

## CHAPTER-IV

### Formation of High-Temperature Stable Benzimidazolium Ionic Liquid-in-Oil Microemulsion and Regioselective Nitration Reaction Therein

#### IV.A.Introduction

Microemulsions are thermodynamically stable ‘nano-dispersions’ of water in oil (or oil in water) stabilized by a surfactant film, frequently in combination with a cosurfactant.<sup>1</sup> There has been considerable interest in the use of microemulsions as media for organic synthesis in recent years. Not only can such a formulation be a way to overcome compatibility problems, the capability of microemulsions to compartmentalize and concentrate reactants can also lead to considerable rate enhancement compared to one-phase systems. A third aspect of interest for preparative organic synthesis is that the large oil-water interface of the system can be used as a template to induce regioselectivity.<sup>2</sup> The dynamic character of these nano-reactors is one of the most important features, which has to be taken into account for a comprehensive understanding of chemical reactions carried out in these media.<sup>3</sup>

In recent years, attempts were made to formulate and characterize waterless/non-aqueous microemulsions, where other polar solvents like methanol, acetonitrile, glycerol, formamide, ethylene glycol etc. were exploited. The first study of non-aqueous microemulsion with ethylene glycol, lecithin and decane were reported by Friberg and Podzimek in 1984.<sup>4</sup> Latter, Falcone et al. studied the properties of non-aqueous reverse micelles (RMs) using six polar solvents, such as glycerol, ethylene glycol, propylene glycol, formamide, dimethyl formamide, dimethylacetamide.<sup>5</sup> Non-aqueous systems have distinct advantages over aqueous ones as: (i) they generally forms larger stable regions of isotropic solutions compared to the analogous aqueous systems; (ii) a large variety of different surfactants can be used to give non-aqueous microemulsions and (iii) these systems can be used as good reaction media, specifically for the reactants which react with water.<sup>6</sup> These pioneer studies stimulated research on the formulation of non-aqueous microemulsions containing room

temperature ionic liquids (RTILs), which also provide hydrophobic or hydrophilic nano-domains. Thus their applications can be extended to fields of reaction and separation or extraction media. Earlier report has shown that surfactant IL-based microemulsions can be used to produce polymer nanoparticles, gels, and open-cell porous materials.<sup>7</sup> Also, IL-in-oil microemulsions were employed to increase the solubility of a sparingly soluble drug to enhance its topical and transdermal delivery and used as template to synthesize starch nanoparticles for investigation of the drug loading and releasing properties.<sup>8-10</sup> ILs are considered suitable solvents for various chemical reactions and catalysis due to their characteristic properties like negligible vapour pressure and tunability in structure by modifying cation and anion moieties.<sup>11, 12</sup> In addition, ILs exhibit excellent chemical and thermal stability, wide polarity and are recyclable.<sup>13, 14</sup> Despite their great potential, reports on the performance of organic reaction in non-aqueous IL microemulsions are still very scarce. In our previous work, we reported Heck reaction in w/o non-ionic microemulsion system in the absence and the presence of an IL (1-Ethyl-3-Propylbenzimidazolium bromide), where the reaction ended with the highest yield (75%) in presence of solute amount of IL, wherein the microemulsion forms spontaneously with the highest stability.<sup>15</sup>

The nitration of phenol is a fundamental unit process of great industrial importance generating commercially valuable intermediates and there is a great need for regioselective pollution free processes. In earlier work on nitration of phenol in microemulsion, it was claimed that in an AOT [sodium bis(2-ethylhexyl)sulfosuccinate]-based microemulsion, ortho nitration was favoured.<sup>16</sup> This was explained as being due to the phenol orienting at the interface with the aromatic ring extending into the organic domain and the hydroxyl group protruding into the aqueous domain. This orientation would make the ortho positions more accessible than the para position to the approaching nitronium ion. However, we have not been able to reproduce these results. A survey of literature shows nitration of phenol lacks positional selectivity for para isomer with majority of processes giving rise to o-isomer as the major product along with minor amounts of p-isomer. Among several nitrating agents employed which include mixed acid, super acids, acyl nitrates and a variety of metal nitrates under different conditions, ferric nitrate in particular either alone or supported on solid matrices such as clays has enjoyed considerable importance.<sup>17, 18</sup> Herein, we formulated the non-aqueous microemulsions using cetyltrimethylammonium bromide (CTAB) as cationic surfactant and n-octanol as cosurfactant in *n*-decane with 1-ethyl-3-propylbenzimidazolium bromide ([EPbim][Br]) as a water-substitute and finally, utilized as reaction media for

regioselective nitration of substituted phenol using nontoxic and inexpensive ferric nitrate. The current studies can help to understand the microstructure of IL microemulsions and thus establish a better way of using them as a new reaction medium.

## **IV.B.Results and discussions**

### **IV.B.1.Distribution of 1-octanol for the formation of stable and spontaneous IL-in-oil microemulsion**

CTAB requires the presence of a cosurfactant, typically a medium chain alcohol, in order to form a stable microemulsion.<sup>22</sup> In IL/O microemulsion system, CTAB are considered to populate at the oil/water interface in partial association with the cosurfactant (1-octanol). On the other hand, 1-octanol further distributes between the interface and the bulk oil, because of the negligible solubility of higher chain length cosurfactant in water.<sup>23</sup> Thus, at a fixed [surfactant(s)], a critical concentration of 1-octanol is required for the stabilization of the IL-based microemulsions. To estimate how much amount of (in moles) 1-octanol is distributed in the interface and oil phase for formation of a stable microemulsion, we perform a simple titrimetric technique (known as the dilution method).<sup>24</sup> The method of dilution is a very simple but informative technique which can derive many useful parameters for the formation of IL-in-oil microemulsions.<sup>25</sup> In this method, by the alternate stabilization and destabilization with the successive addition of cosurfactant and oil, one can obtain the partition coefficient of 1-octanol between oil and IL interface. By suitably analyzing the distribution constant in the form of different standard thermodynamic equations, the corresponding thermodynamic parameters for the formation process can easily be evaluated.<sup>26, 27</sup> However, similar studies involving ILs as polar component instead of water are not common in literature. Thus the dilution studies involving the evaluation of interfacial behaviour, thermodynamic and structural parameters of IL-in-oil microemulsion are considered to be significant. The basic mathematical formalism to determine the thermodynamics of microemulsion formation and evaluation of structural parameters for the presently studied IL -in-oil microemulsion systems can be found in earlier reports.<sup>26-28</sup>

In the present report, this method is used for the estimation of different parameters concerning to the formation of IL-in-oil microemulsion at 358 K with varying molar ratio of IL to surfactant, R (= 1→5). The following equations are helpful to rationalize the

distribution vis-à-vis transfer process of 1-octanol from the continuous oil phase to the interfacial region:

$$k_o = \frac{n_a^o}{n_o} \quad (2)$$

$$\frac{n_a}{n_s} = \frac{n_a^i}{n_s} + k_o \frac{n_o}{n_s} \quad (3)$$

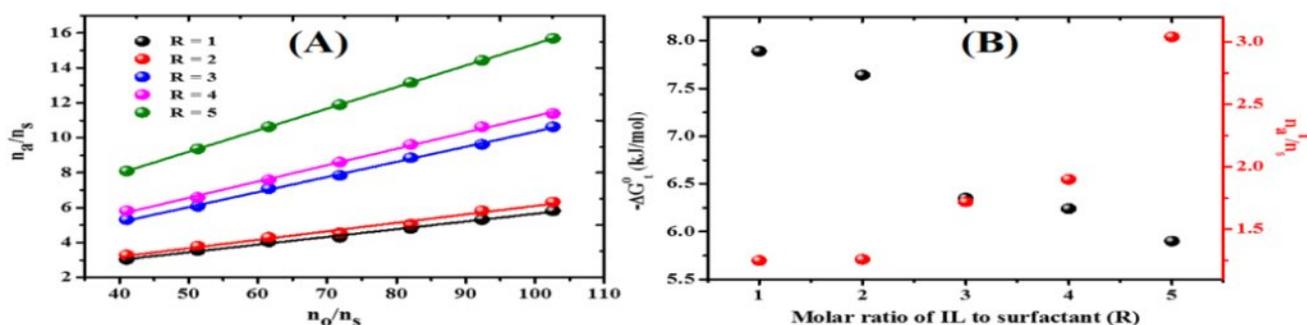
$$K_d = \frac{X_a^i}{X_a^o} = \frac{\frac{n_a^i}{n_a^i + n_s}}{\frac{n_a^o}{n_a^o + n_o}} = \frac{n_a^i(n_a^o + n_o)}{n_a^o(n_a^i + n_s)} \quad (4)$$

$$\Delta G_t^0 = -RT \ln K_d = -RT \ln \frac{X_a^i}{X_a^o} = -RT \ln \frac{I(1+S)}{S(1+I)} \quad (5)$$

Where,  $n_a$ ,  $n_a^i$  and Gibbs free energy of transfer of cosurfactant from oil to interface ( $-\Delta G_t^0$ ),  $n_a^o$ ,  $n_o$ ,  $n_s$  denote the total number of moles of cosurfactant, its number at the interface, in the oil phase, the total number of moles of oil and the total number of moles of surfactant, respectively. A plot of  $n_a/n_s$  against  $n_o/n_s$  at different R (Fig. 1A) according to equation (3) yields the values of the slope ( $S$ ) and the intercept ( $I$ ). Slope ( $S$ ) is actually  $k_o$  and  $n_a^o$  can be determined from equation (2). On the other hand,  $n_a^i$  can be calculated from the intercept ( $I$ ), which is equal to  $n_a^i/n_s$ . The partition of cosurfactant between the continuous oil phase and the interface of the droplet can be expressed in terms of the distribution constant, which is represented by  $K_d$ . The values of  $X_a^i$  and  $X_a^o$  are the mole fraction of cosurfactant in the interfacial layer and in the oil, respectively. It is evident from Fig. 1B that  $n_a^i$  or  $n_a^i/n_s$  values increase with increase in R for all these systems. This indicates that with the increase in IL content, more  $n_a^i$  are required for the formation of stable IL-in-oil microemulsion systems at constant temperature. With increasing IL content, in turn, the interfacial areas are extended (which has been calculated in subsequent section with the help of droplet diameter measured by DLS), and the requirement of cosurfactant at the interface to stabilize the droplets is gradually increased. In other words, hydrophilic property of the system is strengthened as R increases. Therefore, more cosurfactant is needed to adjust the hydrophile-lipophile balance of the microemulsion, resulting in the increase in  $n_a^i$  values.<sup>29</sup> Similar behaviour was reported for [bmim][BF<sub>4</sub>]/Brij-35/1-butanol/toluene<sup>30</sup> and [bmim][BF<sub>4</sub>]/[C<sub>12</sub>mim]Br/pentan-1-ol/octane microemulsions.<sup>29</sup>

The  $\Delta G_t^0$  values for all studied compositions are negative, and hence, spontaneous formation of IL-in-oil microemulsion is suggested at 358 K. It is also evident from Fig. 1B that the values of  $-\Delta G_t^0$ , which is indicative of spontaneity of the cosurfactant transfer process (1-octanol<sub>oil</sub> → 1-octanol<sub>int</sub>), decrease with increasing R (= 1 → 5) for the studied systems. In other

words, association between surfactant and cosurfactant molecules at the interface becomes less favorable with increase in  $\omega$ . This type of variation was reported by Hait et al.,<sup>[27]</sup> Zheng et al.<sup>24</sup> and Paul et al.<sup>28</sup> for water-in-oil microemulsion. From comparative study, the  $-\Delta G_t^0$  values obtained for the present system are comparable with those reported for [bmim][BF<sub>4</sub>]/[C<sub>12</sub>mim]Br/pentan-1-ol/octane IL-in-oil microemulsions;<sup>29</sup> however, are higher than [bmim][BF<sub>4</sub>]/Brij-35/1-butanol/toluene,<sup>30</sup> [bmim][BF<sub>4</sub>]/CTAB/alkanol (ethanol, 1-propanol, 1-butanol)/toluene<sup>31</sup> and [bmim]methanesulfonate±water/(Tween-20+n-pentanol)/n-heptane microemulsion systems.<sup>20</sup> Thus, the present system possesses a relatively better thermodynamic stability at higher temperature.

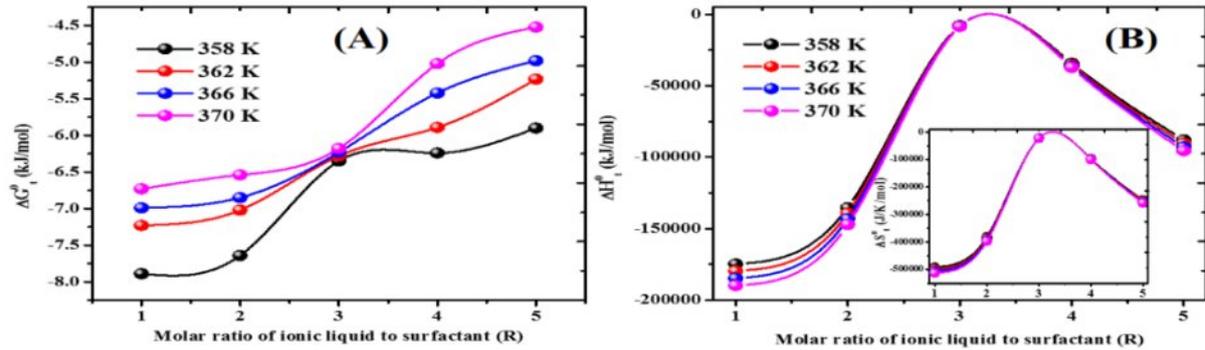


**Figure-IV.1.** (A) Plot of  $n_a/n_s$  vs.  $n_o/n_s$  at varied molar ratio of IL to surfactant (R); (B) Plots of  $\Delta G_t^0$  and interfacial composition ( $n_a^i/n_s$ ) as a function of R for IL/CTAB/1-octanol/decane microemulsion system at fixed temperature of 358K.

#### IV.B.2. Energetic parameters for IL/O microemulsion reveals organized oil/water interface along with temperature-independent formulation at a critical R

The thermodynamic studies on the formation behaviour of IL-in-oil (IL/O) microemulsions and the energetics of the interaction of the components are comparatively rare. Extensive knowledge on formation of IL/O microemulsions and their internal structures and particle aggregation, are of very much significant for their preparation, application, and use. However, the knowledge of their internal arrangement, structure, and interaction needs augmentation through thermodynamic studies. The complex nature of microemulsions has

restricted rapid growth of the thermodynamic viewpoint, which has not been sufficiently explored.<sup>32</sup> In this section, analysis of energetic parameters of the transfer of 1-octanol from decane to the IL-oil interface of CTAB microemulsion at higher temperature range (358→370 K) is presented in detail, which is not reported earlier. However, such reports for IL/O microemulsions at the temperature range of 293 K to 323 K are available in literature, which were recently reviewed by our group.<sup>33</sup>



**Figure-IV.2.** (A) Plots of  $\Delta G_t^0$  and (B)  $\Delta H_t^0$  (inset:  $\Delta S_t^0$ ) as a function of molar ratio of IL to surfactant for IL/CTAB/1-octanol/decane microemulsion system at four different temperatures (358→370 K).

The following equations are helpful to rationalize the temperature dependent energetic parameters transfer process of cosurfactant (herein, 1-octanol) from the continuous oil phase to the interfacial region for stabilization of IL-droplets: the  $\Delta H_t^0$  (standard enthalpy change of transfer process) can be evaluated by the van't Hoff equation. Thus,

$$\left[ \frac{\partial \left( \frac{\Delta G_t^0}{T} \right)}{\partial \left( \frac{1}{T} \right)} \right]_p = \Delta H_t^0 \quad (6)$$

Since the dependencies of  $(\Delta G_t^0/T)$  on  $(1/T)$  are nonlinear for all these systems (plots are shown for brevity), a two-degree polynomial equation of following form is used.

$$\left( \frac{\Delta G_t^0}{T} \right) = A + B_1 \left( \frac{1}{T} \right) + B_2 \left( \frac{1}{T} \right)^2 \quad (7)$$

The differential form of the relation helps to evaluate  $\Delta H_t^0$ . Thus,

$$\left[ \frac{\partial \left( \frac{\Delta G_t^0}{T} \right)}{\partial \left( \frac{1}{T} \right)} \right]_p = B_1 + 2B_2 \left( \frac{1}{T} \right) = \Delta H_t^0 \quad (8)$$

Where, A, B<sub>1</sub> and B<sub>2</sub> are the polynomial coefficients. Then the Gibbs-Helmholtz equation is used to evaluate  $\Delta S_t^0$  (standard entropy change of transfer process),

$$\Delta S_t^0 = \frac{(\Delta H_t^0 - \Delta G_t^0)}{T} \quad (9)$$

The standard state herein considered is the hypothetical ideal state of the unit mole fraction. The dependence of  $\Delta G_t^0$  along with  $\Delta H_t^0$  and  $\Delta S_t^0$  as a function of IL content (R) at four different temperatures are illustrated in Figure-IV.2A and 2B. The negative  $\Delta G_t^0$  value at all elevated temperatures implies that the successful formulation of “high-temperature stable IL/O microemulsions” due to spontaneous transfer of 1-octanol from the oil phase to the interfacial region. For all systems, the absolute values of  $\Delta G_t^0$  decrease with increase in temperature. Hence, the formation of microemulsion was less favorable with increase in temperature, which indicates a weaker interaction between surfactant and cosurfactant at the interface at higher temperature, which corroborated well with the degree of spontaneity of the transfer process. The reduced spontaneity at elevated temperature was earlier reported for microemulsions with the oil isopropylmyristate (IPM), stabilized by trihexyl (tetradecyl) phosphonium bis 2,4,4-(trimethylpentyl)phosphinate (surfactant) + isopropanol (IP as a cosurfactant) like the triisobutyl (methyl)phosphonium tosylate/IPM/(IL-2+IP) system.<sup>34</sup> Further, overall transfer process is found to be exothermic in nature at all experimental temperatures along with negative entropy change with progressive addition of IL. So, 1-octanol causes release of heat during the cosurfactant transfer process. Consequently, the negative entropy change is due to more organization of the interface and its surroundings inside the IL/O droplets. Dissolution of IL into amphiphile-Dc medium can be modelled as consisting of four major processes: (i) endothermic dispersion of IL, (ii) endothermic penetration of IL in the interior of IL/O microemulsions (aggregates), (iii) exothermic reorganization of the amphiphiles at the oil /IL interface, and (iv) exothermic organization of the penetrated IL. The total heat shows exothermicity, which means that the sum of the contributions of processes one and two are, therefore, lower than those of three and four. Such negative standard enthalpy and entropy changes for w/o microemulsions stabilized by cationic cetyltrimethylammonium-based surfactant and 1-octanol were also reported in

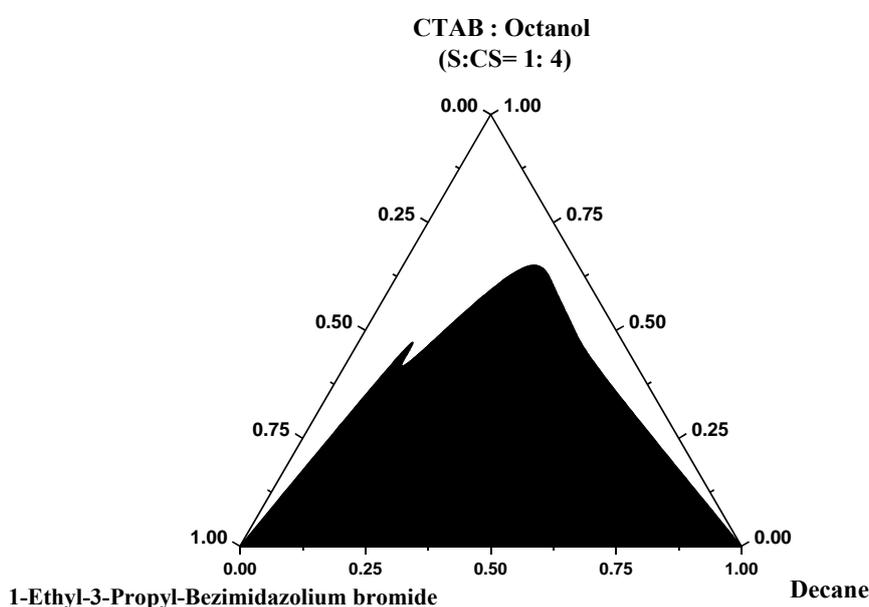
literatures.<sup>35,36</sup> However from comparative study, it can be concluded that 1-octanol/cetyltrimethylammonium-based w/o systems showed much lower free energy of formation than currently studied IL/O systems even at much higher temperatures.<sup>35</sup>

An interesting feature reveals from Fig. 3B and its inset that both  $\Delta H_t^0$  and  $\Delta S_t^0$  values decrease with increase in temperature for all these systems. In other words, the transfer process (1-octanol<sub>oil</sub>→1-octanol<sub>int</sub>) changes from less exothermic to more exothermic with increase in temperature. It can be argued that the degree of hydrogen bonding of water around the surfactant molecules decreases with increase in temperature, and therefore, the energy required to break it diminishes i.e.,  $\Delta H_t^0$  decreases with increase in temperature.<sup>37</sup> Subsequently, variation of  $\Delta S_t^0$  values with increase in temperature can be rationalized as follows: as temperature increases, the extensive hydrogen bonding in ion pair of IL molecules gradually breaks down; affecting the importance of the entropic term due to decrease in IL-hydration around the head group of surfactant.<sup>37</sup> It is also interesting to note that both  $-\Delta H_t^0$  and  $-\Delta S_t^0$  values increase with increase in IL content (R) before reaching a maximum at R = 3 and after that they gradually decrease at higher IL content. Most importantly, the enthalpic processes are quantitatively identical at the maximum, i.e., at R = 3; which indicates that the transfer events of cosurfactant from oil to the interface are physicochemically same and isenthalpic at R = 3. The mixing fraction at the interface is not greatly changed in ionic surfactant-cosurfactant systems with increasing temperature. However, the monomeric solubility of cosurfactant in oil increases monotonically in the ionic surfactant systems. In order to attain a temperature-insensitive microemulsion, the monomeric solubility of cosurfactant in oil has to be reduced by using an appropriate cosurfactant.<sup>38</sup> Earlier, Maiti et al. reported a couple of isenthalpic formulations for cationic w/o microemulsion composed of octadecyltrimethylammonium bromide (C<sub>18</sub>TAB), n-butanol, and n-heptane.<sup>39</sup>

### **IV.B.3. Determination of extent single phase microemulsion region**

From the application point of view, construction of the phase diagram is a primary task towards a microemulsion formulation. Herein, Figure-IV.3 illustrates the pseudoternary phase diagram of 1-ethyl-3-propylbenzimidazolium bromide ([EPbim][Br])-(CTAB + 1-octanol)-*n*-decane systems at fixed surfactant-cosurfactant ratios (1:4, w/w). The shaded areas under the curves represent the two-phase turbid region, where the stable microemulsions are not formed. The unshaded portions correspond to the microemulsion zone. In the currently

studied systems, oil-rich (IL-in-oil microemulsion), IL-rich (oil-in-IL microemulsion) as well as bicontinuous states are observed. However, for simplicity, all these three different regions are represented as a single phase (microemulsion zone; the unshaded portion in the pseudoternary phase diagram). All further experiments are carried out using the oil-rich (i.e., IL-in-oil) microemulsion systems. The areas under the microemulsion region (unshaded portion) and the turbid regions are calculated by simply weighing the individual areas. Similar type of phase characteristic is also reported by Zech et al. for dodecane/[C<sub>16</sub>mim][Cl]/decanol at 1:4, w/w)/ethylammonium nitrate (EAN) microemulsion.<sup>40</sup>



**Figure-IV.3.** The pseudoternary phase diagram of IL/CTAB/1-octanol/decanol microemulsion system at fixed surfactant-cosurfactant ratio (1:4, w/w) and temperature (358K).

#### **IV.B.4. Anomalous behaviour of aggregated droplet size as a function of IL content (R)**

DLS is used to assess whether the ILs are encapsulated by the surfactant to create microemulsions media, because it is a powerful technique to evaluate the formation of these new organized systems. To identify and characterize the [EPbim][Br]/oil microemulsions formed by CTAB/1-octanol (1:4,w/w), the size of the aggregates formed is investigated as a function of [EPbim][Br] content (i.e., molar ratio of IL to surfactant, R) using DLS technique. Variation in the diameter of IL-in-oil microemulsion with the volume fraction of the IL (R) at

360 K is presented in Figure-IV.5. Droplets are fairly monodispersed as exemplified from the size distribution plots, which are not shown here for brevity. Earlier reports exhibit how hydrodynamic diameter of IL based reverse micelles stabilized by ionic surfactant increases as R increases.<sup>40-44</sup> However in the present study, it is observed from Figure-IV.5 that the size of microemulsions decreases almost linearly as R increases. Now the question arises why hydrodynamic diameter of CTAB surfactants are decreasing with increasing R? This can be envisaged considering two effects. First, the lowering of size with increasing R can primarily be resulted by poor encapsulation of [EPbim][Br] over the microemulsions. Secondly, lowering of the values of hydrodynamic diameter is a characteristic feature for formation of microemulsions in highly immiscible non-aqueous solvents.<sup>45</sup> For these systems, the polar solvent predominantly stays in microemulsion core instead of locating near the interfacial region of microemulsion. Here, [EPbim][Br] and *n*-decane are immiscible. So, with increasing [EPbim][Br] concentration, more and more [EPbim][Br] molecules are solubilized in microemulsion core instead of staying near the micellar interface. Increasing concentration of [EPbim][Br] leads to more favourable H-bond interaction with polar head group  $[N(CH_3)_3^+]$  of surfactant, CTAB. So, favourable and strong H-bonding interaction with [EPbim][Br] helps to hold the polar head groups much near to the micellar core. This fact is manifested by the lowering of hydrodynamic diameter of the microemulsions.<sup>45</sup> Earlier, Ghosh noticed similar behaviour for non-aqueous reverse micelles of Brij surfactants prepared in benzene and EAN.<sup>46</sup>

#### **IV.B.5. Geometrical model for the determination of aggregation number and surfactant interfacial molecular area**

The efficient use of newly formulated microemulsions requires a sound knowledge of the basic physicochemical properties of the specific system. For example, in order to model the distribution of various chemical species within the system, parameters such as droplet size, aggregation number, and surfactant molecular interfacial area must be known.<sup>47</sup> Recent work of Lemyre and coworkers confirmed that hydrodynamic diameter of reverse micelles is in direct proportion with aggregation number.<sup>47</sup> According to them, the relationship between hydrodynamic diameter ( $D_h$ ) and aggregation number ( $N_{agg}$ ) for IL-in-oil microemulsions can be expressed using the following equation,

$$\frac{D_h}{2} = \left[ \frac{3N_{agg}}{4\pi} \left( \frac{V_{IL,total}}{n_{surf,in,MEs}} + V_S \right) \right]^{\frac{1}{3}} \quad (6)$$

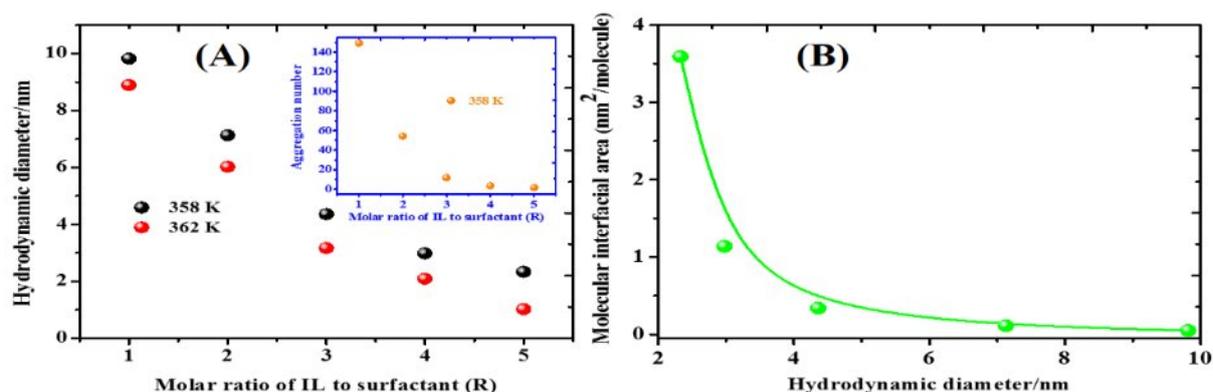
Where,  $V_{IL,total}$ ,  $n_{surf}$ , in MEs, and  $V_s$  are the total volume of water, number of surfactant molecules in microemulsions (MEs) and molecular volumes of surfactant(s), respectively. This equation is based on a model assuming the micelles as a compact sphere and neglects presence of any polar solvent molecules between the surfactant hydrophobic tails which would be the ideal case if two perfectly immiscible solvents are used. Molecular volume of CTAB ( $V_{CTAB}$ ) can be calculated as,

$$V_{CTAB} = (V_{tail} + V_{head}) \quad (7)$$

Where,  $V_{tail}$  and  $V_{head}$  are the molecular volume of hydrocarbon chain and polar head of CTAB.  $V_{head}$  of CTAB has been determined from head group area of CTAB,<sup>27</sup> whereas  $V_{tail}$  can be expressed as,

$$V_{tail} = V_{CH3} - (16 - 1)V_{CH2} \quad (8)$$

Group molar volumes (i.e.  $V_{CH3}$ , and  $V_{CH2}$ ) used for the estimation of molecular volume of CTAB are taken from Preu et al.<sup>48</sup> A representative plot of  $N_{agg}$  as a function of R (i.e.,  $[IL]/[CTAB]$ ) for these systems is depicted in inset of Fig. 4A. Therefore, as hydrodynamic diameter decreases with increasing R, aggregation number also decreases. Since surfactant concentration is fixed, a decrease in aggregation number with R is indicative of an increase in the number of IL droplets which provides additional support to the decreased droplet size as evidenced from DLS measurements.



**Figure-IV.4.** (A) Variation in the hydrodynamic diameter with the molar ratio of IL to surfactant (R) at two different temperatures (358 and 362 K), and (B) Variation of molecular interfacial area of the surfactant as a function of hydrodynamic diameter for IL/CTAB/1-octanol/decane microemulsion system.

Once the micellar composition has been established, equation (9) can be used to determine the molecular interfacial area of the surfactant if the volume occupied by the hydrophilic part of a surfactant molecule ( $V_{surf, hydrophilic}$  or  $V_{head}$ ) and the effective length of the hydrophobic chain of the surfactant ( $l_{hydrophobe}$ ) are known. This leads to following equation;<sup>47</sup>

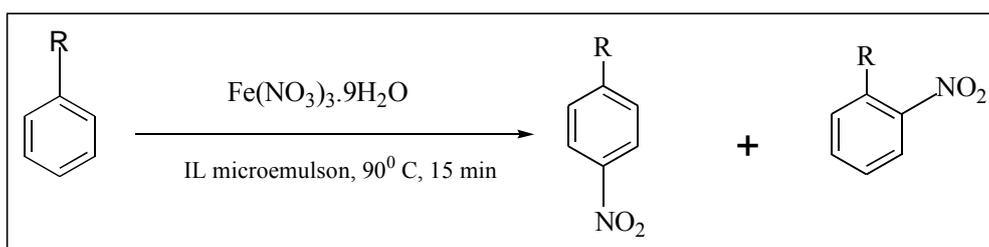
$$\frac{D_h}{2} = \frac{3}{\sigma} \left( \frac{V_{IL, total}}{n_{surf, MEs}} + V_{surf, hydrophilic} \right) + l_{hydrophobe} \quad (9)$$

Where,  $\sigma$  is the surfactant molecular interfacial area and  $l_{hydrophobe}$  can be estimated from Tanford's formula<sup>49</sup> for the maximum extension of the alkyl chain of surfactant. The molecular interfacial area of the surfactant is plotted in Figure-4.B as a function of droplet size. It is clearly evident that, the interfacial area is not constant. A limiting value is reached for droplet size larger than 5 nm, but the interfacial area increases sharply with increasing IL content (R) and decreasing droplet size. The primary reason for the variation of the molecular interfacial area is the dependence of the conformation of the anchored surfactant chains on the radius of curvature.<sup>47</sup> The variation of these parameters with droplet size of microemulsion indicates that the decrease in thermodynamic stability (as evidenced from dilution method) with decreasing size can be attributed to the steric confinement of the hydrophilic quaternary ammonium chain of CTAB and 1-ethyl-3-propylbenzimidazolium cation ([EPbim]<sup>+</sup>) of IL.

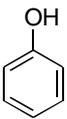
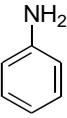
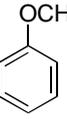
#### IV.B.6.Nitration of aromatic compounds in IL/O microemulsion offers regioselectivity

A nitration reaction was performed in the cationic surfactant-based IL/O microemulsion system with three different aromatic compounds and the ortho-to-para ratio was examined. The results are summarized in Table-IV.1. The corresponding conversion observed for the nitration of phenol at the end of 15 min was 81% for the para isomer and 19% for the ortho isomer.

**Scheme-IV.1.** Pictorial representation of the nitration reaction in IL/CTAB/1-octanol/decane microemulsion system.



**Table-IV.1.** Regioselectivity in product obtained from nitration reaction in IL/CTAB/1-octanol/decane microemulsion system.

| Entry | Reactant  | Reaction Yield (%) |      |
|-------|---|--------------------|------|
|       |   | Ortho              | Para |
| 1.    | <br>[Phenol]   | 19                 | 81   |
| 2.    | <br>[Aniline]  | 23                 | 77   |
| 3.    | <br>[Anisole] | 30                 | 70   |

Mechanistically, we proposed that in situ formation of nitronium ions is a major factor for effective nitration of aromatic compounds with ferric nitrate.<sup>50</sup> An efficient electrophilic substitution reaction of aromatic compounds, specially phenols, anilines and anisole with ferric nitrate as the nitrating agent in reverse micelle has been developed. As can be seen from Table-IV.1, the cationic surfactant-based microemulsion favours para substitution, i.e., regioselectivity. The para-directing effect is stronger for the phenols than for the others. It is supposed that the para-directing effect is due to an attractive interaction between the aromatic ring and the cationic headgroup of the surfactant.<sup>18</sup> The positively charged surfactant headgroup interacts with the electron-rich face of the aromatic ring. Because of the electronegative side of the substance, the electron cloud of the aromatic ring is pulled towards these groups. In order to obtain optimal matching of the charges, the ring will be positioned so that the cationic surfactant headgroup is closer to the ortho positions than to the para position. This will make the approach by the positively charged attacking species, the nitronium ion, more favourable at the para position than at the ortho position. The reactions went to completion in around 15 min. It is noteworthy that the reactions proceeded fast in the microemulsions despite the fact that the surfactant used carried the same charge as the

reacting nitronium ion. Evidently, the positive effect of the large oil–IL interface dominates over the charge repulsion between the surfactant head groups and the attacking nitronium ion.

## IV.C. Materials and Methods

**IV.C.1. Materials** Cetyltrimethylammonium bromide, CTAB ( $\geq 99\%$ , CAS No. 57-09-0, *Sigma*), 1-octanol (anhydrous,  $\geq 99\%$ , CAS No. 111-87-5, *Sigma-Aldrich*) and decane (anhydrous,  $\geq 99\%$ , CAS No. 124-18-5, *Sigma-Aldrich*) were used without further purification.

### IV.C.2. Methods

**IV.C.2.1. Synthesis of ILs** The IL, 1-ethyl-3-propylbenzimidazolium bromide ([EPbim][Br]), is synthesized in accordance with our reported method.<sup>19</sup> It is important to note that the synthesized pure IL ([EPbim][Br]) is white solid at room temperature<sup>19</sup> and it melts around 359 K. In order to make non-aqueous IL based microheterogeneous system, all the studies are carried out at the high temperature. Nevertheless, the solubility of CTAB in the *n*-decane/1-octanol mixture is improved drastically by increasing the temperature to 360 K. This is also the reason for the necessity of tempering the system for getting optically clear solutions of IL based non-aqueous microemulsion. However, these effects can principally not be assigned to electrostatic interactions, which are most of all temperature independent in ionic surfactant-based microemulsions in contrast to non-ionic-based ones.

**IV.C.2.2. Construction of phase diagram of ternary surfactant, oil and IL system** The pseudoternary phase diagram comprising oil (*n*-decane/Dc), benzimidazolium IL (1-ethyl-3-propylbenzimidazolium bromide, [EPbim][Br]), cationic surfactant (CTAB), and cosurfactant (1-octanol/1-On) has been constructed by the method of titration and direct observation. In a typical experiment, mixtures of oil and surfactant (including the cosurfactant) with varying mass ratios of 4:1 are prepared in a series of stoppered test tubes. To construct the pseudoternary phase diagrams for the IL based “water-free” microemulsions, the samples are placed in a thermostatic water bath at  $(360 \pm 0.5)$  K for 10 min, and then the mixture is titrated by IL under moderate agitation. The IL volumes causing the solutions to turn to turbid from clear transparent are noted to determine the phase boundaries. In each plotted phase diagram, the upper part of the phase boundary represents a single-phase region (microemulsion,  $1\phi$ ), and the lower part is a multiphase region ( $2\phi$ ). The compositions in the phase diagrams are represented in weight fractions. The same procedure was repeated for 2 to

3 times for each mixture, and an average of these results was taken for the construction of phase diagrams.

#### **IV.C.2.3. Dilution method study for estimation of interfacial composition and spontaneity of formation of microemulsion**

In the dilution experiments, 0.00025 mole of surfactant (CTAB) is placed in a dry test tube, followed by addition of fixed 2 ml of *n*-decane and different amount of [EPbim][Br] (at different molar ratio of [EPbim][Br] to surfactant  $R = 1 \rightarrow 5$ ), respectively. The sample is placed in a thermostated water bath, stirred constantly with a magnetic stirrer, and kept covered to prevent loss due to evaporation. The cosurfactant (1-octanol) is then added slowly from an auto pipette to the initially viscous and turbid mixture until the solution becomes clear, which is indicative of the formation of the single phase. Sufficient time is given for equilibrium and then the volume of cosurfactant is noted at that point. A known but small volume of oil is again added to the system to destabilize it. A cloudy sample is made just clear by the addition of cosurfactant. The quantity of cosurfactant is recorded. The experiment is monitored at fixed temperature of 360 K. The entire experiment is then repeated for a second time to ensure accuracy, and the average values obtained are used for data processing and analysis. In order to estimate various thermodynamic parameters for the formation of IL-in-oil microemulsion, the above-mentioned experiment is carried out at three other temperatures, such as 365, 370 and 375 K.

#### **IV.C.2.4. Dynamic light scattering (DLS) studies**

DLS measurements are carried out using a Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd, U.K.). A 2.5 mmol of CTAB mixed with appropriate amount of 1-octanol dissolved in 2ml of *n*-decane is used for such studies. The same set of CTAB/1-octanol ratio (w/w), as used for the construction of phase diagram is employed for droplet size analysis at 360 K. Samples are filtered thrice before each measurement using Milipore<sup>TM</sup> hydrophobic membrane filter of 0.25  $\mu\text{m}$  pore size to remove possible dust particles. A He-Ne laser operating at a wavelength of 632.8 nm was used and the data were collected at a  $90^\circ$  angle. Temperature is controlled to within  $\pm 0.05$  K using a built-in Peltier heating-cooling device. Hydrodynamic diameter ( $D_h$ ) of the microemulsion solutions is estimated from the intensity autocorrelation function of the time-dependent fluctuation in intensity. According to Stokes-Einstein equation,  $D_h$  is defined as <sup>20, 21</sup>:

$$D = kT / 3\pi\eta D_h \quad (1)$$

Where,  $k$ ,  $T$ ,  $D$  and  $\eta$  indicate the Boltzmann constant, temperature, diffusion coefficient and viscosity of the solvent (herein *n*-decane) respectively. To check the reproducibility of the results at least 6 measurements are performed.

#### **IV.C.2.5. General procedure for nitration reaction**

Fe (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O (0.5 mmol) and the substrate (1 mmol) were placed in a 10 mL round bottom flask containing the IL-in-Oil microemulsion (3 ml). The mixture was placed on a magnetic stirrer at 90<sup>0</sup> C and stirring continued for 15 min. Then the reaction mixture was diluted with water and extracted with dichloromethane (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using the mixture of petroleum ether and ethyl acetate as eluent.

#### **IV.D. Summary**

Present study is focused on the formulation and characterization of a high-temperature stable quaternary IL-in-oil microemulsions comprising of IL ([EpBzim]Br), CTAB, 1-On and Dc with a detailed description of the interfacial composition and energetic parameters for the transfer of 1-On from bulk oil phase to the interface as a function of system composition and temperatures. Additionally, nitration reaction of some aromatic compound has been performed in the IL/O microemulsion. The reaction ends up with the highest regioselectivity of para isomer. The confinement of IL imparts the regioselectivity on the nitrated product.

#### **IV.E. References**

References are given in BIBLIOGRAPHY under Chapter IV (pp. 111-113).