

ABSTRACT

Microemulsions are thermodynamically stable, macroscopically homogeneous but microscopically heterogeneous, mixtures of water and oil stabilized by surfactant monolayer. They have unique properties like ultralow interfacial tension, large interfacial area and the ability to solubilize otherwise immiscible liquids. In spite of several studies on microemulsions, knowledge on this domain of research are still fragmentary in research. Recently ionic liquids have been found to be good substituent as the polar component. Such a combined potential of ionic liquid and microemulsion have instigated to undertake different physicochemical studies on ionic liquid microemulsion. Sometimes ionic liquids as single polar components suffer from some limitations which may be overcome through the usage of ionic liquid in combination with another polar solvent, e.g., water. With this purview, it was thought to be worthy to carry out the works as outlined below:

Detailed studies on the pseudo-ternary water-in-oil microemulsion system, comprising water/(Tween-20+n-alkanol)/n-heptane, have been carried out by way of phase manifestation, method of dilution, viscosity and dynamic light scattering techniques. Such an initiative was made as point of reference so that the data set could be compared with the similar systems comprising ionic liquid in lieu of water. Tween-20, in combination with cosurfactants (of varying chain length, from n-butanol to n-octanol) were used in studying such systems in the temperature range 303 – 323 K. A clear dependence of the different phases on cosurfactant chain length was noted. By employing the method of dilution, associated thermodynamic parameters for the formation of water-in-oil microemulsion droplets were derived. Different associated structural parameters were derived through further computation of the data derived from the method of dilution. Unusual behavior of Tween 20, compared to the conventional ionic surfactants, was noted. Viscosity measurements, as carried out at different composition and temperature, revealed the temperature and water pool size dependency of the microemulsion systems. Viscosity data did not follow the same

trend during heating and the cooling process, due to condensation effect. This phenomenon was further confirmed by dynamic light scattering studies.

Although several studies on imidazolium based ionic liquid-in-oil microemulsion are available in the literature, however, studies on pyridinium bases ionic liquid microemulsion are not so common. Pyridinium based ionic liquids have superior yet unexplored properties when considered in the polar domain of microemulsion. 1-butyl-4-methyl pyridinium tetrafluoroborate ([b4mpy][BF₄]) / (Tween 20 + n-pentanol) / n-heptane microemulsion system has been studied by combined phase behavior, dynamic light scattering, viscosity and spectroscopic probing techniques. With the increasing amount of Tween 20/n-pentanol (S/CS) ratio, turbidity increased, although it was not possible to achieve a stable microemulsion without the cosurfactant. Dynamic light scattering and viscosity study revealed that the size of the μE droplets increased with increasing volume fraction (ϕ_d) of ionic liquid. Both the size and viscosity increased with ϕ_d . With the increasing amount of n-pentanol, the variation became less sensitive due to the better stabilizing effect induced by the alkanol. Increase in size of the microemulsion droplets was overshadowed by the increase in the fluidity of the medium, for which viscosity decreased with increasing temperature, as common for Newtonian fluids. State of the ionic liquid in the microemulsion was monitored by absorption and fluorescence spectroscopy with and without curcumin as the molecular probe. While a continuous increase in polarity of the IL domain occurred with increasing amount of IL, the fluorescence anisotropy results revealed that the rigidity of the domain passed through maxima for all S/CS ratio.

Physicochemical properties of an ionic liquid (IL) 1-butyl-3-methylimidazolium methanesulfonate, ([bmim][MS]), in combination with water, were evaluated through the density, viscosity, surface tension, conductance, cyclic voltammetry, absorption and emission spectroscopic measurements. Binary mixtures were studied both in the water rich and [bmim][MS] rich regions (0.01 mM to 4.96 M). The static and dynamic properties of the binary combinations were evaluated through density and viscosity measurements. [bmim][MS] decreased the surface tension of water wherefrom the surface excess and area per

molecule of the ionic liquid were determined at the air-liquid surface. Equivalent conductance of [bmim][MS] at infinite dilution was determined from the conductance data as the system obeyed Debye-Hückel-Onsager formalism. Cyclic voltammetry measurements revealed the formation of some metastable organized structures at specific compositions. Absorption and emission spectral behavior of the anionic dye eosin Y was found to be dependent on the concentration of [bmim][MS] in the water rich region. A significant change in steady state anisotropy and excited state life time of the fluorophore occurred above 1.0 M [bmim][MS] in water, which was correlated with the viscosity of the medium. It was concluded that aggregation of [bmim][MS] into micelle like aggregates above the specific concentration occurred, which significantly altered the different physiochemical parameters of [bmim][MS] binary mixture.

Combined phase behavior, method of dilution, viscosity, dynamic light scattering, electrical conductance and spectroscopic probing techniques were employed in understanding the physicochemical properties of pseudo ternary microemulsion system 1-butyl-3-methyl imidazolium methanesulfonate ([bmim][MS] \pm water) / (Tween-20+n-pentanol) / n-heptane. Phase manifestation revealed that the area under the clear region depended on ionic liquid (IL) / water mole ratio. Thermodynamic and structural parameters for the formation of (IL+water)-in-oil μ E system were evaluated employing the method of dilution at different [polar domain]/[Tween-20] mole ratio and temperature; the parameters depended on the composition of the polar domain. IL+water comprising μ E behaved differently, compared to the conventional water-in-oil μ E system, especially at higher mole fraction of IL. Both the size and viscosity increased with the increasing volume fraction of the dispersed phase (IL+water), while they decreased with increasing temperature. Although having IL, the μ Es were less conducting due to the strong interaction between the IL cation and the oxyethylene groups of the surfactants. Formation of micelle like aggregates within the polar domain further suppressed the conductivity. Combined studies on the absorption and emission spectra of eosinY, along with the excited state lifetime and anisotropy measurements, revealed the existence of different states of IL+water in the polar domain.