

## Summary

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The low melting salts that are considered vital from 'Green Chemistry' perspective are known as room temperature ionic liquids (RTILs) owing to their unique and extraordinary physicochemical properties. Room temperature ionic liquids are environment friendly solvents because of their excellent solvation behaviour, non-flammability, high thermal stability, low vapour pressure, high ionic conductivity and wide electrochemical window. These attributes of ionic liquids offer various benefits and hence they play an excellent role as greener alternative compared to that of volatile organic compounds that are employed as catalyst, electrolytes, lubricant and solvent media for liquid/liquid extraction and organic synthesis to name a few. Ionic liquids' chemical structure can be tuned to suit the application by simply adjusting the cations and anions, making them a useful material for a variety of industrial applications. As a consequence, ionic liquids are frequently referred to as "designer solvents." They also allow for the control of physical properties by the precise mixing of constituent ions and appropriate functionalization.

Researchers have used ionic liquids as a substitute for polar and non-polar solvents to modify the physicochemical properties of distinct micellar aggregates a decade ago when they were looking for an alternative to organic solvents and water. In particular, non-aqueous microemulsion systems containing ionic liquids were formulated and reported in a number of studies, which were encouraged by the fact that, despite many important properties of ionic liquids, one of the major roadblocks to their potential application was the poor solubility of apolar solutes in clean and pure ionic liquid.

The significance of using ionic liquids as one of the three components required for the formulation of a microemulsion system: the water-like solvent, the hydrophobic solvent, and the surfactant is very well recognized. From both theoretical (thermodynamics, particle interactions) and practical (possible use as novel reaction media) perspectives, ionic liquids have attracted a lot of attention of researchers worldwide resulting in a substantial increase in studies on microemulsions using ionic liquid as one of the components. As a contribution to these efforts, we have developed a microemulsion system in which alkyl polyglycol ether ( $C_iE_j$ ) surfactants have been substituted with "greener alternatives," such as alkyl glycoside or sugar-based non-ionic surfactants ( $C_nG_m$ ), which are stable throughout a wide temperature range. Subsequently, the current effort also aims to reduce the sugar-based surfactant concentration

required to solubilize the two immiscible solvents (Ionic Liquid and water) in order to improve the surfactant's efficiency. Sugar-based non-ionic surfactants (containing alkyl maltoside and alkyl glucoside) are becoming increasingly popular due to their favourable performance characteristics, such as dermatological compatibility and biodegradability, non-toxicity, and environmental friendliness, which renders microemulsions greener and more beneficial than those prepared with conventional non-ionic surfactants.

In terms of raw ingredients, alkyl polyglycosides (APGs) are non-ionic sugar-based surfactants that differ from traditional non-ionic surfactants, fatty alcohol ethoxylates. In contrast to fatty alcohol ethoxylates, APGs are derived from renewable raw materials for both hydrophobic and hydrophilic molecular components. Surfactants containing alkyl polyglucosides are classified as maltosides, which are glycosides with maltose as the glycone (sugar) functional group. The most common is alkyl maltoside, which is an aglycone that comprises hydrophobic alkyl chains. This class of surfactants contains a modification in the alkyl chain that confers a range of detergent qualities such as low CMC (critical micelle concentration) and solubility due to their amphoteric capabilities.

Chapter II-IV of the present thesis deals with different types of microemulsion systems that have been formulated using different hydrophobic chain lengths of non-ionic sugar-based surfactants as well as different types of room temperature ionic liquids which act as the polar phase instead of water and also act as non-polar phase instead of organic solvents. Whereas, the Chapter-V deals with the application of the formulated microemulsion systems.

In the present work, the room temperature ionic liquids that have been used are ethylammonium nitrate (EAN) and 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF<sub>6</sub>]. The sugar-based non-ionic surfactants that were used are Decyl  $\beta$ -D-maltoside ( $\beta$ -C<sub>10</sub>G<sub>2</sub>), Dodecyl  $\beta$ -D-maltoside ( $\beta$ -C<sub>12</sub>G<sub>2</sub>) and PLANTACARE<sup>®</sup>810-UP (UP-810). PLANTACARE<sup>®</sup>810-UP, an industrial grade surfactant, is a sugar-based non-ionic surfactant manufactured from 100 percent renewable plant-derived feedstocks. It has excellent environmental and skin compatibility profiles, resulting in a great balance of mildness, foam performance, and cleansing effectiveness. PLANTACARE<sup>®</sup> 810 -UP (UP-810) C<sub>8-10</sub> has an average chain length of C<sub>8-10</sub>. It's a glucoside of fatty alcohol. Along with this we have used industrial-grade sugar-based lauryl glucoside (and) Cocamidopropyl betaine zwitterionic surfactant, PLANTACARE<sup>®</sup> K-55. Furthermore, we examined the efficiency of

PLANTACARE<sup>®</sup> K-55 by comparing the microemulsion studies with that of the sugar-based non-ionic surfactants as well as with conventional surfactant.

Despite the fact that conventional non-ionic surfactants have a better detergency and solubilisation efficiency, they are hazardous and harmful to the environment. Furthermore, the temperature dependency of the hydration shell of the ethoxylated head group, which is substantially temperature-dependent, is a distinct feature of the microemulsion formulation utilising typical non-ionic surfactants. The alkyl polyglycoside sugar-based non-ionic surfactants, on the other hand, are only mildly affected by temperature. As a result, in the microemulsion generated with alkyl polyglycosides sugar-based surfactants, there is no substantial temperature-dependent phase inversion.

Firstly, we have formulated the microemulsions comprising of water as polar phase, hydrophobic ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) in place of organic solvents, as non-polar phase, and non-ionic sugar-based surfactant instead of conventional surfactant. The ternary phase behaviour of the microemulsion system was examined as a function of temperature and surfactant mass fraction. While formulating microemulsion systems with sugar-based non-ionic surfactant, we found that the surfactant efficiency increases in terms of consumption when compared to traditional non-ionic surfactant. We've also formulated a microemulsion system using a zwitterionic surfactant, room temperature ionic liquid (RTIL), and water.

The microstructure of the samples was examined using polarising microscopy and we have detected lamellar liquid crystalline phases ( $L_\alpha$ ) at lower temperatures, for the microemulsion system; *n*-Decyl  $\beta$ -D-maltoside/[Bmim][PF<sub>6</sub>]/H<sub>2</sub>O and *n*-Dodecyl  $\beta$ -D-maltoside/[Bmim][PF<sub>6</sub>]/H<sub>2</sub>O. Polarisation microscopy tests revealed the absence of liquid crystalline phases (and high viscosity) when a sugar-based non-ionic surfactant, PLANTACARE<sup>®</sup>810-UP, was used to form a microemulsion system.

In addition, the percolative behaviour of the hydrophobic microemulsion system was also investigated. The creation of percolation clusters of water droplets interacting in the oil medium causes percolation in a micellar phase of an oil-continuous microemulsion. At a constant temperature, the electrical conductivity of typical w/o systems remains low up to a certain fraction of water, then increases by two to three orders of magnitude once the water reaches the system's threshold concentration ( $w_t$ ), resulting in a sigmoidal electrical conductivity–water content (volume, mass) profile.

Furthermore, we also have studied the phase behaviour and surfactant efficiency of five different microemulsion systems that were comprised of water, the hydrophobic ionic liquid [Bmim][PF<sub>6</sub>], and sugar-based non-ionic surfactants PLANTACARE<sup>®</sup>810–UP in detail, as a function of temperature and surfactant concentration by varying the mass fraction of ionic liquid ( $\alpha$ ). The result obtained revealed that the surfactant concentration utilised to solubilize both water and hydrophobic ionic liquid [Bmim][PF<sub>6</sub>], i.e.,  $\bar{X}$  or  $\bar{\gamma}$ , remains virtually constant in all the five distinct microemulsion systems where the mass fraction of the ionic liquid ( $\alpha$ ) is altered. Moreover, with an increase in the concentration of the mass fraction of the ionic liquid ( $\alpha$ ), there is only a slight rise in  $\bar{X}$  or  $\bar{\gamma}$ . The high  $\bar{X}$  or  $\bar{\gamma}$  values in case of microemulsions formulated using conventional non-ionic surfactants indicate that the surfactants are relatively less efficient. However, when sugar-based non-ionic surfactants are employed instead of traditional surfactants, the efficiency improves. With an increase in the mass fraction of the ionic liquid ( $\alpha$ ), only a modest increase in  $\bar{X}$  or  $\bar{\gamma}$  has been noticed. The fish-shaped three-phase area is now also observed to be deformed at low and high  $\alpha$  (mass fraction of ionic liquid) values, whereas it exhibits an asymmetric form at intermediate values of  $\alpha$  (mass fraction of ionic liquid).

Furthermore, an effort was made to gain insights on the effect of alkanols with variable chain lengths (octanol, decanol, and dodecanol) as co-surfactants on the phase behaviour and microstructure of hydrophobic ionic liquid microemulsion systems using various non-ionic surfactants, including conventional, sugar-based non-ionic surfactants as well as Lauryl Glucoside (and) Cocamidopropyl Betaine Zwitterionic surfactant was also investigated. We observed that addition of a long-chain length alkanol (co-surfactant) to a ternary microemulsion system reduces the  $\bar{X}$ -point while concurrently increasing the sugar surfactant's efficiency. It indicates that the amount of surfactant concentration needed to solubilize oil and water is reduced, resulting in increased surfactant efficiency.

As a result, it can be concluded that sugar-based non-ionic surfactants are superior to zwitterionic and conventional non-ionic surfactants in terms of environmental as well as economic considerations. Hence, a microemulsion was successfully formulated using the hydrophobic ionic liquid [Bmim][PF<sub>6</sub>] instead of traditional organic solvents. The formulation of an ionic liquid microemulsion system overcomes the constraints of ionic liquids in terms of their ability to dissolve diverse types of compounds, allowing it to be employed in a variety of industrial applications.

We have observed that when conventional non-ionic surfactant Triton X-100 was utilised in combination with the co-surfactant, the surfactant concentration necessary to solubilize both water and hydrophobic ionic liquid [Bmim][PF<sub>6</sub>] (IL) phases, i.e.,  $\bar{X}$  or  $\bar{\gamma}$  was found to be 0.49. (dodecanol). Whereas, when the industrial-grade sugar-based zwitterionic surfactant PLANTACARE<sup>®</sup>K-55, which is Lauryl Glucoside (and) Cocamidopropyl Betaine, was utilised in the system in combination with the co-surfactant,  $\bar{X}$  or  $\bar{\gamma}$  was determined to be 0.41 (dodecanol). Further, when sugar-based non-ionic surfactants like PLANTACARE<sup>®</sup>810-UP were used,  $\bar{X}$  or  $\bar{\gamma}$  was obtained to be 0.35.

Hence, it can be inferred that in the presence of a co-surfactant, only 35% of the sugar-based non-ionic surfactant was consumed to formulate a microemulsion system (dodecanol). Surfactant efficiency improves as the amount of surfactant concentration necessary for solubilizing oil and water lowers. Henceforth, it can be stated that sugar-based non-ionic surfactants are superior to zwitterionic sugar surfactants and conventional non-ionic surfactant and can be employed as an efficient alternative owing to both environmental and economic considerations.

Additionally, we have formulated the ternary microemulsion systems comprising of non-ionic sugar-based surfactants, *n*-alkanes (oils), and polar ionic liquid, i.e., ethylammonium nitrate (EAN), wherein we have replaced water with room temperature ionic liquid (RTILs), ethylammonium nitrate (EAN) and have used EAN as polar phase. Consequently, we have explored the effect of different alkane chain lengths and different hydrophobic chain lengths of sugar-based non-ionic surfactants on the microemulsion system. The results obtained showed that, for a ternary microemulsion system formulated using a sugar-based non-ionic surfactant, the surfactant efficiency increases with an increase in surfactant amphiphilicity ( $\bar{X}$  changes from 0.63 to 0.43, almost a 20% reduction in surfactant concentration, correspondingly a 20% increase in surfactant efficiency). The results obtained for the formulated microemulsion system while modifying the hydrocarbon chain of surfactants and varying the chain lengths of *n*-alkanes are strikingly similar to those obtained for a microemulsion system formulated with water as a polar solvent.

Furthermore, it has been discovered that the surfactant efficiency diminishes when *n*-alkanes with long-chain length hydrocarbons are added. Our results indicate that even in the absence of a co-surfactant, polar ionic liquids can form microemulsions using sugar-based non-ionic surfactant. Furthermore, the results were obtained by combining a longer hydrophobic chain of

a sugar-based non-ionic surfactant, *n*-Dodecyl  $\beta$ -D-maltoside ( $\beta$ -C<sub>12</sub>G<sub>2</sub>), with a shorter alkyl chain alkane, i.e., octane, which has the highest surfactant efficiency and may be employed in a variety of applications.

Thus, it can be inferred that ethylammonium nitrate (EAN), a polar ionic liquid, can be successfully used for replacement of water as a polar phase. Hence, such a microemulsion system finds its best applications as nanoreactors and many organic reactions wherein water is exempted. The polarisation microscopy studies reveal that liquid crystalline lamellar phases (*LC*) are absent in microemulsion systems formulated with a short alkyl chain non-ionic sugar-based surfactant, such as PLANTACARE<sup>®</sup>810-UP (UP-810), whereas *LC* phases were formed in polar ionic liquid ethylammonium nitrate (EAN) when sugar-based non-ionic surfactant having longer hydrocarbon chains,  $\beta$ -C<sub>10</sub>G<sub>2</sub> and  $\beta$ -C<sub>12</sub>G<sub>2</sub> were used for the formulation of a microemulsion system.

Finally, we have used a ternary microemulsion system comprising of PLANTACARE<sup>®</sup>810-UP/[Bmim][PF<sub>6</sub>]/ water to investigate the solubilization of Sudan Red G, a hydrophobic lysochrome azo dye. For the ternary microemulsion system, the solubilization of an otherwise hydrophobic lysochrome azo dye, Sudan Red G, is enhanced with an increase in surfactant mass fraction,  $\gamma$ . The solubilization of a hydrophobic lysochrome azo dye, Sudan Red G was monitored by determining absorbance at a wavelength of 504 nm using a UV-Visible spectrophotometer. Sudan Red G solubilization was observed to be greater in a microemulsion formulated using a sugar-based non-ionic surfactant, PLANTACARE<sup>®</sup>810-UP than in a microemulsion formulated with a conventional non-ionic surfactant, Triton X-100. The formation of ionic liquid microemulsions allows ionic liquids to dissolve a wide range of substances despite their restrictions. Bio-compatible, ecologically friendly, biodegradable greener surfactants with minimal toxicity were used to solubilize an ordinarily water-insoluble dye, Sudan Red g. These results and the microemulsion systems can provide a green alternative to the present solubilization procedures that are widely used in textiles and other associated industries such as imaging, displays, memory technologies, analytical chemistry, biological indicators, and so on.

In addition to the solubilization technique, we evaluated the recovery efficiency of heavy metal ions using microemulsion system. PLANTACARE<sup>®</sup>810-UP, a sugar-based non-ionic surfactant, was combined with water and the organic solvent ethyl acetate (EtOAc) to formulate a microemulsion that was used to extract the inorganic metal ions. The UV-Visible

spectrophotometric experiments revealed that the absorbance increases with an increase in metal ion concentration in the aqueous phase and decreases with an increase in potassium thiocyanate concentration in the aqueous phase. Furthermore, it has been determined that a concentration of 4.0 mol/L potassium thiocyanate is necessary for the efficient recovery of 0.05 mol/L cobalt and nickel salts. We were able to recover 93.9% (~94%) of the nickel ions and 97% of the cobalt ions from the designed microemulsion system in this study. Our research endeavour is an attempt to reduce the aftereffects on public health and the environment by extracting metal ions from various other industrial effluents and wastes. These findings can also help overcome the lack of metals in the industrial region where they have been employed as raw materials.

In conclusion, to summarise the whole thesis, our research studies shows that room temperature ionic liquids (RTILs) serve an important function as a polar and non-polar phase. To top it off, sugar-based non-ionic surfactants have played a crucial part in these investigations, where they have been successfully used in place of traditional non-ionic surfactants of alkyl polyoxyethylene type. Furthermore, it has also been observed that the use of co-surfactant leads to substantial reduction in the need of sugar-based non-ionic surfactant. The sugar-based non-ionic surfactants that we utilised in this study serve a significant role as a greener alternative when formulating a microemulsion system.