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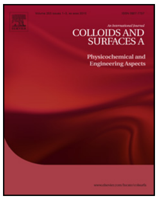

Influence of chemical architecture of oils and ionic liquid on the physicochemical and thermodynamic properties and microenvironment of anionic surfactant based microemulsion

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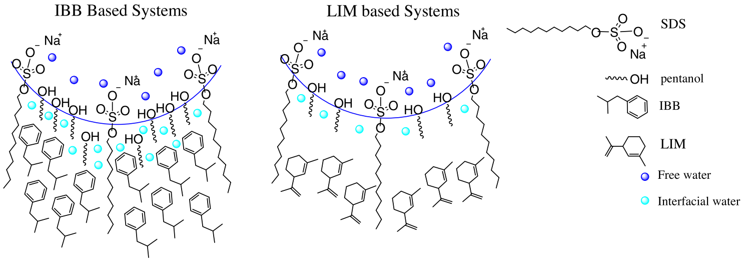
HIGHLIGHTS

- Formation of microemulsions reveals exothermic with negative entropy change.
- Isobutyl benzene penetrates more easily in the surfactant palisade layer than *R*-(+)-limonene.
- Ionic liquid behaves as water structure maker salt due to increase in proportion of bound water.
- Polarity of oil affects microstructures of microemulsions.
- Rotation of fluoroprobe restricts in presence of ionic liquid due to rigidity of interfacial layer.

GRAPHICAL ABSTRACT

Pictorial representation of different extent of penetration of *R*-(+)-limonene (LIM) or isobutyl benzene (IBB) in SDS derived microemulsions.



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ABSTRACT

Hypothesis: Although several studies on water-in-hydrocarbon oil microemulsions stabilized by anionic surfactant are available in literature, such study on oils possess comparable molar volumes with different chemical architectures and physicochemical properties, herein *R*-(+)-limonene (LIM) and isobutyl benzene (IBB) derived microemulsions in absence or presence of ionic liquid (IL) warrants uniqueness of this report.

Experiments: The present study delineates interfacial composition and thermodynamics properties of sodium dodecylsulfate, SDS/1-pentanol/LIM or IBB/water microemulsions in absence or presence of IL, 1-butyl-3-methylimidazolium chloride (bmimCl) as additive by the dilution method. Further, precise characterization of these systems is accomplished by conductivity and DLS studies as function of ω, [bmimCl] and temperature, which provide an insight into unique features of the oil/water interface. Finally, the influence of distinctive features of oils and the states of water organization in nanopool of these microemulsions have been explored from steady state fluorescence emission, fluorescence anisotropy and FTIR measurements.

Findings: bmimCl containing microemulsions are more spontaneous than aqueous microemulsions. Addition of bmimCl yields smaller droplets compared to aqueous system. Fluorescence measurements reveal penetration of oil molecules in the surfactant palisade layer vis-a-vis interfacial micropolarity and their consequential effects in microenvironment of microemulsions in absence or presence of bmimCl, using

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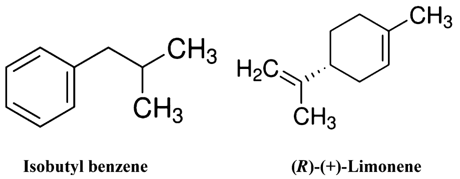
suitable molecular probes. Apart from reciprocal variation in free and bound water with increasing water content, results exhibit mild variation in interfacial water (which is basically trapped water in the hydrophobic tail region of surfactant) by changing oil continuum. Finally, correlation of the results in terms of evaluated physicochemical and thermodynamic parameters has been presented.

1. Introduction

Surfactant mediated self-assemblies are of central interest due to a variety of nano-, micro-, and macrostructures and play generous role in diverse applications, such as nanomaterial synthesis, drug delivery, separations, pharmaceutical formulations, and other dispersant technologies [1–4]. Of these, most widely reported systems are normal (aqueous) micelles and microemulsions. Microemulsions are optically isotropic, transparent, thermodynamically stable dispersions with two or more immiscible liquids, which are stabilized by an adsorbed amphiphilic film (comprising of surfactant either in single or mixed state or frequently in combination with a cosurfactant) at the liquid–liquid interface. Depending upon the types of components, these nanoscale aggregates may comprise oil-in-water (o/w) or water-in-oil (w/o) microemulsions. The o/w microemulsions stake many features of normal (aqueous) micelles and possess similar applications. On the other hand, w/o microemulsions contain polar solvent molecules (water) trapped in a confinement created by the self-aggregation of the surfactant head groups (called water pool), while the alkyl chain (or tail) of the surfactant molecules remain in the bulk nonpolar solvent (oil). The shape and size of this pool are governed by the ratio of the water-to-surfactant concentrations (ω), and also, by the types of surfactant and oil [5,6]. These w/o microemulsions with nanometer-sized water pool represent a classical compartmentalized systems, and find applications in biochemistry, nanochemistry, synthesis, extractions, separations, oil recovery, polymerization and in pharmaceutical, cosmetic, agrochemical, and food industries [7,8]. The majority of these studies involve water and volatile organic solvents as polar and nonpolar solvents, respectively. However, one can increase the number of these solvents by understanding and manipulating the molecular interactions involved in amphiphile self-assembly. Due to the proposed environmentally benign nature along with many unique and attractive physicochemical properties [9,10], ionic liquids (ILs) have emerged as an obvious choice for tuning the molecular interactions to form IL based self-assembled systems.

It is worthy to mention that a series of studies have been reported on the interaction between ionic surfactants (of different chemical structures and charges, for example, anionic, cationic, non-ionic, and zwitterionic) and ILs (comprising of imidazolium cation with variation in alkyl chains and also differ in configuration of anionic constituents) for alteration or modification of the physicochemical properties of surfactant based self-assembled systems, particularly micelles (aqueous) during a past decade. Such studies have clearly demonstrated the effectiveness of ILs in tuning the key physicochemical properties of these systems because of their impressive solvation ability which facilitates interaction with classical surfactants and have attracted widespread attention due to the multifaceted practical uses of such systems [11–16]. Interestingly, most of these studies were involved with a conventional anionic surfactant, sodium dodecylsulphate (SDS) [14,17–20].

The formation of IL based microemulsions is generally hindered by the low miscibility of most conventional surfactants, particularly the ionic and zwitterionic ones in ILs [11,12]. However, a very few using these kind of surfactants in absence and presence of a cosurfactant/co-solvent/additive have been reported in literature [21–24].



Scheme 1. Chemical structures of oils.

In view of these reports, we contemplate to undertake a study, which underlines the influence of an imidazolium based IL [hydrophilic, 1-butyl-3-methylimidazolium chloride (bmimCl)] and polar lipophilic oils [*R*-(+)-limonene (herein, LIM) or isobutyl benzene (herein, IBB)] on the formation and characterization of anionic surfactant, SDS derived w/o microemulsion. 1-pentanol (Pn) was used as cosurfactant. SDS was chosen in order to extend the study from well reported micelles (aqueous) to w/o microemulsions. However, use of LIM and IBB as oil in these formulations is not arbitrary. Reports on formation and properties of microemulsions in LIM and IBB oils are not much reported in literature [25–30]. LIM, the main constituent of peel oil from oranges and other citrus fruits, is an inexpensive monoterpenic hydrocarbon produced from a renewable source and widely available in the market. The distilled peel oil contains 95% LIM together with other terpenes, mainly myrcene. It finds applications in perfumes, soaps, foods and beverages as an additive due to its pleasant citrus fragrance [31]. LIM is also used as a solvent and industrial defatting agent [32]. On the other hand, molecular diffusion in aromatic hydrocarbon (such as, IBB) might be essential for a wide range of physical and chemical processes, for example, chemical and electrochemical reactions, crystal growth and dissolution, distillation, absorption, extraction, and transport across membranes [33]. The novelty of these studies is as follows; both oils possess almost comparable molar volume, but they differ in chemical structures/architectures (Scheme 1) and physicochemical properties (vide. Table S1, Supplementary Material). Unlike linear hydrocarbons, penetration of these aromatic hydrocarbon oils into the palisade layer of surfactant molecules at the water–oil interface is not expected to be straightforward, because of their variation in aromaticity, chemical structure and polarity [29]. Further, this penetration effect makes the spontaneous curvature of the microemulsion droplets negative (or less positive) [34]. In addition, the bulky imidazolium cation with butyl alkyl chain may induce a significant impact on the well-balanced between hydrophobic and electrostatic interactions among the constituents within the confined environment of the anionic surfactant aggregates, leading to characteristics modification of the oil–water interface, microstructure, micropolarity, states of water therein. In view of these backgrounds, we contemplate to undertake the evaluation of interfacial composition and thermodynamic parameters of above mentioned systems under varied physicochemical conditions by the dilution method or the Schulman cosurfactant titration of the oil/water interface. Further, microstructures of these systems have been determined from electrical conductivity and DLS measurements at different physicochemical conditions. In order to find out the unique features of both oil and bmimCl in these formulations, and also to underline consequential changes in interfacial micropolarity around fluoroprobe vis-a-vis physicochemical changes in microenvironment