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# CHAPTER I

## INTRODUCTION

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***I. INTRODUCTION***

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In the past few years, the substitution of hazardous and volatile solvents that were conventionally used in industrial processes is an important subject of concern amongst the researchers (Hejazifar et al., 2020). There are countless factors that affect the solvent selection, such as, concerns regarding the safety for the properties of the solvent, viz. environmental impact on both aqueous as well as non-aqueous solvents, other exposure that have hazardous effect on health, quality of the desired product, solvent flammability or reactivity, waste management and treatment of other industrially relevant constraints and other financial aspects (Alder et al., 2016; Prat et al., 2014). There is an enormous increase in the number of studies dealing with the microemulsions, in which either the aqueous phase or the oil phase has been substituted by an ionic liquid as a solvent. Ionic Liquids are generally referred to as “greener solvents” or “designer solvents” (Freemantle, 1998; Rogers, 2002; Earle & Seddon, 2002; Aki et al., 2007). Furthermore, ionic liquids are also considered as future solvents for various industrial applications such as in catalysis (van Rantwijk & Sheldon, 2007; Pârvulescu & Hardacre, 2007), extractions (Blanchard et al., 1999), chemical reactions (Haumann & Riisager, 2008; Martins et al., 2008), and various other potential applications (Wasserscheid & Keim, 2000; Hallett & Welton, 2011). Specifically, the room temperature ionic liquids (RTILs) have attracted more interest from the researchers. In industries, about 600 conventional solvents are used as compared to at least 10 (Earle et al., 2000) viable simple ionic liquids (Plechkova & Seddon, 2008). The RTILs are non-volatile and have gained popularity as "green solvents" as they are easy to handle and less toxic to the environment as compared to traditional hydrocarbon based organic solvents. It should be emphasized however, that a low vapour pressure does not turn an ionic liquid green.

However, some ILs might be called greener solvents depending on the application, recovery, sustainability, and ability to customise for a specific task. The formation of amphiphilic association structures with ionic liquids, such as micelles, vesicles, microemulsions, and liquid crystalline phases, has received significant attention from researchers in recent years (Evans et al., 1982; Qiu & Texter, 2008; Greaves & Drummond, 2008; Hao & Zemb, 2007). In 1980s, Evans and co-workers (1981; 1982; 1983) have reported the formation of micelles and liquid crystals in ethylammonium nitrate (EAN). In imidazolium-based ionic liquids, self-aggregation of general ionic and non-ionic surfactants was also reported (Anderson et al., 2003; Patrascu et al., 2006; Hao & Zemb, 2007).

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Anderson et al. (2003) investigated the association colloid/micelle formation of SDS in 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and Brij 30 in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]). Patrascu et al. (2006) carried out a detailed investigation on the aggregation behaviour of Poly (ethyleneglycol)-ethers in [Bmim][BF<sub>4</sub>], [Bmim][PF<sub>6</sub>], and 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) amide ([bmim][Tf<sub>2</sub>N]). Later, Hao et al. (2007) ascertained how Zn<sup>2+</sup> fluoros- and zwitterionic surfactants form vesicles in [Bmim][BF<sub>4</sub>] and [Bmim][PF<sub>6</sub>], respectively. Greaves et al. (2008) observed that different protic ionic liquids (PILs) facilitated the self-assembly of amphiphiles. Thomaier et al. (2007) reported the production of aggregation of the surfactant-like ionic liquid 1-hexadecyl-3-methylimidazolium chloride [C<sub>16</sub>mim][Cl] in EAN. According to their findings, the values for critical micelle concentrations (cmc) in RTILs are much greater than those in water. Moreover, the micelle aggregation numbers in RTILs are found to be smaller than those in water, hence, the area per molecule is also lowered compared to that of water. S. Thomaier's PhD thesis (Thomaier, 2009) documents thorough studies on the shape and size of aggregates of the binary system [C<sub>16</sub>mim][Cl]/EAN.

Zhao et al. (2009) recently published a thorough phase diagram of the binary system [C<sub>16</sub>mim][Cl]/EAN. It has been observed that on increasing [C<sub>16</sub>mim][Cl] concentration, aggregates of different morphologies exhibit many similarities to that observed in aqueous systems. The standard liquid crystalline phases, such as regular hexagonal (H<sub>1</sub>), lamellar (L<sub>α</sub>) and reverse bicontinuous cubic (V<sub>2</sub>) phases, have also been described in addition to micellar regions. The attractiveness of aggregate formation in room temperature ionic liquids is highlighted by the capability of forming high temperature stable self-assembled structures (RTILs). As a result, the wider range of RTILs have been examined and found to allow the formation of either high temperature stable or low temperature stable colloidal systems that are not possible in traditional binary surfactant/water mixtures.

Using these earlier findings as a guide, in the present work of thesis, we report the formulation of different types of microemulsions, namely non-aqueous ionic liquid microemulsions, aqueous ionic liquid microemulsions and ionic liquid/oil/water microemulsions using different non-ionic sugar-based surfactants. The phase studies were carried out to confirm the formation of the microemulsion system. Also, the detailed elucidation of their phases is discussed herein. Last but not least, the manufacturing of various hazardous and harmful chemicals that have been generated from varied industrial areas around the world has unbalanced the environment and the life of living organism in water. So, we are focusing into the utilizations of microemulsion systems formulated

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using non-ionic sugar-based surfactants that are environment friendly and have better surface properties compared to conventional surfactants. These microemulsion systems are a standout amongst the most flexible choices for such purposes. The inspiration of the present thesis is to use such microemulsion system for various recent applications like solubilization of hydrophobic dye, extraction of insoluble metal ions and recovery efficiency of metal ions. This part manages the fundamental comprehension of the topic and literature survey limited to the present aim of the thesis.

### ***1.1. Microemulsions***

The unique qualities of non-ionic sugar-based surfactants, room temperature ionic liquid, and microemulsion have drawn considerable attention of researchers from the academia as well as industries around the world due to the advancement of the current science and technology and its development. According to several reports in the literature, there has been a spike in interest in the subject of microemulsion systems with ionic liquid as a main component from both theoretical (thermodynamics, particle interactions) as well as practical (possible use as novel reaction media) perspectives (Qiu & Texter, 2008; Kahlweit et al., 1999; Sottmann & Stubenrauch, 2008; Rakshit et al., 2019; Zech et al., 2010b; Mehta & Kaur, 2010; Cheng et al., 2007). From the fundamental research point of view, there has been great progression crafted in the last three decades about understanding the properties of the microemulsion systems through numerous systematic experiments which aimed at generalizing the behaviour of the microemulsion system formulated by various researchers across the world (Zech et al., 2011; Kahlweit et al., 1988; Fanun, 2008; Rodriguez-Abreu et al., 2007).

Before proposing the term microemulsion, the terms that were used for microemulsion are transparent water and oil dispersion, oleopathic hydro micelles which nowadays are called as reverse microemulsion, or hydroopathic oleo micelles, having one phase system. Also, it was spotted that when the combinations of all the four components added are correct, results into clear, transparent, single-phase system. In 1943, Hoar and Schulman (Hoar & Schulman, 1943) were credited to bring forward the recognition of the term microemulsion through their breakthrough work of initiating transparent and single phase solution by mixing an emulsion with organic solvent named hexanol. For supporting a multiple phase system comprising of water, oil, surfactant, and alcohol that results into one phase transparent solution, the term "microemulsion" was initially proposed by Schulman et al. in 1959 (Schulman et al., 1959). In the beginning, a quaternary solution was formulated which consists of water, benzene, hexanol, and *K*-oleate and

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it was stable homogenous, relatively transparent mixture. Further, on addition of the short-chain length alcohol, the solution appeared to be clear and transparent. They tried to formulate the emulsion system and to it, a co-surfactant was added to make the system clear. Schulman et al (Schulman et al., 1959) later, came up with a statement that when a surfactant and a co-surfactant, are taken in an accurate amount, there is a formation of mixed film at the oil/water interface which results in the formation of interfacial pressure that exceeds the initial positive interfacial tension. As the interfacial tension reduces to zero, a bicontinuous microemulsion is observed, wherein the monolayer of the surfactant gets separated and as a result the filtration of domains of the oil and water takes place. Also, it has been concluded from the observation that these systems formed are made up of the spherical micro droplets having a diameter between 600 and 800 nm due to which the solution can be seen as one –phase system.

Later, a more recent definition of microemulsion was put forth by Danielsson and Lindmann (Danielsson et al., 1981), and it has been used in recent years. They defined microemulsion as a thermodynamically, stable isotropic solution comprised of water, oil and an amphiphile. The water was used as a polar medium containing electrolytes and other additives. The term amphiphile was coined by Winsor (1954) to characterise compounds that have affinity for both non-polar and polar phases. Surfactants are thus fundamentally amphiphiles since they have a strong amphiphilic nature that drives the interface when the polar component is at the polar phase and vice versa. An organic phase that is immiscible or partially miscible with the polar phase is referred to as oil. Nonpolar oil phases can thus be made up of hydrocarbons, partially or completely chlorinated or fluorinated hydrocarbons, single-chain alkanes, cyclic or aromatic hydrocarbons, triglyceride natural oils, and so on (Malmsten et al., 1999). The *n*-alkanes are the most commonly employed non-polar phases in microemulsion systems. It's also been discovered that the polar phase isn't always water, and the non-polar phase isn't always oil.

There have been several attempts to formulate and characterise water-free microemulsions (Friberg et al., 1984; Escoula et al., 1984; Friberg & Liang, 1987; Rico & Lattes, 1987), such as replacing water with ethylene glycerol (Saidi et al., 1990), glycol or formamide (Friberg & Liang, 1987; Ray & Moulik, 1994). Formulating non-aqueous microemulsions with Ionic Liquids has made a significant progress (Atkin & Warr, 2007; Rakshit et al., 2019; Mehta & Kaur, 2010; Thater et al., 2014; Thater et al., 2019; Anjum et al., 2009; Marsh et al., 2002; Zech et al., 2010; Li et al., 2007; Gao et al., 2006). In this chapter, an overview of the current status of research on ionic liquids in microemulsions is presented.

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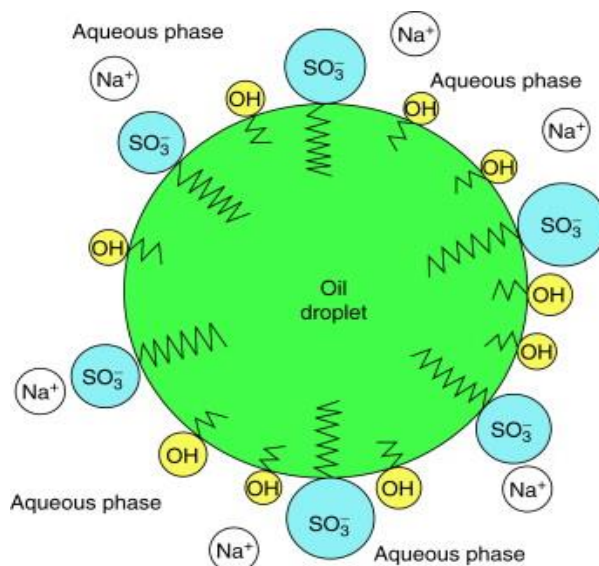
### 1.1.1. Types of microemulsion systems

Since past 100 years, it was believed that mixing of oil and water was not possible. It was observed that on addition of little energy to the mixture in form of stirring, leads to formation of an unstable dispersion and once the system is kept at rest position, the phases get separated out. The interfacial tension between the two immiscible liquids is reduced substantially when a surfactant is added, resulting in the formation of a dispersion. The proportions of the ingredients determine whether the dispersion is oil-in-water (o/w) or water-in-oil (w/o). The system formed is turbid and thermodynamically unstable generally having the dimensions between (0.2-10)  $\mu\text{m}$  (Bellocq et al., 1984; Paul & Moulik, 1997) and hence called as macroemulsions. However, microemulsions remain stable as they are kinetically stable for a considerable amount of time (Prince, 2012). On the other hand, there is no need for any mechanical effort when formulating a microemulsion system. Microemulsions typically have diameters ranging from 3 nm to 10 nm (Paul & Moulik, 1997).

### 1.1.2. Oil-in-water microemulsion system

In the literature, there are reports pertaining to different ranges of colloidal structures in a microemulsion system. Oil-in-water (o/w) and water-in-oil (w/o) microemulsions are examples of some of the microemulsions. The continuous phase of an O/W microemulsion system is water, which is accompanied by oil droplets that are stabilised by a surfactant molecule. Non-ionic surfactants and ionic double chain surfactants, such as sodium bis (2-ethylhexyl) sulfosuccinate, do not require a co-surfactant (AOT).

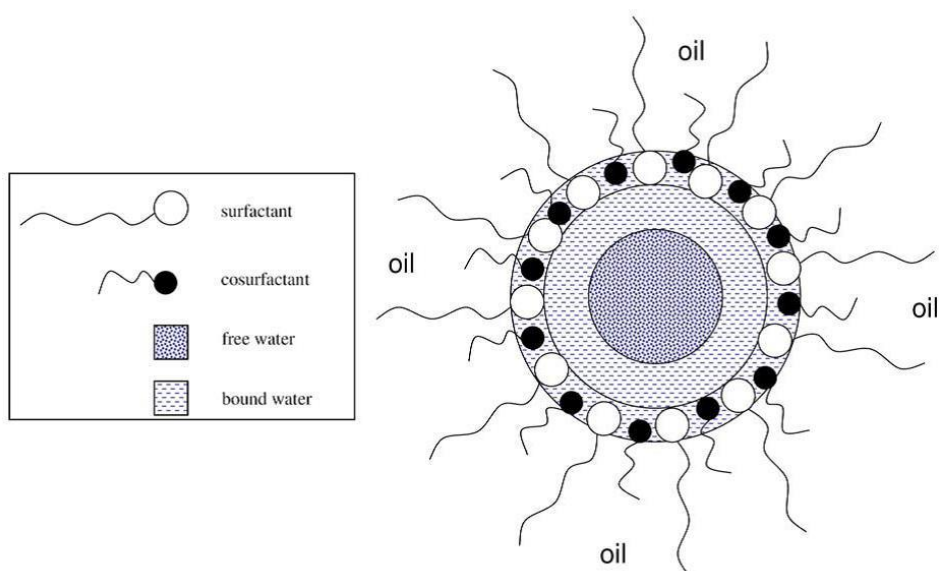
However, the co-surfactant is viable and a required component for the formation of a microemulsion in a single-chain ionic surfactant, as there is strong repulsion of the charged surfactant head groups. The *n*-alcohols are often used as a co-surfactant. Figure 1 describes the simplest one, which is a spherical micellar aggregate with oil in the core of the swelling micelle.



**Figure 1.** Schematic diagram representing the formation of O/W microemulsion system (Langevin et al., 2012).

### 1.1.3. Water-in-Oil microemulsion system

The continuous phase in case of W/O microemulsion is oil accompanied with water droplets that are dispersed and are stabilized by the surfactant molecules. The example of such W/O microemulsions are illustrated in Figure 2.



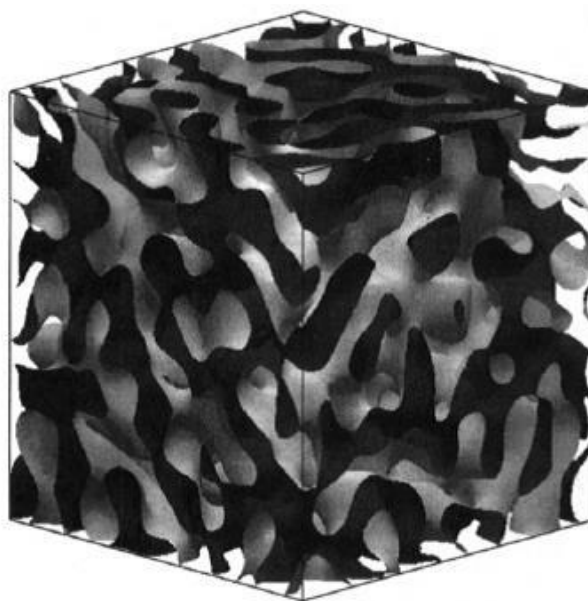
**Figure 2.** Schematic diagram representing the formation of W/O microemulsion system (Langevin et al., 2012; Zech et al., 2010b).

#### 1.1.4. Bicontinuous microemulsion system

The microemulsion areas in the phase diagram of microemulsions, where the structure is complex and which cannot easily be shown as spherical aggregates based on the relative ratios of the constituent components.

In these areas on phase diagram, called as microemulsion, there are several structures that have been reported, like rod-like structure, bicontinuous structures and the formation of the aggregates due to clusters droplet. Moreover, the liquid crystalline phases have also been seen. In roughly equal volumes of water and oil, bicontinuous formations can be seen. A surfactant interfacial coating with a net curvature near to zero separates and stabilises networks of oil and water nanodomains. Figure 3 is a three-dimensional representation of such a bicontinuous structure (Pieruschka & Marcelja, 1994).

The Lamellar phases ( $L\alpha$ -phases) are not always associated with microemulsions, although they do have a significant relationship with them. Dubois and Zemb (2000) have looked through these.



**Figure 3.** Three-dimensional image of a bicontinuous structure (Pieruschka & Marcelja, 1994).

#### 1.1.5. Winsor phases in a microemulsion system

According to Winsor (Winsor, 1948), various types of microemulsion phases co-exist in equilibria and these phases were termed as Winsor phases.

The following are the Winsor phases observed in the microemulsion system:

- 1) Winsor I or oil-in-water microemulsion
- 2) Winsor II or water-in-oil microemulsion



- 3) Winsor III or bicontinuous microemulsion
- 4) Winsor IV or single-phase homogeneous mixture

**1) Winsor I or oil-in-water microemulsion**

In this type of phase, the microemulsion droplets made up of oil (dispersed phase) are encircled by a surfactant layer (often in the merger with a co-surfactant) that permits the formation of internal phase dispersed in water, wherein water is a continuous phase/dispersion medium.

**2) Winsor II or water-in-oil microemulsion**

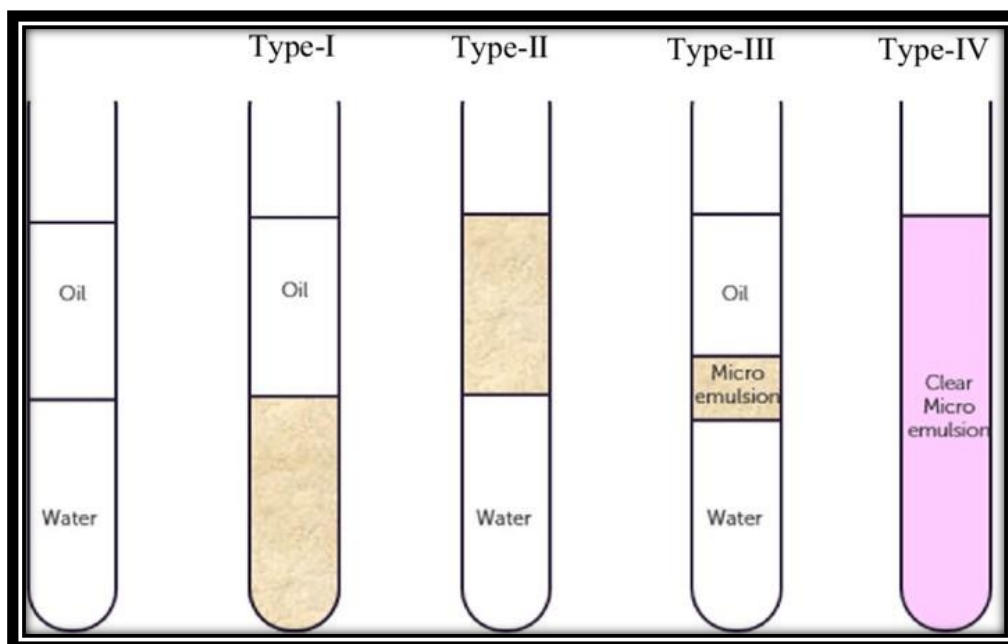
The microemulsion droplets consisting of water (dispersed phase) are constantly ringed by the oil phase (continuous phase/dispersion medium) in this type of microemulsion, which is referred to as “reverse micelles.” The surfactant’s polar head groups are pointing towards the water droplets, while the fatty acid tails are pointing toward the oil phase.

**3) Winsor III or bicontinuous microemulsion**

The amount of water and oil present in this sort of microemulsion system is similar in quantity and exists as a continuous phase, with an irregular flow of oil and water visible. These eventually mix and form a “sponge-phase.” The transitions that occur from o/w to w/o microemulsions pass from this bicontinuous state.

**4) Winsor IV or single-phase homogeneous mixture**

A microemulsion system is a single phase, thermodynamically stable isotropically transparent liquid mixture, consisting of oil, water, and surfactant, sometimes in combination with a co-surfactant.



**Figure 4.** Representation of Winsor phases observed in a microemulsion system (Winsor, 1948; Salleh et al., 2019).

As cited in the various literature studies (Kahlweit, 1999; Kahlweit et al., 1985; Kahlweit et al., 1993; Kahlweit, 1988), usually the microemulsion system comprises of polar water phase, non-polar organic phase (very often *n*-alkanes) and a non-ionic surfactant. It has been proclaimed that the number of surfactants utilised in formulation of the microemulsion system is much higher. The ternary phase behaviour of ionic liquid microemulsion systems is poorly understood, and likewise, the structural variation within the microemulsion phase as a function of surfactant concentration and the temperature is unknown.

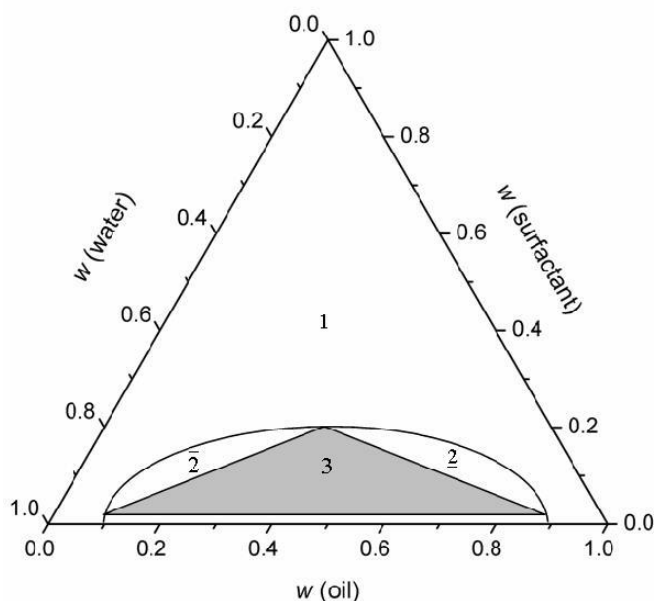
In one of the literature report, it has been reported that, due to change in the interfacial film's curvature, the formulated microemulsion systems changes their microstructure with respect to temperature (Strey, 1994). Hence, the phase diagram of the microemulsion system was constructed and owing to this, the microstructure of a water/*n*-alkanes/ $C_iE_j$  microemulsion system could be recognised (Kahlweit et al., 1985 ; Kahlweit et al., 1988 ; Tessendorf, 2007 ; Strey et al., 1985 ; Kahlweit et al., 1986; Kahlweit, 1999; Kahlweit & Strey, 1987).

However, the studies on the phase behaviour and microstructure of a microemulsion system is increasing progressively (Kazarian et al., 2000; Niga et al., 2010 ; Atkin & Warr, 2007b ; Behera et al., 2009 ; Rai & Pandey, 2014 ; Atkin & Warr, 2007a ; Gao et al., 2009 ; Kusano et al., 2014 ; Ali et al., 2020 ; Islam et al., 2020 ; Zhu et al., 2020 ; Guo et al., 2020; Hejazifar et al., 2020; Langevin et al., 2012 ; Thater et al., 2019 ; Solanki & Patil, 2020 ; Solanki & Patil, 2021). At

first, a ternary microemulsion system consisting of polar ionic liquid; ethyl ammonium nitrate (EAN),  $C_{12}E_3$  as surfactant, and an  $n$ -alkane as oil, namely  $n$ -dodecane or  $n$ -octane was formulated by Thater et.al (2014; 2019), wherein the composition of the coexisting phases from the phase volume and phase densities at a constant surfactant mass fraction were determined. Thereafter, several enhancements have been made by different researchers regarding the formulation of non-aqueous microemulsions even by substituting the water incorporated into conventional microemulsions with other non-aqueous solvents (Li et al., 2005; Zech et al., 2011 ; Thater et al., 2019 ; Solanki & Patil, 2021 ; Chen & Zhao, 2014 ; Anjum et al., 2009; Seth et al., 2007). These neoteric microemulsion systems have gained a lot of research attraction and contemplation from both the theoretical as well as practical points of view (Cheng et al., 2007 ; Malik et al., 2012 ; Xue et al., 2011 ; Mandal et al., 2013).

### 1.1.6. Phase diagrams of microemulsion system

Earlier, the ‘‘Gibb’s triangle’’, was used to study the phase behaviour of three component systems containing water, oil and surfactant as illustrated in Figure 5. The compositions of the added components are expressed in terms of weight, molar or volume fraction. Mostly, it is represented in terms of weight fractions,  $w$ , whereas temperature and pressure are the variables that are always kept constant. The corners of the triangle represent three pure compounds, and the edges of the triangle depict the three binary compositions.



**Figure 5.** Schematic representation of a phase diagram of comprising of water, oil and surfactant depicting the 1, 2 and 3 phase regions (Zech et al., 2010b).

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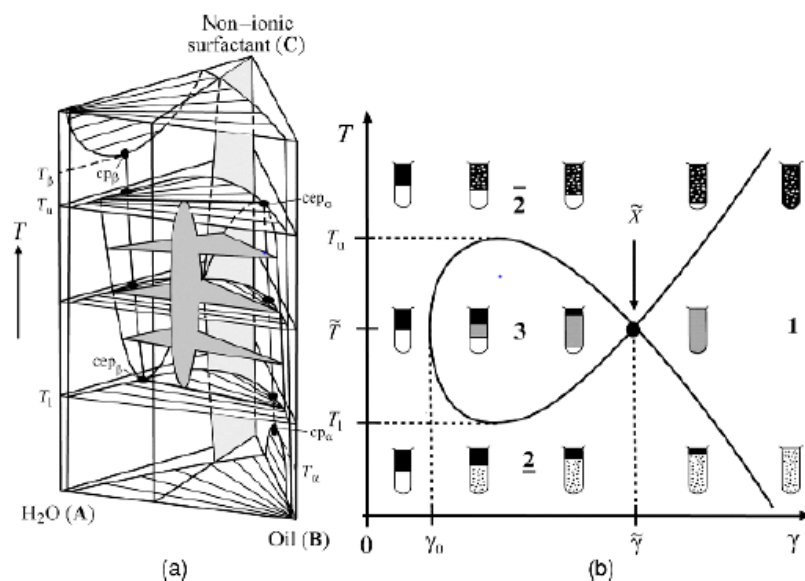
From the above figure, it can be inferred that the lower edge of the diagram represents water-oil mixtures, whereas the left edge shows the water-surfactant mixtures while the right edge represents the oil-surfactant mixtures. Moreover, it can be noticed that compositions of all the three components are observed at the inner side of the triangle. For example, as seen in the figure, the exact point at the middle of the triangle represents equal amounts of water, oil and surfactant (each 33.33 wt%). As we go towards one of the corners, the composition of particular component becomes higher in amount. It is very essential to differentiate the phase behaviour of microemulsion system that are being formed with non-ionic surfactants as well as with ionic ones, due to enormous similarities and few systematic differences.

### 1.1.7. *Microemulsions with non-ionic surfactants*

As already discussed in most of the literature reports, the microemulsion systems are formed with non-ionic surfactants, particularly with  $C_iE_j$  without adding any co-surfactant (Bagha et al., 2016 ; Hejazifar et al., 2020 ; Kahlweit & Strey, 1987 ; Atkin & Warr, 2007a ; Li et al., 2005 ; Mehta & Kaur, 2010; Ali et al., 2007 ; Kahlweit, et al., 1985 ; Rao et al., 2015 ; Gao et al., 2004 ; Zech et al., 2010a ; Prince, 2012; Danielsson et al., 2019 ; Zech et al., 2010b). The primary requirement to study the behaviour of such microemulsion system is to study about its different phases as it depends on various parameters, like temperature, pressure and the nature of each component. Temperature is one of very important variables in non-ionic microemulsions (Hellweg, 2002; Leaver et al., 1995), whereas the effect of the pressure is considered to be less important compared with that of temperature (Kahlweit et al., 1987). The interaction between water and the oligo (ethylene oxide) head group of the surfactant is linked to the temperature dependency of phase behaviour studies of the system containing  $C_iE_j$  type non-ionic surfactant (Olsson & Wennerström, 1994). During the studies, those days water was considered as better solvent for oligo (ethylene oxide) surfactant at low temperatures while it gets worse at high temperatures, leading to form a miscibility gap in the binary water-  $C_iE_j$  system (Saeki et al., 1976; Karlström, 1985). Hence, the phase separation takes place into surfactant rich and a surfactant lean phase at a point called as cloud point.

Furthermore, the phase behaviour of ternary non-ionic microemulsion system was studied by some of the researchers (Kahlweit et al., 1988; Kahlweit et al., 1985; Kahlweit et al., 1989). After their studies, the phase behaviour studies of  $C_iE_j$  surfactants, role of oil and water in a microemulsion was better understood. The temperature dependent phase diagram was described

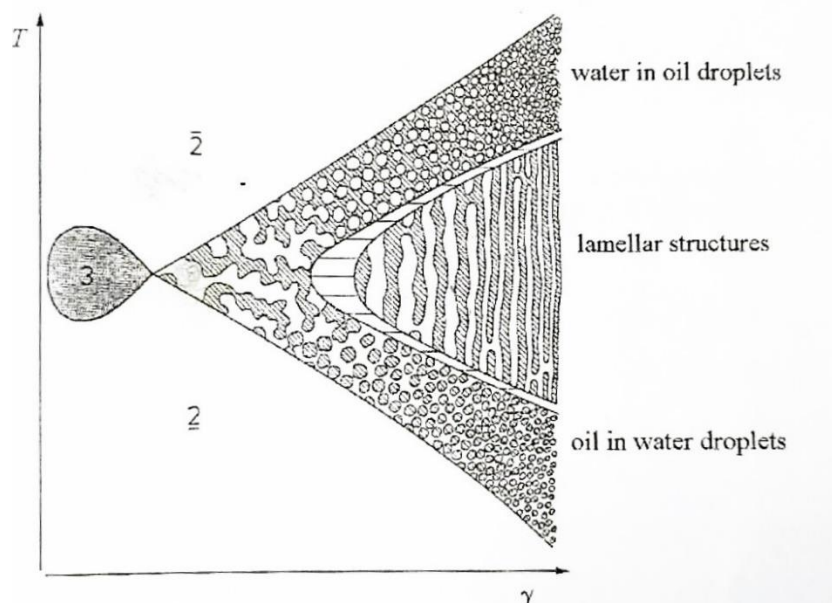
by Kahlweit *et al.* (1985) by stacking the Gibbs triangles vertically into a prism, as seen in Figure 6.



**Figure 6.** An illustrative phase prism involving water, oil and non-ionic surfactant as a function of temperature (Kahlweit *et al.*, 1985; Sottmann & Stubenrauch, 2008).

These phase prisms have a complex structure, making it difficult to comprehend the phase behaviour of the ternary system, containing critical points, critical endpoints, and three phase triangles. It shows that at lower temperatures, the water excess phase is responsible for dissolution of the amphiphiles, i.e., the non-ionic surfactant. As the temperature rises, a nose of water-non-ionic surfactant is observed. Finally, at a lower temperature  $T_l$ , the three-phase triangle can be visible, but it vanishes at an upper critical temperature  $T_u$ . The microemulsion system development shows the Winsor type I phase diagram below  $T_l$  according to the Winsor phase classification. A Winsor type III system emerges between  $T_l$  and  $T_u$ , with a type II system above  $T_u$ . The most essential component in determining the width of the three-phase temperature is the type of the surfactant and oil.

Later, the interpretation of these phase prisms became more difficult and complicated. However, the identification of the experimental phases and their transitions is essential in formulating a microemulsion system. Thus, the study of the phase behaviour of ternary mixtures was conducted to observe the various phases and their transitions in a microemulsion system by various studies by taking the slices of these phase prism and observing it under optical microscope (Atkin & Warr, 2007a; Anjum *et al.*, 2009 ; Solanki & Patil, 2020 ; Solanki Patil ; 2021 ; Thater *et al.*, 2014 ; Thater *et al.*, 2019).



**Figure 7.** An overview of the microstructure of a microemulsion system generated by mixing equal amounts of water and oil (1:1), where a sponge-like phase can be seen in the one-phase area. The lamellar phase ( $L_{\alpha}$ ) appears as the surfactant concentration rises (Tessendorf, 2007).

It has been documented (Tessendorf, 2007) that as the surfactant concentration is increased, the domain size of the microemulsion decreases as the interfacial tension rises. At low surfactant mass fractions in the one phase area, a sponge-like phase dubbed the bicontinuous phase is found, which is separated by the surfactant film and consists of water and oil domains. The bicontinuous phase transitions to the lamellar phase as the surfactant concentration rises. When non-ionic surfactants are concentrated at low temperatures, oil-in-water droplets form, and as the temperature rises, the transition to water-in-oil droplets occurs.

#### 1.1.8. *Microemulsions with ionic surfactants*

The hydrophilic lipophilic character of the non-ionic surfactant can be modified with temperature, as seen in the above section on microemulsions with non-ionic surfactants. As a result, just changing the temperature scale allows you to enfold the entire spectrum of microemulsion droplets from O/W to W/O. The ionic surfactants do not form wider micelles and are strongly hydrophilic. Examples of the ionic surfactants are sodium dodecyl sulphate (SDS) and dodecyl trimethyl ammonium bromide ( $C_{12}TAB$ ) (Sjöblom et al., 1996). However, in the case of ionic surfactants, the size and the structure of the micelles formed do not alter with the temperature and also there is no significant observation for the upper critical solution temperature

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an aqueous solution. It is reported that the hydrophilic lipophilic balance cannot be changed just by tuning the temperature. It has been reported that the microemulsion is not formed just by compensating the hydrophilicity with increasing the hydrocarbon tail of ionic surfactants. Though there is no evidence of a microemulsion system, however due to longer hydrocarbon tails, there is formation of viscous liquid crystalline phases (Ekwall, 1975). Hence, it has been observed that on adding the fourth component in the system containing ionic surfactant, called as co-surfactant which is an alcohol, then only the microemulsion formation takes place. On addition of the double tails to the surfactant molecule, the ability of forming liquid crystalline phases is lowered whereas the hydrophobicity of the surfactant is increased.

However, the ionic double-chain surfactants, namely AOT and dodecyl dimethyl ammonium bromide (DDAB) contributes to a vital type of surfactant class which can form three-component microemulsion system (Zulauf & Eicke, 1979; Eicke & Markovic, 1981; Brown et al., 2012; Ali et al., 2008 ; Chen et al., 1986 ; Fontell et al., 1986 ; Rao et al., 2012b ; Chen et al., 1988 ; Rakshit et al., 2019). The packing parameter, which should be close to 1 (Mitchell & Ninham, 1981), is the most important criterion for the presence of a three-component microemulsion system, and this is achieved by most double-chain length ionic surfactants. Herein, there will no requirement of using a co-surfactant for formulating a microemulsion system (Khan et al., 1989).

On the flip side, generally the addition of a co-surfactant is required for single chain ionic surfactants in order to form a stable microemulsion system (Iglauer et al., 2009; Rakshit & Moulik, 2009). The strong electrostatic interaction of the charged surfactant head groups of ionic surfactants causes changes in the spontaneous curvature as well as a reduction in repulsion when the co-surfactant is added (Carlsson et al., 1999). Generally, low molecular weight aliphatic alcohols are preferred as co-surfactants, but short chain amines can also be used as co-surfactant in formation of microemulsion system with ionic surfactant as an amphiphiles (Rakshit & Moulik, 2009; Wormuth & Kaler, 1987). The major role of the co-surfactant, i.e., alcohol is that it lowers the hydrophilicity of the ionic surfactant and hence the microemulsion is formed. Co-surfactant molecules are contributed between oil, water, and the interface depending on solubility, whereas surfactant molecules are found at the interface between the continuous phase and the dispersed droplet.

Moreover, it has been observed that the smaller droplet size is due to the presence of higher amount of co-surfactant and thus affected by the presence of the co-surfactants. Further, the salt is added in presence of the co-surfactant to obtain a middle phase microemulsion (Hellweg, 2002).

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The phase behaviour of both ionic and non-ionic microemulsions is affected in the same way by the addition of salts. Ionic surfactants, on the other hand, respond to temperature differently than non-ionic surfactants. As a result, it is observed that on increasing the temperature, the hydrophilicity of non-ionic surfactants is increased whereas the solubility of water decreases. Therefore, on increasing the temperature, the ionic surfactants tends to solubilise better in water (Kahlweit et al., 1988). Thus, it can infer that, addition of the co-surfactant and the salt concentration are the essential parameters for this type of microemulsion system where oil, water and ionic surfactants are employed.

## 22.2. *Applications of microemulsion systems*

Microemulsions' outstanding features, such as their excellent ability to solubilize water and oil, large interfacial area, spontaneous production, low interfacial tension, and fine microstructure, make them ideal for a wide range of applications, as summarised in several review papers and books (Langevin et al., 2012 ; Prince, 2012 ; Paul & Moulik, 2001 ; Rakshit et al., 2019 ; Fanun, 2008). Herein, the essential, viable and promising applications mentioned in the literature are summarized in order to explain and highlight their significance and potential.

The dimensions of the microemulsion and its applications is the key reason for its investigation (Paul & Moulik, 2001). It is obvious and noticeable from vast database of literature that the microemulsion systems have been utilized in diverse fields, viz. cosmetics and synthesis of bimetallic nano catalyst (Solanki & Murthy, 2011), semiconductors (Paul & Moulik, 2001), micro colloids (Paul & Moulik, 2001), solar energy conversion (Malik et al., 2012), different chemical reactions including organic as well as inorganic (Paul & Moulik, 2001; Holmberg, 1994; Dutta et al., 2018; Dutta et al., 2003 ; Boon et al., 1986 ; Newington et al., 2007 ; Schwarze et al., 2015), extraction of the metal ions as well as metal recovery (Cadar et al., 2017; Shang et al., 2012; Xia et al., 2008; Vinhal & Cassella, 2019; Kallay et al., 1990; Shan et al., 2005; Mihaly et al., 2010), to remove pollutants from solids and to extract organohalide contaminants (Bonkhoff et al., 1997), solubilization of insoluble salts and organic entities (Wormuth et al., 1990; Bagha & Holmberg, 2013; Paul et al., 2005; Noritomi et al., 2013; Li et al., 2010; Bagha et al., 2016), as microreactors for applications in food industry (Garti, 2003), etc. The uniqueness and versatility of microemulsions have led to their use as templates for synthesis of nanomaterial's owing to flexible tuning of the structure and size of domains (Kahlweit et al., 1987; Schwering et al., 2015; Tessendorf, 2007; Kahlweit, 1988; Kahlweit et al., 1985; Kahlweit et al., 1989).



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Along with the above, the use of microemulsions in enhancement of oil recovery (EOR) represents an encouraging application (Shah, 1981; Mitchell & Ninham, 1981; Ali et al., 2007; Li et al., 2010; Solans & Kunieda, 1996). The data reported indicates that apparently 30 % of an oil reservoir can be extracted by primary recovery and another 20 % can be obtained by EOR (Sjöblom et al., 1996; Solans & Kunieda, 1996).

Furthermore, the important application of a microemulsion system is the synthesis of nanoparticles and nanomaterial's (Mehta & Kaur, 2010; Fanun, 2008; Malik et al., 2012 ; Qiu et al., 2008 ; Schwering et al., 2015 ; Mori et al., 2001 ; Eastoe & Warne, 1996). The W/O type microemulsion systems are employed for this, and it has been proposed that the W/O droplets act as templates and control the nucleation for the particle formation of mostly inorganic nanoparticles (Solans & Kunieda, 1996; Eastoe & Warne, 1996). Further, for synthesis of polymer particles, both W/O as well as O/W microemulsions are utilised in similar manner. In addition, the microemulsion systems are employed in targeted medication delivery systems (Ali et al., 2020; Kogan & Garti, 2006; Kemken et al., 1991; Carlfors et al., 1991), skin care products and agricultural spray formulations (Iglauer et al., 2009). Enzymatic reactions is another research field wherein microemulsion systems are significantly utilized (Schwarze et al., 2015; Hall et al., 2007).

Unlike emulsions, microemulsions are thermodynamically stable due to low interfacial tension between oil-water which is not enough to compensate for the dispersion entropy. The interfacial tension between the two immiscible phases emerges because of the pressure created due to the monomolecular film of surfactant molecules that separates the two immiscible liquids. On the contrary side, the emulsions are thermodynamically unstable liquid-liquid dispersions. The microemulsions have minimal viscosity when compared with that of emulsions. Furthermore, microemulsions are thermodynamically equilibrated systems and the disadvantageous (positive) free energy of increasing the interfacial area is exactly balanced by the favourable (negative) free energy of mixing oil droplets with solvent water.

The entropy of solubilizing the oil and water increases with rise in the number of dissolved droplets, that is equivalent to a reduction in droplet size, and the corresponding contribution to the free energy becomes more and more negative with decreasing the droplet size. As a result, the interfacial tension must decrease in magnitude with increasing droplet size. Hence, microemulsion is elucidated as clear, isotropically transparent, thermodynamically stable dispersions of two immiscible solvents that are stabilized by an interfacial film of a surfactant (often in combination

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with a co-surfactant) which is observed at the liquid-liquid interface (Qiu & Texter, 2008; Cheng, Zhang, et al., 2007 ; Schulman et al., 1959 ; Paul & Moulik, 1997 ; Kahlweit, 1999 ; Lü et al., 2008 ; Rao et al., 2015; Rojas & Koetz, 2010; Rakshit et al., 2019 ; Li et al., 2005 ; Xue et al., 2011).

### **1.3. Room temperature Ionic Liquids (RTILs)**

#### **1.3.1. History of Room temperature Ionic Liquids (RTILs)**

The preliminary substance that would meet our present definition of ionic liquid was first reported in mid-19<sup>th</sup> century in Friedel-Crafts reaction as a separate liquid phase which was named as “red oil.” Despite the fact that the red oil was a salt, it was determined only when NMR spectroscopy was available as tool for characterization (Welton & Wasserscheid, 2002). Decades ago, in the year 1914, the history of ionic liquids commenced, when the physical properties of one of the compound named, ethyl ammonium nitrate [(EAN); m. p. 13–14°C] were reported in the first place by Paul Walden (Walden, 1914). In 1951, Hurley and Wler at Rice Institute in Texas produced AlCl<sub>3</sub>-based ionic liquids as a bath solution for electroplating aluminium (Hurley & Wler Jr, 1951).

In 1963 the U.S. Air Force Academy have shown interest into it and they have reproduced it with the purpose of searching new electrolytes for batteries (Sligh & Brenner, 1963). The first generation of room temperature ionic liquids, named chloro aluminate was successfully formulated by Osteryoung and Wilkes in 1970s (Zawodzinski et al., 1987). The use of ionic liquid, alkylpyridinium tetrahalidoaluminate, [Rpy][AlCl<sub>3</sub>X] as solvent during study of transition metal complexes, was initiated by Hussey and Seddon in 1980s (Holbrey & Seddon, 1999).

The Friedel-Crafts alkylation was the first organic reaction that was carried out in an acidic tetra chloroaluminate ionic liquid and henceforth the ionic liquids have been used as reaction solvents in various organic reactions (Boon et al., 1986). Initially the ionic liquids consisting of aluminium used were difficult to handle as they were highly hygroscopic and air sensitive. Few years later, Wilkes and Zaworotko (Wilkes & Zaworotko, 1992) introduced new air- and water-stable anions, such as halides, [PF<sub>6</sub>]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, and [CF<sub>3</sub>CO<sub>2</sub>]<sup>-</sup> and the problem of handling of ionic liquid was sorted out. After this, ample selections of various ionic liquids have been synthesized and were called as second generation of ionic liquid (IIs). Thereafter, the term “ionic liquid” was used by the researchers. The ionic liquids that melt at and below room temperature are known as room temperature ionic liquids (RTILs). The low melting points of these liquids are a result of the

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intrinsic properties of organic ions in strong electrostatic coupling (Dupont, 2011; Newington et al., 2007; Greaves & Drummond, 2008; Hallett & Welton, 2011; Zech et al., 2010b; Anderson et al., 2002). Due to the low melting point of ionic liquids (ILs), they can act as a solvent for diverse reactions. Ionic liquid based systems offer varying reactivity as well as selectivity when compared with selectivity and reactivity of conventional organic solvents (Dupont, 2011; Newington et al., 2007; Greaves & Drummond, 2008; Hallett & Welton, 2011; Zech et al., 2010b; Anderson et al., 2002; Hao & Zemb, 2007), since the RTILs are made of ions instead of molecules (Stark, 2007; Hao & Zemb, 2007; Greaves & Drummond, 2008; Freemantle, 1998). Generally, the positive ions and the negative ions of RTILs are organic and inorganic respectively (Zech et al., 2010a; Marsh et al., 2004; Rogers, 2003; Pramanik, Sarkar et al., 2011; Pramanik, Ghatak et al., 2011).

The synthesis of RTILs of desired property is practicable by simply making some adjustments in cationic and anionic constituents that can be regulated as per the required properties that enable the dissolution of many sparingly soluble substrates. Hence, they are considered designer solvents (Pramanik, Ghatak, et al., 2011; Atkin & Warr, 2007b; Freemantle, 1998; Hao & Zemb, 2007; Wei et al., 2003 ; Rao et al., 2012a ; Fletcher & Pandey, 2004 ; Welton, 1999 ; Brown et al., 2012). In addition to this, ionic liquids are providing enormous freedom at the interface of chemistry with the life sciences as well viz. role as solvent in enzymatic reaction (van Rantwijk & Sheldon, 2007) as well as whole-cell biocatalysis, (Bräutigam et al., 2007; Pfruender et al., 2006) and as stabilizing media for protein (Fujita, 2005).

Further, their potential applications in the field of pharma industries as active pharmaceutical ingredients as well as in studies of biochemical sciences (Hough et al., 2007) have been explored. As it is a challenging and a crucial mechanism to deliver environmentally safer synthetic chemicals with enhanced performance, the design of the chemicals as well as its structure reactivity plays an important role (Freemantle, 1998; Atkin & Warr, 2007b; Hao & Zemb, 2007). These are ingrained in the Twelve Principles of Green Chemistry (Anastas & Kirchhoff, 2002), which strengthens the new advancement for creating innovative solutions to promote the older ones (Poliakoff et al., 2002). There are noteworthy results observed with the room temperature ionic liquids as it satisfies all the conditions for better environmental sustainability. The room temperature ionic liquids (RTILs) have become a leading scientific discipline which was already bloomed in the last two decades. On one hand, researchers have formulated non-aqueous microemulsions by substituting the water incorporated into the conventional microemulsion system with some other anhydrous solvents (Gao et al., 2004; Atkin & Warr, 2007a; Aki et al.,

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2001; Araos & Warr, 2008; Thater et al., 2011; Thater et al., 2014; Velasco et al., 2006; Langevin et al., 2007; Thater et al., 2019; Araos & Warr, 2005 ; Li et al., 2007 ; Schubert et al., 1993).

On the other hand, due to environmental concerns, researchers are in quest for alternatives to organic solvents. Being environmentally safe, a neoteric solvent, called as room temperature ionic liquids (RTILs) were used for the replacement of conventional volatile organic solvents that had resulted into significantly less evaporation of volatile organic compounds into the environment (Zheng & Eli, 2009; Hao & Zemb, 2007 ; Pramanik, Ghatak, et al., 2011 ; Anjum et al., 2009 ; Porada et al., 2011 ; Sun et al., 2014; Welton, 1999; Marsh et al., 2002).

Room temperature ionic liquids (RTILs) continue to be a great source of interest and is gaining more attention amongst the researchers in diverse areas of academic and industrial fora (Rakshit et al., 2019 ; Pramanik et al., 2011 ; Marsh et al., 2002 ; Marsh et al., 2004; Zech et al., 2009; Atkin & Warr, 2007b; Atkin & Warr, 2007a; Solanki & Patil, 2020; Freemantle, 1998; H. Gao et al., 2004; Aki et al., 2001; Liu et al., 2009). One such research area of interest to researchers is use of room temperature ionic liquids (RTILs), to formulate a microemulsion system wherein ionic liquid has been efficiently utilized as an alternative for either water or organic solvent.

These room temperature ionic liquids are immiscible with either water or nonpolar organic solvents (Behera et al., 2009; Rai & Pandey, 2014; Atkin & Warr, 2007a; Yanan Gao et al., 2009; Kusano et al., 2014; Rao et al., 2012a; Hallett & Welton, 2011; Thater et al., 2014; Thater et al., 2019; Rai & Pandey, 2014; Mandal et al., 2013; Porada et al., 2017). Furthermore, the property of the room temperature ionic liquids (RTILs) is changed in systematic and controlled manner, by adjusting the length of the alkyl groups that are incorporated into the cation. As a result, during the formulation of a microemulsion system, RTILs can be utilised as either hydrophilic or hydrophobic solvents (Porada et al., 2017; Han, 2005; Atkin & Warr, 2007a; Gao et al., 2004; Ghosh et al., 2013).

The physicochemical properties of the ionic liquids, especially room temperature Ionic Liquids (RTILs), serves them as excellent candidates for potential applications (Rogers & Seddon, 2003; Earle et al., 2000). In industry, around 600 traditional solvents are used, compared to at least 106 simple IIs (Plechkova & Seddon, 2008). The brief comparison of the organic solvents and the ionic liquids is discussed in the given table.

**Table 1.** A quick comparison of organic solvents with ionic liquids.

| Property           | Organic solvents (o.s.)          | Ionic liquids                       |
|--------------------|----------------------------------|-------------------------------------|
| Number of solvents | > 10 <sup>3</sup>                | > 10 <sup>6</sup>                   |
| Flammability       | Frequently flammable             | Non-flammable in most cases         |
| Vapor pressure     | Exceptional is usually the case. | Negligible                          |
| Cost               | Commonly inexpensive             | 2-100 times more powerful than o.s. |
| Chirality          | Scarce                           | Adjustable                          |
| Solvation          | Weakly solvating                 | Strongly solvating                  |
| Catalytic ability  | Unusual                          | Common and adaptable                |
| Recyclability      | Green is a must-have             | It's an economic need               |
| Viscosity / mPa s  | 0.2 – 100                        | 22 – 40000                          |

Here, the table describes the properties of the organic solvents that are compared with IIs. Such a comparison helps in understanding the advantages and disadvantages of the ionic liquid's usage. IIs can be utilised as media in extraction procedures (Blanchard et al., 1999) and can also substitute traditional organic solvents in chemical reactions or catalysis (van Rantwijk & Sheldon, 2007; Pârvulescu & Hardacre, 2007). IIs are also being used in a variety of other industrial applications, including dye-sensitized solar cells, lubricant formulations, and lithium-ion battery additives (Plechkova & Seddon, 2008).

### ***1.3.2. Advantages of Room Temperature Ionic Liquid (RTILs)***

Owing to the versatile properties as solvents, Room Temperature Ionic Liquid (RTILs) are used as a green alternative for various applications in many multidisciplinary areas of chemistry and industries such as electrochemistry, biopolymers, molecular self-assembly, electrolytes in batteries and solar cells, as surface coatings and lubricating agents, as media for catalytic reactions, also as solvents for chemical synthesis and in separation technologies (Dantas et al., 1984; Friberg & Liang, 1987; Rico & Lattes, 1987; Saidi et al., 1990; Ray & Moulik, 1994).

The following are some of the key points of interest over traditional organic solvents, which make them environmentally more perfect (Boon et al., 1986; Newington et al., 2007; Schwarze et al., 2015).

- Room Temperature Ionic Liquid (RTILs) are environment-friendly solvents having near-zero vapor pressure.
- They have potentiality to solubilize various kinds of organic, inorganic, polymeric and organometallic materials and possess broad liquidous range.
- Ability to reproduce infinite ionic liquid (ILs) having their own characteristic properties, by connecting distinctive anions and cations.
- RTILs possess high thermal stability (300°C or more).
- Many of the ionic liquids (ILs) are extremely polar and it involves loosely coordinating bulky ions.
- As they are non-volatile as well as non-flammable at elevated temperatures, they do not evaporate.
- RTILs have excellent thermal conductivity wide electrochemical window.
- RTILs are immiscible with many of the organic solvents and hence provide a non-aqueous, polar alternative for two-phase systems.
- They act as solvent and catalyst for specific chemical reactions.
- Additionally, hydrophobic RTILs can also be utilized as immiscible polar stages with water.
- As compared to other organic solvents, RTILs can be recycled straightforwardly and reused consequently urging to decrease the waste.

### ***1.3.3. Synthesis of Room Temperature Ionic Liquid (RTIL), Ethylammonium nitrate [EAN] ( $C_2H_8N_2O_3$ , purity $\geq 97.0\%$ ):***

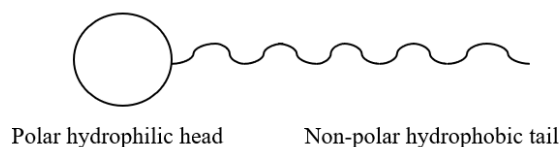
In the present study, the polar ionic liquid used, i.e. ethyl ammonium nitrate (EAN) (M.P. = 12°C) was synthesized in our laboratory by reacting equimolar amounts of ethylamine (70% water solution) and concentrated nitric acid (69.5% water solution) to produce an aqueous solution (Garlitz et al., 1999). The product is a viscous solution of the ionic liquid in water. Upon completion of the reaction, an excess of ethylamine solution is added until the pH becomes plainly basic ( $\approx 10-12$ ). This ensures a stoichiometric reaction between the two species. Excess water was eliminated by first purging the EAN solution with nitrogen; whereas excess amine removal was carried out via rotary evaporation taking care as not to heat the water bath over 40°C, as it helps

reduce the risk of degradation of the ammonium moiety (Atkin & Warr, 2007a). This caution also leads to minimizing the water content to negligible amounts and prevents the formation of nitrous oxide impurities that, if present, produce a yellow discoloration. 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF<sub>6</sub>] and 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF<sub>4</sub>] are the other two room temperature ionic liquids (RTILs). We have procured these RTILs from Sigma Aldrich, USA.

#### 1.4. Surfactants

There is a wide category of surface-active agents, called as surfactants, which have been used in day-to-day life in various applications viz. household and personal care products, as well as drug dosage forms. Surfactants lower the surface tension and have tendency to adsorb at the interface/surface even when present in low concentrations. They are amphiphilic molecules, and the molecular structure comprises of water-soluble head (hydrophilic or lipophobic) and a water insoluble tail (hydrophobic or lipophilic) in the same molecule. The structural representation of surfactant molecule is represented in Figure 7.

Generally, the hydrophobic water-insoluble tail is branched or linear long-chain hydrocarbon having varying chain length of 8-18 carbon atoms, which is connected to a polar head group of a surfactant which either ionic or non-ionic (Rosen et al., 2004; Tadros, 2006; Kronberg & Lindman, 2003). The fluorocarbon or silicone chain can also be used as a hydrophobic water-insoluble tail part instead of the hydrocarbon chain. Hence they act as detergents (cleansers), providing removal of soil from a substrate; solubility enhancers, enabling direct absorption of substances into micelles; and/or stabilizers (often called emulsifiers), assuring stability of various colloidal systems, foaming and wetting agents, and so on (Shah et al., 2011; Bagha et al., 2016; Söderlind et al., 2003; Weerawardena et al., 2000).



**Figure 8.** Structural representation of a surfactant.

As the surfactant dissolves in an aqueous environment, the hydrophobic tail interacts weakly with the water molecules by virtue of the van der Waals forces. On the flip side, the polar

hydrophilic head interacts strongly with the water molecules due to dipole-dipole or ion-dipole forces. Therefore, surfactants are said to be water soluble as it has strong interaction with the water molecules (Tadros, 2006). However, the much weaker van der Waals forces breaks the much stronger hydrogen bonds between water molecules. The surfactants are therefore forced to the interfaces of the system, where the hydrophobic tails get oriented in a way to keep minimum contact with water (Rosen, et al., 2012; Tadros, 2006).

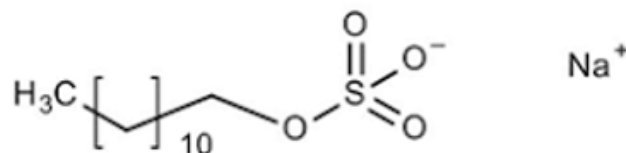
## Classifications of Surfactants

Depending on the charge of the polar head group, surfactants are categorized into four major groups. They are as follows:

### 1.4.1.1 Anionic surfactants (negatively charged)

These types of the surfactants involve anionic (negatively charged ions) on the polar hydrophilic head group such as sulfonate, sulphate, carboxyl or phosphate along with positive charge counter ion such as potassium, sodium, calcium, ammonium and various protonated alkyl amines. They are excellent alternative for household purposes as they castigate varied ranges of the soil. Generally, the anionic surfactants are utilised in manufacturing of cleaning and detergent products as it is economical and valuable. In addition to this, they are also used in other industries such as textiles, agriculture, and construction for applications such as dyeing, bleaching, demulsifying, corrosion prevention and as a fuel additive.

One of the examples of the anionic surfactant containing anionic charge on polar hydrophilic head group is Sodium Lauryl Sulphate (SLS) and the structure is represented in Figure 8.



**Figure 9.** Structure of Anionic surfactant: Sodium Lauryl Sulphate (SLS)

### 1.4.1.2 Cationic Surfactants (positively charged)

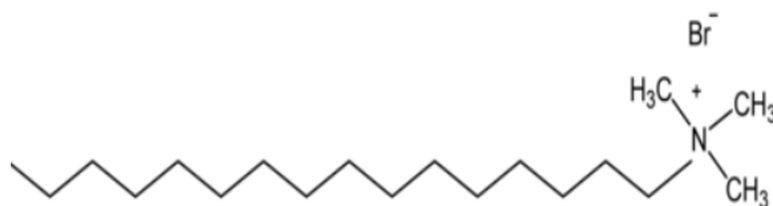
Cationic surfactants are usually quaternary ammonia compounds with positively charged surface-active moieties on polar hydrophilic head group and negative charge as counter ion. Long



chain amines and quaternary ammonium salts are the two most frequent forms of cationic surfactants. The quaternary ammonium salts based cationic surfactants are not pH sensitive as compared to that of long chain amines.

Cationic surfactants are considered as an ideal surfactant for some of the products like fabric softeners, antistatic agents, anticorrosion agent, flotation collector, antiseptic agents, anticaking agents, bactericides, and hair softener because of its outstanding adsorption properties.

Figure 9 represents one of most used cationic surfactants i.e., Cetyltrimethylammonium bromide (CTAB).

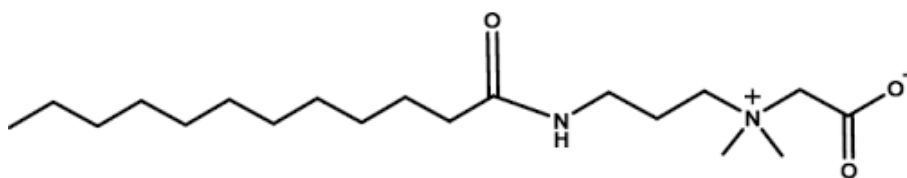


**Figure 10.** Structure of Cationic surfactant: Cetyl trimethylammonium bromide (CTAB)

#### 1.4.1.3 Amphoteric or Zwitterionic Surfactant (both positively and negatively charged)

The surfactants that carry dual charge (both positive and a negative charge) on their hydrophilic end, is termed as Amphoteric or Zwitterionic surfactants. The zwitterionic net charge is zero because the dual charges cancel each other out. These positive and negative charges can either be permanent or it can be dependent on the pH value of the given solution and it will determine how the amphoteric surfactants reacts. Here, usually the cationic component is either an amine or a quaternary ammonium cation, whereas the anionic part is mainly a carboxylic, sulphuric, or phosphoric acid. They are still progressing as they are newest to the market, and in the last few years they have come up with a numerous remarkable quality that includes biodegradability, resistance to hard water, acting as an emulsifier. Amongst the other surfactants, these qualities make amphoteric surfactants most appropriate for using it in shampoos, dyes, pharmaceuticals and many more. Amphoteric surfactants like betaines offer good detergency coupled with high foaming capacity and mildness to the skin

Example of this type is Cocamidopropyl betaine, and the structure is shown in Figure 10.



**Figure 11.** Structure of Amphoteric Surfactant: Cocoamidopropyl betaine.

#### 1.4.1.4 Non-ionic surfactant (No Charge)

This type of surfactant on dissolution in water, do not ionise, as it does not possess any charges. Therefore, they are highly stable and experience limited reaction towards acids and strong electrolytes. Owing to its better emulsifying qualities compared to that of anionic surfactant, they are beneficial for removing both oily and organic dirt. Almost 50% of surfactant production is attributed towards non-ionic surfactants. Hence, they are present in perfumes as well as in beauty products like make-up where they assist in diffusing the pigment across the skin. In addition to this, they are mainly used as industrial cleansers, dispersants, agrochemical emulsifiers, stabilizers, sanitizers, wetting agents and defoaming agents. They are repeatedly used as an emulsifier in non-polar systems containing oil and water and also as a solubilisation agent for oil in water. Polyglycerol alkyl ethers, glucosyl dialkyl ethers, crown ethers, ester-linked surfactants, polyoxyethylene alkyl ethers, Brij, Spans (sorbitan esters), and Tweens (Polysorbates), Triton X-100, and others are examples of non-ionic surfactants.

The amount of surfactant needed to solubilize water in non-polar oil, resulting in a one-phase microemulsion system, is determined by two factors: (a) the micelles' ability to assimilate water, and (b) the amount of surfactant employed for micellization (Aveyard et al., 1992). Moreover, there are various reports wherein they have utilized conventional non-ionic  $C_{12}E_7$  type of surfactants to formulate aqueous as well as non-aqueous microemulsion systems (Friberg et al., 1984; Zech et al., 2010a; Atkin & Warr, 2007a; Anjum et al., 2009; Gao et al., 2008; Gao et al., 2007; Fukuto et al., 2012). The use of a typical surfactant, Triton X-100, for the formulation of a microemulsion system containing [Bmim][PF<sub>6</sub>]/TX-100/water has been effectively proven in the literature (Li et al., 2005; Bilgili et al., 2016; Burauer et al., 2003; Gao et al., 2005; Rao et al., 2012a). The phase behaviour of a ternary system including ethylene glycol (EG), 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF<sub>6</sub>], and TX-100 was determined at 30.0°C in one of the studies (Cheng et al., 2007). The researchers compared H<sub>2</sub>O/TX-100/IL microemulsions to EG/TX-100/IL microemulsions and discovered that non-ionic conventional surfactants were the driving forces for the production of microemulsion systems.

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As reported in various literature studies wherein the non-ionic conventional surfactant was employed for formulation of a microemulsion system, it has been observed that the amount of surfactant used were higher. In the present thesis, we have brought forward this problem and to reduce the use of the surfactant along with considering the environmental factors into account, we have formulated a microemulsion system using non-ionic sugar-based surfactant.

#### **1.4.1.5 Alkyl Polyglycoside non-ionic sugar-based surfactants**

Over the past years, researchers aimed at the development of new amphiphilic molecules that have brought advancement on several fronts. They have designed and synthesized it in such a manner to incorporate it in certain structural manifest that is borrowed from nature, such as sugars, peptides and/or nucleic acid sequences, which has optimized their performance and led to a range of novel applications (Luk & Abbott, 2002). Natural origin, dermal tolerability and biodegradability are the fundamental criteria for novel surfactants. Sugar-based surfactants represent a growing market. Among these, Alkyl Polyglycosides (APGs), produced from vegetable oils and starch, are in demand. They are claimed to possess advantages over other classes of surfactants in terms of dermatological and ocular safety, biodegradability, wettability, foam production, and cleaning ability. These desirable properties have attracted considerable interest from the research community.

Alkyl glycosides constitute a very potent group of nonionic surfactants. On commercial scale, alkyl glycosides are available as alkyl polyglycosides (APG). The industrial production of these surfactants is usually based on Fischer glycosylation, where a fatty alcohol (C<sub>8</sub>–C<sub>16</sub>) is reacted with a carbohydrate (typically starch or glucose) through a condensation reaction. The Fischer process gives a very complex mixture of alkyl glycosides due to the polyfunctionality of carbohydrates (Steytler et al., 2001; Svensson & Adlercreutz, 2011). Alkyl polyglycoside surfactants also known as sugar-based non-ionic surfactants have lately been of particular interest from viewpoint of both fundamental science and industrial applications owing to their excellent dermatological compatibility and biodegradability in addition to their exceptional physical properties such as low surface tension and good electrolyte tolerance (von Rybinski & Hill, 1998) (Hill et al., 2008). The rationale behind phase studies of microemulsion systems that are derived from alkyl glycoside or sugar-based (C<sub>n</sub>G<sub>m</sub>) surfactants instead of the conventional polyoxyethylene ether non-ionic (C<sub>i</sub>E<sub>j</sub>) surfactants is that they have different physico-chemical properties, although they are both non-ionic surfactants. APGs are low in toxicity and biodegradable and they are used in a wide range of applications especially within detergency and

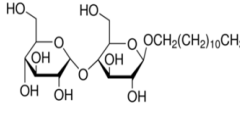
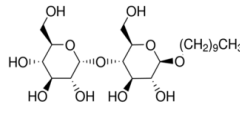
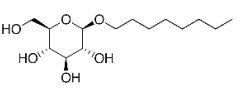
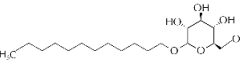
personal care (Messinger et al., 2007; von Rybinski & Hill, 1998; Hill et al., 2008; Balzer, 1991; Sierra & Svensson, 1999; Li et al., 2019). The physico-chemical properties of aqueous solutions of sugar-based non-ionic surfactants are not temperature sensitive whereas of  $C_iE_j$  type surfactant are temperature-sensitive.

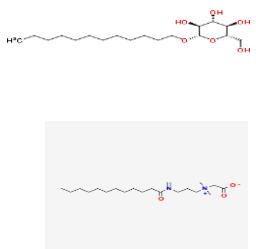
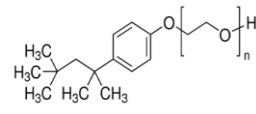
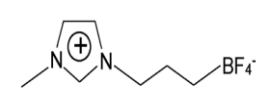
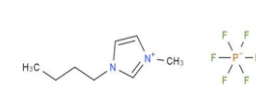
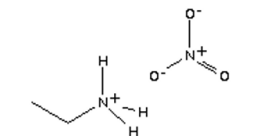

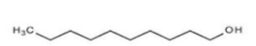
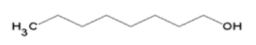
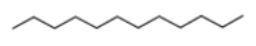
## 1.5. Materials and Methods

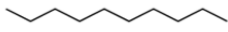
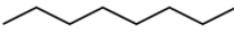
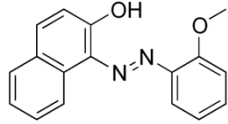
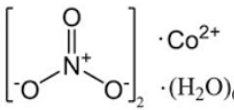
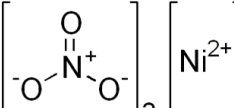
### 1.5.1. Materials

The materials utilized in the present thesis are represented in Table 2.1 below along with their CAS number, supplier and their purity.

**Table 2.** Chemical component used in the present thesis.

| Component  | CAS Number  | Abbreviation                            | Structure  | Manufacturer        | Purity  |
|--|-------------|---|--|---------------------|---------|
| <i>n</i> -Dodecyl $\beta$ -D-maltoside                             | 69227-93-6  | $\beta$ -C <sub>12</sub> G <sub>2</sub> |   | Sigma Aldrich, USA. | ≥ 98%   |
| <i>n</i> -Decyl- $\beta$ -D-maltoside                              | 82494-09-5  | $\beta$ -C <sub>10</sub> G <sub>2</sub> |  | Sigma Aldrich, USA. | ≥ 98%   |
| PLANTACARE <sup>®</sup> 810<br>– UP<br>(caprylyl/capryl glucoside) | 68515-73-1  | UP - 810                                |  | BASF, Germany       | ≥ 98%   |
| PLANTACARE <sup>®</sup> 818–<br>UP<br>(Coco-Glucoside)             | 141464-42-8 | UP - 818                                |  | BASF, Germany       | ≥ 97.0% |

|  |             |                          |  |                           |         |
|--|-------------|--------------------------|--|---------------------------|---------|
| PLANTACARE®K-55<br>(Lauryl Glucoside (and)<br>Cocamidopropyl<br>Betaine) | 110615-47-9 | -                        |    | BASF,<br>Germany          |         |
| Triton X-100   | 9002-93-1   | TX-100                   |    | Sigma Aldrich,<br>USA.    | ≥ 97.0% |
| 1-butyl-3-<br>methylimidazolium<br>tetrafluoroborate                     | 174501-65-6 | [Bmim][BF <sub>4</sub> ] |    | Sigma Aldrich,<br>USA.    | ≥ 97.0% |
| 1-butyl-3-<br>methylimidazolium<br>hexafluorophosphate                   | 174501-64-5 | [Bmim][PF <sub>6</sub> ] |   | Sigma Aldrich,<br>USA.    | ≥ 97.0% |
| Ethylammonium Nitrate  | 22113-86-6  | [EAN]                    |  | Synthesized in<br>our Lab |         |
| 1-dodecanol  | 112-53-8;   | -                        |  | Sigma Aldrich,<br>USA.    | 99%     |
| 1-decanol  | 112-30-1    | -                        |  | Sigma Aldrich,<br>USA.    | 99%     |
| 1-octanol  | 111-87-5    | -                        |  | Sigma Aldrich,<br>USA.    | 99%     |
| Dodecane   | 112-40-3    | -                        |  | Sigma Aldrich,<br>USA.    | 99%     |

|                            |            |  |   |                     |     |
|----------------------------|------------|--|---|---------------------|-----|
| Decane                     | 124-18-5   | -  |   | Sigma Aldrich, USA. | 99% |
| Octane                     | 11-65-9    | -  |   | Sigma Aldrich, USA. | 99% |
| Sudan Red Dye              | 1229-55-6  | -  |   | Alps Industries Ltd | -   |
| cobalt nitrate hexahydrate | 10026-22-9 | $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ |   | Sigma Aldrich, USA. | 99% |
| nickel nitrate hexahydrate | 13478-00-7 | $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$   |  | Sigma Aldrich, USA. | 99% |
| potassium thiocyanate      | 333-20-0   | KSCN   | $\text{K}-\text{S}\equiv\text{N}$   | Sigma Aldrich, USA. | 99% |

### 1.5.2. Experimental techniques

#### 1.5.2.1 Construction of Phase diagrams for microemulsion formulation

Identification of the experimental phases and their transitions is essential in formulating a microemulsion system. Thus, the study of the phase behaviour of ternary mixtures was conducted to observe the various phases and their transitions in a microemulsion system. In the present work, to formulate a microemulsion system, we have weighed an equal portion of polar/non-polar solvents in a ratio of 1:1, by varying the surfactant mass fraction in the test tubes. The test specimens were sealed and placed in a transparent thermostat water bath (Julabo ED-5 heating circulator with an open bath). Subsequently, through visual examination of the phase limits, various phases ( $1\phi$ ,  $2\phi$  and  $3\phi$ ) were resolved at different temperatures ranging from 30 to 60°C.



**Figure 12.** Pictorial representation of a thermostat water bath for phase studies of microemulsions (Anjum et al., 2009; Tessendorf, 2007).

As shown in Figure 13, the distinctive fish-shaped diagram is formed by these phase boundaries, which is in accordance with the data reported in the literature (Atkin & Warr, 2007a; Solanki & Patil, 2020; Solanki & Patil, 2021; Anjum et al., 2009). The phase behaviour was investigated depending on the temperature and mass fraction of the surfactant,  $\gamma$ .

When ionic liquid acts as a non-polar solvent in the solvent mixtures, the weight fraction of ionic liquid (IL) ( $\alpha$ ) is calculated by,

$$\alpha = \frac{m_{\text{Ionic Liquid}}}{m_{\text{Ionic Liquid}} + m_{\text{H}_2\text{O}}} \quad (1)$$

and the weight fraction of the surfactant ( $\gamma$ ) in the total system is calculated by,

$$\gamma = \frac{m_{\text{surfactant}}}{m_{\text{Ionic Liquid}} + m_{\text{H}_2\text{O}} + m_{\text{surfactant}}} \quad (2)$$

Whereas, when ionic liquid acts as a polar solvent in the system, the weight fraction of the ionic liquid (IL) ( $\alpha$ ) is calculated by,

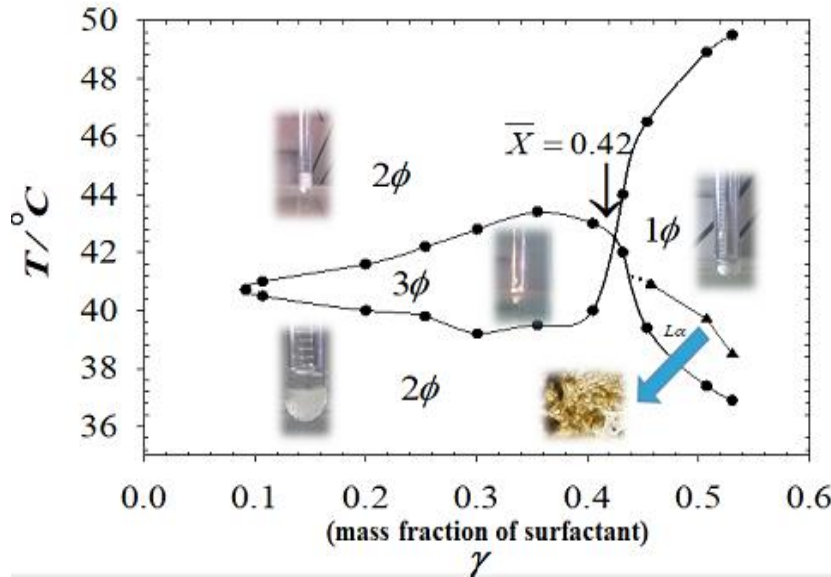
$$\alpha = \frac{m_{\text{Ionic Liquid}}}{m_{\text{Ionic Liquid}} + m_{(n\text{-Alkanes})}} \quad (3)$$

and the weight fraction of the surfactant ( $\gamma$ ) in this system is calculated by,

$$\gamma = \frac{m_{\text{surfactant}}}{m_{\text{Ionic Liquid}} + m_{\text{Oil (n-Alkanes)}} + m_{\text{surfactant}}} \quad (4)$$

The quaternary mixed sample compositions are specified as the mass fraction of a surfactant ( $\gamma$ ) in the total mixture as,

$$\gamma = \frac{m_{\text{surfactant}}}{m_{IL} + m_{H_2O} + m_{\text{co-surfactant}} + m_{\text{surfactant}}} \quad (5)$$



**Figure 13.** Fish-shaped phase diagram obtained by cutting a vertical section through the phase prism for equal amounts of polar and non-polar solvents, where one-phase microemulsion is marked by  $1\phi$ , two-phase is denoted by  $2\phi$  whereas three-phase is represented as  $3\phi$ . The surfactant's mass fraction in the whole mixture is represented by  $\gamma$  (Atkin & Warr, 2007a). The point ( $\bar{X}$ ) denotes the amount of surfactant utilised in the solubilization of two immiscible liquids, at which microemulsion formation takes place.

The characteristic values of a microemulsion system are determined by the dimensions and the position of the three-phase fish-shaped body as shown in Figure 1. The maximum temperature interval over which the three phases occur is defined as  $\Delta T = T_u - T_l$  where  $T_u$  and  $T_l$  are the maximum and minimum temperatures at which the three phases appear, respectively. At the mean temperature,  $\bar{T}$ , the effectiveness of the surfactants to solubilize both polar/non-polar solvents, i.e., water and oil is magnified. As the surfactant concentration is increased, the surfactant-rich middle phase increases in volume, eventually producing a single phase. The microemulsion is said to be balanced at this point in the phase diagram,  $\bar{X}$ , with zero mean curvature of the surfactant layer, and the bicontinuous microemulsion forms. Surfactant efficiency, or the minimal surfactant concentration required to solubilize the two immiscible liquids, is denoted by  $\bar{X}$ .  $\bar{T}$  is defined as



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the phase inversion temperature. Along with this, we have also determined the characteristic parameters ( $\bar{T}$ ,  $\bar{X}$ ,  $\Delta\gamma$ ).

### **1.5.2.2 Polarization Microscopy**

The formulated microemulsion system samples were placed on a glass slide covered with a coverslip for studying the optical microscopy. The presence of liquid crystalline phases in the microemulsion systems was observed between crossed polarizers under a Leica DM-750 P polarization microscope.

### **1.5.2.3 Electrical conductivity measurements**

Electrical conductivity measurements of a typical w/o or o/w microemulsion system provide information on the percolative behaviour of the system (Borkovec et al., 1988 ; Naouli et al., 2011; Jeirani et al., 2013; Chen & Zhao, 2014). The electrical conductivity measurements were carried out using Hanna (HI5321-02) research grade benchtop EC/TDS/resistivity/salinity meter capable of millesimal measuring resolution of conductivity with an extended range from 0.001  $\mu\text{S}/\text{cm}$  to 1 S/cm. The deionized double distilled water having conductivity (5.2– 6.1)  $\mu\text{S}\cdot\text{cm}^{-1}$  is used for all experimental solutions.

It was observed that for typical w/o systems, the electrical conductivity values remain low up to a certain fraction of water, and increases by two to three orders of magnitude once the water reaches the threshold concentration ( $w_t$ ) in the system, at a constant temperature, yielding a sigmoidal electrical conductivity–water content (volume, mass) profile (Dogra & Rakshit, 2004). The electrical conductivity measurements of the microemulsion systems were performed to gain insights regarding a peculiar feature of the system, i.e. dynamic percolation (structural transitions from water in ionic liquid dispersion through bicontinuous microstructure towards the water in ionic liquid microemulsion) (Jeirani et al., 2013).

### **1.5.2.4 Solubilization of dye using microemulsions**

UV-Visible spectroscopy measurements were carried out to study the solubilization of an otherwise water-insoluble organic dye using Perkin- Elmer Lambda-35 UV-Visible Spectrophotometer. The instinctive dissolution of an insoluble materials into a solvent that creates thermodynamically stable isotropic solution with the use of surface-active agents is called as solubilization. Since, there has been an interest manifested towards the application of various dyes due to their bio-degradability and higher compatibility with the environment (Bagha et al., 2013).

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The natural dyes are generally found to be environmentally friendly and have many advantages over synthetic dyes with respect to the production and application (Paul et al., 2005; Bagha & Holmberg, 2013; Wormuth et al., 1990; Petcu et al., 2016; Dil et al., 2017). A dye is usually a coloured organic compound that is used to colour a substrate, e.g., fabric, paper or plastic in a permanent way. Thus, it should be able to resist outer forces which can be caused by washing, rubbing etc. The dye must possess some specific groups that create bonds to the substrate. The dye has an affinity to the substrate to which it is applied to and is applied in an aqueous solution (Wormuth et al., 1990). The dye adsorption mainly depends on the surface and bulk properties of the fibre, the molecular structure of dyes, and the medium in which the dye molecules are dispersed or dissolve (Dantas et al., 2004).

It has been extensively studied in various literature about the solubilization of the dye into a micellar surfactant systems and microemulsion systems (Wormuth et al., 1990; Paul et al., 2005; Dantas et al., 2004; Friberg et al., 1992; Hosseinzadeh et al., 2008). The process named as solubilization of water-insoluble materials in the microemulsion system is implemented in many of the industries viz. detergency, emulsion polymerization, enhanced oil recovery (Nazar et al., 2011), drug delivery and textile dyeing (Carlfors et al., 1991; Kemken et al., 1991; Kogan et al., 2006; Hosseinzadeh et al., 2008; Solans et al., 1996). Microemulsions have been proposed as a media for solubilising inkjet inks (Nir et al., 2010; Noritomi et al., 2013; Paul et al., 2005) and also as a carrier in low temperature dyeing of polyester (Petcu et al., 2016). The ability of dye to get solubilised in micelles (Mitchell et al., 1981; Wormuth et al., 1990; Paul et al., 2005), vesicles (Mitchell et al., 1981; Evans et al., 1981), reverse micelles (Evans et al., 1983; Anderson et al., 2003, microemulsion precursors and microemulsion-based systems (Wormuth et al., 1990; Paul et al., 2005) has been studied previously. However, there is no clear indication in the literature regarding the dye ability or the dyeing mechanism of a dye solubilised in o/w microemulsions. Moreover, it is still not very clear, whether the solubilised dye in o/w microemulsion is transferred directly from the oil-swollen micelles to the substrate or a breakdown of these micelles is needed in order to release the dye into the dye bath so that it can interact with the substrate later.

Some of the natural dyes used in various industrial processes are water soluble whereas others are not. These water insoluble dyes can create problems during their application, leading to non-uniform and uneven dyeing. In this context, it is interesting to know whether microemulsion systems can be used as solubilisation media for such dyes. The microemulsion system is more beneficial as the usage of the toxic solvent is reduced, that were used for solubilization. The solubilization mainly depends upon the most effective parameters like temperature and surfactant

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concentration. An increase in temperature and addition of electrolytes increases the solubilization (Paul et al., 2005; Bagha et al., 2013).

In other words, a hydrophobic substance that are insoluble in water, are solubilised in a microemulsion system where non-ionic sugar-based surfactants has been used. Below the CMC of the surfactant, the solubility (amount of substance that is incorporated in the solution) is slightly higher than in the pure insoluble solvent. However, just above the CMC, the solubility increases dramatically. On addition of more amount of the surfactant, the solubility increases in a linear fashion. The reason for this is due to formation of micelles that accommodate the insoluble dye into its core which is already been studied in the literature where conventional surfactant is used (Tadros, 2006).

Microemulsions are excellent solvents for dyes. All the polar dyes are more soluble in microemulsions than in pure solvents, and the solubility increases strongly with increasing dye polarity. The surfactant-rich interface separating oil and water domains is probably the preferred site for solubilization of the polar dyes. One of the important advantages of microemulsion system is a reduction in the number of toxic solvents upon dispersion of the solvent in a water rich microemulsion. Hence, the possibility that water rich microemulsions may be good solvents for dyes was examined (Solanki & Patil, 2021).

In the present thesis, we have studied the solubilisation of an otherwise water insoluble dye, Sudan Red in the microemulsion system, wherein we have formulated one microemulsion system using non-ionic conventional surfactant and the other microemulsion system using non-ionic sugar-based surfactant using Perkin- Elmer Lambda-35 UV-Visible Spectrophotometer. It has been observed that the absorbance increases with the increase in surfactant mass fraction,  $\gamma$  for both the microemulsion systems i.e., water/1-butyl-3 methylimidazolium hexafluorophosphate [Bmim][PF<sub>6</sub>]/ PLANTACARE®810-UP and water/1-butyl-3 methylimidazolium hexafluoro phosphate [Bmim][PF<sub>6</sub>]/TX-100 containing Sudan Red dye.

This effectively means that the solubilization of dye increases by varying the  $\gamma$  values. It is reported that the non-polar, water insoluble dyes are mainly soluble in the oil-swollen micelles, while water soluble polar dyes are highly soluble in the surfactant-rich interfacial region coating these micelles. The solubility of non-polar dyes is reported to vary as a function of the polarity of the oil component of the microemulsion system.

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### 1.5.2.5 *Metal Extraction and Recovery using microemulsions*

Currently, owing to the increase in the world market, the growth in the industrialization have become vital source for release of the heavy metals that leads to destruction of the environment. (Zaib et al., 2013). There are various other industries like dyes, explosives, tannery, paints, textiles, metallurgy, ceramics, etc. that use to discard the compelling amounts of heavy metals both as aqueous waste stream and solid waste in the environment (Dantas et al., 2003; Dantas et al., 2010).

Hence, by recycling the elements from these wastes, the environmental threat environmental as well as the threat to the public health could be evaded as well as the deficit of the metals that are used as the raw materials for the production of electronic devices could be consummated (Tao et al., 2006). There are many studies reported in the literature wherein the removal of metal ions from industrial effluents were studied and it has been found that the traditional methods such as ion exchange, chemical precipitation, adsorption, bio sorption, reverse osmosis, and membrane filtration was used for treating such effluents (Zaib et al., 2013; Shen et al., 2016). However, the traditional method shows less reactivity, fewer bio-degradability, huge thermal, chemical as well as photolytic stability. Consequently, the use of the microemulsion system was initiated as an economical and contemporary method (Dantas et al., 2004; Al-Ghouti et al., 2013; Radi et al., 2016; Mukherjee et al., 2016). Hence, the microemulsion system used for the recovery of the metals from the aqueous phase ought to be in an oil continuous phase.

Owing to this, in one of the literature studies, the two-phase ( $2\phi$ ) system, i.e. (W/O) which represents water in oil microemulsion with an excess of water is usually used. As a result of increasing interfacial area of the W/O microemulsion phase, this two- phase system has become very effective and economical for the enhancement of extraction process of the metal ion from microemulsion system (Beltrame et al., 2005). In the studies, it has been reported that solubilization of metals in the aqueous phase of the microemulsion system is one of the essential factor that is chosen for extraction of different types of metallic cations like chromium (Dantas et al., 2001; Li et al., 2009), copper (Al-Ghouti et al., 2016), gold (Lu et al., 2011), lanthanide (Shan et al., 2005; Xia et al., 2008), and few other metals (Dantas et al., 2003; Kara et al., 2015).

The most important properties of microemulsions in the textile field are the solubilization capacity for both water and oil-soluble compounds, and the extremely low values of interfacial tensions achieved in contact with aqueous or oil phases. Thus, these microemulsion systems could be ideal solubilization media for a water-insoluble natural dye as well as inorganic metal ions. In

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addition to this, many of the papers in the literature (Mihaly et al., 2010; Tao et al., 2006; Lu et al., 2011; Cadar et al., 2017; Xia et al., 2008; Al-Ghouthi et al., 2016; Shang et al., 2012), it has been reported that microemulsion system used for solubilization must be oil continuous phase. Thus, it is a very effective process for the improvement of extractability as well as for the acceleration of extraction due to an enormous rise of the interfacial surface area in the W/O microemulsion phase in order to recover the metallic cations from the aqueous phase (Tao et al., 2006; Shang et al., 2012; Xia et al., 2008; Steytler et al., 2016).

Therefore, the aim of the present work is to lower the adequate cost of the process as well as the toxicity of the systems by recommending environmentally friendly microemulsion systems. This can be used to probe the recovery of cobalt and nickel ions by extracting and trapping in the inner aqueous phase microemulsion system. The microemulsion systems used are comprised of a non-ionic surfactant and ethyl acetate as organic phases. The optimum potassium thiocyanate concentration and the maximum metal ions concentration which was extracted, and the recovery efficiency data were using certain thiocyanate concentration.

In the present work, we have formulated a ternary microemulsion system that comprises of non-ionic sugar-based surfactants, water as polar phase, and ethyl acetate (EtOAc) as organic phase. Further, the fish-shaped diagram was constructed and the phase diagram of the microemulsion system was investigated. Also, the  $\bar{X}$  value which is the minimum surfactant concentration needed for solubilizing the two immiscible solvents at which the microemulsion forms was determined. Moreover, the recovery efficiency of inorganic metal ions was calculated. The optimum potassium thiocyanate concentration and the maximum metal ions concentration that can be removed using certain thiocyanate concentration were also investigated in detail.

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### 1.6 Scope of the Present work

- To replace conventional solvents (*n*-alkanes) as a non-polar phase with a hydrophobic ionic liquid in ternary microemulsion systems containing alkyl glycoside or sugar surfactant and water.
- To compare and correlate the phase behaviour of the alkyl glycoside surfactant/ionic liquid/water microemulsion system and conventional polyoxyethylene alkyl ether surfactant ( $C_iE_j$ )/ionic liquid/water microemulsion system.
- Ethylammonium nitrate (EAN) as a polar phase in a ternary microemulsion system including alkyl glycoside surfactants to replace water with a room-temperature ionic liquid.
- To formulate microemulsion systems that are stable across a wide temperature range using alkyl glycoside or sugar-based non-ionic surfactants.
- To achieve reduction in surfactant concentration required to solubilize two immiscible solvents.
- To determine the effect of the length of the nonionic surfactant's hydrophobic chain, oil chain length, ionic liquid type, co-surfactant (*n*-alkanols), and ionic liquid concentration on the phase behaviour and microstructure of microemulsion systems.
- To carry out electrical conductivity measurements of typical w/o or o/w microemulsions to provide information on percolative behaviour of the system three-phase systems.
- To use ionic liquid-containing microemulsion system to solubilize Sudan Red G, an organic water-insoluble dye.
- Utilization of w/o microemulsion for extraction as well as efficient recovery of inorganic metal ions.
- To verify the effect of increasing the metal salts concentration and potassium thiocyanate salt concentration on recovery efficiency of the metal ions from metal complexes using a UV-Visible spectrophotometer.