of mixed surfactant microemulsions. Further, phase behavior, thermodynamic properties, structural and packing parameters, transport properties (viscosity, conductance), percolation with related energetics, water solubilization capacity, nature or state of water in the water pool and several other parameters of microemulsion systems can be varied over a wide range with the use of mixed surfactant systems in comparison with single one. Further, there is a wide scope to elaborate such studies using ionic and

non-ionic of different configuration of polar head groups and hydrophobic moieties in solvents with different physical and chemical properties under varied physicochemical conditions. Further, the addition of cosurfactant (alcohol) fine-tunes the surfactant hydrophile-lipophile balance (HLB) and effectively changes the originally unfavorable packing geometry of the surfactant molecules, which in turn, adjust the spontaneous curvature of the film to a negative value (curvature towards aqueous domain) and produces a stable surfactant/alcohol mixed interfacial film. Hence, phase behavior studies of such multicomponent systems comprising single or mixed surfactants, cosurfactants, oil(s), water (additives) are very much significant from the view point of their formulations, stability and characterizations. Generally, cosurfactant molecules partition themselves among the oil, water and the interface domains depending upon the lipophilicity. Adsorption of cosurfactant at the interface essentially depends on its distribution between the oleic phase and the oil/water interface. Therefore, without a quantitative description of the dependence of the partition equilibria on the system composition under varied physicochemical environments, a full understanding of quaternary microemulsions cannot be attained. To explicate the nature of the oil/water interface, detailed knowledge on (a) the interfacial composition (relative population of surfactant and cosurfactant in the interfacial region), (b) the distribution of the cosurfactant between the oil and water in water-in-oil (w/o) microemulsion systems and (c) thermodynamics of transfer of cosurfactant from the oleic phase to the interface are essential. In addition, the water solubilization capacity, transport properties (conductance and viscosity), microstructure and dynamic H-bonding network of confined water are the important parameters of w/o microemulsion system, which determines the size of water core, the rigidity of the oil/water interface, inter-droplet interactions and the morphology of surfactant aggregates. Hence, a comprehensive physicochemical study of some single and mixed surfactant microemulsion systems comprising conventional or biocompatible amphiphiles stabilized in alkanes or polar lipophilic oils in absence or presence of electrolyte/salts is needed. To this end, a simple but elegant method of dilution, conductivity, viscosity, dynamic light scattering (DLS), fluorescence probing techniques (lifetime and steady state anisotropy measurements), fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) techniques have been used

to elucidate the dynamics and internal structure of single and mixed surfactant microemulsions. Microemulsions are membrane-active, antimicrobial, self-preserving in their own right. Further, the antimicrobial activity of the single and mixed microemulsions has been examined against the gram-positive and gram-negative bacterial strains. In the present dissertation, an attempt has been made to formulate and characterize a series of single and mixed surfactant microemulsion systems in oils of different types (in absence or presence of salts/electrolytes) at different physicochemical conditions by employing different techniques as mentioned above. The broad objectives of the present investigation are mentioned below. Chapter III 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) cationic/non-ionic 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 303K. 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. 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 contemplated 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. In Chapter IV, an attempt has been made to underline the influence of the variation in alkyl chain length of alkyltrimethylammonium bromide based cationic surfactant (C_nTAB , $n = 12, 14, 16$ and 18) and oils of different chemical structures and polarity [viz. heptane (Hp) is a short chain (C_7) linear hydrocarbon, whereas isopropyl myristate (IPM) commonly known as a fatty acid ester or polar lipophilic oil, consists of branched alkyl chain (isopropyl) and longer fatty acid chain (myristate, C_{14}) associated with either side of the ester moiety, which is polar] on formation vis-à-vis the constitution of the interfacial film, microstructure and states of the encapsulated water inside the pool of equimolar (1:1) w/o

cationic/non-ionic mixed surfactant microemulsions, water/ C_n TAB ($n = 12 \rightarrow 18$) + polyoxyethylene (20) cetyl alcohol ($C_{16}E_{20}$) (1:1)/pentanol/heptane (or isopropyl myristate) in absence and presence of different inorganic salts [sodium chloride (NaCl), potassium fluoride (KF), potassium iodide (KI), nickel (II) chloride ($NiCl_2$), and iron (III) chloride ($FeCl_3$) at a fixed concentration] at ω (= 25) and 303 K, by employing different methods and techniques (such as, dilution method, phase study, viscosity, DLS and FTIR measurements). However, the additives (inorganic salts) are not chosen arbitrarily. NaCl is a strong electrolyte and influences the interfacial composition of (w/o) microemulsion system. KF and KI are reported to behave as salts of ‘water structure maker’ (kosmotropes) and ‘water structure breaker’ (chaotropes) respectively. $NiCl_2$ and $FeCl_3$ are used, as they are interesting precursor salts for nanoparticle synthesis in w/o microemulsion media. In Chapter V, we contemplate to undertake a precise investigation on the formation vis-à-vis nature of the oil/water interface, transport property and microstructure of anionic/non-ionic 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 (ω), content of nonionic ($X_{nonionic}$), and temperature by means of phase study, the dilution method, conductivity, and DLS measurements. 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 gets minimized. Also, IPM has been widely used in the formulation of biocompatible microemulsions for pharmaceutical, drug delivery and biological applications. However, studies on IPM (which is structurally and physicochemically different from conventional hydrocarbons) derived w/o mixed surfactant microemulsion is not much reported in literature. In continuation of our previous study Chapter VI aims at a precise characterization of the molecular interactions among the constituents, and enlightens the formation vis-à-vis nature of the oil/water interface in the microenvironment of mixed cationic (cetyltrimethylammonium bromide, CTAB) and nonionic (Brij-35) microemulsions stabilized in Pn and IPM as a function of ω , composition (mole fraction of nonionic surfactant in mixed surfactant system, $X_{nonionic}$),

and temperature, and comparison of the results in the light of changes in size and type of polar head group of basic surfactants (viz. CTAB with CTA⁺ and SDS with DS⁻) as well as unequal hydrocarbon chain lengths of CTAB (C₁₆) and Brij-35 (C₁₂). The present investigation sheds on the formation and composition of mixed interfacial film, complete analysis of thermodynamics of the transfer process of cosurfactant from bulk oil to the interface, transport property, microstructure and the physicochemical properties of solubilised water of these systems by means of phase study, dilution method, conductivity, DLS, FTIR (with HOD probing) and ¹H NMR spectroscopic measurements. Further, an attempt has been made to examine the antimicrobial activity or inhibitory effect of the microemulsion systems against the strains gram-positive - *Bacillus subtilis* (*B. subtilis*) and gram-negative - *Escherichia coli* (*E. coli*) bacteria has been in individual constituents and also at different compositions of mixed surfactants [$X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$, S/CS = 1:2 (w/w)] of microemulsions at 303K, by measuring the diameter of the inhibition zone (“diz”). In Chapter VII (final chapter), we contemplate to undertake studies on the formation and precise characterization vis-à-vis the nature of the oil/ water interface and water in the confined environment of nonionic/cationic mixed surfactant w/o microemulsions [water/polyoxyethylene (20) cetyl ether (Brij-58)/cetyltrimethylammonium bromide (CTAB)/1-pentanol (Pn)/heptane (Hp) or decane (Dc)] as a function of different mixing ratios of Brij-58: CTAB (5:0 \rightarrow 0:5, w/w) at 303K. In this report, we intended to address non-ionic (Brij-58)/ionic surfactant (CTAB) mixed surfactant microemulsions (that is, the addition of a cationic surfactant to a nonionic surfactant at different proportions, which differs from other studies) that exhibit synergism in solubilization of water in these systems. An attempt has also been made to correlate the solubilization capacity of water as a function of mixed surfactant composition with percolation of conductance to underline the microstructure of these mixed surfactant microemulsions. In addition, microstructure, internal dynamics (dynamics of the confined water) and interfacial composition of the mixed interfacial film of these systems have been characterized by means of the phase study, DLS, FTIR measurements and dilution method as a function of different mixing ratios of surfactant(s). An attempt has been made to rationalize the results in a comprehensive manner.