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# Ionic liquids in microemulsions: Formulation and characterization

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ABSTRACT

In the last few decades ionic liquids (ILs) have been widely considered as a "green solvents" and they are used in various fields. ILs can be used in the formation of microemulsion as a dispersed medium, polar domain and recently as a surfactant. In this particular review our discussion is about the novel IL-based aqueous and non-aqueous microemulsions which are quite fascinating and interesting research field for scientists. Synthesis of double and triple chain containing surface active ionic liquid (SAILs) and formation of microemulsion as a surfactant with ILs as a polar core have been elaborated in this review. ILs with a certain surface activity having long alkyl chain substituents can self-aggregate and form ILs microemulsion with high-temperature stability and temperature insensitivity. Characterization of these ILs in oil microemulsion and different ultrafast processes which are performed inside these characterized systems are documented very well. We have highlighted the similarities and differences between the nonaqueous microemulsions and the aqueous microemulsions. Addition of water and effect of temperature are quite important in case of the ILs containing microemulsions.


## 1. Introduction

The existence of microemulsions (MEs) was first described by Schulman [1] and Winsor [2] and the definition of microemulsion described by Lindman as "microemulsion is a system of water, oil and amphiphile which has a single optically isotropic and thermodynamically stable liquid solution" [3]. However, the history of discovery of microemulsions was well before the study of Schulman and the first commercial microemulsion, liquid waxes was discovered in 1928 and later, it gained significant attention in the oil industry [4]. Nowadays, it has potential application in separation science, environmental science, material science and reaction engineering with certain unique advantages [5]. They can be used as a nanoreactor to form a monodisperse nanoparticles or drug delivery vehicle due to the fast exchange between the droplets in microemulsions [6,7].

Microemulsions are generally classified as water-in-oil (w/o), oil in water (o/w) or bicontinuous system depending on surfactant type, sample environment etc. and they are characterized by ultra low interfacial tension between oil and water phases [2]. In w/o microemulsion, the surfactant rich oil phases coexists with the surfactant-poor aqueous phase and in o/w microemulsion, surfactant rich water phase coexists with the oil phase where surfactant is only present as monomers at small concentration. Microemulsions, which contain water or highly polar solvents like methanol ($CH_3OH$), acetonitrile (ACN), dimethyl formamide (DMF) in the core, have been studied extensively [8–15]. The size of the microemulsions is varied in the order of nanometer and it is generally characterized by the R/W value (R/W = [water or polar solvents] / [Surfactant]). Recently, several attempts have been made for the preparation of microemulsions where various polar solvents with high dielectric constants and which are immiscible in non polar solvents are used instead of water in the polar core [16–18]. These microemulsions are important in theoretical as well as experimental point of view [19] and recently, they are widely applied to semiconductors, solar energy conversion, microcolloids etc. [20]. Moreover, these waterless microemulsions have significant advantages over water based microemulsion in different organic reactions such as Diels–Alder reaction, esterification, polymerization etc. [21].

In this review article, we focused on the Ionic Liquid (IL) based microemulsions and the role of ionic liquid in formation of microemulsions. Recently, room temperature ionic liquids (RTILs) received an increasing number of attentions because of their unique physiochemical properties such as low volatility, high thermal stability and high ionic conductivity and the drawbacks associated with the non-aqueous solvents or organic solvents related to environment, health or safety can be conquered by using the RTILs [22–27]. More importantly, the cationic and anionic constituents of the RTILs can be modified to obtain the desired property of the solvent and therefore, they are often termed as "designer solvent". For this reason, they are frequently used in organic synthesis, catalysis, electrochemical studies, and other chemical and technological applications [28–32]. ILs exist as liquid in room temperature because of their chemical structure. The cation and anions of the ILs are chosen in such a way that they destabilize the

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solid-phase crystal and they are stabilized by the strong electrostatic interaction and other weak non-specific interaction (van der Waals interaction) between them. At first, researchers were attempting to solubilize different ionic liquids replacing water from the core of the microemulsions [18,33,34]. Later, it is established that IL can also play the role of organic solvent and from the green chemistry point of view it is very much promising for applications. Besides this, water and oil can also solubilize in IL based surfactant. Thus, IL plays a versatile character in IL-based microemulsion and for this reason, the publication based on IL in microemulsion is increased rapidly in recent times. Few recent review articles are also available in literatures which give an excellent overview of the relevant literature [35–41].

## 2. Different role of IL in the formulation of microemulsion

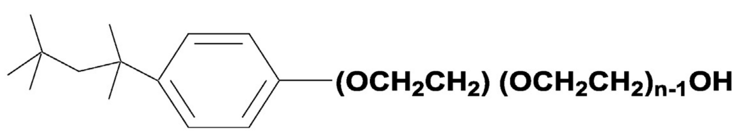
Based on the role of ILs, microemulsions can be classified into three categories. The chemical structures of the various surfactants and ionic liquids are shown in Scheme 1.

(a) Non aqueous IL microemulsions: the polar domain of the microemulsion constitutes the IL.
(b) Aqueous IL microemulsion: the nonpolar part constituents the IL and water is used in polar domain.
(c) Microemulsions with IL as surfactants: different surface active Ionic liquids (SAILs) are used as surfactant and in the polar domain aqueous as well as non aqueous solvents including IL are used.

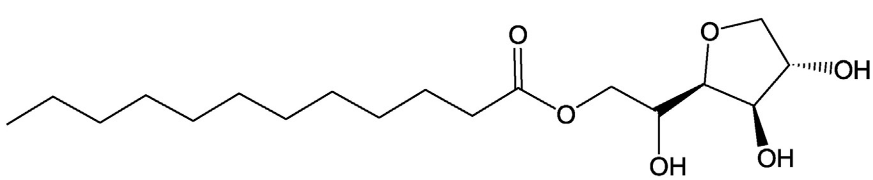
We have described each category in the following sections:

### 2.1. Non aqueous IL microemulsion

For the preparation of non aqueous IL microemulsion, imidazolium based hydrophilic IL, 1-Butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim]BF_4$) is most frequently used. Gao et al. first reported the non aqueous IL microemulsion where $[C_4mim]BF_4$ was used as polar media and the system was characterized by phase diagram, conductivity measurement and DLS (dynamic light scattering) measurement and freeze-fracture transmission electron microscopy (FF-TEM) measurements [42**]. Later, Eastoe et al. performed SANS (small angle neutron scattering) experiment on this microemulsion ($[C_4mim]BF_4$/TX-100/cyclohexane) to demonstrate the surfactant stabilized dispersed nanodroplet with IL core [43]. Chakrabarty et al. also studied the effect of confinement on solvation and rotational relaxation of probe molecule in this microemulsion [44]. Different organic solvents such as toluene, benzene, p-xylene have also been used to investigate the role of organic solvent in this microemulsion [45–49]. Ghosh et al. [50*] have prepared different IL microemulsions composed of TX-100, cyclohexane and IL with the variation of alkyl chain length and the IL they have used in their study are 1-ethyl-3-methylimidazolium n-butyl sulfate $[C_2mim][C_4SO_4]$, 1-ethyl-3-methylimidazolium n-hexyl sulfate $[C_2mim][C_6SO_4]$, and 1-ethyl-3-methylimidazolium n-octyl sulfate $[C_2mim][C_8SO_4]$ and they have proposed that the long octayl chain of octayl sulfate allows the anion to align itself along with the TX-100 surfactant which increase the rigidity of the system. The sulfate based IL




Triton X-100 (TX-100)

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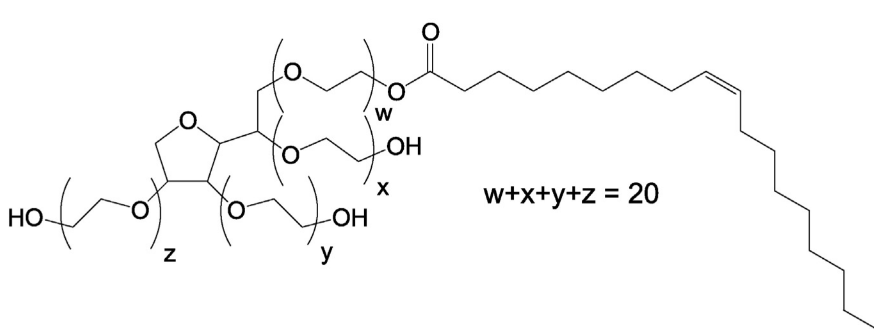


**Tween 80**

**Scheme 1.** Structure of various surfactants and RTILs.