CHAPTER-IV

MICROEMULSION WITH ROOM-TEMPERATURE IONIC LIQUID AS A POLAR PHASE: EFFECT OF VARIATION IN SURFACTANT AMPHIPHILICITY AND OIL LENGTH

Microemulsion with room-temperature ionic liquid as a polar phase: effect of variation in surfactant amphiphilicity and oil length

The work reported in the present chapter involves utilization of an ionic liquid, ethylammonium nitrate (EAN) as a polar phase instead of water, a hydrocarbon solvent (*n-alkanes*), and sugar-based alkyl polyglycoside non-ionic surfactant to formulate microemulsions. Phase transitions and microstructure of the formulated microemulsions were investigated in detail. The sugar-based non-ionic surfactants are non-toxic, biodegradable, and environmentally benign and thus a viable alternative to typical non-ionic surfactants belonging to the alkyl polyoxyethylene ether class (C_iE_j) for forming a microemulsion system. The impact of varying chain lengths of alkanes and varying hydrophobic chain lengths of sugar-based non-ionic surfactants on the microemulsion system was also examined. The experimental data obtained for the formulated microemulsions upon altering the hydrocarbon chain of surfactants and the chain lengths of *n*-alkanes are quite similar to those obtained for a microemulsion system formulated with water as a polar solvent. The liquid crystalline (*LC*) phases were detected using sugar-based alkyl polyglycoside non-ionic surfactants possessing longer hydrocarbon chains, at lower temperatures, and higher surfactant mass fraction in the microemulsion system.

4.1. Introduction

Microemulsions are macroscopically homogenous mixtures that typically contain at least three components: a polar solvent (usually water), a non-polar solvent (oil), and an amphiphilic molecule (surfactant). A surfactant layer stabilizes the liquid-liquid interface between the two immiscible liquid phases, namely the polar solvent (water) and the non-polar hydrocarbon solvent (oil). Microemulsions are thermodynamically stable, isotropic, transparent, and clear (homogeneous, single-phase) dispersions (Atkin & Warr, 2007; Gao et al., 2005; Qui & Texter, 2008) whereas ordinary emulsions are thermodynamically unstable liquid-liquid dispersions. Microemulsions have applications in a variety of fields, viz. micro reactors for chemical reactions and the synthesis of nanomaterials (Mehta & Kaur, 2010; Spiro & Jesus, 2000; Fanun, 2008; Binks et al., 2003; Schulman et al., 1959; Malik et al., 2012; Stubenrauch et al., 2008) , microcolloids (Paul & Moulik, 2001), solar energy conversion (Malik et al., 2012), and various other chemical reactions involving organic and inorganic compounds (Malik et al., 2012) (Stubenrauch et al., 2008; Paul & Moulik, 2001; Holmberg, 1994; Dutta et al., 2018; Li et al., 2007), as evidenced from a large database in the literature.

Researchers have attempted to formulate and study non-aqueous microemulsions in which water is replaced by various non-aqueous solvents in conventional microemulsions (Thater et al., 2014; Thater et al., 2019; Zheng & Eli, 2009).

Furthermore, because traditional oil phase (hydrocarbon solvents) is toxic and volatile, several researchers have used apolar ionic liquids instead of hydrocarbon solvents to in a microemulsion system (Gao et al., 2006; Kahlweit et al., 1988; Kahlweit et al., 1989; Solanki & Patil, 2021; Anjum et al., 2009; Porada et al., 2017; Porada et al., 2011). This unique ionic liquid based microemulsions have piqued researchers' curiosity from both a theoretical and practical standpoint (Zech et al., 2011; Safavi et al., 2010; Rojas & Koetz, 2010; Kuchlyan et al., 2016; Marsh et al., 2002; Zech et al., 2010; Gao et al., 2009). The ternary microemulsion system formulated with polar ionic liquid instead of water has been reported to be used in a variety of high-temperature applications (Li et al., 2005; Marsh et al., 2004; Zech et al., 2010; Gao et al., 2004). Because of their specific physicochemical features, ionic liquids are considered an environmentally friendly media as well as a greener solvent (Petkovic et al., 2011; Anderson et al., 2003). Non-volatility, greatest solvating potential for both organic and inorganic compounds, low vapour pressure and melting point, easy recyclability, strong ionic conductivity, high thermal stability, wide electrochemical window, and nearly negligible flammability are among these remarkable attributes (Petkovic et al., 2011; Anderson et al., 2003; Welton, 1999; Niga et al., 2010; Najjar et al., 2020; Anderson et al., 2002; Atkin & Warr, 2007b; Gao et al., 2006). Ethylammonium nitrate (EAN) and imidazolium salts with short alkyl chains are the polar ionic liquids used in the formulation of these microemulsion systems.

However, only a few studies have dealt with investigations pertaining to the relationship between phase behaviour as well as its structural variation as a function of temperature, surfactant concentration, and microstructure within the microemulsion phase for the polar ionic liquid/*n*-alkanes/non-ionic surfactant ternary microemulsion system. The database from literature on the studies in which the microemulsion was created using a typical non-ionic surfactant/polar ionic liquid/oil has been tabulated in Table 1.

Table 1. The database on microemulsion formulated using conventional non-ionic surfactant/polar ionic liquid/oil.

Non-aqueous microemulsion systems studied in the literature	Reference cited
1) Triton X-100/[Bmim][BF_4/ Tween 20	(Mehta & Kaur, 2010)
2) $C_{12}E_3$/EAN/ dodecane 3) $C_{12}E_3$/EAN/ octane	(Thater et al., 2014) (Thater et al., 2019)
4) $C_{14}E_4$/EAN/dodecane 5) $C_{14}E_4$/EAN/octane 6) $C_{12}E_3$/EAN/dodecane 7) $C_{12}E_3$/EAN/octane	(Anjum et al., 2009)
8) 1-hexadecyl-3-methyl imidazolium chloride([C_{16}mim][Cl])/EAN/dodecane/decanol 9) 1-hexadecyl-3-methyl imidazolium chloride ([C_{16}mim][Cl])/ [Bmim][BF_4]/ dodecane/decanol	(Marsh et al., 2002)
10) Triton X-100 /[Bmim][BF_4]/cyclohexane	(Zech et al., 2010)
11) Triton X-100 /[Bmim][BF_4]/Toluene 12) Triton X-100 /[Bmim][BF_4]/P-Xylene 13) Triton X-100 /[Bmim][BF_4]/Benzene	(Li et al., 2007) (Atkin & Warr, 2007b) (Gao et al., 2006)

Our findings complement those of Thater et al. (2014; 2019), who investigated the phase behaviour and microstructure of a microemulsion generated by solubilizing two immiscible fluids using a non-ionic conventional surfactant (*n*-alkanes and polar ionic liquid). The main goal of this study was to replace the traditional non-ionic alkyl polyglycol ether (C_iE_j) surfactant required for the solubilization of an equal amount of two immiscible liquids (polar ionic liquid and oil) to form a microemulsion system with a sugar-based non-ionic surfactant based on data published in the literature. Sugar-based non-ionic surfactants (containing alkyl maltoside and alkyl glucoside) are becoming increasingly popular due to their favourable performance properties, such as dermatological compatibility and biodegradability (Gao et al., 2007; Balzer, 1991; Balzer, 1996; Rybinski, 1996; Claessom et al., 2002; Sierra et al., 1999; Rybinski, 1998), non-toxicity, and environmental friendliness, which makes microemulsions greener and more beneficial than those made with conventional non-ionic surfactants (Li et al., 2001).

Alkyl polyglycosides (APGs) are non-ionic sugar-based surfactants that differ from fatty alcohol ethoxylates, which are the most common non-ionic surfactants. For both hydrophobic and hydrophilic molecular components, APGs are synthesized using renewable basic resources (Balzer, 1996). Surfactants containing alkyl polyglycosides are classified as maltoside, which are glycosides with maltose as the glycone (sugar) functional group. The most common is alkyl maltoside, which is a glycone that comprises of hydrophobic alkyl chains. This class of surfactants contains a modification in the alkyl chain that confers a range of detergent qualities such as CMC (critical micelle concentration) and solubility due to their amphoteric capabilities. PLANTACARE ® 810 -UP (UP-810), *n*-Decyl β-D-maltoside (β-$C_{10}G_2$), and *n*-Dodecyl β-D-maltoside (β-$C_{12}G_2$) are the sugar-based non-ionic surfactants employed in this investigation. PLANTACARE ® 810 -UP (UP-810) is a non-ionic sugar surfactant made entirely of renewable plant-based feed stocks. The environmental and skin compatibility characteristics of PLANTACARE ® 810 -UP (UP-810) are outstanding, resulting in a superb mix of mildness, foam performance, and cleansing effectiveness. PLANTACARE® 810-UP (UP-810) has an average chain length of $C_{8\text{-}10}$. It has a molecular weight of 292.37 g and is a fatty alcohol glucoside.

The second sugar-based non-ionic alkyl polyglycoside surfactant employed is *n*-Decyl β-D-maltoside having molecular formula $C_{22}H_{42}O_{11}$ is made by attaching a dodecyl group to the reducing-end anomeric centre of a beta-maltose molecule and has a molecular weight of 482.6 g. It is a glycoside and disaccharide derivative generated from a beta-maltose hydride. The third sugar-based non-ionic alkyl polyglycoside surfactant used in this study is *n*-Dodecyl β-D-maltoside with chemical formula $C_{24}H_{46}O_{11}$ and has a molecular weight of 510.62 g. Despite the fact that non-ionic conventional surfactants have a better 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 conventional non-ionic surfactants. The alkyl polyglycoside sugar-based non-ionic surfactant, on the other hand, is only mildly affected by change in temperature. As a result, in the microemulsion formulated with alkyl polyglycosides sugar-based surfactants, there is no substantial temperature-dependent phase inversion.

We developed a microemulsion system consisting of room temperature ionic liquid ethylammonium nitrate (EAN)/sugar-based non-ionic surfactant/*n*-alkanes. The aforesaid systems' phase behaviour and microstructure were explored, and the results compared to those reported in the literature. The effects of varying alkane chain lengths, such as octane, decane, and dodecane, on the phase behaviour of the ternary microemulsion system was also investigated. Visual inspection of the phase boundaries led to identification of the three microregions known as phases: ionic liquid/oil, bicontinuous, and oil/ionic liquid. Furthermore, the ability of sugar-based non-ionic surfactants to significantly lower interfacial tension and thereby solubilize both non-polar and polar ionic liquid (IL) phases, i.e., $\overline{X}$ or $\overline{\gamma}$ (the minimum quantity of surfactant required to solubilize the two immiscible liquids), was assessed. Furthermore, using a polarisation microscope, presence of lamellar phases was confirmed in ternary microemulsion systems made using a sugar-based non-ionic surfactant with longer hydrocarbon chains.

4.2. Materials and methods.

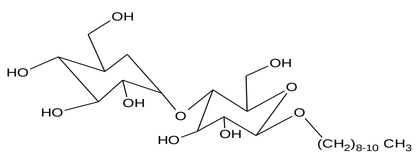
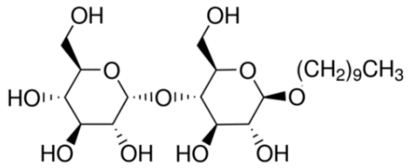
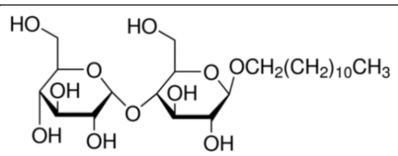
PLANTACARE® 810 – UP (UP-810), a sugar-based non-ionic surfactant, was obtained as a gift sample from BASF, Germany. The sugar-based non-ionic surfactants, *n*-dodecyl β-D-maltoside (β-$C_{12}G_2$) ($C_{24}H_{46}O_{11}$, purity ≥ 98%); *n*-decyl−β-D-maltoside (β-$C_{10}G_2$) ($C_{22}H_{42}O_{11}$, purity ≥ 98%), and various chain length *n*-alkanes, i.e. Octane [$CH_3(CH_2)_6CH_3$, purity 99%] Decane [$CH_3(CH_2)_8CH_3$, purity 99 %] and Dodecane [$CH_3(CH_2)_{10}CH_3$, purity 99 %], Sigma Aldrich provided the ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF_4] ($C_8H_{15}F_6N_2P$, purity ≥97.0%). All the chemicals were used as received.

Synthesis of Room Temperature Ionic Liquid (Polar Ionic Liquid, Ethylammonium nitrate [EAN] ($C_2H_8N_2O_3$, purity ≥ 97.0%)

In the present work, the polar ionic liquid, i.e., ethylammonium nitrate (EAN) (M.P. = 12°C) was prepared by reacting equimolar amounts of ethylamine (70% v/v aqueous solution) and conc. nitric acid (69.5% v/v aqueous solution) to produce an aqueous solution (Matsumura et al., 1990; Evans et al., 1993). The resultant product is a solution of the ionic liquid in water. Upon completion of the reaction, an excess of ethylamine solution is added until the pH becomes basic (≈ 10-12). Excess water was removed by purging the EAN solution with nitrogen; whereas excess amine removal was carried out via rotary evaporation ensuring the temperature of the water bath doesn't cross the 40°C mark, thereby reducing the risk of degradation of the ammonium moiety (Anderson et al., 2002; Garlitz et al., 1999).

The average chain length, molecular weight and other properties of the non-ionic surfactants utilized for the formulation of microemulsion have been mentioned in table 2. The low molecular weight sugar-based non-ionic surfactant, i.e., PLANTACARE® 810-UP (UP-810) & *n*-Decyl *β*-D-maltoside (*β* – $C_{10}G_2$) with the average chain length C_{8-10} have bigger hydration shell whereas as the average chain length increases i.e., C_{8-12} in case of *n*-Dodecyl *β*-D- maltoside (*β*–$C_{12}G_2$), the hydration shell tends to shrink and hence solubilize both immiscible liquids, i.e., polar ionic liquid (EAN) and oil readily. Therefore, higher the alkyl chain length of the non-ionic sugar-based surfactant, *n*-dodecyl *β*-D-maltoside (*β*–$C_{12}G_2$), lesser will be the consumption of the surfactant in formation of one phase microemulsion system due to smaller hydration shell resulting into an increase in the hydrophobicity of the surfactant. Hence, longer the hydrocarbon chain length of a surfactant, better will be the efficiency of the surfactant in terms of consumption of the surfactant in formulating a microemulsion system.

Table 2. Properties of the sugar-based non-ionic surfactants utilized for formulation of microemulsion system.

Name of the Surfactants	Molecular Structure	Molecular weight	Molecular Formula	Average Chain Length
PLANTACARE® 810 – UP (UP-810)		292.37 g	-	C_{8-10}
n-Decyl−*β*-D-maltoside (*β*-$C_{10}G_2$)		482.6 g	$C_{22}H_{42}O_{11}$	C_{8-10}
n-Dodecyl−*β*-D-maltoside (*β*-$C_{12}G_2$)		510.62g	$C_{24}H_{46}O_{11}$	C_{8-12}

Phase Studies of ternary microemulsion system

For the formation of a microemulsion, the experimental identification of phases and phase transitions is vital. By taking an equal quantity of oil/polar ionic liquid (1:1) ratio and altering the surfactant mass fraction, phase behavioural investigations of the ternary mixture were carried out as a function of temperature and surfactant mass fraction, γ. A characteristic fish-shaped outline emerges from the phase boundaries.

In the solvent mixture, the weight fraction of the ionic liquid (α) is calculated by,

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

and in the whole mixture, the mass fraction of the surfactant (γ) is calculated by,

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

Polarization Microscopy

The samples were prepared by placing them on a glass slide and covering them with a coverslip for optical microscopy examinations. Between crossed polarizers, the samples were viewed using a Leica DM750 P polarisation microscope.

4.3. Results and Discussion

Phase behaviour as a function of varying the hydrocarbon chain length of sugar-based non-ionic surfactant using Ionic Liquid as a polar phase

Figure 1 represents the fish-shaped phase diagram of a microemulsion system containing equal quantities of polar ionic liquid, EAN/dodecane (1:1), and non-ionic sugar-based surfactant with changing hydrocarbon chain length. These fish-shaped frameworks match those reported in recent literature (Thater et al., 2014) (Thater et al., 2019), in which a non-ionic alkyl polyglycol ether (C_iE_j) was utilised as a surfactant in the development of an EAN/dodecane/ C_iE_j microemulsion system. Due to its short alkyl chain length, the non-ionic sugar-based surfactant PLANTACARE® 810-UP (UP-810) can only be divided into two phases in the graph shown in Figure 1, whereas *n*-Decyl β-D- maltoside ($\beta - C_{10}G_2$) and *n*-Dodecyl β-D-maltoside ($\beta - C_{12}G_2$) can form a three-phase body. These findings were corroborated by studies reported in the literature claiming the existence of a tri-critical point (Bhattacharya et al., 2020; Kahlweit et al., 1996; Kahlweit, 1988; Langevin, 1988; Kahlweit et al., 1985; Strey et al., 1985), which is located between the amphiphilicity of non-ionic sugar-based surfactants such as *n*-Decyl *β*-D- maltoside ($\beta - C_{10}G_2$) and *n*-Dodecyl *β*-D-maltoside ($\beta - C_{12}G_2$).

According to Thater et al. (Thater et al., 2014) (Thater et al., 2019), the $\overline{X}$, i.e., the point at which the two immiscible liquids can be solubilized with the minimum amount of surfactant, decreases from >45 wt % for C_8E_2 to ~40 wt % for $C_{12}E_3$ and ~30 wt % for $C_{14}E_4$, as the surfactant amphiphilicity increases. These findings are similar to those reported in the literature (Kunz et al., 2012), in which water is used as a polar phase with oil and non-ionic conventional surfactant to form a microemulsion system; the phase transition occurs between C_5E_2 and C_6E_3 non-ionic surfactants in the case of forma, and between $C_{10}E_4$ and $C_{12}E_4$ in the case of formamide as reported by Schubert et. al (1993). Similar results were obtained in the current study. From a shorter chain length non-ionic sugar-based surfactant, PLANTACARE® 810 (UP-810), to a longer chain length non-ionic sugar-based surfactant, *n*-Decyl *β*-D- maltoside ($\beta - C_{10}G_2$) and *n*-Dodecyl *β*-D-maltoside ($\beta - C_{12}G_2$), the size of the fish increases, implying that the microemulsion changes from weakly structured to strongly structured.

The shift of the microemulsion from weakly structured to highly structured, like the tri-critical point, has been attributed to higher amphiphilicity for polar ionic liquid, EAN, and compared to water, which is commensurate with lower surfactant solvophobicity. In the instance of the PLANTACARE® 810-UP (UP-810)/EAN/dodecane system, the $\overline{X}$ is found to be ~63 wt %. In the case of the *n*-Decyl *β*-D- maltoside ($\beta - C_{10}G_2$)/EAN/dodecane system, the $\overline{X}$ drops to ~48wt %. In the case of the *n*-Dodecyl *β*-D-maltoside (β–$C_{12}G_2$) /EAN/dodecane system, the $\overline{X}$ drops to ~43 wt %.

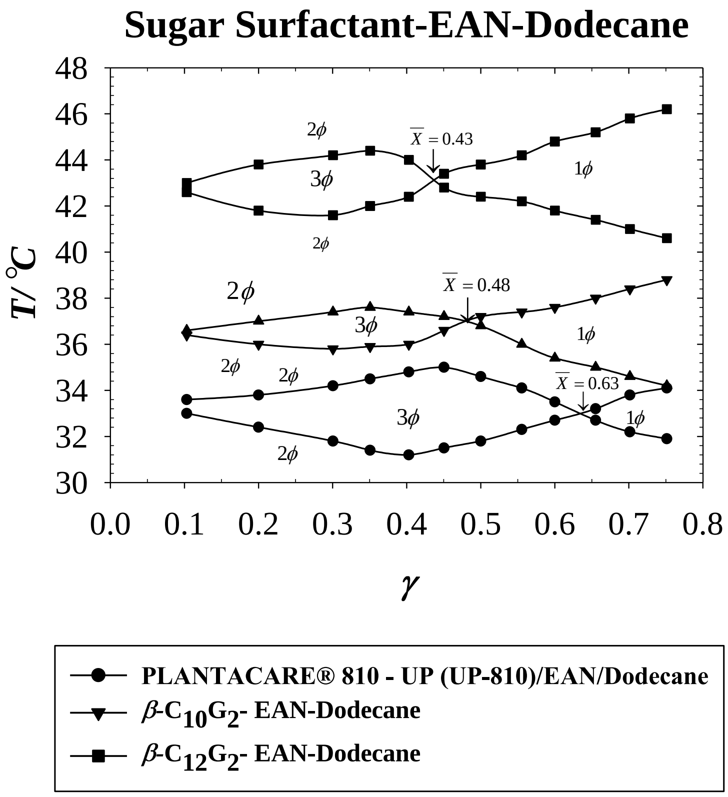


Figure 1. Phase diagram of a [*Temperature (T/°C)- wt% of surfactant* (γ)] ternary microemulsion constructed for equal masses of polar ionic liquid, ethylammonium nitrate (EAN) as polar phase and alkane (dodecane) as the non-polar phase in presence of non-ionic sugar-based surfactants with varying hydrocarbon chain lengths, viz. PLANTACARE® 810 – UP (UP-810)/EAN/Dodecane, *n*-Decyl β-D-maltoside (β–$C_{10}G_2$)/EAN/Dodecane and *n*-Dodecyl β-D-maltoside (β–$C_{12}G_2$)/EAN/Dodecane. T/°C represents the temperature and γ is the mass fractions of surfactant. 1Ø corresponds to one phase, 2Ø corresponds lower two-phase (O/IL droplet μE), 2Ø corresponds upper two phases (IL/O droplet μE), and 3Ø corresponds to three-phase regions, respectively.

The lower phase (2Ø), which is oil-in-polar ionic liquid (EAN) (oil excess phase), is formed in the ternary microemulsion system composed of polar ionic liquid (EAN), oil, and non-ionic sugar-based surfactant at low temperatures (below 35°C), according to phase studies of the fish-shaped microemulsion system. Because oils (non-polar solvents) and polar ionic liquid (EAN) are incompatible under the experimental conditions, all of the oil in the lower phase (2Ø) phase is distributed as microemulsion droplets. The miscibility gap between oil and non-ionic surfactants is narrower, with an upper critical point.

The sugar-based non-ionic surfactant has a larger hydration shell at low temperatures, but as the temperature rises, the hydration shell shrinks. The mixture of EAN-sugar-based non-ionic surfactant has an upper miscibility gap with a lower critical point, which alters the phase behaviour of a ternary mixture. The surfactant tends to grow more hydrophilic as the size of the head group increases, whilst the oil solubility decreases. As a result, the surfactant becomes solubilized in the polar ionic liquid (EAN) phase after the addition of the non-ionic sugar-based surfactant. A large amount of surfactant is required to generate the microemulsion at an average temperature (between 35 and 45°C) (three-phase area). When more non-ionic sugar-based surfactant is added, the surfactant concentration rises to the mass fraction of the surfactant, i.e., $\gamma = \gamma_0$ (where γ is the mass fraction of the surfactant and γ_0 is the coordinates of the fish head), indicating that both phases (oil and polar ionic liquid (EAN) in the ternary microemulsion system are saturated. The concentration of the non-ionic sugar-based surfactant ($\gamma < \gamma_0$) was found to be relatively low at T= $\bar{T}$ temperature. Because both the oil (non-polar solvent) and the polar ionic liquid (EAN) phases are at intermediate temperatures, the non-ionic sugar-based surfactant had an enormously high solubilizing capability in both the polar ionic liquid and the oil phase, resulting in a surfactant-rich middle phase (3∅), which is found to be in equilibrium with an excess of the polar ionic liquid (EAN) and the oil phase.

Furthermore, as the temperature rises and the amount of non-ionic sugar-based surfactant with enhanced amphiphilicity is increased, the middle phase begins to rise, subsequently the interfacial tension between the phases decreases. This phenomenon continues until the whole amount of polar ionic liquid and oil is dissolved in this phase, resulting in the formation of the one-phase region (1∅) ($\gamma > \bar{\gamma}$), i.e., $\bar{X}$ or $\bar{\gamma}$ (coordinates of fishtail), at which time the entire sample is now referred to as a microemulsion system. As a result, increasing the alkyl chain length of a sugar-based non-ionic surfactant increases the hydrophobicity of the surfactant, resulting in a significant improvement in the surfactant's efficiency. Henceforth, the higher chain length of the non-ionic sugar-based surfactant, *n*-dodecyl *β*-D-maltoside ($\beta - C_{12}G_2$), can readily solubilize both immiscible liquids, i.e., polar ionic liquid (EAN) and oil, resulting in the formation of a one-phase microemulsion system.

The above-mentioned microemulsion system has some unique characteristics, which are listed in Table 3. The parameters are: ∅ (IL volume fraction); γ_0 and T_0 (co-ordinates of the fish head); $\bar{\gamma}$, $\bar{T}$ is (co-ordinates of the fishtail), and $\Delta\gamma$, ΔT (maximum extension of surfactant concentration and temperature of the 3-phase body). Table 1 shows that for formed ternary microemulsion systems, the ΔT value falls as the hydrocarbon chain length of the non-ionic sugar-based surfactant increases. The concentration ranges across which the three-phase body of a microemulsion occurs, $\Delta\gamma$, reduces as ΔT lowers, i.e., the length of fish diminishes.

Table 3. Distinctive parameters of the phase diagrams (*T*-γ section) constructed for a ternary microemulsion formulation.

Microemulsion System	$\emptyset$	γ_0	T_0/°C	$\bar{\gamma}$	$\bar{T}$/°C	$\Delta\gamma$	ΔT/°C
PLANTACARE® 810 – UP (UP-810) / EAN/ Dodecane	0.5	0.1	31.3	0.63	34.9	0.53	3.6
β-$C_{10}G_2$,/EAN/ Dodecane	0.5	0.1	35.9	0.48	37.7	0.38	1.8
β-$C_{12}G_2$,/EAN/ Dodecane	0.5	0.1	41.5	0.43	44.4	0.33	2.9

$\emptyset$ represent the volume fraction of the polar ionic liquid (EAN)/oil (1:1); γ_0, T_0 represent the coordinates of the fish head; $\bar{\gamma}$, $\bar{T}$ represent the coordinates of fishtail; and $\Delta\gamma$, ΔT represent the maximum extension of surfactant concentration and temperature of the three-phase fish-shaped body.

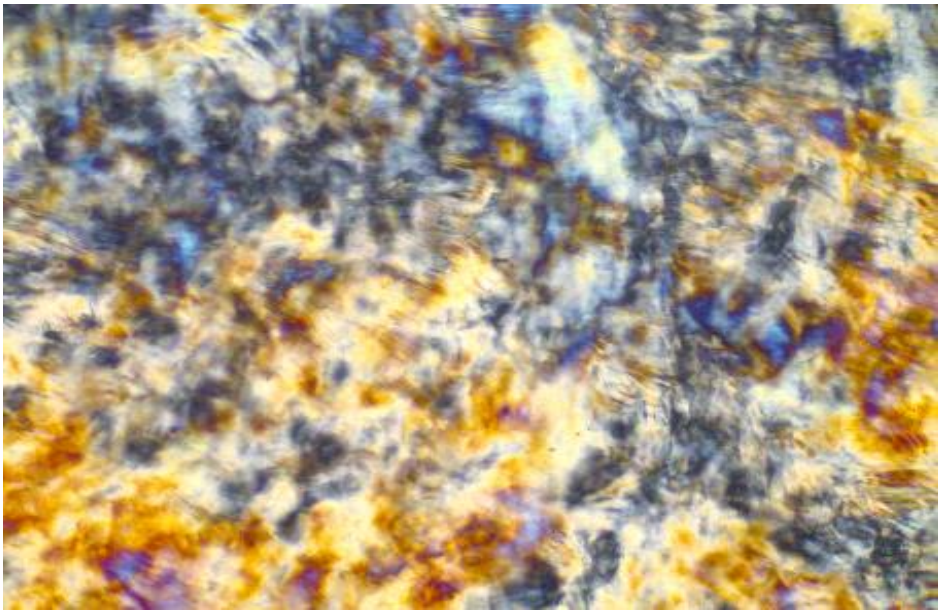


Figure 2. Polarization microscopy images revealing the presence of lamellar phases for the ternary microemulsion system, i.e., β-$C_{12}G_2$/EAN/Octane at γ = > 0.35 in the low-temperature regime (below 40°C).

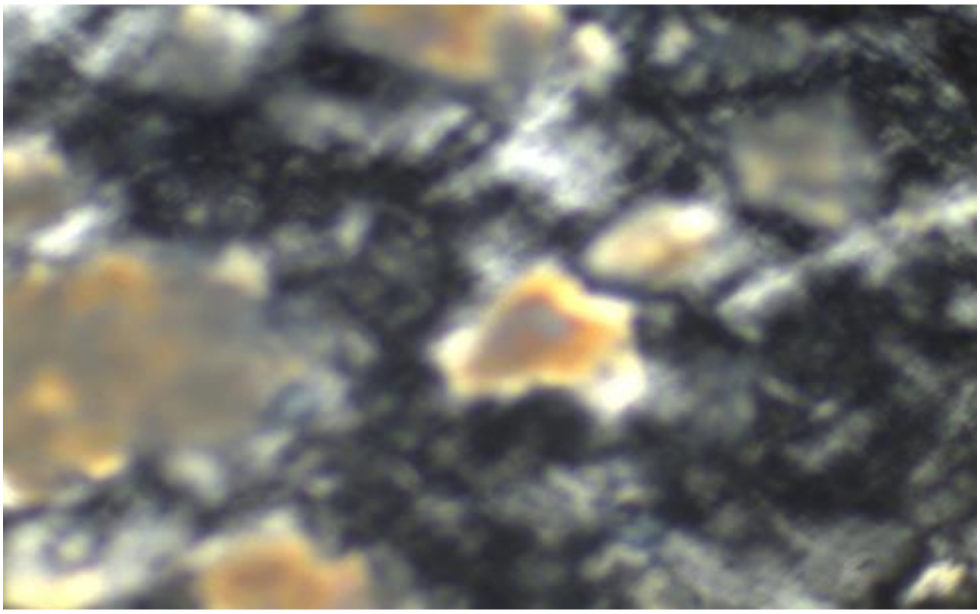


Figure 3. Polarization microscopy images revealing the presence of lamellar phases for the ternary microemulsion system, i.e., β-$C_{10}G_2$/EAN/Octane at γ = > 0.35 in the low-temperature regime (below 40°C).

Figure 4. Polarization microscopy images as a shred of evidence showing the absence of Liquid Crystalline phases (*LC*) for PLANTACARE®810–UP /EAN/Octane microemulsion system. i.e., γ = > 0.35 in the low-temperature as well as high temperature regime.

In the low-temperature zone (below 40°C), polarisation microscopy studies revealed the occurrence of liquid crystalline lamellar phases (*LC*) at large concentrations or mass fractions of sugar-based non-ionic surfactant, i.e., γ = > 0.35. Figure 2 shows images of lamellar phases in the case of *n*-Dodecyl β-D-maltoside ($\beta - C_{12}G_2$)/EAN/octane microemulsion system, whereas Figure 3 shows images of lamellar phases in the case of *n*-decyl β-D-maltoside (β-$C_{10}G_2$)/ EAN/octane microemulsion system. Since the birefringence phenomena is noticed when the sample is held between the crossed polarizers, the lamellar phases were easier to investigate using a polarisation microscope. When the microemulsion is formulated utilising a short alkyl chain non-ionic sugar-based surfactant (i.e., PLANTACARE® 810 – UP (UP-810) as shown in Figure 4, polarisation microscopy tests confirmed the absence of lamellar phase.

Phase behaviour as a function of Oil chain Length

Figure 5 shows vertical sections through phase prisms observed in the presence of non-ionic sugar-based surfactant PLANTACARE® 810-UP (UP-810) at equal masses of polar ionic liquid ethylammonium nitrate (EAN) and various chain lengths of *n*-alkanes as non-polar phase. The $\bar{X}$ was determined to be ~47 wt % in the PLANTACARE® 810-UP (UP-810)/EAN/Octane microemulsion system, ~56 wt % in the PLANTACARE® 810-UP (UP-810)/EAN/Decane microemulsion system, and ~63 wt % in the PLANTACARE® 810-UP (UP-810) /EAN/Dodecane microemulsion system.

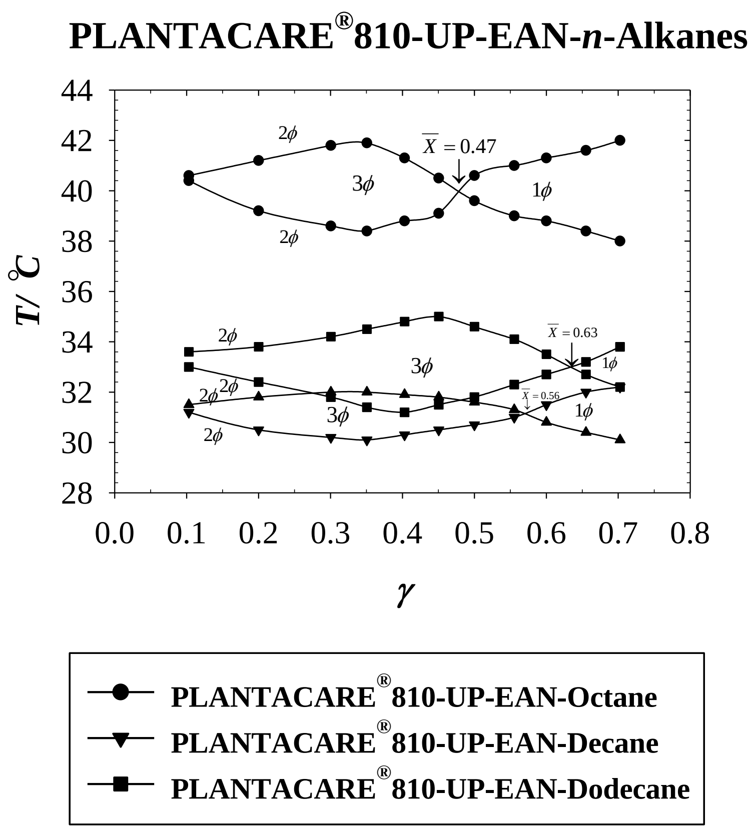
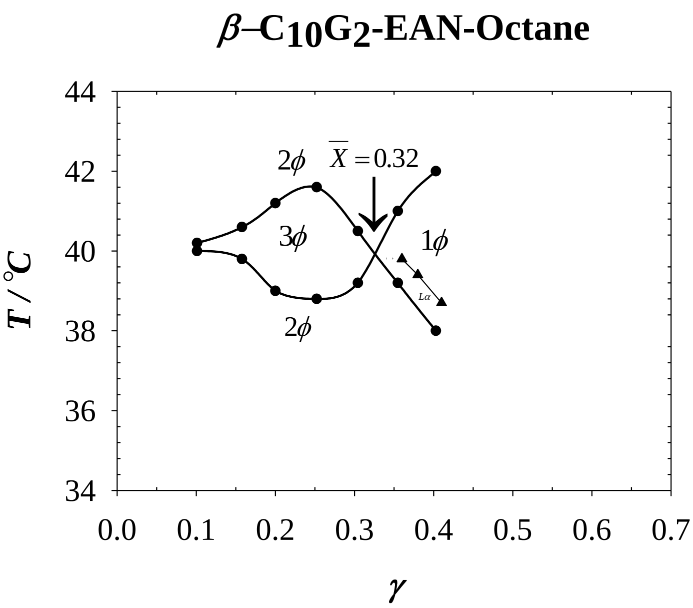


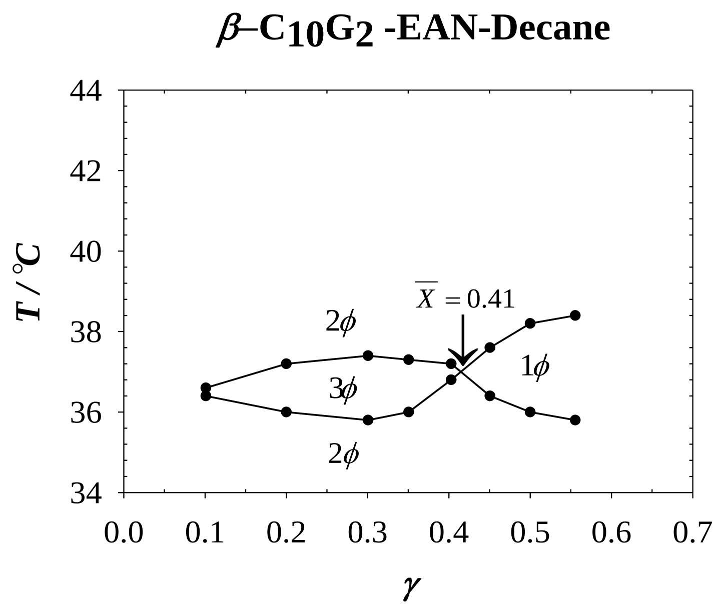
Figure 5. Phase diagram of a [*Temperature (T/°C)- wt% of surfactant* (γ)] ternary microemulsion constructed for equal masses of polar ionic liquid, ethylammonium nitrate (EAN) as polar phase and alkane (dodecane) as the non-polar phase in presence of non-ionic sugar-based surfactants with varying chain lengths of *n*- alkanes as non-polar phase, viz. PLANTACARE® 810 – UP (UP-810)/EAN/Octane, PLANTACARE® 810 – UP (UP-810)/EAN/Decane and PLANTACARE® 810 – UP (UP-810)/EAN/Dodecane. T/°C represents the temperature and γ is the mass fractions of surfactant. 1Ø corresponds to one phase, 2Ø corresponds lower two-phase (O/IL droplet μE), 2Ø corresponds upper two phases (IL/O droplet μE), and 3Ø corresponds to three-phase regions, respectively.

Similarly, in the presence of non-ionic sugar-based surfactant *n*-Decyl β-D-maltoside (β–$C_{10}G_2$), phase studies were conducted for equal masses of polar ionic liquid ethylammonium nitrate (EAN) and varying chain lengths of *n*-alkanes as non-polar phase, where the $\bar{X}$ was found to be ~32 wt % in the case of *n*-Decyl β-D-maltoside (β-$C_{10}G_2$)/ EAN/octane microemulsion system, while in the case of *n*-Decyl β-D-maltoside (β-$C_{10}G_2$)/ EAN/Decane, the $\bar{X}$ was found to be ~41 wt % and later in the case of *n*-Decyl β-D-maltoside (β-$C_{10}G_2$)/ EAN/Dodecane, the $\bar{X}$ is found to be ~48 wt % as shown in Fig. 6 (a), 6 (b) and 6 (c).

(a)



(b)



(c)

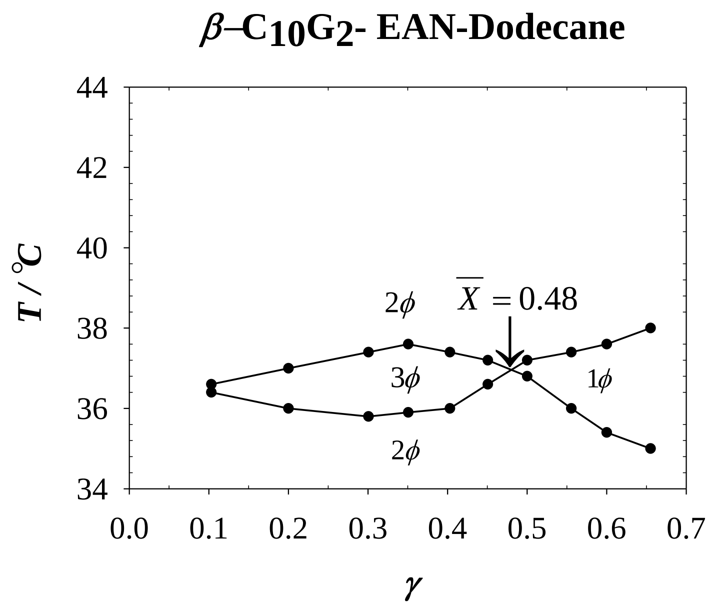
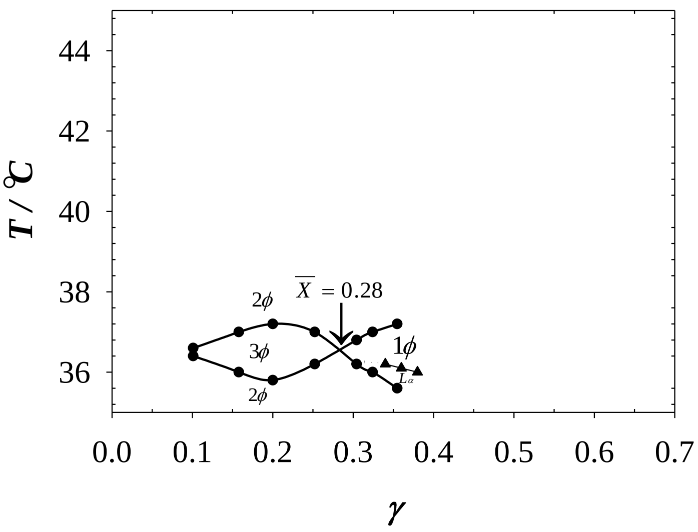


Figure 6. Phase diagram [*Temperature (T/°C)- wt% of surfactant* (γ)] of a ternary microemulsion system constructed for equal masses of polar ionic liquid, ethylammonium nitrate (EAN) as polar phase and varying chain lengths, *n*- alkanes as non-polar phase in presence of non-ionic sugar-based surfactant, *n*-Decyl β-D-maltoside (β-$C_{10}G_2$). T/°C represents the temperature and γ is the mass fractions of surfactant. 1∅ corresponds to one phase, 2∅ corresponds lower two-phase (O/IL droplet μE), 2∅ corresponds upper two phases (IL/O droplet μE), and 3∅ corresponds to three-phase regions, respectively.

In addition, phase behaviour studies were conducted for a sugar-based non-ionic surfactant with a longer alkyl chain length, namely *n*-Dodecyl β-D-maltoside (β-$C_{12}G_2$), with equal quantities of polar ionic liquid ethylammonium nitrate (EAN) and various chain lengths of n- alkanes. The $\bar{X}$ value for *n*-Dodecyl β-D-maltoside (β-$C_{12}G_2$)/ EAN/octane microemulsion system is found to be ~28 wt %, while the $\bar{X}$ value for *n*-Dodecyl β-D-maltoside (β-$C_{12}G_2$)/ EAN/decane microemulsion system is found to be ~34 wt %, and it reaches ~43 wt % for n *n*-Dodecyl β-D-maltoside (β-$C_{12}G_2$)/ EAN/dodecane microemulsion system.

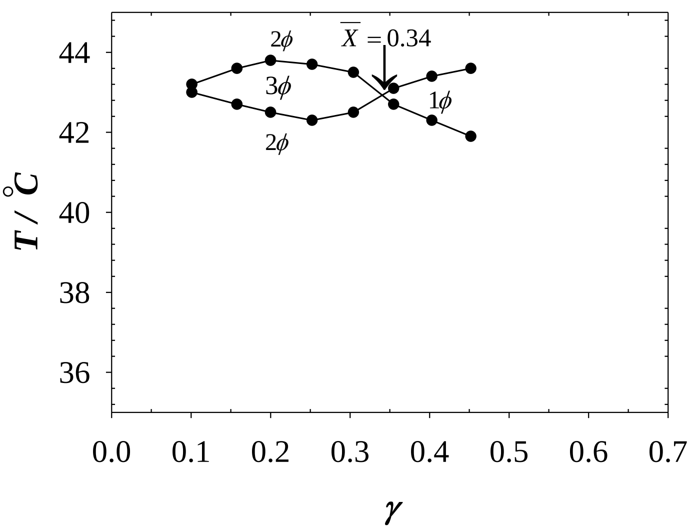
β–$C_{12}G_2$- EAN-Octane

(a)



β–$C_{12}G_2$- EAN-Decane

(b)



(c)

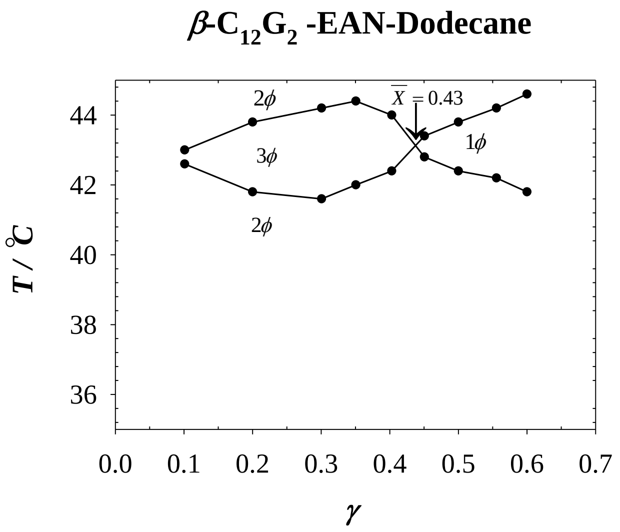


Figure 6. Phase diagram [*Temperature (T/°C)- wt% of surfactant* (γ)] of a ternary microemulsion system constructed for equal masses of polar ionic liquid, ethylammonium nitrate (EAN) as polar phase and varying chain lengths, *n*- alkanes as non-polar phase in presence of non-ionic sugar-based surfactant, *n*-Dodecyl β-D-maltoside (β-$C_{12}G_2$).

Table 4. Distinctive parameters of the phase diagrams (T-γ section) constructed for a ternary microemulsion formulation.

Microemulsion System	$\emptyset$	γ_0	T_0/°C	$\bar{\gamma}$	$\bar{T}$/°C	$\Delta\gamma$	ΔT/°C
PLANTACARE® 810 – UP/ EAN/ Octane	0.5	0.1	38.4	0.47	41.9	0.37	3.5
PLANTACARE® 810 – UP/ EAN/ Decane	0.5	0.1	30.2	0.56	32.0	0.46	1.8
PLANTACARE® 810 – UP/ EAN/ Dodecane	0.5	0.1	31.2	0.63	35.0	0.53	3.8
n-Decyl β-D-maltoside (β–$C_{10}G_2$)/ EAN/ Octane	0.5	0.1	38.8	0.32	41.6	0.22	2.8

n-Decyl *β*-D-maltoside (*β*–$C_{10}G_2$)/ EAN/ Decane	0.5	0.1	35.8	0.41	37.4	0.31	1.6
n-Decyl *β*-D-maltoside (*β*–$C_{10}G_2$)/ EAN/ Dodecane	0.5	0.1	35.8	0.48	37.6	0.38	1.8
n-Dodecyl *β*-D-maltoside (*β*–$C_{12}G_2$)/ EAN/ Octane	0.5	0.1	35.8	0.28	37.2	0.18	1.4
n-Dodecyl *β*-D-maltoside (*β*–$C_{12}G_2$)/ EAN/ Decane	0.5	0.1	43.8	0.34	44.2	0.24	0.4
n-Dodecyl *β*-D-maltoside (*β*–$C_{12}G_2$)/ EAN/ Dodecane	0.5	0.1	41.6	0.43	44.3	0.33	2.7

$\emptyset$ represents the volume fraction of the polar ionic liquid (EAN)/oil (1:1); γ_0, T_0 represents the coordinates of the fish head; $\overline{\gamma}, \overline{T}$ represents the coordinates of fishtail; and $\Delta\gamma$, ΔT represents the maximum extension of surfactant concentration and temperature of the three-phase fish-shaped body.

Table 4 lists the unique parameters for the formulated microemulsion system. The surfactant efficiency diminishes as the length of the oil chain increases, as shown in Figures 4, 5, and 6. This is because as the oil chain lengthens, the one-phase region swings toward higher temperatures, lowering surfactant efficiency. The decline in the efficiency of sugar-based surfactants is due to the increased hydrophobicity of oil, which makes surfactant difficult to solubilize in it, requiring more surfactant to solubilize the same amount of oil in order to formulate a microemulsion system.

Furthermore, as the length of the oil chain increases, the oil becomes more hydrophobic, reducing surfactant efficiency and pushing the one-phase region to higher temperatures (Hejazifer et al., 2020; Tessendorf, 2007). These findings are consistent with those of Thater et al (2014; 2019), who found that surfactant effectiveness falls as alkyl chain length of alkanes increases, and that surfactant efficiency can be enhanced by constructing a microemulsion system with a shorter alkyl chain length alkane, such as octane. As a result, it can be concluded that sugar-based non-ionic surfactants, such as PLANTACARE® 810-UP (UP-810), n-Decyl β-D-maltoside (β-$C_{10}G_2$), and n-Dodecyl β-D-maltoside (β-$C_{12}G_2$), in combination with polar ionic liquid, are a preferable alternative for forming a non-aqueous microemulsion system from the standpoint of the environment. As a safer and greener option, such a microemulsion system can be used in a variety of applications.

4.4. Conclusions

In the present study, the ternary microemulsion systems comprising of non-ionic sugar-based surfactants, *n*-alkanes (oils), and polar ionic liquid, i.e., ethylammonium nitrate (EAN) were formulated. The phase behaviour and microstructure of the formulated ternary microemulsion system were determined. The ternary microemulsion systems formation in this investigation included non-ionic sugar-based surfactants, *n*-alkanes (oils), and a polar ionic liquid, ethylammonium nitrate (EAN). The formulated ternary microemulsion system's phase behaviour and microstructure was investigated. However, for the 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).

Furthermore, it has been discovered that the surfactant efficiency diminishes when *n*-alkanes with long-chain length hydrocarbons are added. In addition, the present study revealed that even in the absence of a co-surfactant, polar ionic liquids can produce microemulsion system with sugar-based non-ionic surfactants. Furthermore, the results were obtained by combining a longer hydrophobic chain of a sugar-based non-ionic surfactant, *n*-Dodecyl β-D-maltoside (β-$C_{12}G_2$), with a shorter alkyl chain alkane, i.e., octane, which has the highest surfactant efficiency and may be employed in a variety of applications.

In addition to this, it is found that ethylammonium nitrate (EAN), a polar ionic liquid, can successfully replace water as a polar phase. As a result, nanoreactors and many chemical reactions that do not require water benefit most from such microemulsion system. Finally, 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®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, β-$C_{10}G_2$ and β-$C_{12}G_2$ were used for the formulation of a microemulsion system.