CHAPTER III

HYDROPHOBIC IONIC LIQUID/ SUGAR SURFACTANT/WATER MICROEMULSIONS: EFFECT OF MASS FRACTION OF IONIC LIQUID (α) AS WELL AS THE EFFECT OF CO-SURFACTANT

Hydrophobic ionic liquid/ sugar surfactant/water microemulsion: effect of mass fraction of ionic liquid (α) as well as the effect of co-surfactant

In the present chapter, the effect of altering the mass fraction of ionic liquid (on the phase behaviour and microstructure of a formulated microemulsion system using hydrophobic ionic liquid as the oil phase, a non-ionic sugar-based surfactant, and a polar solvent, i.e., water, has been evaluated. Furthermore, a thorough investigation the effect of *n*-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 traditional sugar-based non-ionic surfactants as well as Lauryl Glucoside (and) Cocamidopropyl Betaine zwitterionic surfactant was also investigated. In addition, the formation of liquid crystalline phases in the microemulsion systems was studied using Polarising Microscopy. The inclusion of a long-chain length alkanol (co-surfactant) lowers the $\overline{X}$-point while concurrently increasing the efficiency of sugar-based surfactant.

3.1 Introduction

Microemulsions are isotropic liquid solutions that are clear, thermodynamically stable, and optically transparent. They are made up of three components: two immiscible liquids, a surfactant, and sometimes a co-surfactant (Bellocq et al., 1984; Paul & Moulik, 1997; Mitchell & Ninham, 1981; Kunz et al., 2012; Kahlweit, 1999; Prince, 2012). When oil and water are present in the mixture, the isotropic mixture of the three components generates nanoscale aggregates such as oil swollen micelles and water-swollen reverse micelles. Such mixtures of water, oil, and surfactant exhibit a wide range of microstructures, as well as a wide range of liquid crystalline or lamellar phases, as well as many other forms of multiple phase domains, inside the single-phase dispersion known as microemulsion (Chen et al., 1986; Hellweg, 2002; Strey, 1994; Saha et al., 2012; Dubois & Zemb, 2000; Kahlweit & Strey, 1985; Kahlweit et al., 1993; Kahlweit et al., 1987; Kahlweit et al., 1989; Kahlweit et al., 1985; Kahlweit et al., 1990; Kahlweit et al., 1986; Rakshit et al., 2019).

Room temperature ionic liquids (RTILs) are liquids made entirely of ions that exist at room temperature. RTILs have organic and inorganic cations and anions, respectively (Holbrey & Seddon, 1999; Earle et al., 2000). When compared to dipolar or multipolar interactions in Volatile Organic Compounds (VOCs), coulombic interactions between ions are significant in RTILs. The nonvolatile character of RTILs is their most essential and distinguishing attribute, as they do not contribute VOCs to the global atmosphere (Marsh et al., 2004; Marsh et al., 2002; Atkin & Warr, 2007; Wasserscheid & Welton, 2008; Gao et al., 2006). Hence RTILs, rather than VOCs or traditional hydrocarbon solvents, are most suited for microemulsion formulation (Kuchlyan et al., 2016; Liu et al., 2009; Marsh et al., 2004; MacFarlane et al., 2007; Welton, 1999; Wasserscheid & Welton, 2008; Plechkova & Seddon, 2007). RTILs have been effectively employed to substitute organic solvents in a microemulsion system due to their beneficial properties, such as low vapour pressure, low volatility, high thermal stability, a broad liquid temperature range of 96–300 °C, superior conductivity and ability to dissolve a wide variety of organic and inorganic material (Marsh et al., 2004; Marsh et al., 2002; Atkin & Warr, 2007; Li et al., 2006; Welton, 1999). In general, the polar phase is water, and the non-polar phase is an organic solvent (very often *n*-alkanes are used) in a microemulsion system (Kahlweit et al., 1985; Kahlweit et al., 1989; Kahlweit & Strey, 1987; Kahlweit et al., 1988; Rao et al., 2012; Kahlweit, Strey, & Haase, 1985; Kumar & Mittal, 1999; Hellweg, 2002; Rai & Pandey., 2014).

The literature already contains several reports on microemulsion systems in which equal amounts of water and a hydrophobic ionic liquids are solubilized in the presence of conventional non-ionic alkyl polyglycol ether (C_iE_j) surfactants to formulate a microemulsion (Anjum et al., 2009; Porada et al., 2011; Sun et al., 2014; Porada et al., 2017; Zheng & Eli., 2009; Rakshit et al., 2019; Porada et al., 2017; Porada et al., 2011; Qiu & Texter, 2008; Hejazifar et al., 2020; Gao et al., 2005; Gao et al., 2007; Barauer et al., 1999; Sjöblom et al., 1996; Solanki & Patil, 2020; Seth et al., 2007; Zech et al., 2011).

In the previous chapter, we explored the formulation of a ternary microemulsion system using a hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate as the oil/non-polar phase and a non-ionic sugar-based alkyl polyglycoside surfactant as the non-polar phase. Phase behaviour and microstructure were investigated. In this chapter, the major objective was to study the effect of varying mass fractions of ionic liquid (α) on the phase behaviour and microstructure of a microemulsion system. In addition, we looked into the phase behaviour and microstructure of a hydrophobic ionic liquid microemulsion system using alkanols with varying chain lengths (octanol, decanol, and dodecanol) as co-surfactants. Additionally, polarizing microscopy studies were conducted to ascertain the formation of liquid crystalline phases in microemulsion systems.

3.2 Materials and methods

The non-ionic surfactant Triton X-100 ($C_{14}H_{22}O(C_2H_4O)n$, purity≥97.0%); the alcohols 1-dodecanol ($C_{12}H_{26}O$, purity 99 %),1-Decanol ($C_{10}H_{22}O$, purity 99 %), *n*-octanol ($C_8H_{18}O$, purity 99%); the Ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] ($C_8H_{15}F_6N_2P$, purity ≥97.0%) and the alkanes, i.e. Tetradecane[$CH_3(CH_2)_{12}CH_3$ (or $C_{14}H_{30}$), purity 99%], [Dodecane [$CH_3(CH_2)_{10}CH_3$ (or $C_{12}H_{26}$), purity 99%], Decane [$CH_3(CH_2)_8CH_3$ (or $C_{10}H_{22}$), purity 99 %], Octane [$CH_3(CH_2)_6CH_3$ (or C_8H_{18}), purity 99 %] were procured from Sigma Aldrich, USA. The industrial grade alkyl glucoside surfactant, PLANTACARE® 810 – UP, i.e., $C_{8\text{-}10}$ fatty alkyl glucoside or UP-810 and Lauryl Glucoside (and) Cocamidopropyl Betaine (PLANTACARE® K-55) was received as gift sample from BASF, Germany.

Phase Studies

In order to examine microemulsions, it is necessary to study phase behaviour, identify phase transitions and phase boundaries. In the preceding chapter, the phase behaviour of self-assembling ternary mixtures (water, hydrophobic ionic liquid, and surfactant) was also discussed. Microemulsions were made by weighing known amounts of water, hydrophobic ionic liquid, and surfactant, or polar ionic liquid, solvent (oil), and surfactant, in test tubes, as described in the previous chapter. In a transparent water bath (± 0.2 ℃), the sealed test tubes were kept. Visual inspection/optical polarised microscopy of phase boundaries at temperatures ranging from 30 to 60°C determined the number of phases, 1∅ (corresponding to one phase), 2∅ (corresponding to lower two-phase) or water/ionic liquid droplet microemulsion, 2∅ (corresponding to upper two-phase) or ionic liquid/water droplet microemulsion), and 3∅ (corresponding to three-phase regions).

The sample compositions of the ternary mixtures are defined as the mass fraction of ionic liquid (α) in the solvent mixture and is given by,

$$\alpha = \frac{m_{[\mathrm{Bmim}][\mathrm{PF}_6]}}{m_{[\mathrm{Bmim}][\mathrm{PF}_6]}+m_{\mathrm{H2O}}}$$

Here, in this study, the sample compositions of the quaternary mixtures are defined as the mass fraction of a surfactant in the total mixture,

$$\gamma = \frac{m_{\mathrm{surfactant}}}{m_{[\mathrm{Bmim}][\mathrm{PF}_6]}+m_{\mathrm{H2O}}+m_{\mathrm{co-surfactant}}+m_{\mathrm{surfactant}}}$$

Polarization Microscopy

The optical microscopy analysis of the prepared microemulsion samples was carried out by placing samples on a glass slide. The glass slide was covered with a coverslip and the sample was observed under Leica DM750 P Polarization microscope between crossed polarizers.

3.3 Results and Discussion

3.3.1 Effect of varying mass fraction of ionic liquid (α) on the microemulsion system

Figure 1 represents the phase diagrams for the ternary system PLANTACARE® 810 – UP/[Bmim][PF_6]/water with varying the mass fraction of the ionic liquid *(α)*, as a function of γ and T/°C. The fish-shaped outlines in Figure 1 are based on temperature scans taken at various γ. Table 1 lists the typical parameters of the phase diagrams. As demonstrated in Figure 1, an IL/W droplet microemulsion coexists (2∅ upper phase) with an IL surplus phase for γ values below 0.5 and at low temperatures (Winsor I system). A bicontinuous microemulsion with an IL excess phase and a water excess phase (3∅ phase or Winsor III) coexists at an intermediate temperature when the temperature is elevated. As the temperature rises, a W/IL droplet microemulsion coexists with a water excess phase (2∅ lower phase or Winsor II system), i.e., at high temperatures. From low to high temperature, increasing the surfactant mass fraction, i.e., γ values above ~0.5, results in the creation of an isotropic, optically transparent 1-phase microemulsion system (1∅ or Winsor IV).

Our findings are consistent with those obtained utilising [Bmim][PF_6]/water/Triton X-100 (Anjum et al., 2009), where the comparison of these phase sequences was reported to be similar to that of the classical water/*n*-alkane/C*i*E*j* system.

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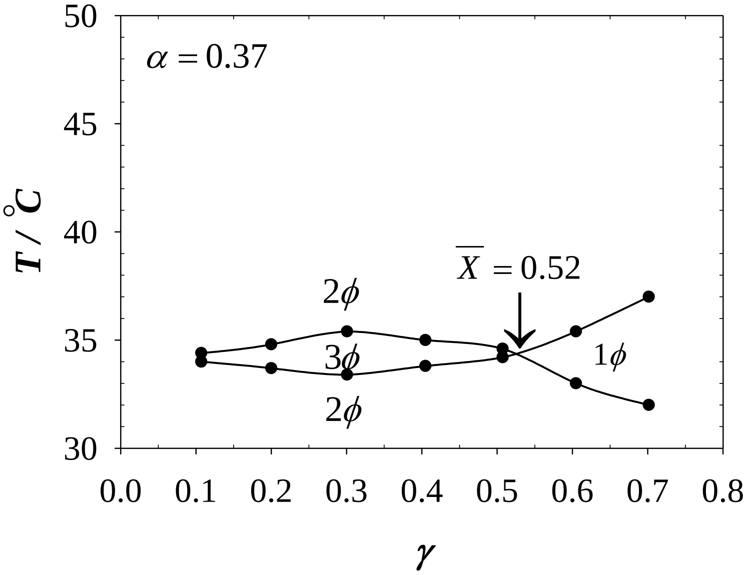

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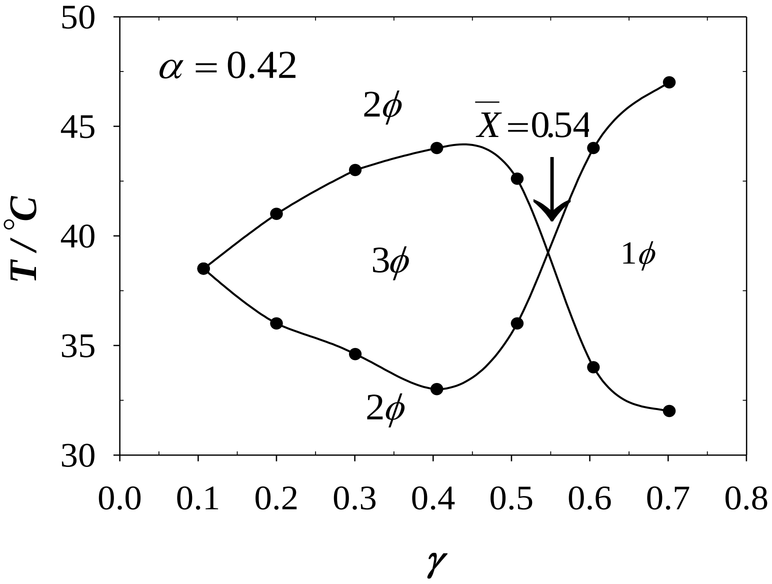
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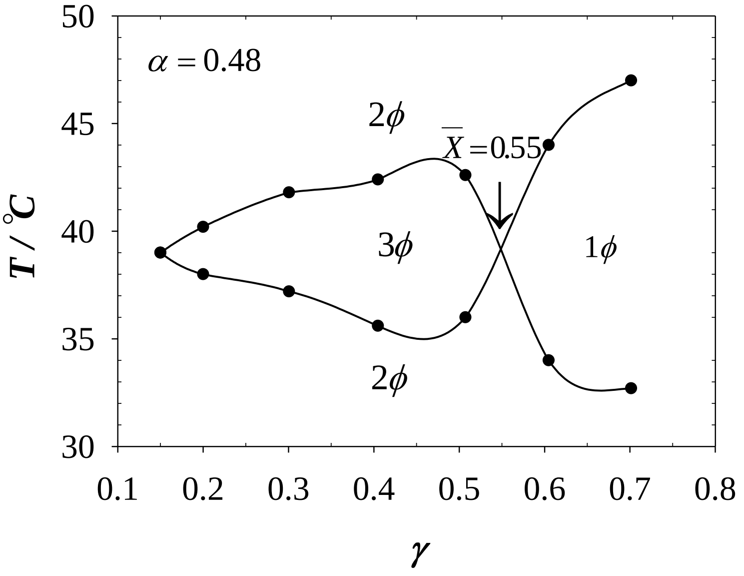
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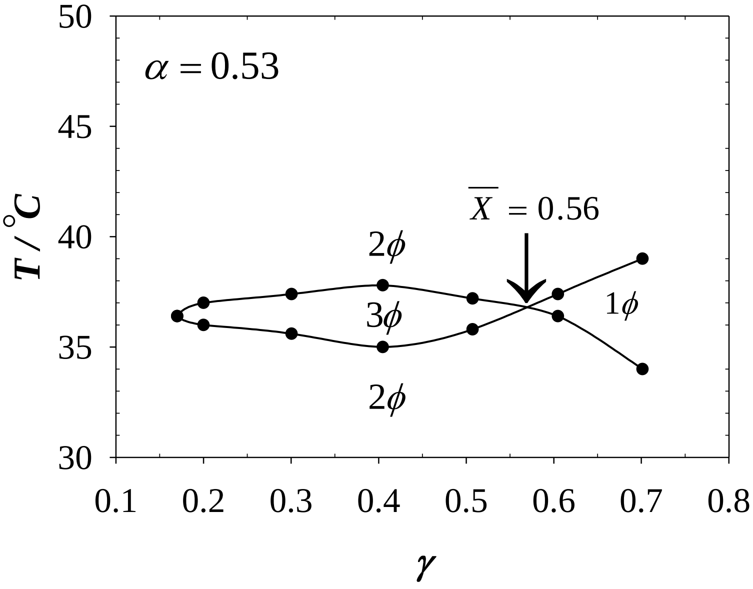
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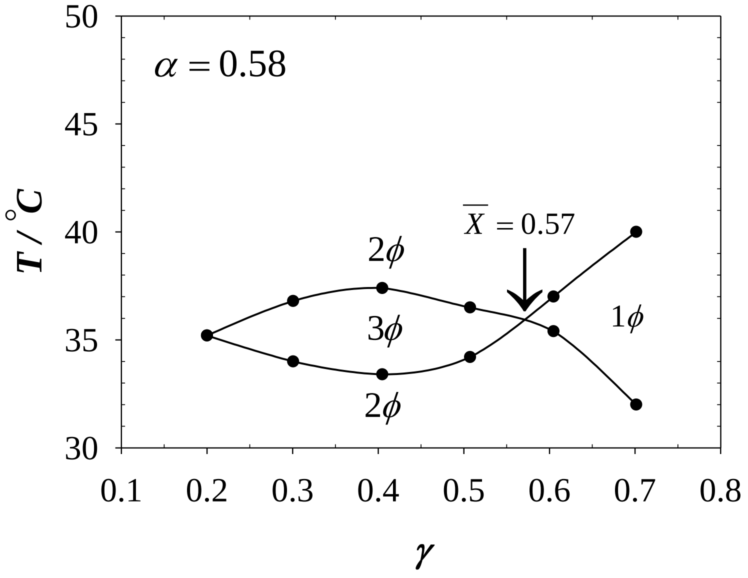

Figure 1. Fish-shaped phase diagrams (*T/°C*-γ section) of the ternary system obtained for equal masses of water and ionic liquid [Bmim][PF_6], in presence of PLANTACARE® 810 – UP surfactant at varying mass fraction of ionic liquid (α) [IL/ (IL + water)] ratios. (α = 0.58 corresponds to equal volumes of water and ionic liquid). *T/°C* represents the temperature and γ is the mass fractions of surfactant. $1\emptyset$ corresponds to one phase, $2\emptyset$ corresponds to lower two-phase (W/IL droplet μE), $2\emptyset$ corresponds to upper two-phase (IL/W droplet μE), and $3\emptyset$ corresponds to three-phase regions, respectively.

Table 1. Characteristic parameters of the constructed Phase diagrams

Microemulsion System	$\boldsymbol{\alpha}$	$\emptyset$	$\boldsymbol{\gamma_0}$	$\boldsymbol{T_0}$/°C	$\boldsymbol{\overline{\gamma}}$	$\boldsymbol{\overline{T}}$/°C	$\Delta\boldsymbol{\gamma}$	$\Delta\boldsymbol{T}$/°C
PLANTACARE® 810 – UP/ [Bmim][PF_6]/ H_2O	0.37	0.30	0.10	35.6	0.52	35.4	0.42	2.0
PLANTACARE® 810 – UP/ [Bmim][PF_6]/ H_2O	0.42	0.35	0.10	35.1	0.54	44.1	0.44	11.1
PLANTACARE® 810 – UP/ [Bmim][PF_6]/ H_2O	0.48	0.40	0.14	33.4	0.55	42.5	0.41	6.9
PLANTACARE® 810 – UP/ [Bmim][PF_6]/ H_2O	0.53	0.45	0.16	33.5	0.56	37.9	0.4	2.8

PLANTACARE® 810 – UP/ [Bmim][PF_6]/ H_2O	0.58	0.50	0.19	33.0	0.57	37.4	0.38	3.9

IL mass fraction α; IL volume fraction $\emptyset$; coordinates of fish head γ_0, T_0; coordinates of fishtail $\overline{\gamma}$, $\overline{T}$; maximum extension of surfactant concentration and temperature of the 3-phase body $\Delta\gamma$, ΔT.

As evident from Figure 1 and Table 1, the fish's head has migrated towards a high mass fraction of surfactant (γ) at low temperatures and an increase in the mass fraction of ionic liquid (α). This is attributed to the higher monomeric solubility of the sugar-based non-ionic surfactant in the ionic liquid. As the mass fraction of the ionic liquid in the ternary system increases, more surfactant is utilised for saturation of the ionic liquid phase with the monomers of the surfactant, as shown in Figure 1 (a) to (e). This raises the coordinates of the fish head γ_0. From the given table, it has been observed that T_0 decreases as the mass fraction of ionic liquid (α) in the system are increased. This is due to the ternary system's increased ability to generate W/IL droplets. Specifically, at lower temperatures, the curvature changes from positive to negative values via an average zero mean curvature. The initial droplet of the middle phase occurs at the coordinates γ_0, T_0, which are the coordinates of the fish head. The volume of the intermediate phase grows as the surfactant mass fraction, γ, increases, without affecting the bicontinuous structure, as seen in Figure 1 (a) to (e).

The coordinates of the fishtail, $\overline{\gamma}$, are moderately influenced by varying the mass fraction of ionic liquid, α, as evident from the details in Table 1. It can be inferred very clearly that, upon changing the mass fraction of the ionic liquid, α, there is no substantial change in the $\bar{X}$ or $\bar{\gamma}$ value, which is the minimum surfactant needed for solubilizing two immiscible solvents (IL and Water). Figure 1 (a) shows that for a mass fraction of ionic liquid, $\alpha = 0.37$, the $\overline{X} = 0.52$ which increases to the $\overline{X} = 0.54$ at $\alpha = 0.42$ (Figure 1 (b)), $\overline{X} = 0.55$ at $\alpha = 0.48$ (Figure 1 (c)), $\overline{X} = 0.56$ at $\alpha = 0.53$ (Figure 1 (d)), $\overline{X} = 0.57$ at $\alpha = 0.58$ (Figure 1 (e)). Thus, as the mass fraction of the ionic liquid (α) grows, the mass fraction of the surfactant (γ) increases as well, resulting in a drop in surfactant efficiency. However, as compared to the traditional surfactants, the amount of sugar-based nonionic surfactant used is smaller. Furthermore, the sugar-based surfactant we employ is non-toxic and environmentally benign, which is apt for a wide range of applications. The ternary microemulsion system PLANTACARE® 810 – UP/ [Bmim][PF_6]/ H_2O does not have a liquid crystalline phase, as mentioned in the preceding chapter. Despite altering the mass fraction of ionic liquid in the current chapter, no indication of a liquid crystalline phase was observed in any of the five systems.

3.3.2 Effect of co-surfactant on hydrophobic Ionic Liquid microemulsion system

The effect of co-surfactants, such as short-chain alcohols, octanol, decanol, and dodecanol, as well as sugar-based non-ionic surfactants, on the phase behaviour of the ternary microemulsion system was examined in this section. The Triton X-100/[Bmim][PF_6]/*n*-alkanols/H_2O microemulsion system was formulated and this system was compared with that of a microemulsion formulated using sugar-based non-ionic surfactant, and the zwitterionic sugar surfactants. Table 2 lists the characteristic parameters for formulated microemulsion systems.

It can be inferred from Figure 2 that, the $\overline{X}$ or $\overline{\gamma}$, for the ternary microemulsion system; Triton X-100/[Bmim][PF_6]/*n*-alkanols/H_2O, decreases as the alkyl chain length of the co-surfactant increases in the presence of the co-surfactants. It is clear from Figure 2 of the previous chapter 2, the amount of conventional surfactant required to solubilize water and 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6], in the ternary microemulsion system, Triton X-100/[Bmim][PF_6]/ H_2O, the $\overline{X}$ or $\overline{\gamma}$ is high (0.57). From Figure 2 (a), it can be noted that the $\overline{X}$ or $\overline{\gamma}$ is reduced to 0.54, when the microemulsion is formulated using conventional, Triton X-100 surfactant along with the use of the co-surfactant (octanol) and it reduces further to 0.52 (Figure 2(b)) using decanol and subsequently decreases to 0.49 (Figure 2(c)) with the use of dodecanol as co-surfactant. The values of $\Delta\gamma$ decrease gradually with an increase in length of the alkanol (co-surfactant) used for the formulation of a microemulsion is shown in Table 1.

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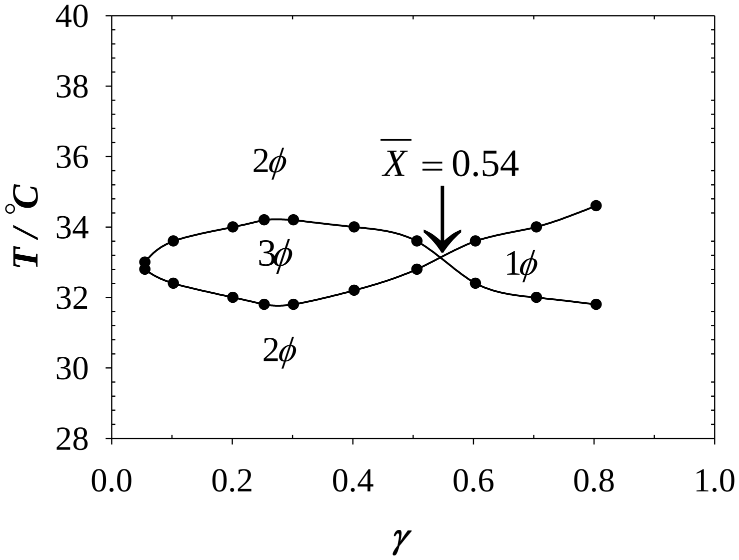
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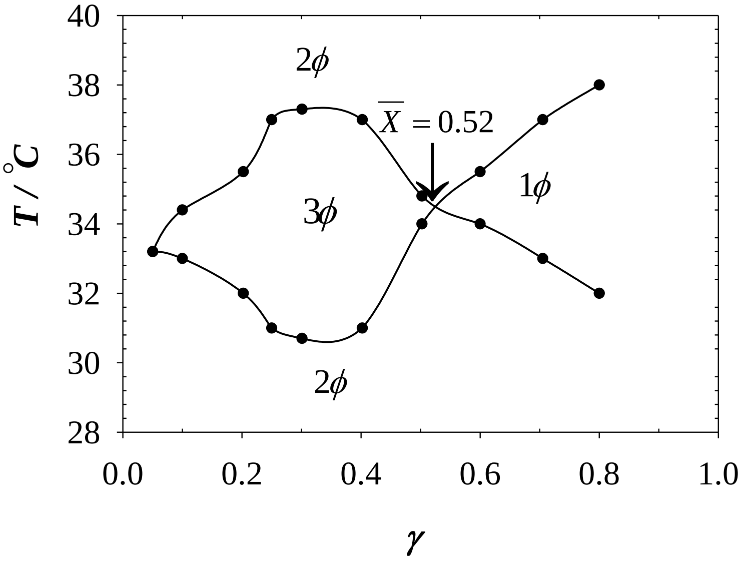
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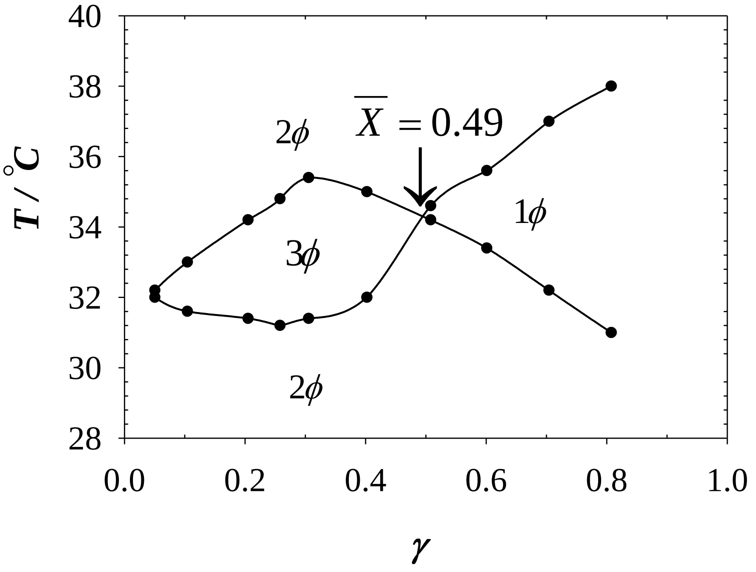


Figure 2. Fish-shaped phase diagram obtained for equal masses of water and IL [Bmim][PF_6], in presence of Triton X-100 and various chain lengths alkanols. (a) Triton X-100/[Bmim][PF_6]/Octanol/H_2O (b) Triton X-100/ [Bmim][PF_6]/Decanol/H_2O (c) Triton X-100/[Bmim][PF_6]/Dodecanol /H_2O. The chosen IL mass fraction α corresponds to equal volumes of water and IL. *T/°C* represents the temperature and γ is the mass fractions of surfactant. 1Ø corresponds to one phase, 2Ø corresponds lower two phases (W/IL droplet μE), 2Ø corresponds upper two-phase (IL/W droplet μE), and 3Ø corresponds to three-phase regions, respectively.

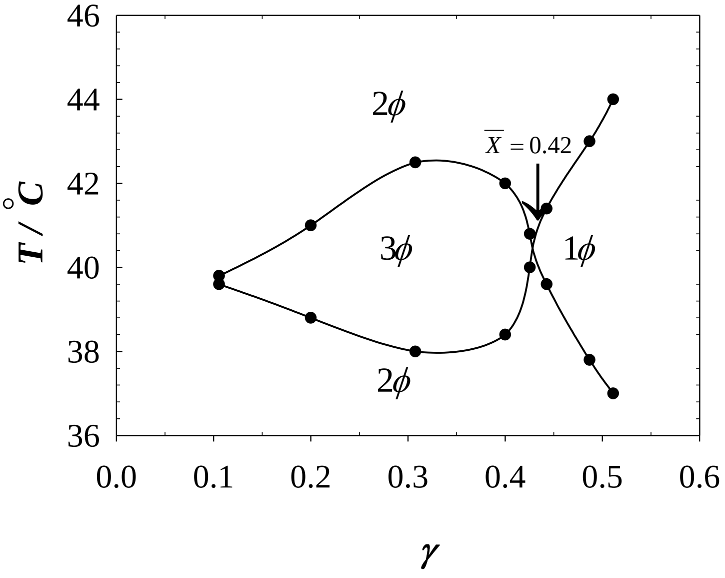
Table 2. Characteristic parameters of the constructed Phase diagrams

Microemulsion System	Ø	γ_0	T_0/°C	$\bar{\gamma}$	$\bar{T}$/°C	$\Delta\gamma$	ΔT/°C
Triton X-100 / [Bmim][PF_6]/ Octanol/ H_2O	0.5	0.05	31.6	0.54	34.3	0.49	2.7
Triton X-100 / [Bmim][PF_6]/ Decanol/ H_2O	0.5	0.05	30.7	0.52	37.3	0.47	6.6
Triton X-100 / [Bmim][PF_6]/ Dodecanol/ H_2O	0.5	0.05	31.1	0.49	35.4	0.44	4.3

When co-surfactants are added in ternary microemulsion systems, such as PLANTACARE®810–UP/[Bmim][PF_6]/*n*-alkanols/H_2O, the $\bar{X}$ or $\bar{\gamma}$, which is the minimum surfactant concentration required to solubilize the two immiscible solvents, decreases as the alkyl chain length of the co-surfactant increases, as shown in Figure 3. It is clear from Figure 3 of chapter

2, that the amount of the amount of sugar-based non-ionic surfactant, i.e., PLANTACARE®810–UP, required to solubilize water and 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6], the $\overline{X}$ or $\overline{\gamma}$ in a ternary microemulsion system is high (0.46) in a ternary microemulsion system, whereas in the current chapter, we have reported that the $\overline{X}$ or $\overline{\gamma}$ is reduced to 0.42 as shown in Figure 3 (a) in a ternary microemulsion system formulated using PLANTACARE®810–UP surfactant along with the co-surfactant (octanol) and it reduces further to 0.39 (Figure 3(b)) using decanol and subsequently decreases to 0.35 (Figure 3 (c)) with the use of dodecanol as co-surfactant. The phase diagrams' distinctive properties are listed in Table 1. As demonstrated in Table 3, the values of Δγ drop gradually as the length of the alkanol (co-surfactant) utilised in the microemulsion formulation increases.

(a)



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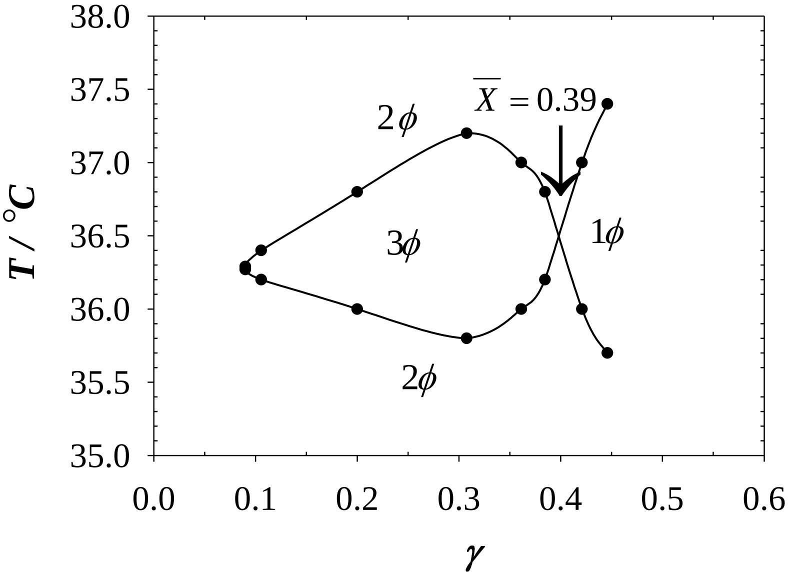

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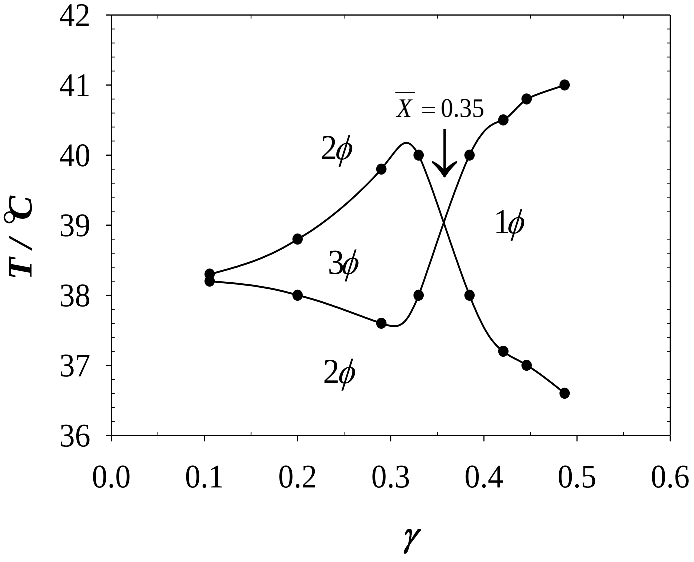


Figure 3. Fish-shaped phase diagram obtained for equal masses of water and IL [Bmim][PF_6], in presence of PLANTACARE®810–UP and various chain lengths alkanols.
(a)PLANTACARE®810–UP/[Bmim][PF_6]/Octanol/H_2O
(b)PLANTACARE®810–UP/[Bmim][PF_6]/Decanol/H_2O
(c) PLANTACARE® 810–UP/[Bmim][PF_6]/Dodecanol /H_2O.

The chosen IL mass fraction α corresponds to equal volumes of water and IL. *T/°C* represents the temperature and γ is the mass fractions of surfactant. 1∅ corresponds to one phase, 2∅ corresponds lower two phases (W/IL droplet μE), 2∅ corresponds upper two phases (IL/W droplet μE), and 3∅ corresponds to three-phase regions, respectively.

Table 3. Characteristic parameters of the constructed Phase diagrams

Microemulsion System	$\emptyset$	γ_0	T_0/°C	$\bar{\gamma}$	$\bar{T}$/°C	$\Delta\gamma$	ΔT/°C
PLANTACARE® 810 – UP/ [Bmim][PF_6]/Octanol/ H_2O	0.5	0.1	39.6	0.42	40.4	0.32	4.5
PLANTACARE® 810 – UP / [Bmim][PF_6]/Decanol/ H_2O	0.5	0.1	38.2	0.39	39.0	0.29	2.0
PLANTACARE® 810 – UP / [Bmim][PF_6]/Dodecanol/ H_2O	0.5	0.1	36.2	0.35	36.4	0.25	1.4

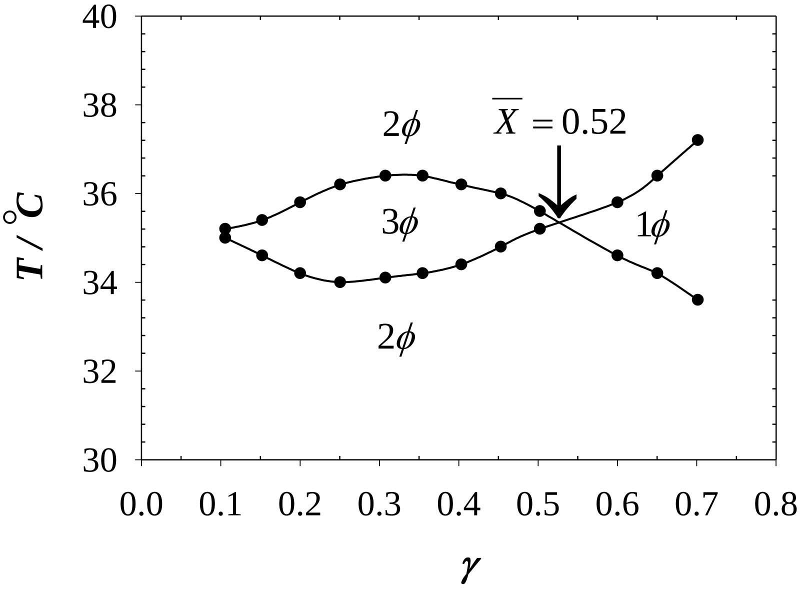
IL volume fraction $\emptyset$; coordinates of fish head γ_0, T_0; coordinates of fishtail $\bar{\gamma}$, $\bar{T}$; maximum extension of surfactant concentration and temperature of the 3-phase body $\Delta\gamma$, ΔT.

In the present work, we have used long-chain length alcohols with various chain lengths, namely octanol, decanol, and dodecanol as a co-surfactant in the formulation of microemulsion systems. Alcohols are known to have surface activity, which is an important characteristic. As a result, they seek out the interfacial region between the oil and water phases. However, because their head group is smaller, they do not tend to form micelles (Tessendorf, 2007; Thater et al., 2016; Iglauer et al., 2009). As a result, they're called co-surfactants rather than surfactants. The solubility of the surfactant employed to formulate the microemulsion system is influenced by the presence of a co-surfactant, in this case alcohols.

It has been observed that the solubility of the PLANTACARE®810–UP increases in the presence of the co-surfactant in the ternary microemulsion system. This results in a drop in the middle phase region's interfacial tension, culminating in the creation of a one-phase region at $\overline{X}$. As the chain length of alcohols rises (from octanol to dodecanol), the orientation in the interfacial region increases as well, allowing for rapid surfactant solubilization in these places, resulting in a one-phase homogeneous microemulsion. As a result, with the addition of the co-surfactant, the surfactant efficiency improves. According to the data illustrated in Figure 2, conventional surfactants increase the efficiency of the surfactant when used in conjunction with a co-surfactant. However, when sugar-based non-ionic surfactants, which are environmentally safe and non-toxic, are used in conjunction with the co-surfactant, the surfactant's efficiency is improved even further, as shown in Figure 3.

Similarly, we have also formulated a microemulsion system utilising Lauryl Glucoside (and) Cocamidopropyl Betaine (PLANTACARE®K-55) sugar-based zwitterionic surfactant to verify the effect of co-surfactant on the phase behaviour and microstructure of microemulsion systems as illustrated in Figure 3.

(a)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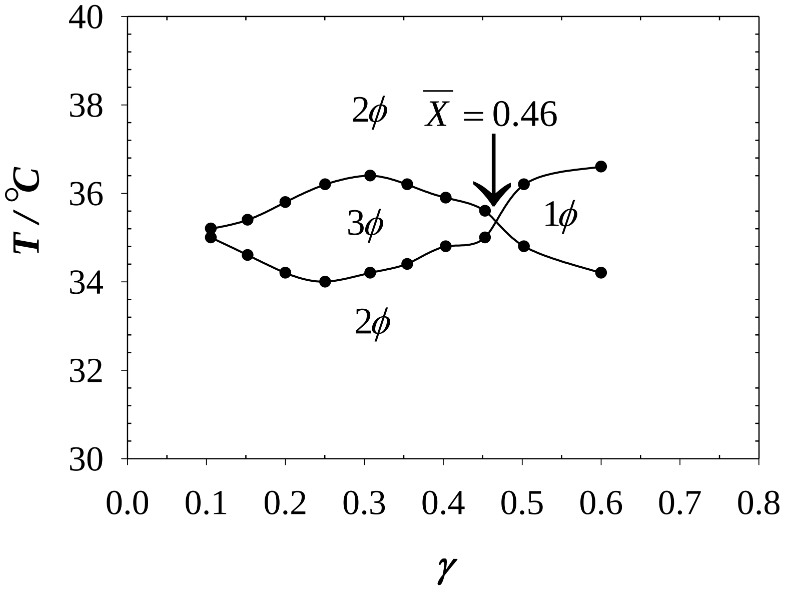
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1ϕ
2ϕ
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
γ

(c)

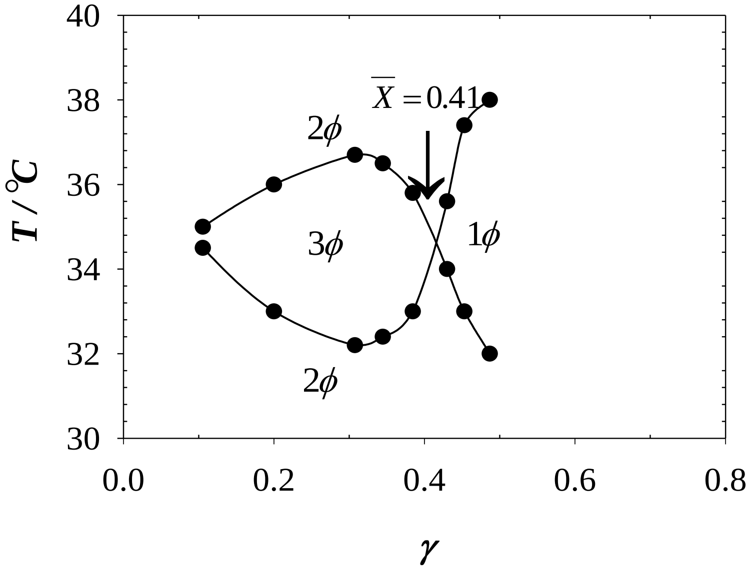
40
38
36
34
32
30
T / °C
$\overline{X} = 0.41$
2ϕ
3ϕ
1ϕ
2ϕ
0.0
0.2
0.4
0.6
0.8
γ

Figure 4. Fish-shaped phase diagram obtained for equal masses of water and IL [Bmim][PF_6], in presence of PLANTACARE® K- 55 and various chain lengths alkanols. (a)PLANTACARE®K-55/[Bmim][PF_6]/Octanol/H_2O

(b)PLANTACARE®K-55/[Bmim][PF_6]/Decanol/H_2O

(c) PLANTACARE®K-55/[Bmim][PF_6]/Dodecanol /H_2O.

The chosen ionic liquid mass fraction α corresponds to equal volumes of water and IL. *T/°C* represents the temperature and γ is the mass fractions of surfactant. 1$\emptyset$ corresponds to one phase, 2$\emptyset$ corresponds to lower two-phase (W/IL droplet μE), 2$\emptyset$ corresponds to upper two-phase (IL/W droplet μE), and 3$\emptyset$ corresponds to three-phase regions, respectively.

It is evident from Figure 4 that, the $\bar{X}$ or $\bar{\gamma}$ which is the minimum surfactant concentration required to solubilize two immiscible solvents (IL and water) obtained is 0.52 in the case of PLANTACARE®K-55/[Bmim][PF_6]/Octanol/H_2O microemulsion system as shown in Figure 4 (a), the $\bar{X}$ or $\bar{\gamma}$ reduces to 0.46 in case of PLANTACARE®K-55/[Bmim][PF_6]/Decanol/H_2O microemulsion system as seen in Figure 4 (b), further the $\bar{X}$ or $\bar{\gamma}$ subsequently reduces to 0.41 of PLANTACARE®K-55/[Bmim][PF_6]/Dodecanol/H_2O as revealed in Figure 4 (c). It has been noticed that for the microemulsion system, PLANTACARE®K-55/[Bmim][PF_6]/ H_2O, the $\bar{X}$ or $\bar{\gamma}$ obtained was 0.68 as mentioned in previous chapter 2, Figure 4.

As a result, the $\bar{X}$ or $\bar{\gamma}$ has been reduced from 0.68 (without co-surfactant) to 0.41 (with co-surfactant), implying that the concentration of industrial-grade sugar-based zwitterionic surfactant required to solubilize two immiscible solvents, namely oil and water, to formulate a microemulsion system has been reduced substantially from 68% to 41%. Table 4 consists of the distinctive parameters *($\emptyset$, γ_0, T_0, $\bar{\gamma}$, T/°C, $\Delta\gamma$, ΔT)* of the fish-shaped phase diagrams of the formulated microemulsion system in presence of co-surfactant. The coordinates for the fish head (lowest surfactant concentration at which a third middle phase emerges) are γ_0 and T_0, while the coordinates for the fishtail (lowest surfactant concentration at which a third middle phase appears) are $\bar{\gamma}$ and $\bar{T}$, respectively.

Table 4. Characteristic parameters of the constructed Phase diagrams

Microemulsion System	$\emptyset$	$\boldsymbol{\gamma_0}$	$\boldsymbol{T_0}/℃$	$\overline{\boldsymbol{\gamma}}$	$\overline{\boldsymbol{T}}/℃$	$\Delta\boldsymbol{\gamma}$	$\Delta\boldsymbol{T}/℃$
PLANTACARE®K-55/ [Bmim][PF_6]/ Octanol/ H_2O	0.5	0.1	34.0	0.52	36.4	0.42	2.4
PLANTACARE®K-55/ [Bmim][PF_6]/ Decanol/ H_2O	0.5	0.1	34.0	0.46	36.4	0.36	2.4
PLANTACARE®K-55/ [Bmim][PF_6]/ Dodecanol/ H_2O	0.5	0.1	34.6	0.41	34.7	0.31	6.4

In the present system, it was discovered that in the presence of the co-surfactant, the solubility of the surfactant used, PLANTACARE® K- 55 increases while the interfacial tension of the middle phase region decreases, resulting in the formation of one phase region at $\bar{X}$ = 0.41. As a result, adding a co-surfactant improves surfactant efficiency.

There is no evidence of the liquid crystalline phases in any of the systems discussed above. However, when the temperature rises, the viscosity of the formed microemulsion systems appears to increase significantly. Last but not least, all of the foregoing microemulsion systems suggest that sugar-based non-ionic surfactants are a better tool for formulating microemulsion systems that can be employed in a variety of applications. In the last chapter of thesis, we will explore some of the applications of these microemulsions formulations.

3.4 Conclusions

By varying the mass fraction of ionic liquid (α)., the phase behaviour and surfactant efficiency of five different microemulsion systems containing water, the hydrophobic ionic liquid [Bmim][PF_6], and sugar-based non-ionic surfactants PLANTACARE®810–UP were studied in detail as a function of temperature and surfactant concentration. The liquid crystalline lamellar phase was not detected in the one-phase areas for all the microemulsion formulations that were prepared. In the five distinct microemulsions reported herein, where the mass fraction of the ionic liquid (α) is altered, the surfactant concentration utilised to solubilize both water and hydrophobic ionic liquid [Bmim][PF_6], i.e., $\overline{\mathrm{X}}$ or $\overline{\gamma}$, remains virtually constant.

Furthermore, with an increase in the concentration of the mass fraction of the ionic liquid (α), there is only a minor rise in $\overline{\mathrm{X}}$ or $\overline{\gamma}$. The presence of high $\overline{\mathrm{X}}$ or $\overline{\gamma}$ values reveals that the surfactants are less efficient, it means the consumption of the surfactant is high in formulation of a microemulsion system. However, when sugar-based non-ionic surfactants are employed instead of traditional surfactants, the efficiency improves. In the second case, the fish-shaped three-phase region is now also observed to be deformed at low and high α (mass fraction of ionic liquid) values, whereas it exhibits an asymmetric form at intermediate values of α. The phase behaviour and surfactant efficiency of a microemulsion system made up of water, the hydrophobic ionic liquid [Bmim][PF_6], and several non-ionic and zwitterionic surfactants were investigated as a function of temperature and surfactant concentration.

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_6] (IL) phases, i.e., $\overline{\mathrm{X}}$ or $\overline{\gamma}$ was analysed and found to be 0.49. (dodecanol). Whereas, when the industrial-grade sugar-based zwitterionic surfactant PLANTACARE®K-55, which is Lauryl Glucoside (and) Cocamidopropyl Betaine, was utilised in the system in combination with the co-surfactant, $\overline{\mathrm{X}}$ or $\overline{\gamma}$ was determined to be 0.41 (dodecanol). When the sugar-based non-ionic surfactants like PLANTACARE®810–UP were used, $\overline{\mathrm{X}}$ or $\overline{\gamma}$ was obtained to be 0.35. In the presence of a co-surfactant, only 35% of the sugar-based non-ionic surfactant was required to produce a microemulsion system (dodecanol). Surfactant efficiency improves as the amount of surfactant concentration necessary for solubilizing oil and water lowers.

As a result, 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. In addition, a microemulsion was successfully formulated using the hydrophobic ionic liquid [Bmim][PF_6] 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.