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## ARTICLE

# Combined Phase Behavior, Dynamic Light Scattering, Viscosity and Spectroscopic Investigations on Pyridinium Based Ionic Liquid-in-Oil Microemulsion

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Although several studies on imidazolium based ionic liquid-in-oil microemulsions are available in literature, however, studies on the pyridinium based ionic liquid microemulsions are uncommon. Pyridinium based ionic liquids have superior yet unexplored properties when considered in the polar domain of microemulsion. *t*-butyl-4-methyl pyridinium tetrafluoroborate ([b<sub>4</sub>mpy][BF<sub>4</sub>]) / (Tween 20 + n-pentanol) / n-heptane ionic liquid-in-oil microemulsion system has been studied by combined phase behavior, dynamic light scattering, viscosity, UV-visible absorption and emission spectroscopic techniques. With decreasing Tween 20/n-pentanol (S/CS) ratio, stability of the microemulsions decreased, although it was not possible to achieve stable microemulsion without the cosurfactant. Dynamic light scattering and viscosity studies revealed that the size of the microemulsion droplets increased with increasing volume fraction ( $\phi_d$ ) of ionic liquid. Both the size and viscosity increased with  $\phi_d$ . With the increasing amount of n-pentanol, the variation was less sensitive due to the reduced polarity of the medium induced by alkanol. Increase in the size of microemulsion droplets were overshadowed by the increase in the fluidity of the medium, for which viscosity decreased with increasing temperature, as common for the Newtonian fluids. State of the ionic liquid in the microemulsion was monitored by absorption and fluorescence spectroscopy without and with curcumin as the molecular probe respectively. 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 combinations. Spherical morphology of the microemulsion droplets were established through the TEM measurements.

## 1. Introduction

A microemulsion can be defined as an optically transparent, thermodynamically stable dispersion of one liquid in otherwise immiscible second liquid, stabilized by a surfactant<sup>1</sup>. Sometimes, short chain alkanols and amines can assist microemulsion formation<sup>1</sup>. It has also been reported that ionic liquid (IL) can substitute the polar component (water) in a microemulsion<sup>2</sup>. Scientific studies involving ILs have reached its credential beyond any doubt for which there has been an exponential growth in the research publication involving ILs. ILs, with melting points below 100°C, are considered as neoteric components for its specific properties, *viz.*, non-flammability, non-corrosiveness, high ionic conductivity and inertness towards different thermal and chemical environments<sup>3</sup>. One of the outstanding properties of ILs lies in its use as an alternate to traditional organic solvents. ILs are also called “designer solvents” because its properties can be tuned by altering

the substituents as well as the counter ions<sup>4</sup>. In spite of significant research contributions on ILs, the lack of complete knowledge is considered to be one of the barriers in utilizing them for practical applications. Thus more fundamental researches on ILs are warranted.

It is needless to mention that microemulsion comprising ILs in the polar domain can have some unknown but some novel properties owing to the unique and combined features of the ILs and microemulsions. Ionic liquid microemulsions find application in various fields, *viz.*, preparation and characterization of polymeric nanoparticles<sup>5</sup>, synthesis of inorganic nanoparticles<sup>6</sup>, renewable lubricants<sup>7</sup>, and catalysis<sup>8</sup>, *etc.* They are in addition to the existing uses of the microemulsions, *viz.*, drug delivery, nanoparticle synthesis, media for organic reaction, biochemical reaction, separation, cosmetics<sup>9</sup>, *etc.*

Most of the studies on ILs are associated with the imidazolium ion. However, there has been a current trend to search for alternate, easily available but low cost ILs other than the imidazolium ion. According Domanska et al.<sup>10</sup>, pyridinium based ILs have specific properties, viz., broad liquidous temperature range, inertness to air, moisture and superior solubilization capacity. These unique features of pyridinium based ILs have already been explored with special reference to antistatic thermoplastic resin<sup>11</sup>, adhesive film<sup>12</sup>, electrochemical probe<sup>13</sup>, electron transfer process<sup>14</sup>, reaction acceleration<sup>15</sup>, organo catalysis<sup>16</sup>, extraction process<sup>17</sup>, etc. In spite of high possible potentials, there have been a little research on *1*-butyl-4-methylpyridinium tetrafluoroborate ([b<sub>4</sub>mpy][BF<sub>4</sub>]) comprising microemulsion although it is one of the most reported pyridinium based IL<sup>18</sup>. In a very recent report of Takumi et al.<sup>19</sup>, mutual miscibility of imidazolium and pyridinium ILs with [BF<sub>4</sub>]<sup>-</sup> as the common counter anion have been explored. Another advantage of using this IL is that the system itself can be investigated without any molecular probe (because of the presence of the pyridinium ring) in the UV-visible region.

Curcumin is a natural polyphenolic compound isolated from the rhizome of turmeric (*Curcuma longa*). Apart from its biological activities, curcumin nowadays are being used as molecular probe<sup>20,21</sup>. Once used in the IL-in-oil microemulsion, curcumin has the only possibility to reside in the polar domain of the microemulsion as it is insoluble in n-heptane. Thus curcumin can conveniently be used as a molecular probe in investigating the microenvironment of the polar domain of the ionic liquid-in-oil microemulsion.

In the formulation of microemulsion, uses of nonionic surfactants are always advantageous as they are stable over a wide pH range with higher solubilisation capability<sup>22-24</sup>. Use of nonionic surfactants in combination with short chain alkanols are well documented in literature<sup>25-38</sup>. Kundu et al.<sup>30-33</sup> and Bardhan et al.<sup>25, 26</sup> have recently reported the studies involving Brij 56, Brij 58, Brij 76, Triton X 100 and Tween 80 in presence of ionic liquids. Bardhan et al.<sup>26</sup> have studied Brij 35/n-pentanol/isopropyl myristate water-in-oil microemulsion systems in combination with an anionic surfactant sodium dodecyl sulfactate. Li et al.<sup>39</sup> have investigated the quaternary mixed systems comprising water, Triton X 100, alkanol and n-heptane. Among the nonionic surfactants polyoxyethylene sorbitan esters (Tweens) are the mostly studied surfactants because of its cheaper price and easy availability<sup>35,40-43</sup>. According to Yaghmur et al.<sup>43</sup>, presence of bulky polyoxyethylene head group, attached to a sorbitan ring, results in hydrophilicity of Tweens. In another report of Shevachman et al.<sup>41</sup>, it has been proposed that Tween based surfactants can form less compact structure at the oil-water interface. In spite of tremendous application potentials, not many works have been carried out using Tween 20 in combination with IL except a few<sup>44,45</sup>. Use of short chain alcohols as cosurfactant in preparing microemulsions are well documented in literature<sup>27,35,36,41,43,46,47</sup>. Short chain alkanols can lower down the polar domain-oil interfacial tension which is otherwise unachievable by single chain commercial surfactants. Thus alcohols can modify the spontaneous curvature of the surfactant film at the interface. Cosurfactant can also act as

spacers between surfactant molecules at the interface<sup>40</sup>. Additionally it can alter the polarity of the polar and apolar phases when used as a cosolvent<sup>41</sup>. Digout et al.<sup>28</sup>, Li et al.<sup>39</sup>, Moulik et al.<sup>36</sup> and Abuin et al.<sup>46</sup> have carried out systematic investigations using n-alkanol to understand the chain length effect on the stability of different microemulsions. According to Digout et al.<sup>28</sup>, among the alkanols minimum size for microemulsion droplets can be achieved using n-pentanol with an enhanced interfacial rigidity. In our present study we therefore used n-pentanol in combination with Tween 20.

In the present manuscript, comprehensive studies on the IL-in-oil type microemulsion comprising *1*-butyl-4-methylpyridinium tetrafluoroborate have been reported. Effect of Tween 20(surfactant)/n-pentanol (cosurfactant) mass ratio, volume fraction of IL and temperature have been studied using a number of techniques, viz., phase manifestation, dynamic light scattering, viscosity, UV-visible absorption and emission spectroscopy. The detailed phase diagram studies helped in identifying the single phase microemulsion and the two phase turbid regions. Dynamic light scattering studies provided the information about the size and its distribution of the droplets at different temperature; viscosity measurements were carried out and correlated with the DLS data. The ionic liquid in the polar domain of the microemulsion was investigated by UV-visible absorption spectroscopy. Fluorescence spectroscopic studies using curcumin in the polar domain helped in understanding the state of polarity and rigidity of the microenvironment.

## 2. Experimental section

**2.1. Materials.** The IL *1*-butyl-4-methyl pyridinium tetrafluoroborate, [b<sub>4</sub>mpy][BF<sub>4</sub>] was purchased from Sigma-Aldrich Chemicals Pvt. Ltd., USA. The nonionic surfactant polyoxyethylene sorbitan monolaurate (Tween 20) and the cosurfactant n-pentanol were products from Fluka, Switzerland and Lancaster, England respectively. They were stated to be more than 99.5% pure. HPLC grade n-heptane was obtained from E. Merck, Germany. Curcumin, [1,7-bis(4-hydroxy-3-methoxy-phenyl)-1,6-heptadiene-3,5-dione] was a product from Sigma-Aldrich Chemicals Pvt. Ltd., USA. All the chemicals, except Tween 20, were used as received. Tween 20, as stated by the supplier, comprised < 3 wt% water. Water was removed following the protocol of Schubert et al.<sup>48</sup> Karl-Fischer titration revealed the presence of < 0.5 wt% water in the purified sample.

### 2.2. Methods

**2.2.1. Phase Manifestation.** In the entire work Tween 20 (S) and n-pentanol (CS) were used in three different mass ratio (1:0.5, 1:1 and 1:2) to explore the effect of cosurfactant in the microemulsion system. Pseudo ternary phase diagram comprising [b<sub>4</sub>mim][BF<sub>4</sub>]/(Tween-20+n-pentanol)/n-heptane was constructed by the method of titration and through visual inspection. Known amount of Tween 20 + n-pentanol and n-heptane or IL were taken in stoppered test tube. IL or n-heptane was then progressively added using a Hamilton (USA) microsyringe under constant stirring<sup>49,50</sup>. The whole process was carried out in a controlled temperature bath (298±0.1K). The phase boundary was detected through the

appearance of turbidity. The same experiment was carried out for a number of compositions by varying the amount of oil or IL as well as in different S/CS ratio.

**2.2.2. Dynamic Light Scattering (DLS) Studies.** DLS measurements were carried out using a Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd, U.K.). A 0.2 M Tween 20 mixed with appropriate amount of n-pentanol dissolved in n-heptane was used for such studies. Tween 20 / n-pentanol ratio (w/w) were the same as in phase manifestation studies. A He-Ne laser of 632.8 nm wavelength was used and the data were collected at 90° 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<sup>49,50</sup>.

$$D = \frac{kT}{3\pi\eta d} \quad (1)$$

where, k, T and η indicate the Boltzmann constant, temperature and viscosity of the solvent (herein n-heptane) respectively.

**2.2.3. Viscosity Measurement.** Viscosity of microemulsion systems were measured with an LVDV-II+PCP cone and plate type roto-viscometer (Brookfield Eng. Lab, USA). The same set of solutions, as used in the DLS measurements, were employed for size analyses. Temperature was controlled by a cryogenic circulatory water bath with a precision of ±0.1K (DC-1006 M/S Hahnstech Corporation, S. Korea). Shear rate (r) was varied in the range 20 – 60 sec<sup>-1</sup> with an increment of 5.0 sec<sup>-1</sup> in each step. Zero shear viscosity (η) was obtained using the relation η = τ / r<sup>49,50</sup>, where τ indicates the shear stress.

**2.2.4. Spectral Studies.**

**2.2.4.1. Absorption Spectra.** UV-visible absorption spectra of the microemulsion systems without any other molecular probes were recorded on a UVD-2950 spectrophotometer (Labomed Inc., USA) in the range 200-400nm using a matched pair cell of 1.0cm path length. While recording the spectra of the IL comprising systems, corresponding surfactant solution without the IL was used as reference.

**2.2.4.2. Emission Spectra.** Steady state fluorescence spectroscopic measurements were carried out using a bench-top spectrofluorimeter (Quantmaster-40, Photon Technology International Inc, NJ, USA). The steady state emission spectra was recorded in the range 400-650nm with an excitation of curcumin at 426nm. While recording the fluorescence spectra, the overall concentration of curcumin was always kept constant at 10 μM. Initially, required amount of curcumin in methanol-chloroform (1:3 v/v) was taken in a test tube. The solvent was evaporated under vacuum. Microemulsion of known composition was then added and homogenized by keeping the solution in an ultrasonic water bath. It is to be mentioned that curcumin is insoluble in n-heptane. Therefore it could be assumed that the dye molecules reside in the polar domain.

To know about the microviscosity of the solvent surrounding the probe molecules, steady state anisotropy (r) values were determined using the following expressions<sup>51</sup>:

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

and,

$$G = I_{HV}/I_{HH} \quad (3)$$

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 ( $\lambda_{em}$ ) of 550 nm. Further details are available in the literature<sup>51</sup>. Both the absorption and fluorescence spectra were recorded at ambient but controlled temperature.

**2.2.5. Morphological studies: transmission electron microscopy (TEM)**

In order to understand the morphology of the microemulsion droplets, transmission electron microscopic studies were further carried out. TEM analyses were carried out. Microemulsion dispersion was diluted 10-fold in n-heptane. 2 μL of the diluted solution was then drop casted on TEM grid (Formavar/Carbon, 300 mesh Cu, Agar Scientific, UK). The solution was allowed to dry in air at room temperature overnight and vacuum dried before imaging. TEM was performed on a Technai F30 UHR version electron microscope, using a field emission gun (FEG) operating at an accelerating voltage of 200 kV. As this method may lead to the disruption of the microemulsion, hence the freeze fractured TEM (FF-TEM) analyses were also carried out. However, due to the very low surface tension of the continuous medium (n-heptane) the freeze replica could not be generated. Hence only the TEM images obtained by the conventional technique have been reported.

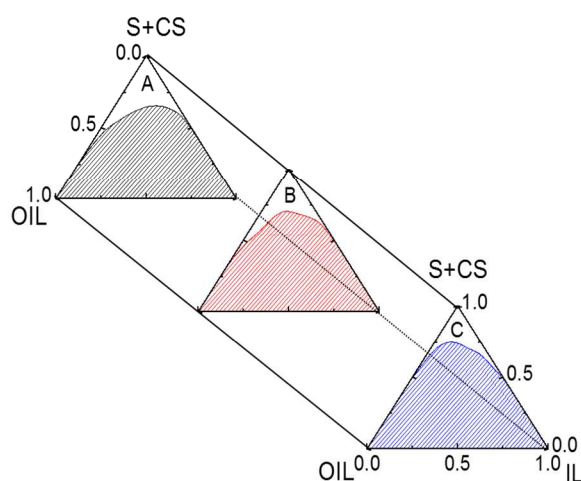
### 3. Results and discussions

**3.1. Phase Manifestation.** From the application point of view, construction of the phase diagram is a primary task towards a microemulsion formulation. Figure 1 describes the pseudo ternary phase diagram of [b<sub>4</sub>mpy][BF<sub>4</sub>]/(Tween-20+n-pentanol)/n-heptane systems at different surfactant-cosurfactant ratio (w/w). The shaded area under the curves represent the two phase turbid region, where the stable microemulsions were not formed. The unshaded portions correspond to the microemulsion zone. In the presently studied systems oil rich (ionic liquid-in-oil microemulsion), ionic liquid rich (oil-in-ionic liquid microemulsion) as well as bicontinuous states were observed. However, for simplicity all these three different regions were represented as a single phase (microemulsion zone; the unshaded portion in the pseudoternary phase diagram). All the



further experiments were carried out using the oil rich (i.e., ionic liquid in oil) microemulsion systems. Area under the microemulsion region (unshaded portion) and the turbid regions were calculated by the simple method of weighing the individual area as previously described<sup>49,50</sup>. With increasing amount of cosurfactant (with respect to surfactant) stability of the microemulsion decreased as revealed through the decrease in the area of the unshaded portions of the phase diagrams. Results have been graphically presented in Figure S1 (supplementary section). Percentage area of the microemulsion zone was plotted against the wt% of the cosurfactant ( $w_{CS}\%$ ) and it was observed that such a profile followed a  $2^0$  polynomial relation whereby the maximum microemulsion zone would have appeared in absence of cosurfactant:

$$\begin{aligned} \text{\% area of microemulsion zone} \\ = 20.34 - 8.46 \times w_{CS} \% + 1.61 \times (w_{CS} \%)^2 \end{aligned} \quad (4)$$



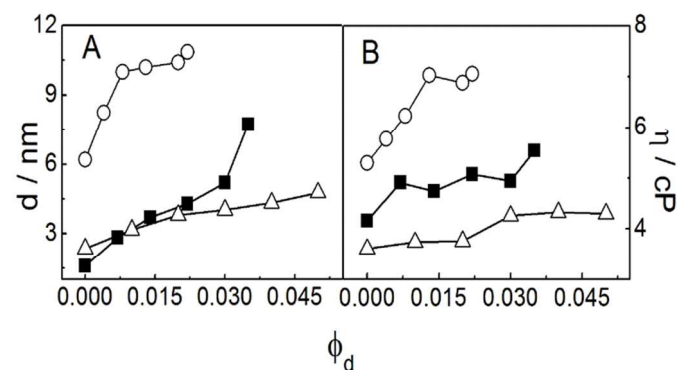
**Figure 1.** Pseudo ternary phase diagram of  $[b_4mpy][BF_4]/(Tween-20+n-pentanol)/n-heptane$  system at different Tween 20 (S) / n-pentanol (CS) ratio (w/w): A, 1:0.5; B, 1:1 and C, 1:2. n-heptane was used as oil (Oil) and  $[b_4mpy][BF_4]$  was used as the ionic liquid (IL). Temp. 298 K.

Apparently it implies that in absence of n-pentanol the area of microemulsion zone would have been 20% while that for the turbid region be 80%. Interestingly a stable microemulsion without n-pentanol was unachievable. Hence, unlike the other systems<sup>2,52</sup>, use of cosurfactant was mandatory in order to achieve a stable microemulsion. Use of cosurfactant for single tailed surfactants is not uncommon in literature<sup>49,50</sup>. Present set of results were also comparable with the similar components where water<sup>49</sup> and another ionic liquid *l*-butyl-3-methyl imidazoliummethane sulphonate  $[bmim][MS]$ <sup>50</sup> were used. Compared to the other systems, the % area of the microemulsion zone was less which could be due to the greater ionicity of the components in the polar domain, compared to water as well as  $[bmim][MS]$ . Although the cation  $[b_4mpy]^+$  was less polar, however, the  $BF_4^-$  ion played a significant role in reducing the

stability of the microemulsion; thus more two phase turbid regions were resulted.

As already mentioned in the introduction section that n-pentanol serves dual purpose in case of nonionic microemulsion: firstly, it reduces the interfacial tension at the oil-polar domain interface through the modification of spontaneous curvature. This phenomenon helps in the formation of stable microemulsion. However the second contribution of cosurfactant, reduction of interfacial polarity in the present case, resulted in destabilization of the microemulsion. Here in the polar domain comprises ionic liquid, hence, it is not unexpected that addition of n-pentanol would destabilise the microemulsion by reducing the interfacial polarity.

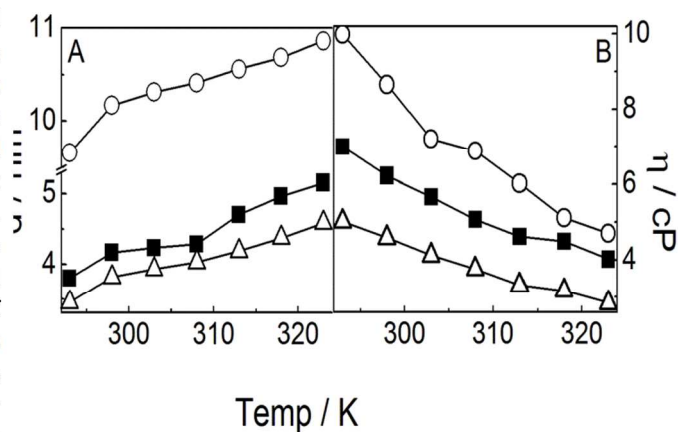
**3.2. Dynamic Light Scattering (DLS) and Viscosity Studies.** DLS studies on microemulsion can provide information on its droplet size, its distribution, and hence the polydispersity index. Variation in the diameter of  $[b_4mpy][BF_4]/(Tween\ 20+n-pentanol)/n-heptane$  IL-in-oil microemulsion with the volume fraction of the IL ( $\phi_d$ ) at 308 K have been graphically presented in Figure 2 at different surfactant cosurfactant ratio (panel A). Droplets were fairly monodispersed as revealed through its size distribution shown in Figure S2 (supplementary section). As under similar condition, there is a correlation between the size of droplets and viscosity, hence the viscosity ( $\eta$ ) –  $\phi_d$  profile for the same systems were also presented in panel B of the same figure (Figure 2). Experiments were carried out in the temperature range 293 – 323K and the results at 308K (intermediate temperature) have been shown as representative. Results for the other systems have been presented in the supplementary section. Size of the microemulsion droplets increased with increasing volume fraction ( $\phi_d$ ) of IL. Increase in size with increasing volume fraction of the dispersed phase is not an uncommon phenomena and have also been documented by others<sup>2,44,50,52,53</sup>.



**Figure 2.** Variation in diameter ( $d$ ) and viscosity ( $\eta$ ) of  $[b_4mpy][BF_4]/(Tween-20+n-pentanol)/n-heptane$  IL-in-oil microemulsion system with the volume fraction ( $\phi_d$ ) of  $[b_4mpy][BF_4]$ . Temp. 308 K. Tween 20/ n-pentanol ratio (w/w): O, 1:0.5; ■, 1:1 and △, 1:2.

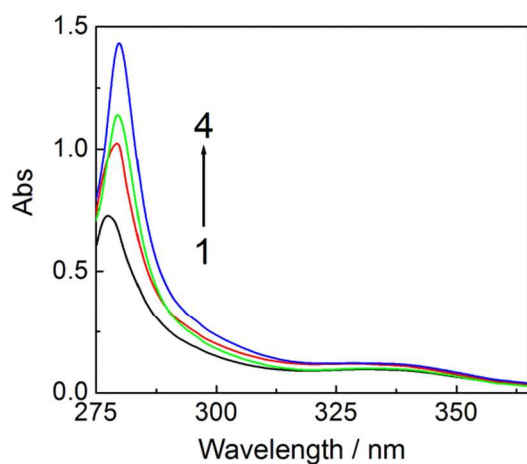
Size -  $\phi_d$  profiles were found to be dependent on S/CS ratio. Size of the microemulsion droplet comprising Tween 20 and n-pentanol for the systems with a S/CS mass ratio of 1:0.5 was found to be larger than 1:1 which was even larger than 1:2. Results clearly indicate that cosurfactants caused size constriction. Larger number of cosurfactant at the IL-oil interface results in the formation of a compact structure. n-pentanol enhances the compactness and hence rigidity of the interface, as also reported by Digout et al.<sup>28</sup> In a previous report we have shown that for the polyoxyethylene head group comprising surfactants (Tween 20), increasing amount of cosurfactant can lead to the formation of larger number of droplets<sup>49,50</sup>. For a fixed amount of surfactants, increasing number of droplets would result only at the expense of bigger droplets. Such an observation further supports the decrease in the area of the microemulsion region with increasing amount of cosurfactant, as in the phase manifestation studies. While giving a closer look at the panel A of Figure 2 it was observed that for an S / CS ratio of 1:0.5, size of the microemulsion droplet increased linearly up to  $\phi_d=0.01$ , after which a change in the slope of increment profile appeared. Initially when IL molecules are added they strongly coordinate with the polyoxyethylene head group of Tween20. With the further addition of IL they become free and behave like bulk material<sup>50</sup>. Almost twice the volume of IL was required for the attainment in the breakpoint in the microemulsion with S/CS ratio 1:1 ( $\phi_d=0.02$ ). However, for such systems the slope after the threshold was higher. Such an ambiguity is beyond explanation with the present level of knowledge.  $d$  vs.  $\phi_d$  profile for the systems with surfactant/cosurfactant ratio 1:2 was almost linear.  $d$ - $\phi_d$  profile for all the systems at different temperature have been graphically presented in Figure S3 (supplementary section). It could be concluded from the results that with the increasing amount of cosurfactant (n-pentanol), size increment with the volume fraction becomes less sensitive. Presence of larger number of n-pentanol at the interface and subsequent enhancement of the interfacial rigidity was the causative factor for such an observation. Viscosity profile for the similar systems followed the same trend line as in the variation of droplet size with  $\phi_d$ . Thus, it could be concluded that variations in the viscosity with  $\phi_d$  was a consequence of the size variation in the microemulsion droplets. In order to understand the effect of temperature, DLS studies were also carried out at different temperatures (293, 298, 303, 308, 313, 318 and 323K). While considering the size variation (as shown in Figure 3 panel A), it was observed that for all the systems  $d$  vs. temperature profiles were almost linear. With increasing temperature size of the droplets increases as also reported by others<sup>54</sup>. Increase in the volume of the dispersed phase as well as the “softening” of the interfacial region with increasing temperature attribute to the increase in droplet size. Additionally, with the increase in temperature, probability of interdroplet contact increases. In dynamic light scattering studies spherical geometries are usually assumed. However according to the proposition of Nazario et al.<sup>55</sup>, Tweens in combination with alkanols can experience reasonable shape fluctuation which eventually impart increased droplet diameter. In the present set of studies size of the microemulsion droplets were comparatively bigger than the conventional water in oil microemulsion droplets or swollen reverse micelle. It is not unexpected that such entities may have different shapes / geometry other than spheres. To address such issues further

studies like cryo-TEM and small angle neutron scattering, etc., are warranted. Parallel nature of the size-temperature profiles imply that the effect of temperature were the same for all the systems (independent of S/CS ratio). Although there occurred size increment with increasing temperature, however, reverse trends were recorded for the viscosity for all the systems. Results for viscosity-temperature profile for the three combinations at  $\phi_d=0.02$  have been shown in Figure 3 (panel B). Decrease in viscosity with the increase in temperature is a common phenomenon for Newtonian fluids. In the present set of studies, increase in droplet size was overshadowed by the increase in the fluidity of the medium. For all the three systems, viscosity decreased almost linearly with increasing temperature, although the slopes were different for the different systems. Differences in the slopes were due to the differences in the rigidity of the microemulsion droplets. Systems with larger proportion of cosurfactant are expected to form more rigid structures. Viscosity variation for all the systems at different volume fractions and temperature have also been graphically presented in Figure S4 (supplementary section).



**Figure 3.** Variation in the size (A) and viscosity (B) with temperature for [b<sub>4</sub>mpy][BF<sub>4</sub>]/(Tween-20+n-pentanol)/n-heptane IL-in-oil microemulsion at different Tween 20/n-pentanol ratio (S/CS, w/w): O, 1:0.5; ■, 1:1 and Δ, 1:2. 0.2 M Tween20 was used in each case where the volume fraction ( $\phi_d$ ) of IL was kept constant at 0.02.

**3.3. Spectral Studies.** Spectroscopic investigation on microemulsion using a suitable probe can provide useful information on the microenvironment, viz., polarity, fluidity, state of the aggregates of the ionic liquid in the polar domain of microemulsion. Substantial reports on such aspects are available in literature<sup>2,44,50,53</sup>. For the present system as the ionic liquid itself exhibits UV-visible absorption band, due to the presence of pyridinium ring, the microemulsion was studied without any probe. Figure 4 describes the absorption spectra of [b<sub>4</sub>mpy][BF<sub>4</sub>] confined in the polar domain at different volume fraction. Two distinct peaks, one at 280nm and another at 335 nm were recorded for the ionic liquid. The peak at

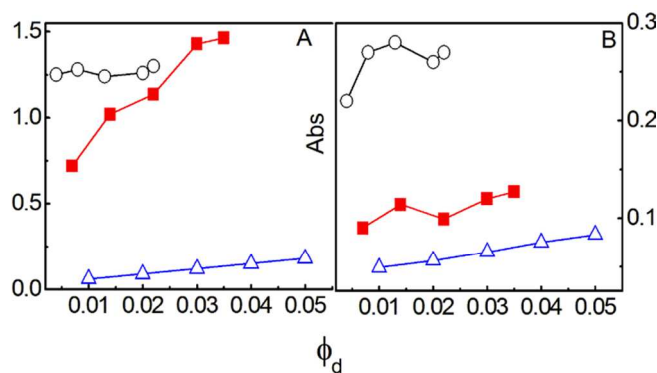


**Figure 4.** Absorption spectra of 1-butyl 4-methyl pyridinium tetrafluoroborate  $[b_4mpy][BF_4]$  confined in the polar domain at different volume fraction ( $\phi_d$ ): 1, 0.007; 2, 0.014; 3, 0.022 and 4, 0.03. System without the IL was used as reference.

3.2.

3.3.

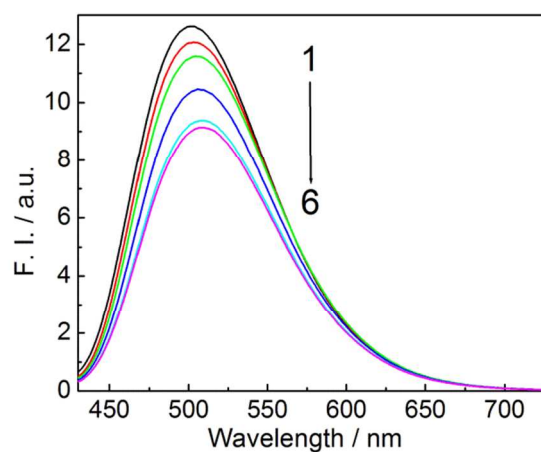
3.4. 280 nm was significantly more intense than the other. Intensity of both the bands increased with increasing volume fraction ( $\phi_d$ ) of the ionic liquid. Absorbance vs.  $\phi_d$  profile for both the peaks have been graphically shown in Figure 5. Increase in the absorbance values were mostly linear except for the system with Tween 20/n-pentanol in a ratio of 1:0.5 (w/w). With the initial addition of IL to reverse micelles, formation of strongly coordinated species between the IL cation and oxyethylene groups of Tween 20 are initiated resulting in the formation of swollen reverse micelles. After substantial amount of IL molecules are added, IL molecules becomes free and behave like bulk liquids; thus the microemulsion is formed. Results were in parity with the phase behaviour, DLS and viscosity studies.



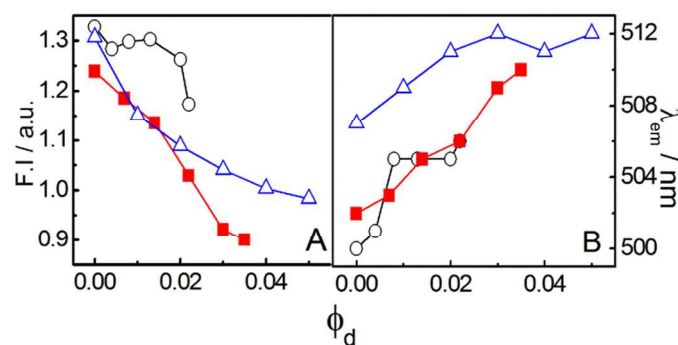
**Figure 5.** Variation in the absorbance of 1-butyl 4-methyl pyridinium tetrafluoroborate  $[b_4mpy][BF_4]$  confined in the polar domain with its volume fraction ( $\phi_d$ ). Absorbance values were recorded at two different wavelengths :one at 283 nm (A) and 335 nm (B). Tween 20/n-pentanol ratio (w/w): O, 1:0.5; ■, 1:1 and Δ, 1:2.

Microenvironment of the polar domain in the reverse micelles are supposed to be different at different ratio of surfactant and

cosurfactant, as the polarity of the interface (oil/IL) are dependent on the relative abundance of cosurfactant at the interface. In order to understand the microheterogeneity of the reverse micelles (herein IL in oil microemulsion) curcumin was used as the fluorescent probe. For such systems the fluorescent probe can have different locations ranging from the IL/oil interface to the core of the polar domain<sup>56</sup>. Fluorescence spectra of curcumin confined in the polar domain of IL in oil microemulsion are shown in Figure 6. When excited at 426 nm, curcumin shows an emission maximum at  $\sim 500$  nm. Results were found to be comparable with the previous report<sup>57</sup>. Red shift in the emission maxima alongwith a decrease in the fluorescence intensity with increasing volume fraction of the ionic liquid were noted as shown in Figure 7. The decrease in fluorescence intensity (panel A) was due to the localized dilution of the probe in the IL pool<sup>2,44,50,53</sup>. The progressive red shift (panel B, Figure 7) in the emission maxima was due to the increased polarity of the domain with increasing volume fraction of the ionic liquid<sup>50</sup>. As already mentioned previously, initially with the progressive addition of the IL to the reverse micelles, strongly coordinated species starts forming between the IL cation and oxyethylene head group of Tween 20, resulting in the formation of swollen reverse micelles. Further addition of IL led to the occurrence of free IL (bulk), as in the case of ionic liquid in oil microemulsion. A transition from the swollen reverse micelle to microemulsion was confirmed through the appearance of breaks/halts in the red shift of the fluorescence maxima of curcumin with increasing volume of IL<sup>56</sup>. Such breakpoints were dependent on the Tween 20/n-pentanol mass ratio. Breakpoints appeared at higher volume fraction of the IL with increasing proportion of n-pentanol.

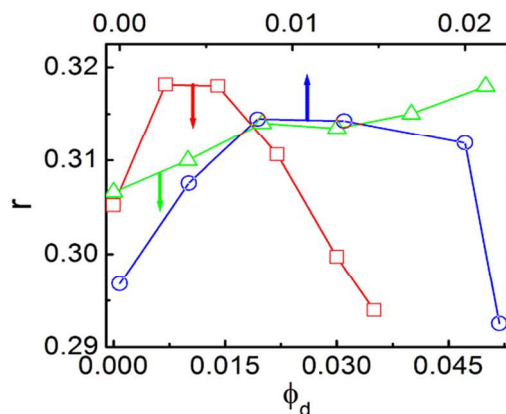


**Figure 6.** Emission spectra of 10  $\mu$ M curcumin in  $[b_4mpy][BF_4]/(Tween-20+n-pentanol)/n-heptane$  IL-in-oil microemulsion at different volume fraction ( $\phi_d$ ) of IL.  $\phi_d$  values: 1, 0.00; 2, 0.007; 3, 0.014; 4, 0.022; 5, 0.03 and 6, 0.035. Tween 20/n-pentanol ratio (w/w): 1:1. Inset: Variation in the fluorescence intensity (panel A) and  $\lambda_{em}$ (panel B) with  $\phi_d$  for different Tween 20/n-pentanol ratio (w/w): O, 1:0.5; □, 1:1 and Δ, 1:2.



**Figure 7.** Variation in the fluorescence intensity (panel A) and  $\lambda_{em}$  (panel B) of 10  $\mu\text{M}$  curcumin with  $\phi_d$  confined in  $[\text{b}_4\text{mpy}][\text{BF}_4]/(\text{Tween-20}+\text{n-pentanol})/\text{n-heptane}$  IL-in-oil microemulsion. Tween 20/n-pentanol ratio (w/w): O, 1:0.5; ■, 1:1 and  $\Delta$ , 1:2.

To know the exact state of the solvent in the pool, fluorescence anisotropy studies on curcumin were carried out. Variation in the fluorescence anisotropy value ( $r$ ) with volume fraction ( $\phi_d$ ) of ionic liquid have been graphically shown in Figure 8.



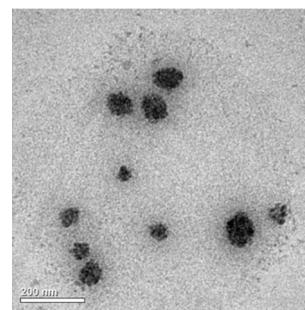
**Figure 8.** Variation in the fluorescence anisotropy ( $r$ ) for 10  $\mu\text{M}$  curcumin with the volume fraction ( $\phi_d$ ) of IL for  $[\text{b}_4\text{mpy}][\text{BF}_4]/(\text{Tween-20}+\text{n-pentanol})/\text{n-heptane}$  IL-in-oil microemulsion system. Tween 20/n-pentanol ratio (w/w): O, 1:0.5; □, 1:1 and  $\Delta$ , 1:2. Temp, 298K.

Anisotropy values passed through maxima with respect to the volume fraction of IL. Initially ILs are used up in forming coordinated species with the oxyethylene head groups of Tween 20 for which structured entities are formed (like swollen reverse micelles). At that stage the dye molecules did not have the freedom of movement. After the process of coordination of surfactant head group by IL cation was over, excess ILs become free for which they can behave as bulk IL, as in the case of ionic liquid in oil microemulsion. Under that situation, the mobility of dye molecules became higher. This eventually led to the decrease in the fluorescence anisotropy values. A linear increase in the anisotropy

value for the system comprising Tween20:n-pentanol in a 1:2 w/w ratio was due to the continued solvation of the cationic component of the ionic liquid, which was assisted by the presence of larger number of alkanol molecules.

### 3.4. Morphological study: TEM analyses

Morphological studies on the microemulsion droplets of different compositions were investigated by transmission electron microscopy. Representative TEM image for a microemulsion system with Tween 20/n-pentanol at equal mass ratio (1:1) are shown in Figure 9.



**Figure 9.** Representative TEM image of  $[\text{b}_4\text{mpy}][\text{BF}_4]/(\text{Tween-20}+\text{n-pentanol})/\text{n-heptane}$  IL-in-oil microemulsion. Tween 20/n-pentanol (w/w): 1:1. Volume fraction ( $\phi_d$ ) of IL: 0.015. Scale bar: 200 nm.

Particles as studied by the transmission electron microscopy, were found to be spherical in nature. However, particle surfaces were not smooth, which was possibly due to the drying up of the solvents. Sizes of the microemulsion droplets as derived from the dynamic light scattering were found to be smaller than the TEM results. Such a difference was due to the variation in the sample preparation and the subsequent analyses. However, spherical morphologies, as obtained from the TEM measurements further supports the assumption as made in the dynamic light scattering studies. Larger as obtained by the TEM measurements was due to the possible aggregation of the droplets.

## 4. Conclusions

Comprehensive studies on *l*-butyl-4-methyl pyridinium tetrafluoroborate ( $[\text{b}_4\text{mpy}][\text{BF}_4]$ ) / (Tween 20 + n-pentanol) / n-heptane microemulsion system were carried out using a number of different physicochemical techniques. Although the added cosurfactant destabilized the microemulsion, however, it was essential for the formation of a stable microemulsion. Cosurfactant



controlled the curvature of the microemulsion droplets; it simultaneously also imparted better stability by solvating the cationic component of the ionic liquid. Larger number of droplet formation was aided by the cosurfactant. Sensitivity towards temperature decreased with increasing proportion of cosurfactant with respect to Tween 20, as revealed through the combined dynamic light scattering and viscosity measurements. Oxyethylene groups of Tween 20 formed coordinate linkages with the IL cation, which resulted in the rigidity enhancement of the polar domain. The IL, in excess of the amount required for coordinating the surfactant head groups, behaved like the bulk component as revealed through the occurrence of red shift in fluorescence maxima and appearance of maxima in fluorescence anisotropy values. Electron microscopic studies could further shed light on the morphology of the microemulsion droplets, where the spherical morphology of the droplets were established.

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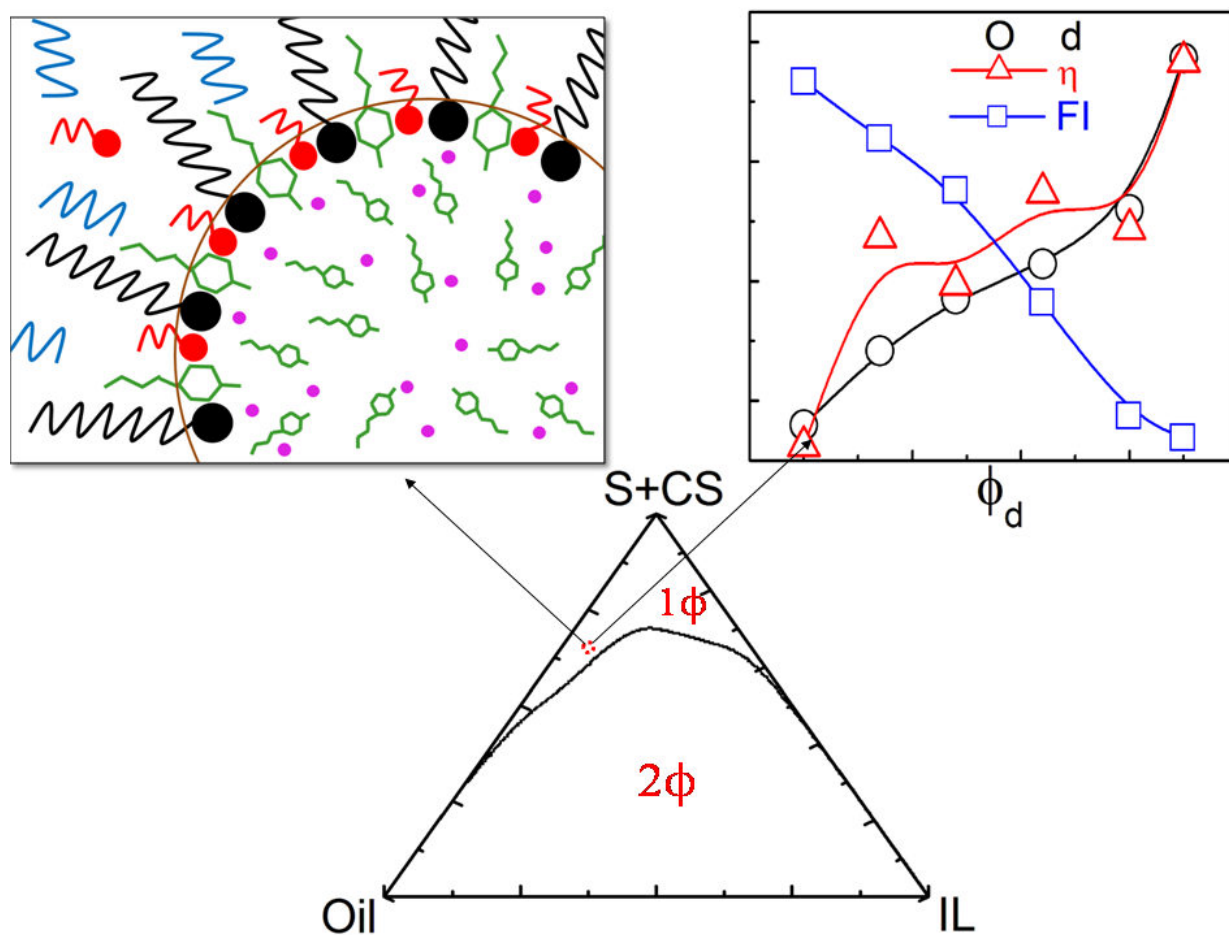
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Proposed model, phase diagram and variation in size ( $d$ ), viscosity ( $\eta$ ) and fluorescence intensity (FI) for *1*-butyl-4-methyl pyridinium tetrafluoroborate ( $[\text{b}_4\text{mpy}][\text{BF}_4]$ ) / (Tween 20 + *n*-pentanol) / *n*-heptane ionic liquid-in-oil microemulsion system.