Phase Studies of Sugar Surfactant Ionic Liquid Microemulsions: A Green Chemistry Approach.

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Abstract

Microemulsions are increasingly gaining importance as templates since a great deal is known about how to tune the structure and size of domains. To understand how the addition of sugar surfactant to the ionic liquid and water to the aqueous phase,respectively,influence the phase behaviour and thus the microstructure, the phase diagrams were studied after each compositional change. The respective phase diagrams are presented and discussed in terms of their potential use as templates. A new approach to achieving this goal entails arresting the oil (aqueous) phase by gelling it, i.e. by forming an organo gel (a hydrogel), and polymerizing the aqueous (oil) phase. In the present work phase diagram of a ternary water – ionic liquid – sugar surfactant microemulsion systemswere studied. Mixing an extremely hydrophobic extractant considered here as ionic liquid with an extremely hydrophilic sugar surfactant we succeed to formulate microemulsion that can be described with the classical Winsor formalism for multiphasic microemulsions.

Introduction :

Room temperature ionic liquids (ILs) are currently attracting considerable scientific interst on several fronts. ILs are green solvents due to their low vapour pressure, and designer solvants because their physical propertoes can vbe varied predictably by incorporation of appropriate functional groups, [1-3] ILs solubilise many organic and inorganic species facilitating reations between unusual combinations of reagents.

Both hydrophilic and hydrophobic ILs that are immiscible with oil and water, respectively, have been identified. [4]

Microemulsions are optically transparent, isotropic, thermodynamically stable solution mixtures of atleast three components, namely, two immiscible solvents and a surfactant. The surfactant (sometimes in combination with a cosurfactant) separates the two solvents by forming a monolayer at the liquid-liquid interface.

Kahlweit, Strey, and coworkers have performed numerous systematic experiments aimed at generalizing the behaviour of microemulsion. [5-6]In the recent review the general pattern of the phase behaviour, properties, and microstructure of microemulsion are summarized.[7]

Gao et al. have used $BmimBF_4$ instead of water to prepare nonaqueous bmimbf4/benzene/Triton X-100 (TX-100)[8] and $bmimbf_4$/cyclohexane/TX-100[9] microemulsion. They studied the phase behaviour of ionic liquid-in oil (IL/O) microemulsion and found properties similar to those of classical water-in-oil (W/O) microemulsion.[13] Here we are using hydrophobic Ionic Liquid such as bmimPF6. This IL have been used to replace typical organic solvents in ternary water/oil/surfactant systems. [10-13]

From the so-called "fish-cuts" inside the phase tetrahedron we observe the phase transition WI-WIII-WII by only increasing the extractant concentration. (WI - oil-in-water μE with excess oil phase ; WII - water-in-oil μE with an excess aqueous phase ; WIII - bicontinuous μE form in equilibrium with both water and oil excess phases). We were particularly interested in the WIII-type microemulsions and their two excess phases(bicontinuous μE form in equilibrium with both water and oil excess phases).This can be obtained around the phase inversion when the system changes from an oil-in-water μE with excess oil phase(Winsor I) to an water-in-oil μE with an excess aqueous phase (Winsor II) Chemical analysis of these excess phases gives us the exact film composition. Neutron scattering experiments of the microemulsion inform about the microemulsion structure as well as characteristic length scales and specific area. Microstructures, structure factors, and mean droplet lifetimes are also determined in some phases. We studied the phase behaviour of the two ternary systems water/bmimPF6/plantacare UP-810 and water/bmimPF6/plantacare UP-818.

Here in order to replace Hydrocarbon solvent like alkanes, dodecane, octane, decane with Ionic Liquid , we used conventional, biodegradable sugar surfactant and microemulsion formed. Thus its phase behaviour was studied. Thus it is Green Chemistry Microemulsion.

Experimental

Materials

The industrial grade surfactants alcohol glucoside (PLANTACARE® 810, i.e. C8-10fatty alcohol glucoside or P-810 UPand PLANTACARE® 818, i.e. C8-

16 fatty alcohol glucoside or P-818 UP)were purchased freom BASF Germany. The sugar surfactant n-dodecyl β-D-maltoside ($C_{24}H_{46}O_{11}$, purity $\geq$ 98%) ; the alcohols 1-dodecanol ($C_{12}H_{26}O$, purity 99%), n-octanol ($C_8H_{18}O$, purity 99%) ; the Ionic liquid 1 – Butyl-3-methyl-imidazolium hexafluorophosphate ($C_8H_{15}F_6N_2P$, purity $\geq$ 97.0%) werepurchasedfrom Sigma Aldrich.All chemicals were used as delivered.

Methodology :

Phase behavior measurement is essential to study microemulsions. The phase behavior of self-assembling ternary mixtures (Water, Hydrophobic IL (Oil), and Surfactant or Water, IL+Solvent (Oil) and Surfactant was studied as a function of temperature and composition at a 1:1 water (polar) to Oil ratio, i.e. polar/apolar 1:1, while varying the surfactant concentration. Microemulsions were be prepared by weighing in known amounts of water, Hydrophobic IL, and surfactant, in test tubes. The sealed test tubes were placed in a transparent water bath & number of phases determined by visual inspection/optical polarized microscopy of phase boundaries at temperatures ranging from 30 to 90 °C.

The sample compositions of the ternary mixtures are given as the mass fraction of IL in the solvent mixture.

$$\gamma = \frac{m \text{ bmimPF } 6}{m \text{ bmimPF } 6 + m \text{ H2O}}$$

and as mass fraction of surfactant in the total mixture

$$\gamma = \frac{m \text{ surfactant}}{m \text{ bmimPF } 6 + m \text{ H2O} + m \text{ surfactant}}$$

The phase boundaries give rise to a characteristic "fish" outline (Figure 1)

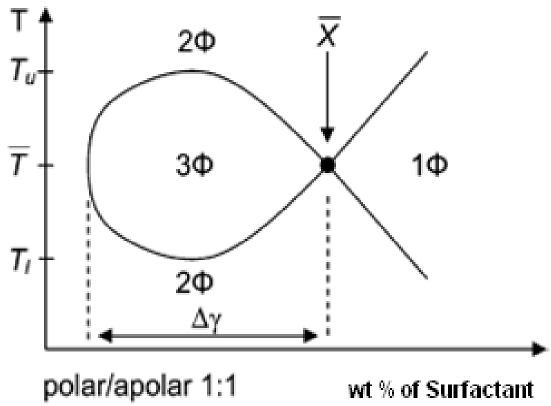


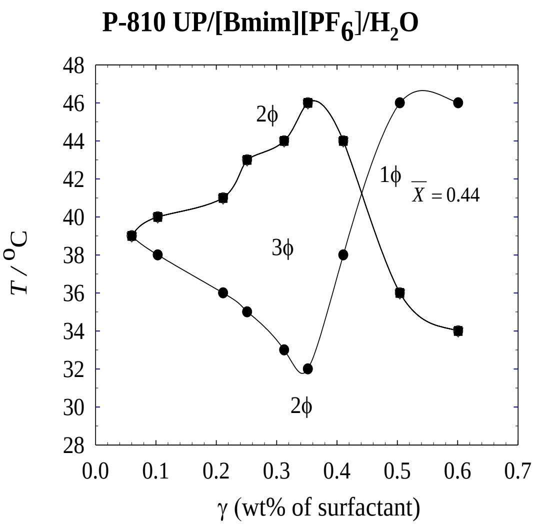
Figure 1. Schematic Fish-shaped phase diagram obtained for equal masses of polar and apolar solvent, showing single phase (1Φ), two phase (2Φ) and three phase (3Φ) regions. 'γ' is the mass fraction of surfactant in the total mixture.

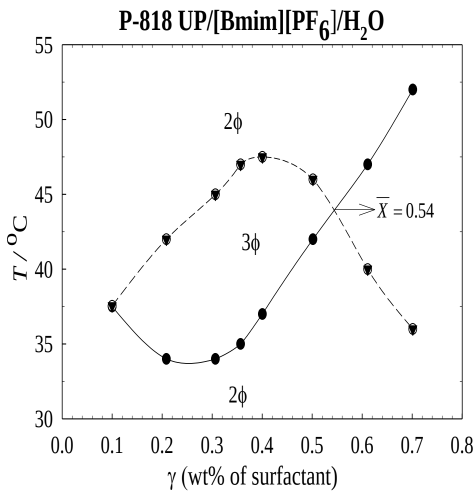
The dimensions and position of the three-phase body define the characteristic values of a microemulsion system, as shown in Figure 1. The maximum temperature interval over which the three phases occur is defined as $\Delta T = T_u - T_1$where T_u and T_1 are the maximum and minimum temperatures at which the three phases appear, respectively. At the mean temperature, $\bar{T}$, the efficiency of the surfactant in dissolving both water and oil is maximized. As the surfactant concentration is increased, the surfactant-rich middle phase increases in volume, eventually producing a single phase. At this position in the phase diagram, $\bar{X}$, the microemulsion is said to be balanced, with zero mean curvature of the surfactant film, and the bicontinuous microemulsion forms. The term $\bar{X}$, defines surfactant efficiency, which is the minimum surfactant concentration required to solubilize the two immiscible solvents. $\bar{T}$ is also defined as the phase inversion temperature. The characteristic parameters ($\bar{T}$, $\bar{X}$) were determined.

Results and Discussion :

a. Phase behavior as a function of type of surfactant type :

To verify the effect of variation surfactant amphiphilicity, on the phase behavior and microstructure of microemulsion systems, a ternary microemulsion involving two different industrial grade surfactants alcohol glucoside (PLANTACARE® 810, i.e. C8-10fatty alcohol glucoside or P-810 UP and PLANTACARE® 818, i.e. C8-16 fatty alcohol glucoside or P-818 UP), hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] and water was formulated. The typical fish shaped phase diagram for these systems is as illustrated below:





b. Hydrophobic Ionic Liquid-in-Water Microemulsions:

Microemulsions of sugar surfactants, water and hydrophobic ionic liquid were formulated. The hydrophobic ionic liquid (e.g. 1-butyl-3-methylimidazolium hexafluorophosphate, bmimPF_6) was used to replace typical organic solvent in ternary water/oil/sugar surfactant systems. The phase behavior and microemulsion formation using equal masses of water and hydrophobic ionic liquid in presence of sugar surfactant i.e. Water/1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6]/n-dodecyl-β-D-maltoside (β-$C_{12}G_2$) was investigated in detail and the resultant characteristic Fish-shaped phase diagram is as shown below:

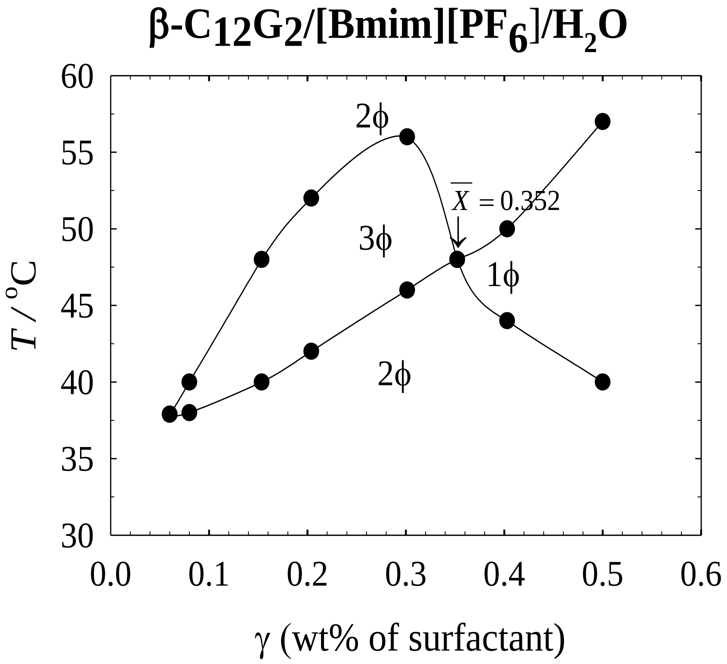


Figure 2. Schematic Fish-shaped phase diagram obtained for equal masses of water and IL [Bmim][PF_6], showing single phase (1Φ), two phase (2Φ) and three phase (3Φ) regions.

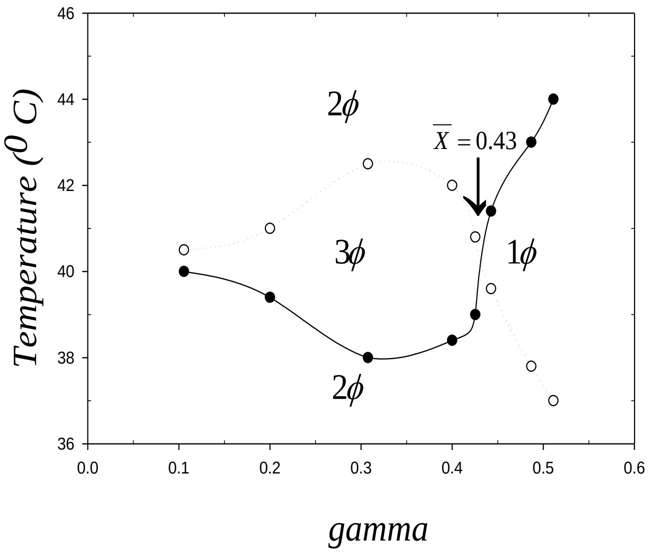
Polarization microscopy studies revealed absence of liquid crystalline phases at lower γ and similar observation was noted at higher γ, for the above ternary microemulsion system. However detailed investigation at higher γ is underway to corroborate this observation.

c. Phase behavior as a function of co-surfactant type:

To verify the effect of variation cosurfactant amphiphilicity, on the phasebehavior and microstructure of microemulsion systems, a ternary microemulsion involving two different industrial grade surfactants alcohol glucoside (PLANTACARE® 810, i.e. C8-10fatty alcohol glucoside or P-810

UP, hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6], n- octanol and water was formulated. The typical fish shaped phase diagram for these systems is as illustrated below:

UP - 810 , BmimPF6 , Octanol , Distill Water



Conclusion :

The $\bar{X}$ or surfactant efficiency, which is the minimum surfactant concentration required to solubilize two immiscible solvents was found to be 0.352 for the ternary microemulsion system,Water/1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6]/n-dodecyl-β-D-maltoside. Hence, the microemulsion formulated by utilizing nonionic sugar surfactant requires much less surfactant as compared to conventional nonionic surfactant of polyoxyethylene type. Another peculiar feature is the absence of liquid crystalline phases (and high viscosity) at higher weight percentage of surfactant in the microemulsion. By addition of co-surfactant we observed that the $\bar{X}$ or surfactant efficiency decreases. So presence of co-surfactant encouraged us to reduce the amount of solvent and also the amount of surfactant is reduced.Thus surfactant content is reduced and thus it is more eco-friendly.

In future we will be doing; Polar Ionic Liquid-in-Oil Microemulsions:

a) ***Phase behavior as a function of type of Ionic Liquids*****:** The phase behavior and microemulsion formation of following ternary systems:

i) Ethylammonium nitrate//*n*-alkane/ *n*-dodecyl-β-D-maltoside and

ii)1-butyl-3-methylimidazolium tetrafluoroborate/n-alkane/ *n*-dodecyl-β-D-maltoside .

b) *Phase behavior as a function of Oil Length*: The phase behavior and microemulsion formation of Ethylammonium nitrate/*n-alkane*/ *n*-dodecyl-β-D-maltoside will be studied in detail, wherein the alkanes of varying chain length (decane, dodecane and tetradecane will be used.

C) *Phase behavior as a function of co-surfactant type:* The phase behavior and microemulsion formation using more homologous series will be studied. By increasing CH_2 group i.e. Decanol, Dodecanol and higher alcohol we will use to decrease the $\bar{X}$ or surfactant efficiency , thus the surfactant amount will be reduced.

References :

(1) Forsyth, S. A.; Pringle, J.; MacFarlane, D. R. *Aust. J. Chem*. 2004, 57 113.

(2) Rodgers, R.D.; Seddon, K. R, *Science* **2003**, 302, 792.

(3) Seddon, K. R.; Stark, A.; Torres, M.-J. *Pure Appl. Chem*. **2000**, 72, 2275.

(4) Wenton, T. Chem. *Rev*. **1999**, 99, 2071.

(5) Kahlweit, M.; Strey, R. *Angrew. Chem. Int. Edn. Engl*. **1985**, 24, 654.

(6) Kahlweit, M.; Strey, R.; Firman, P.; Haase, D.; Jen,; Schomacker, R. Kahlweit, M.; Strey, R.; Firman, P *Langmuir* **1988**, 4 499.

(7) Kahlweit, M.; Strey, R.; Firman, P. *J. Phys. Chem*. **1986**, 90, 671.

(8) Kahlweit, M.; Strey, R.; Busse, G. *J. Phys. Chem*. **1990**, 94, 3881.

(9) Seth, D.; Chakraborty, A.; Setua, P.; Sarkar, N. *J. Chem. Phy*.**2007**, 126, 224512.

(10) Gao, Y.; Li, N.; Zheng, L.; Zhao, X.; Zhang, J.; Cao, Q.; Zhao, M.; Li, Z.; Zhang, G. Chem. – Eur. J. **2007**, 13, 2661.

(11) M. Subinya, A. K. Steudle, B. Nestl, B. Nebel, B. Hauer, C. Stubenrauch, S. Engelskirchen, *Langmuir***2014**, 30, 2993-3000.

(12) O. Zech, S. Thomaier, A. Kolodziejski, D. Touraud, I. Grillo and W. Kunz, *Chem. –Eur*. J., **2010**, 16, 7863-786.

(13) L. Y. Xue, H. J. Qui, Y. Li, Lu, X. R. Huang and Y. B. Qu, *colloids Surf., B*, **2011**, 82, 432-437.