

CHAPTER 4

Physico-chemical Studies on Ionic Liquid Microemulsion: Phase Manifestation, Formation Dynamics, Size, Viscosity, Percolation of Electrical Conductance and Spectroscopic Investigations on 1-butyl-3-methyl imidazolium methanesulfonate + water / Tween-20 +n-pentanol / n-heptane Pseudoternary System

Abstract

Combined phase behavior, method of dilution, viscosity, dynamic light scattering, electrical conductance and spectroscopic probing techniques were employed in understanding the physico-chemical 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.

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1. Introduction

Ionic liquids (ILs) are environmentally benign materials³⁴⁴ with some specific properties, viz., low melting point (less than 100°C), ionic nature, low volatility and easy recyclability, etc., for which they have gained special pedigree as “green solvent”¹⁹¹. ILs are gaining importance for their applications, viz., as alternate solvent for chemical reaction and separation³⁴⁵, in electrochemistry³⁴⁶ and nanoparticle synthesis²³¹, etc. Advantages of using IL as media for chemical reaction have been reviewed by Hao³⁴⁷ and Welton.¹⁷⁹ Imidazolium based ILs are used because of its tunability; tailor made ILs can be prepared using imidazolium cation. However, use of neat IL has some limitations; they are inefficient in dissolving a wide variety of compounds²⁰⁴. This could be overcome by using them in the form of microemulsion (μ E). The term μ E was first coined by Schülman⁵⁶ and subsequently by Lindman⁶⁰. μ E is defined as thermodynamically stable, clear and isotropic dispersion of one liquid into another immiscible liquid stabilized by a surfactant monolayer^{30,34,348,349}. μ Es also find various applications in the field of cosmetics, pharmaceuticals, chemical reaction in compartmentalized systems and synthesis of nanoparticles. Although a large number of articles on μ E are available in the literature, however the review works of Moulik et al.^{224,350,351}, Gradzielsky et al.³⁵², Stubenrauch et al.³⁵³, Fanun et al.³⁵⁴ and Lindman et al.^{219,355} are worth reading.

The limitations of ILs, in respect of their capabilities to dissolve a wide variety of compounds, can easily be overcome through the formation of μ E²¹¹. Research works involving IL microemulsion are ever increasing^{202,210,214-216,348,356}. Han and co-workers²⁰³ first reported the formation of μ E comprising IL. Very recently Sarkar and co-workers²¹² have reported a new strategy to prepare IL-in-oil μ Es. Different review works on IL μ Es are available in the literature^{191,213,347,349,357,358}. IL based μ Es in drug formulation has been explored by the research group of Moniruzzaman et al.¹⁸⁷ and Althanyan et al.³⁵⁹ Estoe et al.³⁴⁸, for the first time, have reported the characterization of IL μ E using small angle neutron scattering (SANS) technique. Koetz and co-workers²¹³ have studied the structure of IL modified μ E. Gao et al.^{176,204,205} undertaken extensive

works on μ Es comprising of [bmim][PF₆] and water by different techniques. While Friberg et al.³⁴⁹ have reported about the works on [bmim][BF₄] based μ E, the structural studies of [bmim][BF₄]-in-oil μ E have been reported by Gao et al.¹⁷⁶. IL-in-oil μ Es have also been extensively studied by Zheng and co-workers³⁶⁰ using Triton X-100 and Tween 20. In the work of Gao et al.⁹¹ comparative studies between the properties of microemulsions comprising TX-100 and Tween 20 have been reported. In another work of Zheng et al.³⁶¹ extensive investigation were carried out on IL μ E comprising Tween 80 as surfactant. It was proposed that the imidazolium cation can get coordinated with the lone pair of electrons of oxyethylene groups in Triton X-100 or Tween 20²¹¹. Such interactions can lead to the formation of structured/rigid/organized entities. Subsequently, the system becomes less sensitive to temperature, compared to the corresponding conventional water-in-oil μ Es. Dynamic light scattering studies, combined with the viscosity measurements, can shed light on the above mentioned characteristics of IL μ E (the size and its temperature sensitivity).

Studies on the microenvironment of IL-in-oil μ E using different solvatochromic probes have been reported by the research groups of Bhattacharyya^{133-135,216,225}, Gao^{140,176,203-205,211,360}, Sarkar^{113,144,193,212,216} and Samanta^{210,214,312}. According to Gao et al.²⁰⁴, with increasing amount of IL, polarity of the microenvironment increases, resulting in a red shift in the absorption spectra of dye molecule (probe). Solvent dynamics studies in reverse micelle can provide information about the different states of the polar domains^{210,214-216,356}. Bhattacharyya et al.^{133,134} have performed solvent dynamics studies using IL μ Es. Similar works have been reported by Sarkar et al.²¹⁶ where different dyes were used in the confined polar domain of μ E. Samanta et al.²¹⁵ have also reported the solvent dynamic studies, both in the neat and in confined ILs. However, all those results may be considered as fragmentary in nature to completely understand the different states of IL in the μ E of oil continuum.

IL based μ E can be formed using any one of the three coexisting pseudo phases: the polar domain, the surfactant and the oil (non polar component). However, till date no μ E is reported where all the three components are ILs³⁶². IL based μ Es have advantages over the pure IL, as well as the corresponding

conventional μE (comprising water). As a result, IL μEs find many applications which include colloidal crystallization³⁶³, synthesis of nanomaterial¹⁸⁶, pharmaceuticals¹⁸⁷, polymers³⁶⁴, catalysis¹⁸⁴, chemical engineering^{365,366} and energy conversion³⁶⁷, etc. However, the most significant application of IL μE lies its use as alternate solvent for organic chemical reaction¹⁷⁹.

Although termed as environmentally benign, fluorinated ILs are toxic because they can generate HF, POF_3 , etc., upon heating¹⁹³. Hence, studies involving non-fluorinated ILs are considered to be more significant. In this aspect, 1-butyl-3-methyl imidazolium methanesulfonate [bmim][MS] is more “green” compared to the conventional fluorinated ILs. However, to the best of our knowledge no reports are available on [bmim][MS] based microemulsion.

Water is the “greenest” among all solvents. In our previous report, we showed that [bmim][MS] in combination with water exhibited some unusual behavior³⁶⁸. The binary mixtures were studied using a number of techniques in the bulk condition. Different properties of the binary mixture could be tuned/alterd by judicious mixing of the components. Previously, we have carried out systematic physico-chemical investigations on water / (Tween 20 + n-pentanol) / n-heptane water-in-oil μE ²⁶¹. It is, therefore, important to undertake the challenge in investigating the polar domain in oil microemulsion comprising the binary mixture of ionic liquid, [bmim][MS], in combination with water. Such studies are important in terms of their application as well as fundamental understanding point of view. However to the best our knowledge, no systematic studies have yet been carried out using a binary mixture of IL and water, which would be the novelty of the present work.

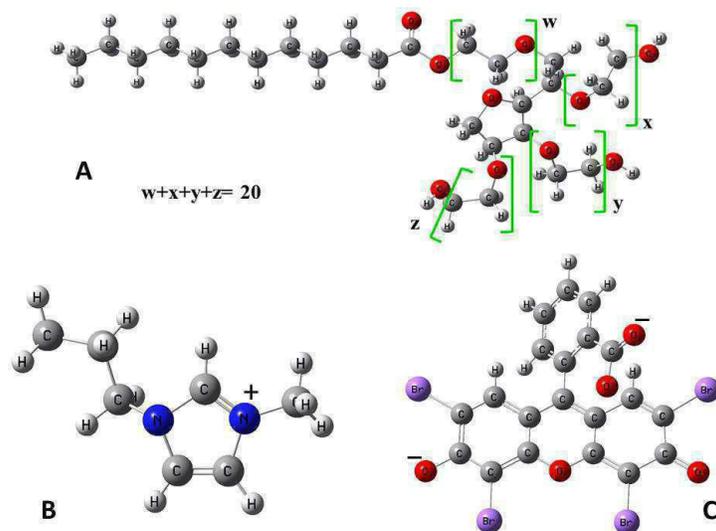
In this paper we report the results of the investigations made on pseudo ternary polar domain-in-oil μE system ([bmim][MS]+water) / (Tween 20+n-pentanol) / n-heptane. Our previously published results on water / (Tween 20+n-pentanol) / n-heptane μE ²⁶¹ alongwith the binary mixture of [bmim][MS] + water³⁶⁹ have been considered as the points of references. There are several reports on the microemulsions comprising TX-100^{176,203,204,211}; however IL microemulsions comprising Tween 20 are not so many. Compared to TX-100, Tween 20 is less toxic. The choice of the anion in the IL is intentional as it is an

inorganic ion linked to an alkyl group. It is needless to mention that such a system will definitely be less toxic compared to the fluorinated ILs. The μ E systems have been studied as functions of the composition of binary mixture of the polar domain, volume of the dispersed phase (polar domain) and temperature. μ Es were characterized using a number of techniques, viz., phase behavior, method of dilution, viscosity, dynamic light scattering (DLS), electrical conductance, absorption and fluorescence spectroscopic measurements. It is believed that such a system will exhibit some unusual properties and will find different potential applications due to the unique features of the binary mixtures as well as of a μ E. Usually IL-in-oil μ Es are more rigid and less temperature sensitive; such limitations can be overcome provided the pure IL is replaced with a binary mixture of IL and water.

2. Experimental

2.1. Materials.

The nonionic surfactant polyoxyethylene sorbitan monolaurate (Tween 20) and the IL 1-butyl-3-methyl-imidazolium methanesulfonate, [bmim][MS] were purchased from M/S Fluka, Switzerland and M/S Sigma-Aldrich Chemicals Pvt. Ltd., USA respectively. They were stated to be more than 99.5% pure and were dried under vacuum at 60⁰C for eight hours^{144,193,369}. HPLC grade n-pentanol was a product from Lancaster, England while n-heptane was obtained from E. Merck, Germany. They were used as received. The dye eosin Y, [2-(2, 4, 5, 7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl) benzoate] was a product from E. Merck, Germany. Structure of Tween 20, [bmim] cation and eosin Y are shown in Scheme 1. Double distilled water with a specific conductance of 2-4 μ S cm^{-1} (at 298K) was used.



Scheme 4.1. Schematic models of A, Tween 20; B, [bmim] cation and C, eosin Y

2.2. Methods

2.2.1. Phase manifestation. The pseudo ternary phase diagram of ([bmim][MS]+water) / (Tween 20+n-pentanol) / n-heptane at different compositions of the polar domain were constructed by titrimetric method as described elsewhere^{101,229,261}. Briefly, known amounts of Tween 20+n-pentanol (1:1, w/w) and n-heptane or (IL+water) were taken in a stoppered test tube. (IL+water) or n-heptane was then progressively added using a Hamilton (USA) microsyringe under constant stirring in a controlled temperature bath (298±0.1K). The phase boundary was detected through the appearance of turbidity, whereby the composition was noted. The same experiment was carried out for a number of compositions by varying the amount of oil or IL+water. Also the experiments were carried out using different combinations of IL and water.

2.2.2. Method of dilution. The simple experiment, capable of providing useful information on the thermodynamics of formation and structural parameters of μ E, was also carried out titrimetrically^{34,101,261}. Different binary mixtures were used as the polar domain in the oil continuum. Also experiments were carried out at different [IL+ water] / [Tween 20] mole ratio, ω (5, 10, 15, 20 and 25) and temperatures (298, 303, 308, 313, 318 and 323K). Known amount of surfactant,

polar component (IL+water) and n-heptane were taken in a stoppered test tube which, after homogenization, appeared turbid. n-pentanol was then progressively added. After saturating the oil continuum (and partly the polar domain) once excess n-pentanol became available, it behaved like cosurfactant and occupied the polar domain/oil interface whereby a clear μE was formed. The required amount of n-pentanol was then noted. Upon further addition of n-heptane, the oil continuum abstracted the cosurfactant from the interface which resulted in the destabilization of the μE . The clarity was regained again by adding cosurfactant. This method of destabilization and re-stabilization was carried out for a number of times, whereby the composition was also noted. The method basically aimed to determine the partition coefficient of n-pentanol between the oil continuum and the interface (strictly speaking, n-pentanol was partly soluble in the polar domain). The previously followed approach of Moulik et al.⁹⁸ was suitably modified in the present case as has been detailed in the supplementary section.

2.2.3. Viscosity measurements. Viscosity of μE was measured using a LVDV-II+PCP cone and plate type roto-viscometer (Brookfield Eng. Lab, USA). A 0.2M Tween20, mixed with 1:1 (w/w) n-pentanol in n-heptane was used. Unlike the dilution experiments, viscosity was measured at varied volume fraction (ϕ_d) of the dispersed phase. This approach was adapted because of the fact that with varying composition of the polar domain, the same molar ratio range of [IL+water] / [Tween 20] could not be maintained for all the binary mixtures. Temperature during the viscosity measurement was controlled by a cryogenic circulatory water bath with a precision of $\pm 0.1\text{K}$ (DC-1006 M/S. Hahntech Corporation, S. Korea). Shear rates (D) were varied within the range $20 - 60 \text{ S}^{-1}$ with an increment of 5.0 S^{-1} in each step. Zero shear viscosity (η) was obtained using the relation $\eta = \tau / D^{114,127,261,370}$, where τ is the shear stress.

2.2.4. Dynamic light scattering (DLS) studies. Size of the μE droplet was determined by dynamic light scattering (DLS) method. The same set of solution, as used in the viscosity measurements, was employed for size analyses. DLS measurements were carried out using a Zetasizer Nano ZS90 (ZEN3690, Malvern

Instruments Ltd, U.K.). A He-Ne laser of 632.8 nm wavelength was used and the data were collected at 90⁰ angle. Temperature was controlled by inbuilt Peltier heating-cooling device with an accuracy of ±0.05K. The instrument actually measures the diffusion coefficient (D) from which the diameter of the microemulsion droplet (d) was determined according to Stokes–Einstein’s formalism^{134,136,225,261,265}.

$$D = \frac{kT}{3\pi\eta d} \quad (4.1)$$

where k, T and η indicate the Boltzmann constant, temperature and viscosity respectively.

2.2.5. Conductance measurements. μE comprising IL and water in the polar domain is expected to be conducting, as reported for the conventional water-in-oil μE having ionic components in the polar domain¹¹⁶. Both the volume and temperature induced percolation studies were carried out using 0.2 M Tween20 (with 1:1 w/w n-pentanol) in n-heptane. 10 mL of Tween 20 solution was taken in a thermostated enclosure. For volume induced percolation, binary mixtures of (IL+water) was progressively added with constant stirring. Specific conductance was measured with an EC-CON510/43S conductivity meter (Cyberscan, TDS/⁰C/⁰F, USA). Volume induced percolation studies were conducted at four different temperatures, viz., 298, 303, 308 and 313 K. In another approach while performing the temperature induced percolation studies, a known amount of the dispersed phase (IL+water) was mixed with the surfactant solution. Conductance was then recorded in the temperature range 283-343 K with an increment of 5 K in each step.

2.2.6. Spectral studies.

2.2.6.1. Absorption spectra. Visible absorption spectra of eosin Y (EY) in the polar domain were recorded on a UVD-2950 Spectrophotometer (Labomed Inc., USA) in the range 400-600 nm using a matched pair cell of 1.0 cm path length. Corresponding (IL+water)-in-n-heptane μE without the dye was used as reference. Overall concentration of eosin Y was always kept constant at 10 μM.

Initially, required amount of eosin Y in methanol was taken in a test tube. The solvent was evaporated under vacuum. μE of known composition was then added and homogenized by vortexing the solution. It is to be mentioned that eosin Y is insoluble in n-heptane³⁴⁰. Therefore it could be assumed that the dye molecules reside in the polar domain³⁶⁰.

2.2.6.2. Emission spectra. The same set of solutions, as used in absorption spectroscopic measurements, was used in the fluorescence measurements. Detail of the experimental techniques is available elsewhere^{340,369}. Both the steady state and time resolved fluorescence measurements were carried out using a bench-top spectrofluorimeter (Quantamaster-40, Photon Technology International Inc, NJ, USA). For recording the steady state fluorescence spectra (500 - 650 nm), eosin Y was excited at 500 nm (λ_{ex}).

Steady state anisotropy (r), which is related to the microviscosity of the solvent surrounding the probe molecule, was determined using the following expressions^{325,326}:

$$r = (I_{VV} - GI_{VH}) / (I_{VV} + 2GI_{VH}) \quad (4.2)$$

$$\text{and, } G = I_{HV}/I_{HH} \quad (4.3)$$

where, I_{VV} , I_{VH} are the intensities obtained with the excitation polarizer oriented vertically and the emission polarizer oriented vertically and horizontally respectively; I_{HV} and I_{HH} refer to the similar parameters as above for the horizontal positions of the excitation polarizer. In case of anisotropy measurements, the fluorescence data were collected at an emission wavelength (λ_{em}) of 550 nm³⁶⁹. Excited state lifetime of eosin Y in the polar domain was determined by analyzing the fluorescence decay curve which was single exponential in nature. A pulsed nano diode emitting at 500nm was used as the light source^{340,369}. Goodness of the fit of the curves were adjudged by χ^2 values which were in between 1 and 1.2¹⁴⁴. Fluorescence decay curves were analyzed by Felix GX (version 2.0) software. Both the absorption and fluorescence data were recorded at ambient but controlled temperature.

3. Results and discussion

3.1. Phase manifestation. Although tedious, however the construction of phase diagram for ternary / pseudo ternary μE systems are essential from the fundamental as well as the application point of view^{28,62}. The pseudo ternary phase diagrams for ([bmim][MS] \pm water)/(Tween-20+n-pentanol)/n-heptane at different [bmim][MS] / water mole fractions have been graphically presented in Figure 4.1. The phase manifestations for water containing μE system have been previously reported by the present research group²⁶¹ and this has been taken as the point of reference. Each pseudo ternary phase diagram comprise of a single phase (1 Φ) clear μE region and a two phase turbid region (2 Φ). The extreme corners of the polar component and oil component corresponded to oil-in-polar domain and polar domain-in-oil μE respectively. In the present system, the oil rich regions, i.e., (IL+water)-in-oil μE s were examined for other set of experiments. Area under the clear and turbid regions were calculated by weighing the individual components in the pseudoternary phase diagram as have been done previously^{229,261}. The area under the turbid region was higher in each case compared to pure water. The increase in the area under turbid regions is due to the presence of the ionic components in the polar domain. However, when one analyses the results in terms of the variation of % area under the clear or turbid region with the composition of the binary mixture, it is observed that the %area under clear region for different microemulsions μE passes through a minimum at 50 mole% [bmim][MS] in combination with water ($x_{\text{IL}}=0.5$), as graphically presented in Figure 4.2.

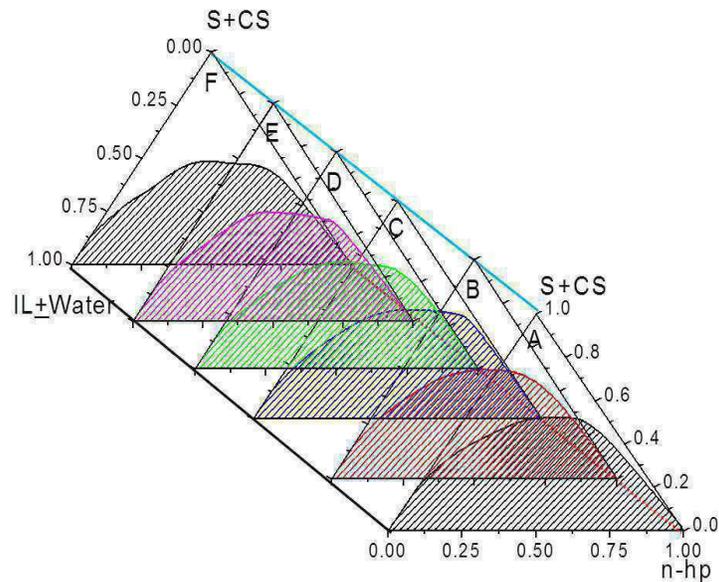


Figure 4.1. Pseudo-ternary phase diagram of $([\text{bmim}][\text{MS}]\pm\text{water})/(\text{Tween-20}+\text{n-pentanol})/\text{n-heptane}$ microemulsion at 298K. 1:1 (w/w) Tween-20 and n-pentanol was used. Mole fraction of $[\text{bmim}][\text{MS}]$ in the binary mixture of $[\text{bmim}][\text{MS}]$ and water: A, 0.2; B, 0.4; C, 0.5; D, 0.6; E, 0.8 and F, 1.0 respectively. The shaded portions represent *biphasic (2Φ)* regions while the clear portions correspond to the *single phase (1Φ)* regions.

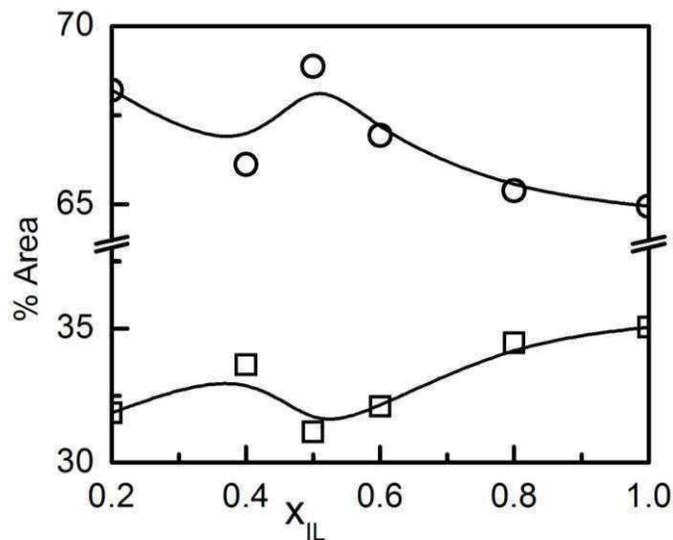


Figure 4.2. Interdependence of the %area under clear (\square) and turbid (O) regions on the mole fraction of $[\text{bmim}][\text{MS}]$ (X_{IL}) in the binary mixture of $[\text{bmim}][\text{MS}]$ and water for $([\text{bmim}][\text{MS}]\pm\text{water})/(\text{Tween-20}+\text{n-pentanol})/\text{n-heptane}$ microemulsion system at 298K.

According to our recent study³⁶⁹ as well as other available reports^{294,295,323}, IL can deactivate water molecules when present in excess amount in a binary mixture. The deactivation of water molecules for binary mixtures comprising of more than 50 mole% IL has recently been modeled by Stark et al.³⁷¹ and Liu et al.^{294,295}.

Above 50 mole% IL, the deactivated water molecules cannot significantly alter the structure of the aggregates. Also there are reports describing the formation of micelle like entities by the IL in binary mixtures^{294,295,298,302,303,306}. Besides, due to amphiphilic nature, IL can also occupy the interface alongwith the surfactant and cosurfactant molecules. Subsequently, clarity of the μE increased further with increasing mole fraction of IL.

3.2. Method of dilution.

3.2.1. Evaluation of thermodynamic parameters. The method of dilution is a very simple but informative technique which can derive many useful parameters for the formation of polar domain-in-oil μE ⁹⁵. In this method, by the alternate stabilization and destabilization with the successive addition of cosurfactant and oil, one can obtain the partition coefficient of n-pentanol between oil and oil / (IL+water) interface. By suitably analyzing the distribution constant in the form of different standard thermodynamic equations, the corresponding thermodynamic parameters for the formation process can be evaluated easily^{98,372,373}. In addition to the thermodynamic parameters, the structural parameters can also be computed from these experimental results^{108,223,228,229}. Although several reports on the method of dilution are available in the literature involving water-in-oil μE , such studies involving ILs are not common and as per our knowledge only one recent report is available in the literature on the IL- μE system³⁶⁴. Thus the dilution studies involving the evaluation of interfacial behavior, thermodynamic and structural parameters of IL μE are considered to be significant.

For a stable μE , the alkanol is distributed in between the interface and oil; the surfactant essentially remains at the interface. In some cases the alkanol molecules may also become partly soluble in the polar domain. In the present case the alkanol molecules get distributed within the (IL+ water) mixture, interface and oil respectively. The total number of moles of n-alkanols (n_a^t) would thus follow the relation^{98,108,223,364}:

$$n_a^t = n_a^p + n_a^i + n_a^o \quad (4.4)$$

where, the superscripts p, i and o stand for polar phase(water+IL), interface and oil respectively.

At a constant temperature and a fixed ω , the ratio of the sum of number of moles of alkanol in the polar phase (n_a^p) and the number of moles of alkanol in oil (n_a^o) will be a constant with the total number of it in the oil (n_o) and total number of polar phase molecules (n_p). Consequently, the mole fraction ratio of alkanol at the interface (X_a^i) and the sum of the mole fraction of alkanol in oil (X_a^o) and polar phase (X_a^p) should also be constant. Thus,

$$\frac{n_a^o + n_a^p}{n_o + n_p} = k \quad (5)$$

and

$$\frac{X_a^i}{X_a^o + X_a^p} = k_d \quad (4.6)$$

where, k and k_d are constant and the distribution constant respectively.

By replacing equation (4.2) in equation (4.1) one sets the following relation:

or,

$$\frac{n_a^t}{n_s} = \frac{n_a^i}{n_s} + k \left(\frac{n_o + n_p}{n_s} \right) \quad (4.7)$$

where n_s represents the number of moles of surfactants.

In the dilution experiments, at a fixed n_s , n_a^t and (n_o+n_p) are varied to have a series of $\frac{n_a^t}{n_s}$ and $\frac{n_o + n_p}{n_s}$ which according to equation (4.7) can give $\frac{n_a^i}{n_s}$

and k from the linear plot between $\frac{n_a^t}{n_s}$ and $\frac{n_o + n_p}{n_s}$ as Intercept (I) and slope

(S), respectively. The plot of $\frac{n_a^t}{n_s}$ vs. $\frac{n_o + n_p}{n_s}$ for $x_{IL}=0.5$ at $\omega = 15$ have been presented in Figure 4.2.

The distribution constant, k_d , can be related with the slope and intercept of equation (4.7) as:

$$k_d = \frac{X_a^i}{X_a^o + X_a^p} = \frac{\frac{n_a^i}{(n_a^i + n_s)}}{\frac{n_a^o}{(n_a^o + n_o)} + \frac{n_a^p}{(n_a^p + n_p)}} = \frac{n_a^i (1 + \frac{n_a^o}{n_o})}{n_a^o (n_a^i + n_s)} \quad (4.8)$$

Or,

$$k_d = \frac{\frac{n_a^i}{(n_a^i + n_s)}}{\frac{(n_a^o + n_a^p)}{(n_a^o + n_a^p + n_o + n_p)}} \quad (4.9)$$

Or,

$$k_d = \frac{(n_a^o + n_a^p + n_o + n_p)}{(n_a^o + n_a^p) \left(\frac{n_a^i + n_s}{n_a^i} \right)} \quad (4.10)$$

We know,

$$S = \frac{n_a^o + n_a^p}{n_o + n_p}$$

Thus,

$$k_d = \frac{[S(n_o + n_p) + (n_o + n_p)]}{S(n_o + n_p) \left(1 + \frac{n_s}{n_a^i} \right)} \quad (4.11)$$

$$k_d = \frac{I(S + 1)}{S(I + 1)} \quad (4.12)$$

Therefore, by knowing I, S one would get the value of k_d

Thus by using equations (7) and (12) one can evaluate the values of n_a^i , n_a^o and k_d for the formation of w/o microemulsion.

Changes in the standard Gibbs free energy of transfer (ΔG_t°) of alkanol from oil to the interface (as well as into the polar domain) could be expressed as:

$$\Delta G_t^\circ = - RT \ln k_d \quad (4.13)$$

Changes in the standard enthalpy of transfer ΔH_t° was evaluated by the van't Hoff equation:

$$\left[\frac{\partial(\Delta G_t^\circ)}{\partial(1/T)} \right]_p = \Delta H_t^\circ \quad (4.14)$$

ΔG_t° vs T profile was found to follow a two degree polynomial equation as:

$$\Delta G_t^\circ = a + bT + cT^2 \quad (4.15)$$

where a, b and c are the polynomial coefficients.

The ΔH_t° values at the different experimental temperatures were determined using the following expression:

$$\left[\frac{d(\Delta G_t^\circ / T)}{d(1/T)} \right]_p = a - cT^2 = \Delta H_t^\circ \quad (4.16)$$

The standard entropy of transfer (ΔS_t°) of the associated process was then evaluated according to the following expression:

$$\Delta S_t^\circ = (\Delta H_t^\circ - \Delta G_t^\circ) / T \quad (4.17)$$

A representative plot of n_a^t/n_s vs. $(n_o+n_p)/n_s$ at $x_{[bmim][MS]}=0.5$ and $\omega=15$ has been shown in Figure 4.3. Herein n_a^t , n_s , n_o , n_p stand for the total number of moles of alkanol, surfactant, oil and the polar component respectively.

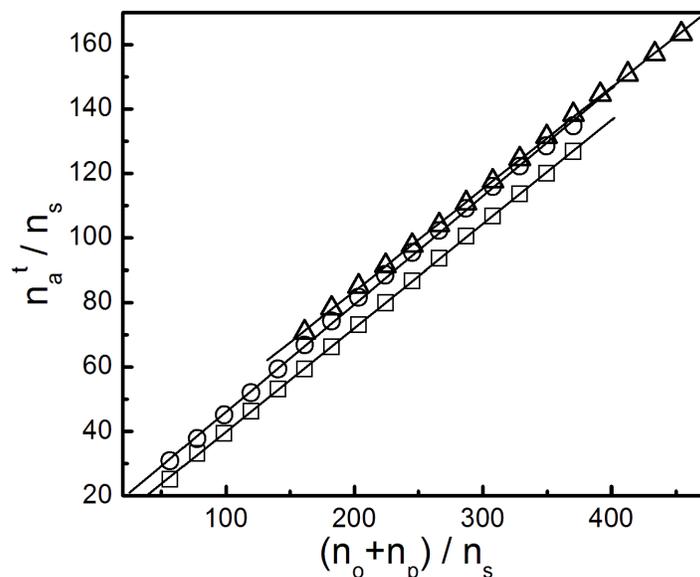


Figure 4.3. Plot of n_a^t/n_s vs. $(n_o+n_p)/n_s$ for $([bmim][MS]+water)/(Tween-20+n-pentanol)/n-heptane$ polar domain-in-oil microemulsion system. $[bmim][MS] / [water]$ mole ratio = 1:1. $([bmim][MS]+water)/Tween20$ mole ratio, $\omega=15$. Temperature (in K): \circ , 298; Δ , 308 and \square , 318. 0.2g Tween 20 was used in each case.

Results are summarized in Table 4.1 for equimolar mixture of IL and water. Other results are provided in Table 4.2.

Table 4.1. Thermodynamic parameters for the transfer of n-pentanol from oil to $([bmim][MS]+water)$ interface during the formation of $[bmim][MS]\pm water/(Tween-20+n-pentanol)/n-heptane$ polar domain-in-oil microemulsion at different temperature and $[IL+water]/[Tween-20]$ mole ratio, ω . IL:water molar ratio = 1:1

Parameter	Temp. / K						
	ω	298	303	308	313	318	323
k_d	5	3.01	3.19	2.93	4.17	3.22	3.45
	10	3.72	3.51	3.79	3.47	3.09	3.57
	15	3.69	3.88	3.97	3.56	3.62	3.90
	20	3.99	3.93	4.15	3.88	3.85	3.98
	25	4.17	4.19	4.00	3.98	3.98	4.24
$-\Delta G_t^0 / kJ mol^{-1}$	5	2.73	2.92	3.25	3.72	3.09	3.33
	10	3.25	3.16	3.41	3.24	2.98	3.42
	15	3.23	3.42	3.53	3.31	3.40	3.66
	20	3.43	3.44	3.65	3.53	3.57	3.71
	25	3.54	3.61	3.55	3.59	3.65	3.88
	5	19.79	-2.02	-24.20	-46.74	-69.65	-92.92
	10	-7.54	-4.91	-2.23	0.49	3.25	6.06

$\Delta H_t^0 / \text{kJ mol}^{-1}$	15	-8.59	-4.65	-0.65	3.41	7.55	11.75
	20	-4.12	-2.58	-1.03	0.56	2.17	3.82
	25	-4.32	-3.05	-1.76	-0.45	0.88	2.24
$\Delta S_t^0 / \text{J K}^{-1} \text{mol}^{-1}$	5	75.59	2.97	-69.66	-137.47	-209.30	-277.38
	10	-14.39	-5.76	3.84	11.91	19.63	29.37
	15	-17.96	-4.08	9.34	21.47	34.44	47.69
	20	-2.33	2.83	8.51	13.07	18.06	23.30
	25	-2.65	1.83	5.81	10.03	14.26	18.93

0.2g Tween-20 was taken in each case. ϕ_d = volume fraction of the dispersed phase (IL+ water).

Results revealed that increasing ω value resulted in the increase of k_d value, except in a few cases. However, while considering all the binary combinations of IL and water, the variation of k_d (and subsequently ΔG_t^0) with ω and temperature were not very straightforward. In our previous studies^{228,261} for water/Tween20+n-pentanol/n-heptane water-in-oil microemulsion, we observed that with the increased volume fraction of polar domain, new droplets were formed. It was due to the capability of the polyoxyethylene groups of Tween 20 to uncoil at larger volume fraction of the polar component. Systems comprising of less than 50 mole% IL behaved similarly to water/Tween20+n-pentanol/n-heptane μE . However, for the systems comprising of more than 50 mole% IL, the variation of thermodynamic parameters was different. Microemulsions comprising more than 50 mole% IL in combination with water behaved more like the IL microemulsion. In this sense, behavior of the systems comprising less than 50 mole% IL were more like the microemulsion with water only.

Table 4.2. Thermodynamic parameters for the transfer of n-pentanol from oil to oil-(IL+ water) interface in the formation of [bmim][MS] \pm water / (Tween-20+n-pentanol) / n-heptane polar domain-in-oil microemulsion at different temperature and [IL+ water]/[Tween-20] mole ratio, ω . IL:water = 2:4, 4:6, 6:4, 8:2 and 1:0

IL:Wa		$k_a / -\Delta G_i^0$ (kJ mol ⁻¹) / ΔH_i^0 (kJ mol ⁻¹) / ΔS_i^0 (J K ⁻¹ mol ⁻¹) at different temperature (in K)						
	ω	Temp. 298	303	308	313	318	323	
2:8	5	3.32/2.97/-1.62/4.54	2.88/2.67/-0.32/7.73	1.22/2.50/0.99/4.87	3.28/3.09/2.33/17.32	3.46/3.28/3.69/21.94	3.44/3.32/5.07/25.99	
	10	2.70/2.84/-76.11/-	2.45/1.59/-52.06/-	2.64/2.67/-27.63/-	2.72/2.94/-2.78/-0.58	3.58/3.06/22.45/81.21	6.04/3.04/48.09/163.8	
	15	3.15/ 2.84 /-0.01/9.50	1.88/1.59/-0.10/4.94	2.84/2.67/-0.19/8.05	3.09/2.94/-0.29/8.47	3.18/3.06/-0.39/8.40	3.09/3.04/-0.49/7.90	
	20	2.14/1.88/33.06/117.2	2.52/2.33/25.24/91.00	0.88/2.30/17.30/55.20	1.98/2.77/9.23/35.16	3.40/3.23/1.03/13.42	3.25/3.17/-7.30/-	
	25	4.45/2.69/-69.99/-	2.83/2.62/-41.60/-	2.40/2.25/-12.73/-	2.75/2.63/16.61/61.48	2.91/2.83/46.43/154.8	2.00/1.87/76.71/243.2	
4:6	5	3.68/3.23/-28.54/-	3.99/3.49/-15.44/-	3.56/3.25/-2.12/3.69	3.22/3.04/11.42/46.22	3.32/3.17/25.18/89.16	4.30/3.92/39.15/133.3	
	10	3.03/3.74/17.11/66.60	3.52/3.17/13.49/55.01	3.83/3.44/9.83/43.09	3.73/3.42/6.11/30.45	3.48/3.30/2.32/17.69	4.09/3.78/-1.52/6.98	
	15	3.52/3.12/-10.44/-	3.42/3.10/-4.67/-5.17	3.32/3.37/1.19/13.86	3.42/3.19/7.16/33.09	3.67/3.44/13.21/52.38	3.38/3.27/19.37/70.08	
	20	3.88/3.36/-6.37/-	3.70/3.29/-4.09/-2.64	3.81/3.43/-1.78/5.33	3.66/3.38/0.56/12.59	3.81/3.54/2.95/20.41	3.77/3.56/5.38/27.68	
	25	3.92/3.38/-35.55/-	3.22/2.95/-17.88/-	2.40/3.24/0.08/7.54	3.93/3.56/18.34/69.96	3.85/3.57/36.89/127.2	4.97/3.31/55.73/185.8	
6:4	5	2.75/2.96/29.59/107.7	3.23/3.17/13.70/54.96	3.27/3.26/-2.46/1.86	3.09/3.38/-18.88/-	3.00/3.48/-35.57/-	3.19/3.49/-52.53/-	
	10	3.40/3.04/315.62/106	3.83/3.38/320.69/106	3.87/3.46/325.86/106	3.96/3.58/331.11/106	3.88/3.58/336.44/106	3.68/3.50/341.86/106	
	15	4.29/3.61/-201.16/-	4.11/3.56/-204.47/-	4.15/3.65/-207.83/-	4.55/3.94/-211.24/-	4.10/3.73/-214.71/-	4.57/4.08/-218.24/-	
	20	4.33/3.63/-159.76/-	4.89/3.99/-162.38/-	4.25/3.71/-165.05/-	4.69/4.02/-167.77/-	4.36/3.89/-170.52/-	4.63/4.12/-173.33/-	
	25	5.14/4.05/-35.52/-	5.49/4.29/-36.07/-	5.35/4.29/-36.63/-	4.92/4.15/-37.19/-	4.89/4.19/-37.77/-	4.77/4.19/-38.35/-	
8:2	5	3.22/2.90/799.82/269	3.73/3.32/812.88/269	3.25/3.02/826.18/269	3.79/3.47/839.69/269	3.25/3.12/853.41/269	2.76/2.73/867.35/269	
	10	3.84/3.33/4.89/27.62	3.93/3.45/4.92/27.60	3.97/3.53/4.94/27.50	4.16/3.71/4.96/27.71	4.18/3.79/4.98/27.58	4.28/3.90/5.01/27.59	
	15	4.04/3.46/-193.19/-	4.01/3.50/-196.41/-	4.31/3.74/-199.68/-	4.15/3.70/-203.01/-	4.37/3.90/-206.38/-	4.48/4.03/-209.81/-	
	20	4.34/3.64/104.27/362.	4.03/3.51/105.83/360.	4.81/4.02/107.42/361.	4.43/3.88/109.03/360.	4.76/4.13/110.67/360.	4.77/4.19/112.34/360.	
	25	4.76/3.87/85.92/301.3	5.24/4.17/87.29/301.8	5.56/4.39/88.68/302.2	4.89/4.13/90.11/301.0	5.02/4.27/91.55/301.3	4.97/4.31/93.01/301.3	
1:0	5	5.64/4.28/-	3.61/3.24/-	3.25/3.02/28.31/29.50	5.01/4.19/97.36/27.39	4.76/4.12/167.53/25.2	3.45/3.32/238.81/22.9	
	10	4.38/4.66/28.77/108.8	5.26/4.18/13.72/59.09	5.23/4.23/-1.58/8.61	4.96/4.16/-17.14/-	4.32/3.87/-32.95/-	7.28/5.33/-49.00/-	
	15	5.83/4.47/-1.54/12.84	5.73/4.39/-2.21/7.24	7.05/4.58/-3.89/3.59	5.51/4.44/-5.61/-3.74	4.80/4.15/-7.36/-	5.03/4.34/-9.13/-	
	20	5.89/4.39/12.14/55.47	6.24/4.61/4.23/29.19	6.49/4.78/-3.80/3.20	4.99/4.18/-11.97/-	5.19/4.35/-20.26/-	4.80/4.21/-28.69/-	
	25	5.33/4.56/3.77/26.57	5.52/4.70/0.85/17.00	5.37/4.86/-2.13/7.07	5.60/4.48/-5.15/-2.12	5.10/4.31/-8.22/-	5.21/4.43/-11.34/-	

The variation was similar to the conventional water-in-oil microemulsions with ionic surfactants. It has already been stated that when the amount of [bmim][MS] exceeds 50 mole% (in the binary mixture), it can deactivate water molecules. The rigidity of IL-in-oil μ Es was due to strong electrostatic interaction between the imidazolium cation and oxyethylene group of Tween 20. Hence, when binary mixture comprising of more than 50 mole% IL was used as the polar domain, size of the microemulsion droplets increased with ω instead of formation of smaller droplets like water / (Tween 20+n-pentanol) / n-heptane²⁶¹ or water-in-oil μ E systems comprising Tweens and Brij^{228,229}. Figure 4.4 describes the variation in the changes of standard free energy (ΔG_r^0) with ω and T for $x_{IL} = 0.2$ and 0.8.

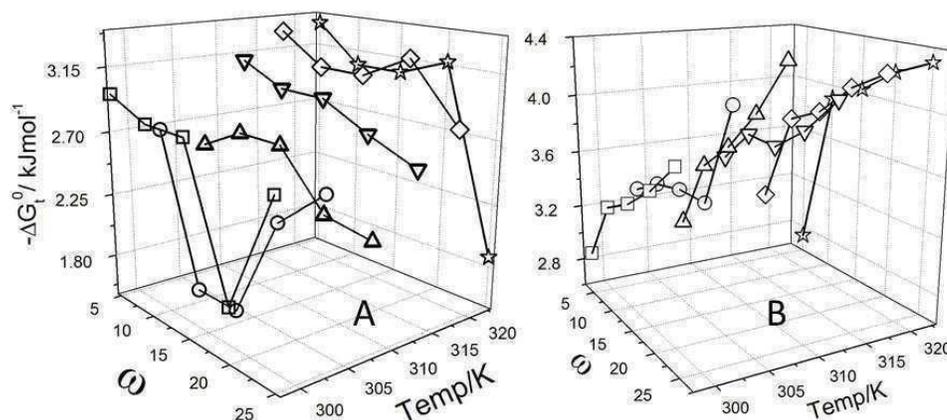


Figure 4.4. ΔG_r^0 - ω -T profile for the formation of ([bmim][MS]±water)/(Tween-20+n-pentanol)/n-heptane polar domain-in-oil microemulsion system. Mole fraction of [bmim][MS] in the polar domain: A, 0.2 and B, 0.8.

Binary mixtures of different compositions ($x_{IL} = 0.2, 0.4, 0.5, 0.6, 0.8$ and 1.0) were used for such studies. Some representative results have been shown in Table 4.1. Other results are summarized in Table 4.2. In all the cases ΔG_r^0 values were negative which implied the spontaneity of the formation of μ E. However, ΔG_r^0 - ω -T profiles were found to be composition dependent. For systems comprising of lower amount of IL (less than 50 mole%) negative values of ΔG_r^0 decreased with increasing ω . This suggests the similarity of the behavior of present μ E system with the corresponding water-in-oil μ Es²⁶¹. No systematic variation in ΔG_r^0 with T was observed in either case. For systems with larger amounts of IL, negative values of ΔG_r^0 increased with ω suggesting the formation of larger droplets without significantly losing their rigidity. However, to make final conclusions in

this regard some other experimental evidences like dynamic light scattering studies are warranted. While considering the formation dynamics, it was observed that behavior of the systems comprising of less than 50 mole% of IL was similar to water comprising μ Es; spontaneity of μ E formation decreased with increasing volume of the dispersed phase (ω or ϕ_d). However, for systems comprising of more than 50 mole% of IL, polarity of the dispersed phase decreased which resulted in the increased ease of μ E formation. The decreased polarity was occurred due to the presence of IL molecules which themselves are amphiphilic in nature. This further supported the inferences drawn from the phase manifestation studies. With increasing ω , the curvature of μ E decreased leading to more accumulation of cosurfactant at the polar domain-oil interface. While considering the enthalpy of transfer process under various conditions (as described in Table 4.1, Table 4.2 and Fig 4.5), it was found that at higher temperature ΔH_t^0 became endothermic which was initially exothermic in nature.

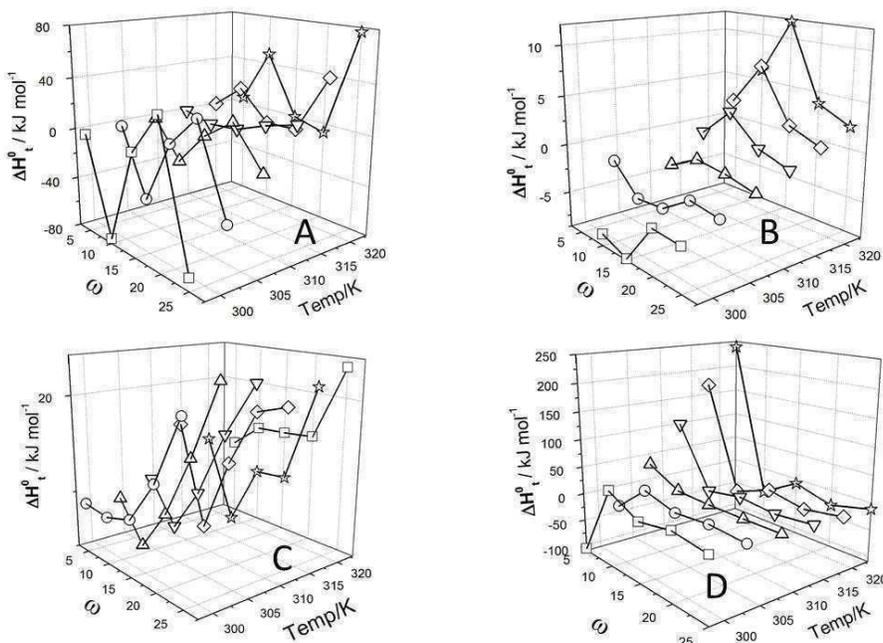


Figure 4.5. ΔH_t^0 - ω -T profile for the formation of [bmim][MS] \pm water/(Tween-20+n-pentanol)/n-heptane polar domain in oil microemulsion system. Mole fraction of [bmim][MS] in the polar domain: A, 0.2; B, 0.5; C, 0.8 and D, 1.0

Our present set of results for the system comprising of more than 50 mole% IL showed similar behavior as in case of [bmim][BF₄] / (Brij-35+1-butanol) / toluene IL-in-oil μ E system³⁶⁴. As there are possibilities for the polar components to get

dispersed into the n-heptane medium, there occurred an effective increase in the area of the droplet surface. The required energy for the positive work is compensated by the absorption of heat. However, in the cases involving size increment, the negative value of ΔH_t^0 was not unexpected to decrease. To justify the similarities / dissimilarities between the behavior of conventional water-in-oil μE and IL-in-oil μE , analysis of the enthalpy-entropy profile was necessary²²⁴. Fig 6 describes the $\Delta H_t^0 - \Delta S_t^0$ profile for all the combinations. Nice correlations were observed for all the sets of values, e.g., different x_{IL} , ω and temperature. Compensation temperature, as obtained from the slope was found to be 311 K which was in good agreement with the average of all the experimental temperatures (298, 303, 308, 313, 318 and 323 K).

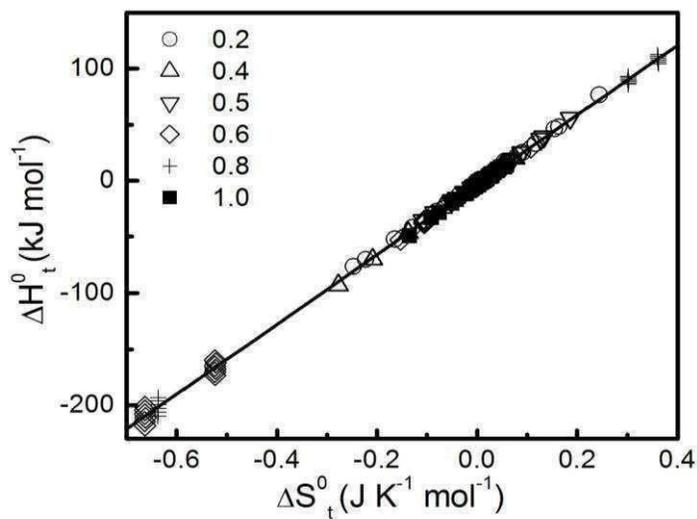


Figure 4.6. Enthalpy–entropy compensation for the formation of ([bmim][MS] + water) / (Tween-20+n-pentanol) / n-heptane polar domain-in-oil microemulsion system. Mole fraction of [bmim][MS] in the binary mixture (present in the polar domain) have been mentioned inside the Figure

3.2.2. Evaluation of structural parameters. The results of dilution experiments can be further computed to determine different structural parameters of the w/o microemulsion. For such evaluation the μE droplets are considered to be spherical, monodispersed and a monomolecular layer comprising surfactant and cosurfactant is present at the interface. The total volume of the dispersed droplets (V_d) per unit volume (here in mL) can be expressed as follows:

$$V_d = \frac{4}{3} \pi R_e^3 N_d \quad (4.18)$$

R_e and N_d represents the effective diameter and total number of the droplets respectively.

The droplet surface area (A_d) of droplets per unit volume is therefore:

$$A_d = 4\pi R_e^2 N_d = (n_s A_s + n_a^i A_a) N_A \quad (4.19)$$

where, A_s and A_a are the cross sectional area of the surfactant and cosurfactant molecules respectively, N_A Avogadro's constant.

The equation for R_e from equation (4.18) and (4.19) can be written as:

$$R_e = 3V_d/A_d \quad (4.20)$$

Total volume of the dispersed phase, herein the water droplet embedded by the surfactant and n-alkanols at the oil-water interface, is the sum of the volume contribution of water (V_{H_2O}), surfactant (V_s) and the interfacial n-alkanol molecules (V_a^i) at the interface respectively. Thus one could write;

$$V_d = V_{H_2O} + V_s + V_a^i \quad (4.21)$$

One can determine the respective volumes using the values of number of moles (n_a^i), molar mass (M_a) and density of the components (ρ_a) according to the relation:

$$V_a^i = n_a^i M_a / \rho_a \quad (4.22)$$

The total droplet surface area (A_d) can be obtained from the equation:

$$A_d = (n_s A_s + n_a^i A_a) N_A \quad (4.23)$$

where, A_s and A_a correspond to the head group area of the surfactant and cosurfactant respectively, N_A is the Avogadro number.

Putting the value of R_e in equation (4.18) one can easily obtain the value of N_d as:

$$N_d = 3V_d/4\pi R_e^3 \quad (4.24)$$

Average aggregation number of surfactant (N_s) and cosurfactant (N_a) can be computed using the following formulae:

$$N_s = \frac{n_s N_A}{N_d} \quad (4.25)$$

$$N_a = \frac{n_o^i N_A}{N_d} \quad (4.26)$$

Volume of a microemulsion droplet can be considered as the additive contributions of the polar components, surfactant and cosurfactant molecules. Thus the radius of polar domain in a microemulsion droplet (R_p) and the effective radius (R_e) are related as:

$$R_p = \left(\frac{V_p + V_s^h + V_a^h}{V_d} \right)^{1/3} R_e \quad (4.27)$$

where, V_p , V_s^h and V_a^h are volume of water droplet, surfactant head group, and alkanol head group, respectively. Volume contribution due to surfactant head group and cosurfactant head group could be evaluated from the following two equations:

$$V_s^h = \frac{4}{3\pi^{1/2}} A_s^{3/2} N_s \quad (4.28)$$

$$V_a^h = \frac{4}{3\pi^{1/2}} A_a^{3/2} N_a \quad (4.29)$$

Results of the dilution experiments were computed using suitable mathematical formulations whereby the different structural parameters, viz., number of droplets per unit volume (N_d), number of surfactants per droplet (N_s), number of cosurfactants per droplet (N_{cs}), effective diameter of the droplet (R_e) and radius of polar domain (R_p) could be determined²²⁴. While computing the structural parameters, the μ E droplets were assumed to be spherical and monodispersed, stabilized by a surfactant and cosurfactant monolayer. Results are summarized in Table 4.3 and Table 4.4. N_d - ω -T profile for the systems comprising of 20 and 80 mole% of [bmim][MS] have been shown in Figure 4.7 as representative.

Table 4.3. Structural parameters of [bmim][MS]+water/(Tween-20+n-pentanol)/n-heptane polar domain-in-oil microemulsion at different temperature and [IL+water]/[Tween-20] mole ratio, ω . Mole ratio of IL : water = 1:1

Parameters	Temp. / K						
	ω	298	303	308	313	318	323
R_e / nm	5	4.74	3.75	3.35	2.83	2.63	2.42
	10	4.30	4.32	3.62	3.45	3.29	2.91
	15	5.25	4.56	3.88	3.88	3.79	3.26
	20	5.31	5.03	4.48	4.09	3.84	3.58
	25	5.65	5.09	5.09	4.35	4.22	3.79
$10^{-18} N_d$ (per mL)	5	0.76	1.744	3.25	6.83	5.08	7.27
	10	1.89	1.56	3.11	3.13	2.93	5.28
	15	1.09	1.75	3.28	2.73	2.53	5.08
	20	1.34	1.512	2.24	3.02	3.63	4.61
	25	1.27	1.783	1.62	2.95	3.04	4.66
N_s (per droplet)	5	67.46	55.99	43.47	14.28	19.23	13.44
	10	51.56	62.63	31.40	31.21	33.35	18.46
	15	89.08	55.89	29.80	35.71	38.53	19.20
	20	72.85	64.58	43.51	32.36	26.86	21.17
	25	76.66	54.75	60.17	33.07	32.12	20.96
N_{cs} (per droplet)	5	5.27	3.67	2.07	3.06	1.29	1.26
	10	8.06	5.94	4.64	3.23	1.52	1.98
	15	11.16	7.95	6.07	4.62	2.92	3.21
	20	12.67	9.97	7.62	6.12	5.01	4.21
	25	14.74	11.25	9.46	7.35	6.10	5.24

0.2g Tween-20 was taken in *each case*. ϕ_d = volume fraction of the dispersed phase (IL+ water).

In both the cases, the number of droplets per unit volume increased with increasing temperature. However, the extent of increase were higher for the systems comprising of lower amount of [bmim][MS]. The decrease in the number of droplet with increasing volume of the dispersed phase was not unexpected. With the increase in the volume of the dispersed phase, larger droplets were formed³⁶⁴. While considering the size of the polar domain as well as the effective size of the μE (as modeled by Wang et al.³⁶⁴), it has been noticed that both R_e and R_p decreased with the increase in temperature and ω for water rich binary mixtures ($x_{\text{IL}} < 0.5$). However, the size of the μE as well as the polar domain increased with increasing volume of the dispersed phase. A systems comprising of 50 mole% of IL comprising system behaved intermediately compared to water rich or IL rich binary mixtures. The reason for such unusual behavior is not certain. Compared to the corresponding water-in-oil μE systems, presently studied (IL+water) μE system was less temperature sensitive as revealed from the variation of R_e values with temperature. The rigidity was contributed by the strong electrostatic attraction between oxyethylene groups of the surfactant and the imidazolium cation.

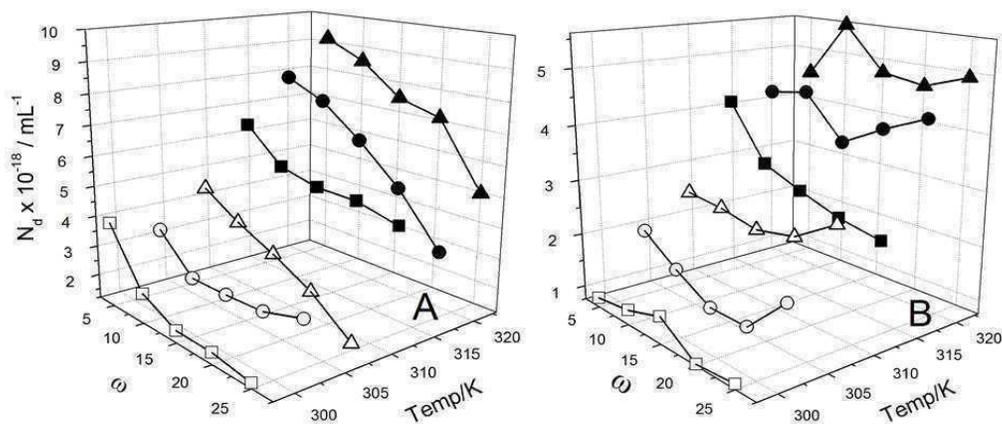


Figure 4.7. N_d - ω - T profile for the formation of ([bmim][MS] \pm water)/(Tween-20+n-pentanol)/n-heptane polar domain-in-oil microemulsion system. Mole fraction of [bmim][MS] in the polar domain: A, 0.2 and B, 0.8. Temperature (in K): \square , 298; O , 303; Δ , 308; \blacksquare , 313; \bullet , 318 and \blacktriangle , 323.

Table 4.4. Structural parameters of [bmim][MS] \pm water/(Tween-20+n-hexanol)/n-heptane polar domain-in-oil microemulsion at different temperature and [IL+water]/[Tween-20] mole ratio, ω . IL:water = 2:4, 4:6, 6:4, 8:2 and 1:0

IL:Water		R_e (nm)/ $10^{-18} N_d$ (per mL)/ N_s (per droplet)/ N_{cs} (per droplet) at different temperature (in K)																							
ω	Temp. 298	303					308					313					318					323			
2:8	5	3.27	3.99	2.45	5.01	3.14	3.38	2.58	3.56	2.96	4.47	2.97	9.7	2.61	6.41	2.52	2.21	2.41	7.87	2.24	1.69	2.18	9.09	2.23	1.04
	10	3.80	2.18	3.47	5.98	3.58	2.24	3.36	4.06	3.19	3.72	3.10	2.88	2.87	5.31	2.81	2.31	2.65	7.31	2.64	2.28	2.55	8.50	2.34	2.65
	15	4.26	1.59	6.11	7.2	3.80	2.25	3.44	5.09	3.34	3.15	3.62	4.01	3.06	4.98	3.17	3.22	2.85	6.26	2.98	2.64	2.67	7.46	2.38	1.98
	20	4.47	1.58	6.18	8.26	3.97	2.32	3.89	6.03	3.58	2.46	3.84	3.18	3.23	4.96	3.36	3.88	3.22	5.03	3.19	1.96	2.85	7.08	2.35	2.73
	25	4.81	1.36	7.16	9.54	4.01	2.71	4.59	6.77	3.79	1.43	4.20	5.35	3.34	4.62	3.84	4.51	3.24	3.39	3.45	3.53	3.11	4.94	2.45	2.49
4:6	5	3.47	3.37	2.89	5.57	3.21	4.22	3.31	4.33	3.08	3.55	3.14	2.81	2.79	4.29	2.27	1.82	2.54	5.95	2.56	1.46	2.49	12.2	2.46	2.47
	10	5.01	0.85	1.14	7.78	3.85	2.33	4.18	5.46	3.21	5.62	3.54	4.53	3.11	5.34	2.83	3.57	2.99	4.43	2.78	2.13	2.73	8.87	2.54	2.7
	15	4.96	1.19	3.16	9.82	4.23	2.10	4.65	6.96	3.99	2.33	4.19	5.23	3.78	2.50	3.09	3.66	3.36	3.91	2.87	3.14	3.23	3.65	2.68	1.69
	20	4.86	1.65	5.92	10.75	4.26	2.64	4.69	8.01	3.95	3.34	4.93	6.49	4.03	2.60	3.55	5.092	3.66	3.63	3.22	4.16	3.44	4.28	2.75	3.32
	25	5.06	1.68	5.78	12.08	5.14	1.44	4.78	10.36	6.15	0.64	5.53	6.32	4.18	2.85	3.72	6.32	3.95	3.31	3.67	5.12	3.47	5.95	2.90	4.59
6:4	5	4.92	0.72	4.55	5.79	3.83	1.75	4.56	4.12	3.32	2.89	4.28	3.08	3.02	3.61	2.71	2.03	2.74	4.41	3.21	1.19	2.50	6.61	2.48	1.26
	10	5.29	0.86	5.29	9.79	4.16	2.10	4.64	6.64	3.90	2.42	4.44	4.95	3.48	3.63	2.88	3.98	3.27	4.20	3.32	3.02	3.05	4.97	2.96	2.29
	15	4.63	1.87	6.21	9.83	4.19	2.58	4.77	7.57	3.94	3.05	4.72	6.08	3.58	4.33	3.25	4.98	3.41	4.82	3.63	4.09	3.16	6.55	2.98	3.58
	20	5.18	1.47	6.62	12.31	4.37	2.81	5.17	8.79	4.54	2.11	5.13	7.66	3.83	4.25	3.59	6.08	3.80	3.84	3.74	5.05	3.46	5.70	3.17	4.42
	25	5.21	1.76	5.54	13.2	4.73	2.44	5.39	10.35	4.42	3.01	5.24	8.57	4.36	2.91	3.95	7.36	3.90	4.50	4.16	6.12	3.67	5.60	3.40	5.3
8:2	5	4.82	0.92	5.59	7.27	3.90	1.97	4.94	5.02	3.54	2.52	4.47	3.47	3.13	4.14	2.86	2.93	2.92	4.22	3.31	1.69	2.66	4.50	2.67	0.52
	10	5.35	1.02	6.56	11.33	4.71	1.52	5.43	8.04	4.11	2.45	4.98	6.07	3.79	3.12	3.13	4.77	3.46	4.35	3.54	3.97	3.23	5.54	2.76	3.35
	15	5.55	1.24	7.86	13.89	5.56	1.13	5.67	11.46	4.57	2.30	4.64	8.29	4.27	2.82	3.46	6.74	3.97	3.56	3.74	5.56	3.67	4.75	2.66	4.74
	20	6.72	0.77	7.61	19.65	5.67	1.12	6.39	14.44	4.83	2.44	4.99	10.12	4.69	2.56	3.81	8.64	4.18	3.97	3.95	7.09	3.98	4.63	2.91	6.13
	25	6.95	0.84	8.61	22.27	5.84	1.87	6.72	14.48	4.89	2.91	5.35	11.25	5.05	2.41	4.04	10.48	4.35	4.33	4.25	8.29	4.17	4.90	3.25	7.33
1:0	5	3.23	0.75	0.91	5.91	4.37	1.57	2.22	6.27	4.19	1.55	2.31	3.84	3.21	5.85	1.67	4.22	3.10	5.65	1.73	3.3	3.01	4.50	2.17	1.76
	10	5.78	1.02	1.58	14.32	4.17	3.71	2.43	8.53	4.11	3.64	2.68	7.52	3.83	4.61	2.12	6.34	3.64	5.37	1.81	5.45	3.31	5.69	2.42	4.84
	15	4.42	4.47	2.18	10.75	4.48	3.92	2.49	10.36	4.08	5.71	2.71	8.52	4.32	4.05	2.41	8.43	3.94	5.86	2.16	7.11	4.12	4.31	2.66	6.55
	20	4.78	4.15	2.36	12.67	4.59	4.68	2.58	11.32	4.21	6.62	2.47	9.44	4.58	4.22	2.71	10.06	4.19	6.01	2.32	8.47	4.32	4.94	2.97	8.13
	25	5.13	3.76	2.59	14.75	5.03	3.93	2.68	13.62	4.67	5.17	2.88	11.55	4.63	5.16	2.89	10.87	4.65	4.82	2.73	10.38	4.35	6.21	3.34	9.05

3.3. Dynamic light scattering studies. Size of the μE droplets were also determined by the dynamic light scattering experiments. As in the present study binary mixtures of [bmim][MS] and water of different compositions were used, hence size variations were considered with respect to the volume fraction of the dispersed phase. Variation in the diameter of the μE droplet with the volume fraction of polar domain has been shown in Figure 4.8 along with the viscosity data.

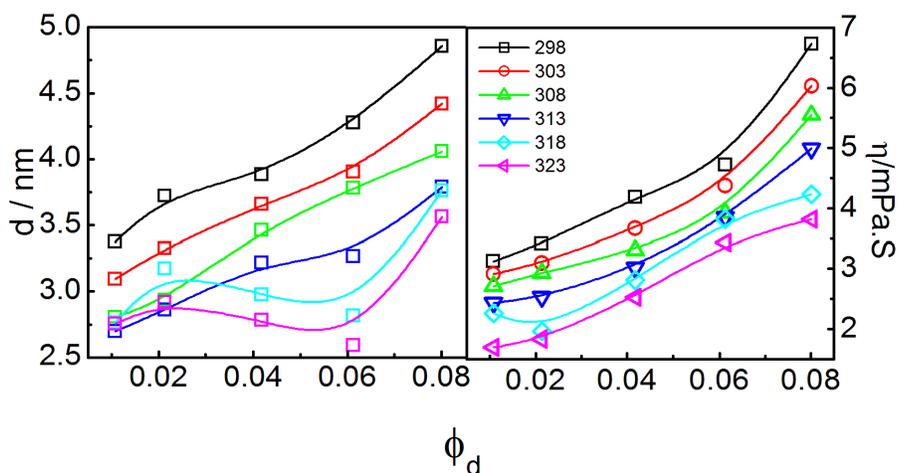
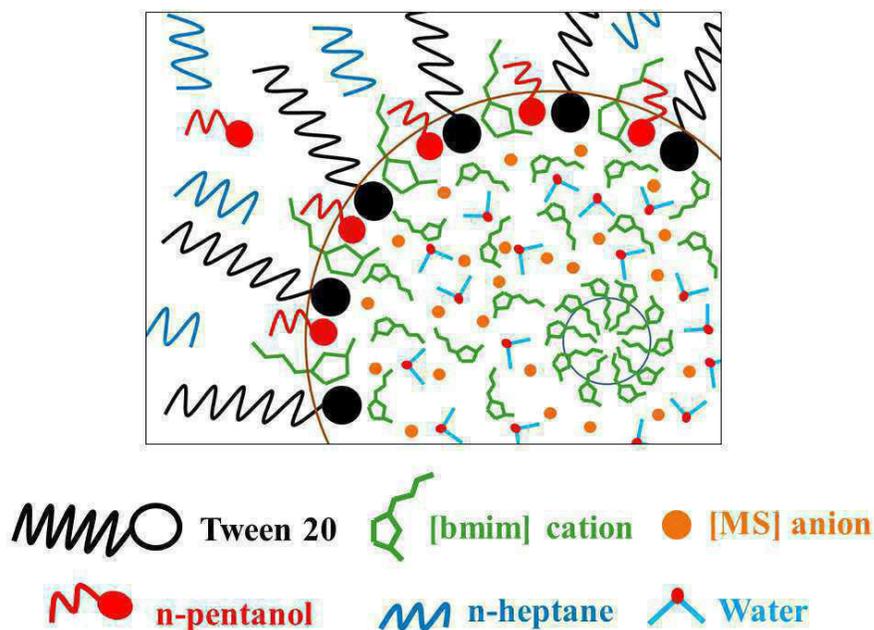


Figure 4.8. Variation in the size (diameter, d) and viscosity (η) of the polar domain-in-oil microemulsion of ([bmim][MS] \pm water)/(Tween-20+n-pentanol)/n-heptane. Mole fraction of [bmim][MS] in the polar domain: 0.5. A 0.2M Tween-20 with 1:1 (w/w) n-pentanol solution was used. Temperatures (in K) are mentioned inside the Figure

With increasing volume fraction, except at the higher temperatures (318 and 323 K), the $d - \phi_d$ profiles were nearly linear. The DLS data closely matched with the size parameters derived from the method of dilution. Size of the μE droplets decreased with increasing temperature for all the compositions, which were quite unusual. The size constriction effect was noted in both the DLS measurements as well as in the method of dilution. This kind of size variation with temperature has never been reported previously for any IL μE systems. We assume that the size constriction upon heating was due to the formation of reorganized entities. Heating of the polar domain decreased the viscosity (as shown in Figure 4.8 right panel) which allowed the IL+water to get reorganized and therefore the structured entities were formed as proposed in Scheme 4.2. Such a proposition for the formation of organized assembly of IL-in-oil μE has been reported by several

authors^{191,211,364,374}. However to make final conclusion in this regard, further studies like freeze fractured electron microscopy or cryo-TEM measurements are warranted. This can be considered as the future perspectives.



Scheme 4.2. Proposed model for the location/organization of the different components in [bmim][MS]+water/Tween 20+n-pentanol/n-heptane polar domain-in-oil microemulsion. The core of the microemulsion is comprised of micelle like aggregates of [bmim] cations.

3.4. Viscosity measurement. Viscosity of microemulsion depends on the size and number of droplets. In the present case, viscosity decreased almost linearly with temperature except a few cases. It is to be noted that in the case of pure binary mixtures in the bulk condition, viscosity variation were entirely different from the present study. Increase in viscosity with increasing volume of the dispersed phase is attributed to the increase in the size of the polar domain (the phenomenon of swelling effect). As the size of the droplets decreased with the increase in temperature hence it is not unexpected that viscosity would decrease with the increase in temperature. Additionally it is known that for all the liquids viscosity usually decreases with the increase in temperature.

3.5. Conductance measurement. Although the continuum is comprised of oil, the μ Es with the ionic components in polar domain is expected to conduct electricity.

The percolation of electrical conductance for a μE in oil continuum can occur either through the “hopping mechanism” or through the mechanism of “fusion, mass transfer and fission”^{28,62}. The effective mean theory with dipole-dipole interaction has been adapted in the present case. In the present set of experiment, both the volume and temperature induced conductance studies were performed. Variation in specific conductance with the volume fraction of (IL+water) at different compositions has been shown in Figure 4.9 at 298 K as representative. In the conductivity studies, ratio of surfactant, cosurfactant and oil were kept constant. Although comprised of ionic species in the polar domain, the present μE systems were found to be less conducting compared to conventional μE s comprising single tailed ionic surfactants.

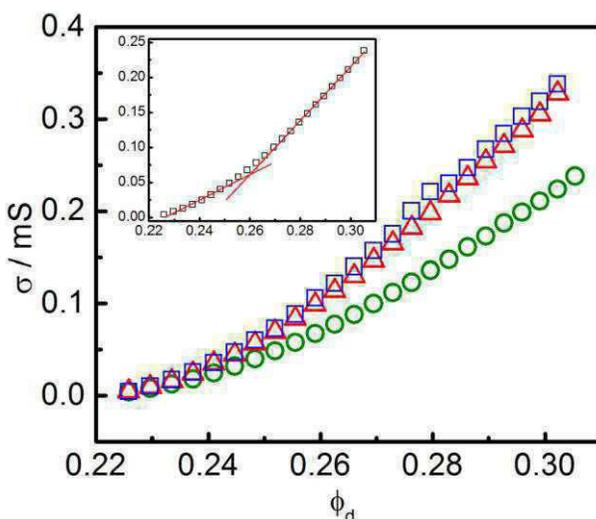


Figure 4.9. Volume induced percolation of $([\text{bmim}][\text{MS}]\pm\text{water})/(\text{Tween-20}+\text{n-pentanol})/\text{n-heptane}$ polar domain-in-oil microemulsion system. Mole fraction of $[\text{bmim}][\text{MS}]$ in the polar domain: O , 0.2; \square , 0.5 and Δ , 0.8. Threshold volume fraction (Φ_d^t) (for $x_{\text{IL}}=0.2$) was determined from the point of intersection of two tangents as shown in the inset. Temperature 298 K.

The depressed conductance was attributed to the dense packing of IL, the surfactant and cosurfactant at the polar domain / oil interface¹¹³. Besides, ILs can strongly interact with the oxyethylene group of Tween 20²¹¹. These three combined factors effectively resulted in the formation of rigid entities. The threshold value for the volume induced percolation was determined from the intersection point of the two tangents as shown in the inset of Fig 9. This method of evaluation of percolation threshold (ϕ_d^t) have been previously reported^{113,229}.

The conductance derived results are summarized in Table 5. The conductance data were processed according to the scaling equation²²⁶:

$$\sigma = k (\phi_d - \phi_d^t)^m \quad (4.30)$$

$$\text{i.e.,} \quad \ln \sigma = \ln k + m \ln(\phi_d - \phi_d^t) \quad (4.31)$$

where, σ is the conductance of the microemulsion, k is a constant which depends on the conductance of the dispersed phase and m is the exponent, ϕ_d and ϕ_d^t are the post threshold and threshold volume fraction respectively. One can thus determine the value of $\ln k$ and m from the linear plot of $\ln \sigma$ vs $\ln(\phi_d - \phi_d^t)$ (Figure not shown to save space). According to the previously published results^{51,103,115,375,376}, higher ϕ_d^t corresponds to static percolation while lower ϕ_d^t indicates dynamic percolation. In the present case ϕ_d^t did not change significantly with the composition as well as the temperature. As predicted, the exponent 'm' remained constant for all the system except a few cases. The negative value of k increased with x_{IL} , which resulted from the decrease in the polarity of the binary mixtures, especially after $x_{IL} > 0.5$. In our previous study³⁶⁸ as well as from the present results, it is known that IL, in combination with water, in polar domain can form micelle like aggregates leading to the decrease in the polarity of the dispersed phase. We failed to determine the threshold value for the temperature induced percolation, as shown in Figure 4.10. However, it was evident from Fig 10 that with increasing volume fraction of the polar domain, conductance increased. Interestingly, μ Es comprising of larger proportion of IL (compared to water) were less conducting [Panel B and C of Figure 4.10]. This observation further reveals that the rigidity of the droplets is enhanced for systems comprising of high proportion of IL.

Table 4.5. Scaling law parameters for volume (IL+ water) induced percolation of ([bmim][MS] \pm water) / (Tween-20+ n-pentanol) / n-heptane polar domain-in-oil microemulsion system at different temperatures.

IL+Water	$\phi_a^t / \ln k / m$			
	298K	303K	308K	313K
2:8	0.276/-0.38 \pm 0.09 / 0.336 \pm 0.02	0.250 / 1.06 \pm 0.04 / 0.87 \pm 0.01	0.252 / 1.25 \pm 0.08 / 0.83 \pm 0.04	0.255 / 1.37 \pm 0.09 / 0.82 \pm 0.03
4:6	0.276 / -0.04 \pm 0.07 / 2.48 \pm 0.05	0.261/ 1.20 \pm 0.07 / 3.10 \pm 0.02	0.253 / -1.08 \pm 0.06/ 1.69 \pm 0.04	0.252/ -1.78 \pm 0.05 / 1.32 \pm 0.04
5:5	0.263 / -0.34 \pm 0.07/ 2.48 \pm 0.05	0.256 /-1.35 \pm 0.08 / 1.25 \pm 0.05	0.257/-2.01 \pm 0.01/ 0.94 \pm 0.007	0.263 /-1.94 \pm 0.04 / 1.18 \pm 0.03
6:4	0.263 / -1.04 \pm 0.05 / 1.34 \pm 0.02	0.258 /-1.79 \pm 0.02 / 1.01 \pm 0.02	0.258/-1.86 \pm 0.02 / 1.03 \pm 0.01	0.258/-2.01 \pm 0.01 / 1.00 \pm 0.008
8:2	0.263 / -1.54 \pm 0.05 / 1.46 \pm 0.04	0.257 /-1.59 \pm 0.02 / 1.39 \pm 0.02	0.258 /-2.02 \pm 0.04 / 1.21 \pm 0.04	0.259 /-2.09 \pm 0.01 / 1.38 \pm 0.02
Pure IL	0.256 /-1.25 \pm 0.04 / 1.49 \pm 0.03	0.259 /-1.44 \pm 0.04 / 1.56 \pm 0.03	0.252 /-1.78 \pm 0.03 / 1.36 \pm 0.03	0.262 /-2.06 \pm 0.04 / 1.57 \pm 0.04

A 0.2 M Tween 20 + n-pentanol (1:1, w/w) in n-heptane was used in each case.

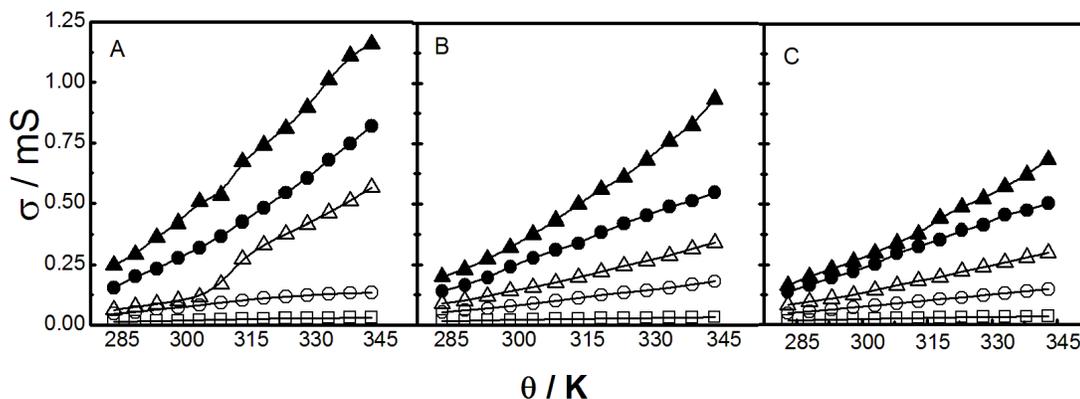


Figure 4.10. Temperature induced percolation of ([bmim][MS] \pm water)/(Tween-20+n-pentanol)/n-heptane polar domain-in-oil microemulsion. Mole fraction of [bmim][MS] in the polar domain: 0.2, panel A; 0.5, panel B and 0.8, panel C. Volume fraction of the polar domain: \square , 0.237; O , 0.252; Δ , 0.266; \bullet , 0.280 and \blacktriangle , 0.293.

3.6. Spectroscopic studies. Absorption and emission spectroscopic probing techniques are considered to provide useful information in understanding the local environment of the polar domain-in-oil continuum. In the present study the anionic xanthene dye eosin Y was used as the probe. Our previous study involving the physico-chemical characterization of [bmim][MS]+water binary mixture was also carried out using eosin Y as the probe³⁶⁹. Such an approach has also been followed by different researchers^{176,202,204,360}. Eosin Y is completely insoluble in n-heptane, therefore, it would predominantly reside in the polar domain^{340,360}. Absorption and emission spectra of eosin Y in different media have been shown in Figure 4.11. While considering the absorption spectra of eosin Y in pure water, it was observed that eosin Y exhibits a strong intense peak at 517 nm with a shoulder appearing at 495 nm. For bulk IL+water mixture, the spectra was red shifted at 537 nm. The peak for eosin Y in the μ E appeared at 530 nm. The red shift in the absorption maxima was due to the increasing polarity of the solvent^{360,369}.

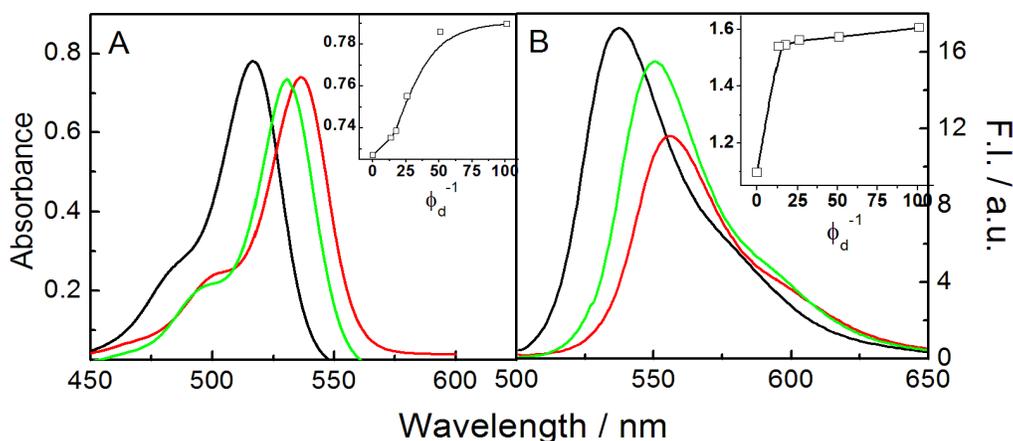


Figure 4.11. Absorption (A) and steady state emission spectra (B) of eosin Y in ([bmim][MS] \pm water)/(Tween-20+n-pentanol)/n-heptane polar domain-in-oil microemulsion system along with the spectra in pure water and IL + water mixture. Spectra in pure water are shown through the black lines while the green lines correspond to the spectra in IL+water in μ E comprising 50 mole% IL and $\phi_d = 0.057$. The red lines represent the spectra of eosin Y in IL + water mixture. In the insets, absorbance (at 517 nm) vs. ϕ_d^{-1} profile (panel A) and fluorescence intensity (at 537 nm) vs. ϕ_d^{-1} (panel B) have been shown. Overall concentration of eosin Y was kept constant at 10 μ M. $\lambda_{ex} = 500$ nm.

When excited at 500 nm, eosin Y in neat water showed an emission maximum at 537 nm. In the case of IL + water, the emission peak appeared at 556 nm. The results were in conformity with our previous reports^{340,368}. Eosin Y in the μ E exhibited intermediate behavior. Red shift in the fluorescence spectra was due to the enhanced polarity of the medium²²⁵. For each binary combination of [bmim][MS] and water, the spectra of eosin Y were recorded at different ϕ_d values for (IL+water)-in-oil μ Es. All the results are not shown to save space. Compared to the absorption and emission intensity of eosin Y in water, the values decreased with increasing volume fraction of the polar domain. Simultaneously there occurred red shifts in both the absorption and emission spectra which suggests that the microenvironment around eosin Y in the μ E are not the same¹¹³. Progressive red shift with increasing ϕ_d value reflects the change in the state of polar domain. Interestingly, decrease in both the absorbance and fluorescence intensity with ϕ_d were nonlinear in the range 0.009 - 0.07. To understand the states of the polar components in the μ E system, absorbance (at 517 nm) and the fluorescence intensity (at 537 nm) were plotted against the reciprocal of the volume fraction of the dispersed phase (ϕ_d^{-1}). Representative plots for 50 mole% [bmim][MS] (with respect to water) have been shown in the insets of Figure 4.11.

In both the cases break points appeared around $\phi_d^{-1} = 25$, above which, especially the fluorescence intensity, increased linearly. Results clearly indicate the change in the state of the polar component in this range. With increasing ϕ_d in the lower range polar components were involved in solvating the surfactant head groups whereby they resided in the palisade layer of the μ E. Once the surfactant head groups were completely solvated, the polar components became free and could behave like bulk entities. Such an observation has not been reported previously and this may be considered as the novelty of the present work. To understand the solvation phenomena in further detail, both the fluorescence anisotropy and lifetime measurements were carried out for the μ Es using eosin Y as the probe. Such studies helped in understanding the microviscosity of the medium as well^{216,356}. Representative plots for the anisotropy and lifetime variation with ϕ_d^{-1} have been shown in Figure 4.12 for μ E comprising of 50 mole% IL. Results for other combinations have been shown in the Figure 4.13.

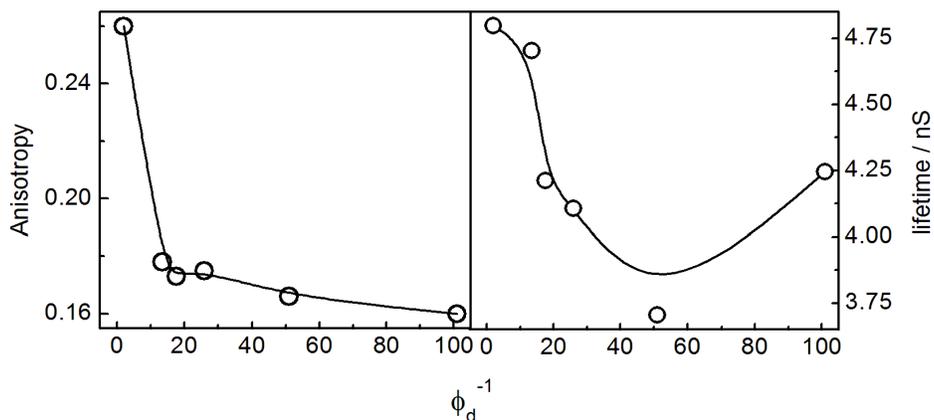


Figure 4.12. Variation in the anisotropy and lifetime for 10 μ M eosin Y with the inverse of volume fraction of the polar domain (ϕ_d^{-1}) for ([bmim][MS] \pm water)/(Tween-20+n-pentanol)/n-heptane polar domain-in-oil microemulsion system. An equimolar mixture of [bmim][MS] and water was used as the polar domain. A 10 μ M eosin Y was used. λ_{ex} = 500nm and λ_{em} = 537nm.

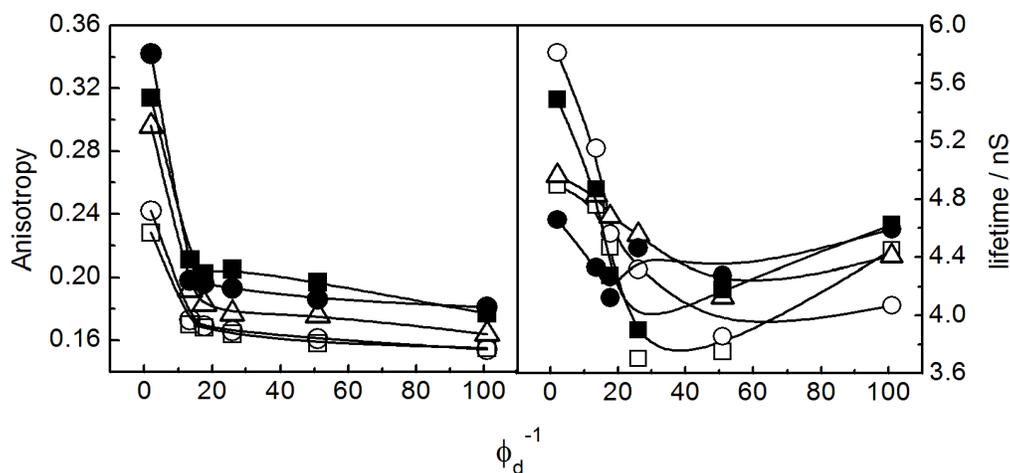


Figure 4.13. Variation in the fluorescence anisotropy and lifetime for 10 μ M eosinY with the inverse of *volume fraction of the polar domain* (ϕ_d^{-1}) for ([bmim][MS] \pm water)/(Tween-20+n-pentanol)/n-heptane polar domain-in-oil microemulsion system. *Mole fraction of [bmim][MS] in the polar domain*: (\square) 0.2; (O) 0.4; (Δ) 0.6; (\blacksquare) 0.8 and (\bullet) 1.0.

Appearance of break point around $\phi_d^{-1} = 20 - 25$ conforms the conclusion as drawn in the absorption and steady state fluorescence measurements. However, to understand such systems completely, further studies like small angle neutron scattering (SANS), transmission electron microscopy (TEM) and ultrafast solvent dynamic studies are warranted and these are considered as future perspectives.