

Hydrophobic Ionic Liquid/Sugar Surfactant (PLANTACARE® K- 55)/Water Microemulsions: Phase Studies and Effect of Co-surfactant

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Abstract

Microemulsions have become more important because it is easier to tune the structure and the size of domains. They are unique and versatile media for various types of chemical reactions including nanoparticle preparation, organic synthesis, bio-organic synthesis, and so on. In the present study, hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate was used to replace conventional hydrocarbon solvent and industrial grade sugar based lauryl glucoside (and) cocamidopropyl betaine surfactant was used instead of a conventional non-ionic surfactant (alkyl polyoxyethylene ether class); while formulating an ionic liquid / sugar surfactant/ water ternary microemulsion system respectively. Moreover, effect of alkanol of higher chain length (dodecanol) as co-surfactant on the phase behaviour of ternary microemulsion system was also investigated. The ability of industrial grade sugar-based surfactant PLANTACARE® K- 55 which is a lauryl glucoside (and) cocamidopropyl betaine to solubilize both water and hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate phases, i.e. \bar{X} or \bar{Y} was evaluated. The addition of long chain length alkanol (co-surfactant) leads to decrease in the \bar{X} -point and simultaneously increases the efficiency of the industrial grade sugar-based surfactant.

Keywords

Microemulsion, hydrophobic Ionic Liquid, Lauryl Glucoside (and) Cocamidopropyl Betaine surfactant, Co-surfactant.

Introduction

Microemulsions are macroscopically isotropic, homogeneous, thermodynamically stable solutions consisting of at least three constituents, namely a polar phase (generally water), a non-polar phase (generally oil), and a surfactant (sometimes a surfactant in combination with a surfactant are used). A surfactant or surface-active agent is a molecule that consists of a water soluble (hydrophilic or polar) part and an oil-soluble (hydrophobic or non-polar) part. The hydrophilic part is called the head group and the hydrophobic part is called the tail group. The two different hydrophilic and hydrophobic parts make the surfactant surface active in the sense that it adsorbs or accumulates at interfaces between polar and non-polar media, so that the head group is solvated in the polar medium and the tail group in the non-polar medium. Examples of such interfaces are those between water and air or between water and oil. On a microscopic level in a microemulsion, the surfactant molecules form an interfacial film separating the non-polar and polar domains. This interfacial layer forms different microstructures ranging from droplets of oil dispersed in a continuous water phase (o/w-microemulsion) over a bicontinuous phase to water droplets dispersed in the continuous oil phase (w/o-microemulsion). The isotropic mixture of the three components usually forms nanoscale aggregates such as oil swollen micelles and water swollen reverse micelles when the immiscible liquids are oil and water. Such mixtures of water, oil, and surfactant show a rich variety of microstructures within the single-phase called as microemulsion and sometimes it exhibits rich variety of liquid crystalline or lamellar phases, in addition to many different kinds of multiple phase domains.¹

Room temperature ionic liquids (RTILs) are liquid at room temperature that consist solely of ions. Cations and anions of RTILs are generally organic and inorganic in nature, respectively. In RTILs, the coulombic interactions between ions are substantial compared to dipolar or multipolar interaction in Volatile Organic Compounds (VOCs). The most important and unique feature of RTILs is their nonvolatile nature, owing to which; they do not contribute VOCs in the global atmosphere. Hence, RTILs are preferred for formulation of microemulsions rather than VOCs or conventional hydrocarbon solvents.² RTILs have been successfully used to replace organic solvents in a microemulsion system because of their beneficial properties, viz. low vapor pressure, low volatility, high thermal stability, broad liquids temperature range 96–300 °C, excellent conductivity and the ability to dissolve a wide variety of organic and inorganic materials.³ 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.^{3,4} The studies on microemulsion systems wherein equal amounts of water and a hydrophobic Ionic Liquid are solubilized in presence of conventional non-ionic alkyl polyglycol ether (C_iE_j) surfactants to formulate a microemulsion are already reported in literature.⁵ However, a thorough investigation on preparation and phase behavior studies of microemulsion systems involving ionic liquid/s, water and industrial grade sugar based lauryl glucoside (and) cocamidopropyl betaine surfactant is lacking.

We have formulated microemulsion formulations, wherein, hydrophobic ionic liquids are used as a non-polar phase to replace oil (organic solvent). The microemulsion is stabilized by an industrial grade lauryl glucoside (and) cocamidopropyl betaine surfactant. The intent of the present work is to determine the conditions under which the surfactant solubilizes the maximum amounts of ionic liquid and water, i.e. to study phase behavior in order to achieve the reduction in surfactant concentration required to solubilize the two immiscible solvents (water and hydrophobic ionic liquid) by replacing the alkyl polyglycoether (C_iE_j) surfactants with a “green alternative”, viz. lauryl glucoside (and) cocamidopropyl betaine surfactant in a ternary system and formulating microemulsion systems that are stable over a wide temperature range.⁶ The conventional nonionic surfactants of the alkyl polyglycol ether (C_iE_j) type exhibit several phenomenon that are temperature dependent and are not ideal for formulating microemulsions that are stable over a wide temperature range.^{6, 7, 8} On the contrary, the properties of sugar surfactants are not temperature sensitive. Hence, a microemulsion formulated using a hydrophobic ionic liquid and water stabilized a sugar surfactant can aid in extending the conventional thermal stability range from room temperature to 150 °C. Ionic liquid microemulsions have been reported to be temperature-independent, offering a possibility of droplet-shaped microstructure in a large temperature range, thus making these systems suitable for broad range of applications.⁹ The formulation of a less toxic, biodegradable microemulsion is of enormous importance and such a microemulsion can be formulated by use of a zwitterionic alkyl polyglucoside and cocamidopropyl betaine surfactant. Moreover, the water-in-bmimPF₆ microemulsions can dissolve compounds such as Ni(NO₃)₂, CoCl₂, K₃Fe(CN)₆ and methyl orange and hence they can be utilized for the solubilization of these compounds.¹⁰ The ionic liquid [Bmim][PF₆] has been reported to serve as a directing or vectoring agent for the formation of silica microrods with nanosized pores using water/TX-100/[Bmim][PF₆] microemulsions.¹ Hence ionic liquid microemulsion

systems are capable of dissolving the above compounds can be explored for applications in different fields, viz. preparation of nanomaterials and chemical reactions.^{1,11,12}

Material and Methods

The industrial grade sugar-based surfactant, Lauryl Glucoside (and) Cocamidopropyl Betaine (PLANTACARE[®] K-55) was received as a gift sample from BASF, Germany. The alcohol, dodecanol (C₁₂H₂₆O, purity 99%) and the Ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim] [PF₆] (C₈H₁₅F₆N₂P, purity ≥97.0%) were procured from Sigma Aldrich, USA. All chemicals were used as received.

Phase Studies of Microemulsions

Phase behavior measurements are a vital aspect during an investigation and formulation of a microemulsion system. A rapid method for quantifying the efficiency of a microemulsion system is to determine the \bar{X} -point by recording a T – γ section of an ionic liquid/ (water + ionic liquid) volume fraction $\phi = 0.5$. Such an approach aids determination of the optimal state \bar{X} by extrapolation of the phase boundaries from $\underline{2}$ to 1 (turbid to clear) and 1 to $\bar{2}$ (clear to turbid), which makes the exact determination of the three-phase region dispensable. Hence, the phase behavior of self-assembling ternary mixtures of water, hydrophobic ionic liquid and surfactant as well as quaternary mixtures of water, hydrophobic ionic liquid, surfactant and alkanol as co-surfactant has been studied as a function of temperature and composition at a 1:1 water to Hydrophobic IL (Oil) ratio, i.e. polar/apolar 1:1, while changing the surfactant concentration. Microemulsion was formulated by weighing in known amounts of water, hydrophobic ionic liquid, and surfactant in test tubes. The sealed test tubes were then placed in a transparent water bath. The number of phases (1 \emptyset , 2 \emptyset , or 3 \emptyset) were determined by visual inspection of phase boundaries at temperatures ranging from 30 to 60°C.^{4,5}

The sample compositions of the ternary mixtures are defined as the mass fraction of IL in the solvent (water- to- oil) mixture.

$$\alpha = \frac{m_{[\text{Bmim}][\text{PF}_6]}}{m_{[\text{Bmim}][\text{PF}_6]} + m_{[\text{H}_2\text{O}]}} \quad (1)$$

and as mass fraction of surfactant in the total mixture

$$\gamma = \frac{m_{\text{surfactant}}}{m_{[\text{Bmim}][\text{PF}_6]} + m_{[\text{H}_2\text{O}]} + m_{\text{surfactant}}} \quad (2)$$

The phase boundaries exhibit a characteristic “fish” shaped outline as illustrated in Figure 1. The phase boundaries of T and γ results in the formation of fish shaped body, which ultimately aids in determination of the phase inversion point, i.e. \bar{T} and $\bar{\gamma}$ which is also known as fish tail point \bar{X} . $\bar{\gamma}$ or \bar{X} represents the minimum surfactant concentration required to solubilize whole amount of two immiscible (water and oil) solvents.^{4,5}

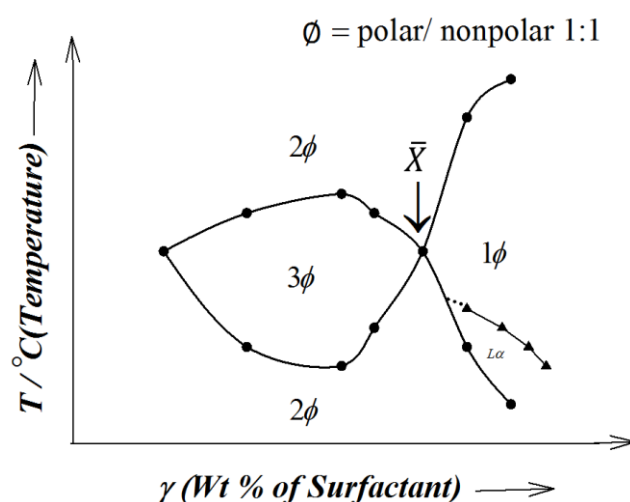


Figure 1: Schematic Fish-shaped phase diagram obtained by taking a vertical section through the phase prism, consisting of equal masses of polar (water) and non polar (Ionic Liquid) solvent, depicting single phase (1ϕ), two phase (2ϕ) and three phase (3ϕ) regions. ‘ γ ’ is the mass fraction of surfactant in the total mixture.

Results and Discussion

Phase behavior studies with industrial grade sugar-based surfactant.

In the present work, we have attempted to formulate a microemulsion system using water, hydrophobic ionic liquid, i.e. 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆] and industrial grade sugar-based surfactant PLANTACARE[®] K- 55, i.e. lauryl glucoside (and) cocamidopropyl betaine. Herein, we wanted to replace organic solvent i.e. an oil phase, so hydrophobic ionic liquid i.e. 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆] was used as oil phase in formulation of the microemulsion system.¹³ In a recent study, the microemulsion system formulated using conventional nonionic surfactant Triton X-100 (TX-100), water and hydrophobic ionic liquid (e.g., 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆]) was compared with the microemulsion system formulated

using nonionic sugar based industrial grade surfactant PLANTACARE 810–UP (UP-810). Upon comparison of the absolute \bar{X} values, it was observed that, when a conventional nonionic surfactant Triton X-100 is used, the \bar{X} value, i.e., the surfactant required to solubilize oil and water is high.¹⁴ Similar observation of lower efficiency of a conventional nonionic surfactant during formulation of a ionic liquid microemulsion has been reported by Anjum et al.⁵ We anticipate enhancement in efficiency while using an industrial grade zwitterionic alkyl polyglycoside and cocamodipropyl betaine surfactant to formulate a water/sugar surfactant/hydrophobic ionic liquid microemulsion.

The typical fish shaped phase diagram obtained for the system, PLANTACARE[®] K- 55/ 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆]/water is illustrated in Figure 2.

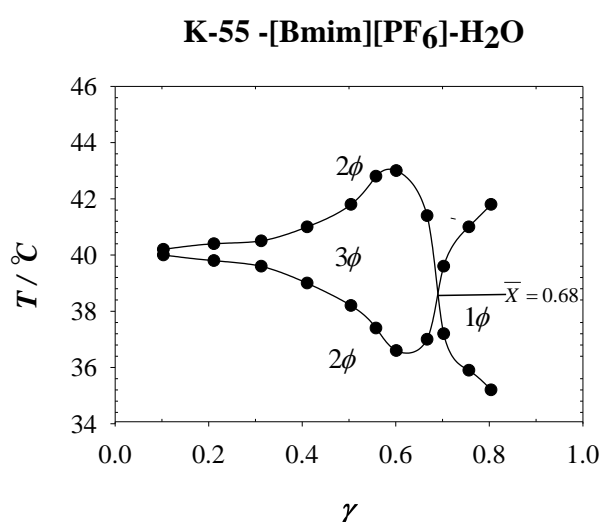


Figure 2: Schematic Fish-shaped phase diagram obtained for equal masses of water and IL [Bmim][PF₆] using industrial grade sugar-based surfactant PLANTACARE[®] K- 55 (K-55).

The corresponding characteristic parameters ($\phi, \gamma_0, T_0, \bar{\gamma}$ or $\bar{X}, \bar{T}, \Delta\gamma, \Delta T$) of the fish shaped phase diagrams of a microemulsion system formulated are presented in Table 1. The coordinates of the so-called fish head (lowest surfactant concentration at which a third middle phase appears) are γ_0 and T_0 , whereas those of the fish tail (lowest surfactant concentration at which one phase is formed) are $\bar{\gamma}$ and \bar{T} , respectively.

Microemulsion System	ϕ	γ_0	$T_0/^\circ\text{C}$	$\bar{\gamma}$	$\bar{T}/^\circ\text{C}$	$\Delta\gamma$	$\Delta T/^\circ\text{C}$
K-55/ [Bmim][PF ₆]/ H ₂ O	0.5	0.09	40.0	0.68	38.3	0.59	10.6

Table 1: Characteristic values for the Phase Behavior of Water/ PLANTACARE[®] K-55(K-55)/1-butyl-3-methylimidazolium hexafluorophosphate microemulsion system.

It is evident that for microemulsion system formulated using 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim] [PF₆] instead of organic solvent as oil, the \bar{X} , which is the minimum surfactant concentration required to solubilize two immiscible solvents obtained is 0.68. Although microemulsion could be formulated, the efficiency of the surfactant in dissolving both water and oil, \bar{X} , value is quite high. It means that 68% of sugar surfactant is required to solubilize two immiscible solvents, oil and water to formulate a microemulsion system.

Here, at $T = \bar{T}$ temperature and a very low surfactant concentration ($\gamma < \gamma_0$), the oil and the water phase are at the intermediate temperatures. Hence, the surfactant will have high solubility in both water phase as well as oil phase which will give rise to a surfactant-rich middle phase in equilibrium with excess of oil and water.^{7, 8} With further increase in temperature, the middle phase also starts to increase until entire amount of water and oil gets solubilized in this phase giving rise to \bar{X} point which is found to be 0.68.

At low temperatures, the lower phase (2ϕ) is water-rich phase and the upper phase (2ϕ) is oil (IL)-excess phase where the surfactant will form oil-swollen micelles also called as microemulsion droplets. Upon addition of surfactant to this binary mixture, the surfactant gets solubilized in both the phases. Later on, with further addition of the surfactant, the concentration of the surfactant increases to surfactant mass fraction i.e. $\gamma = \gamma_0$, and it can be observed that at the fish head, both oil and water phases are being saturated. With further addition of the surfactant, the third phase which is the middle phase (3ϕ) appears.^{11, 12}

When the temperature is increased, the surfactant tends to get solubilized until the three-phase region (3ϕ) ($\gamma < \bar{\gamma}$) is observed. Further addition of the surfactant, now decreases the interfacial tension between the phases which results into formation of one-phase region (1ϕ) ($\gamma > \bar{\gamma}$) as shown in Figure 2. At higher temperatures, ionic liquid (oil) is a superior solvent for the surfactant, and IL-swollen reverse micelles form in an oil continuous phase, in equilibrium with a lower phase of excess IL.

Phase behavior of sugar surfactant in presence of Co-surfactant (Dodecanol):

To verify the effect of co-surfactant on the phase behavior and microstructure of microemulsion systems, a microemulsion involving dodecanol, i.e. PLANTACARE® K-55/1-butyl-3-methylimidazoliumhexafluorophosphate [Bmim] [PF₆]/Dodecanol/water was formulated as illustrated in Figure 3. The ratio of surfactant to co-surfactant (dodecanol) was 1:1.

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

$$\gamma = \frac{m_{surfactant}}{m_{[Bmim][PF_6]} + m_{[H_2O]} + m_{surfactant} + m_{co-surfactant}} \tag{3}$$

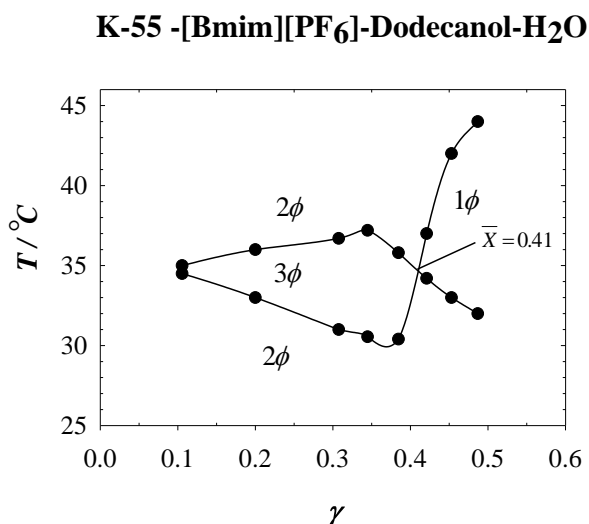


Figure 3: Schematic Fish-shaped phase diagram obtained for equal masses of water and Ionic Liquid [Bmim][PF₆]in presence of co-surfactant (Dodecanol) using sugar based non-ionic surfactant PLANTACARE® K- 55 (K-55).

It is reported that the efficiency of the ionic liquid microemulsion system did not improve by addition of octanol as a co-surfactant and the efficiency is too low for technical applications.¹³ However, it is evident from Figure 3 for a microemulsion formulated by us that, the \bar{X} or $\bar{\gamma}$ which is the minimum surfactant concentration required to solubilize two immiscible solvents (IL as oil and water) obtained is 0.41 when co-surfactant is used along with the surfactant. It can be inferred that the \bar{X} or $\bar{\gamma}$ is reduced 0.68 to 0.41 in presence of co-surfactant, implying

that the concentration of industrial grade sugar surfactant required to solubilize two immiscible solvents i.e. oil and water, to formulate a microemulsion system has been reduced from 68% to 41%. The co-surfactant, dodecanol is itself surface active, orients itself at the hydrophobic ionic liquid/water interface and also influences the surfactant solubility. The addition of co-surfactant leads to a decrease in the interfacial tension and subsequently reduces the amount of surfactant required to solubilize two immiscible solvents, oil and water.^{11, 12}

The characteristic parameters ($\phi, \gamma_0, T_0, \bar{\gamma}, \bar{T}, \Delta\gamma, \Delta T$) of the fish shaped phase diagrams of a microemulsion system formed are presented in Table 2. The coordinates of the fish head (lowest surfactant concentration at which a third middle phase appears) are γ_0 and T_0 , whereas those of the fish tail (lowest surfactant concentration at which one phase is formed) are $\bar{\gamma}$ and \bar{T} , respectively.

Microemulsion System	ϕ	γ_0	$T_0/^\circ\text{C}$	$\bar{\gamma}$	$\bar{T}/^\circ\text{C}$	$\Delta\gamma$	$\Delta T/^\circ\text{C}$
K-55/ [Bmim][PF ₆]/ Dodecanol/ H ₂ O	0.5	0.1	34.6	0.41	34.7	0.31	6.4

Table 2: Characteristic values for the Phase Behavior of Water/ PLANTACARE[®] K- 55 (K-55)/IL/Dodecanol microemulsion system.

In the present system, it has been observed that in presence of the co-surfactant, the solubility of the surfactant used, i.e. PLANTACARE[®] K- 55 which is lauryl glucoside (and) cocamidopropyl betaine, increases and it decreases the interfacial tension of the middle phase region and results into formation of one phase region at \bar{X} (which is the minimum surfactant concentration required to solubilize two immiscible solvents, oil and water) 0.41. Thus the surfactant efficiency increases on addition of co-surfactant.

Thus compiling the data for both the system, i.e. 1) PLANTACARE[®] K- 55/ 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆]/ water, and 2) PLANTACARE[®] K- 55/ 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆]/dodecanol/water, it can be concluded that on addition of the higher chain length co-surfactant, i.e. dodecanol (alkanol), the surfactant efficiency increases as the \bar{X} which is the minimum surfactant concentration required to solubilize two immiscible solvents decreases.

Conclusions

The phase behaviour and the surfactant efficiency of microemulsion system consisting of water, the hydrophobic ionic liquid [Bmim][PF₆] and industrial grade sugar-based surfactant PLANTACARE[®]K-55 which is a lauryl glucoside (and) cocamidopropyl betaine, were studied as a function of temperature and surfactant mass concentration. A microemulsion was successfully formulated wherein, the conventional organic solvent was replaced with the hydrophobic ionic liquid [Bmim] [PF₆].

The effect of alkanol (dodecanol) as a co-surfactant on the phase behavior of water/1-butyl-3-methylimidazolium hexafluorophosphate/PLANTACARE[®]K-55 was investigated. Substantial reduction in surfactant concentration required to solubilize the two immiscible solvents was achieved upon addition of long chain co-surfactant to the ternary microemulsion system; water/1-butyl-3-methylimidazolium hexafluorophosphate/PLANTACARE[®]K-55.

The formulation of ionic liquid microemulsion system enables to overcome the limitations of ionic liquids alone to dissolve various types of compounds and thus can be used for several industrial applications. It is evident from our studies that ionic liquids play a role not only as a polar phase but it can also be used as a replacement of an organic solvent. The sugar-based surfactant used in the present work plays a role as a greener alternative while formulating a microemulsion. The microemulsion system formulated can be explored for use in various applications, viz. solubilization of an otherwise water insoluble dye and as a template for preparation of nanomaterials and chemical reactions.

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