

CHAPTER-II

Physicochemical studies of water-in-oil nonionic microemulsion in presence of benzimidazole-based ionic liquid and probing of microenvironment using model C-C cross coupling (Heck) reaction

II.A. Introduction

Ionic liquids (ILs) are organic salts/solvents being constituted of distinct cations and anions, having low vapor pressure, high thermal and chemical stability. They are non-flammable and of good catalytic and solvation.¹ The importance and application of ILs are reflected by the contribution of different myriads of researchers.² A number of physicochemical investigations of imidazolium-based ILs have been reported.³ On the other hand, the example of benzimidazole-based ILs is relatively new and scarcely reported in literature.⁴ Benzimidazole is an important motif which is found both in naturally occurring and biologically active compounds. It is an important pharmacophore as well.⁵

In the field of colloid and interface science, the investigation of surfactant molecular assemblies in room temperature ionic liquid (RTIL) is of great interest because the former systems can solubilize substances being essentially insoluble in the latter and thus, solubilizing power of surfactant assemblies may widen the application of RTILs. From this point of view, the elucidation of self-assembling phenomena of surfactant molecules in ILs and its applications have become an interesting area of research.⁶ Furthermore, IL based microemulsions are used as reaction media in various organic transformations, viz. aminolysis of esters,⁷ Diels-Alder reaction,⁸ Matsuda-Heck reaction⁹ etc. Water-in-oil (w/o) microemulsions or reverse micelles (RMs) are macroscopically homogeneous mixtures of oil, water, surfactant and/or cosurfactant, whereas in the microscopic level it consists of individual domains of oil and water separated by a monolayer of surfactant and/or cosurfactant. The stability, flexibility and microheterogeneity of microemulsions make them convenient for biological and technological applications.¹⁰ The microstructure of microemulsions critically depends on the system composition, temperature, and additives.¹⁰ Very recently, we have reported the characteristic roles of surfactant (s), cosurfactant and

oils for the formation and stabilization of w/o microemulsions in absence or presence of additive by employing the Schulman's method of cosurfactant titration of the oil/water interface (or, the dilution method).¹¹⁻¹³ Wang et.al.¹⁴ employed the dilution method for the first time to investigate the physicochemical parameters of [bmim][BF₄]/ Brij-35/1-butanol/toluene-based IL/O microemulsion.

In view of these studies, we contemplate to undertake the study of the formation of a water-in-oil (w/o) nonionic surfactant microemulsion, water/Tween-20/Pn/Cy with special reference to its characteristics features of the oil/water interface under different physicochemical conditions in absence or presence of IL, 1-butyl-3-propylbenzimidazolium bromide ([bpBzim]Br) as an additive. Thermodynamics of formation, microstructure, transport properties and dynamics of H-bonding of this system, water-IL/Tween-20/Pn/Cy w/o microemulsion, have been investigated by employing the dilution method, conductivity, DLS, FTIR. Further, an in-depth characterization of the microenvironment of the system in absence or presence of IL has been made by performing a model C-C cross coupling reaction (Heck reaction). The famed name reaction, Heck, is one of the fine studied responses in the meadow of organic synthesis.¹⁵ Report on study of Heck reaction in IL-microemulsion is available in literature.¹⁶ The yield of Heck coupled product depends on the type of surfactant used as well as the nature of confinement of these systems.^{9,16} An attempt has been made to monitor the effective physicochemical changes in microemulsion, leading to microenvironmental changes during the course of reaction. Finally, a correlation of the results in terms of the evaluated physicochemical parameters vis-à-vis microstructural features during Heck reaction has been drawn and provides a new horizon to understand the most plausible location/site as well as to determine the actual reaction parameter required for effective reaction in the studied micro-heterogeneous system. To the best of our knowledge, such a comprehensive study on w/o microemulsion in presence of benzimidazole- based IL has not been reported earlier.

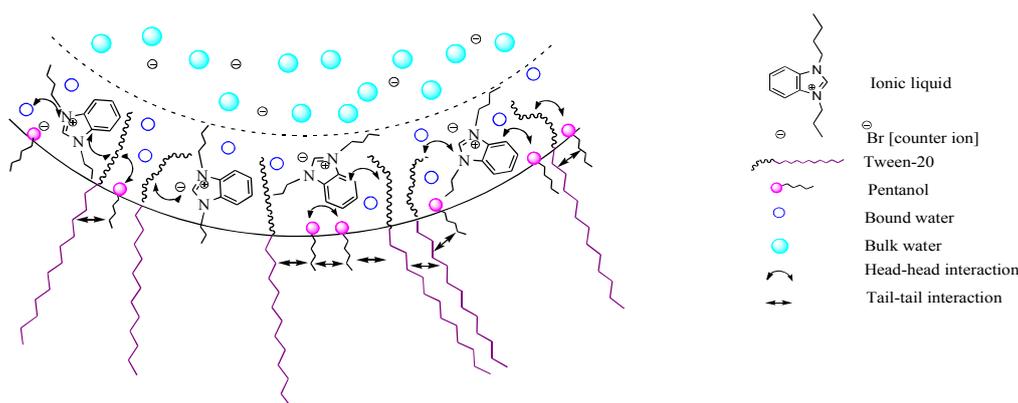
II.B. Results and discussions

II.B.1. The Schulman's cosurfactant titration at the oil/water interface (The dilution method)

In order to underline the influence of IL and its content on the interfacial composition of Tween-20-based w/o microemulsion stabilized in Pn and Cy under various physicochemical conditions (i.e., at different temperatures and fixed molar ratio of water to surfactant, ω), n_a^i/n_s values [i.e. compositional variations of amphiphiles (both Tween-20 and Pn) at the interface] are plotted against [IL] ($0.0 \rightarrow 0.20 \text{ mol dm}^{-3}$) and respective plots are depicted in Figure-II.1 (inset A). The mathematical evaluation and the results of interfacial composition have been discussed elaborately indicating all possible interactions among the constituents in the microenvironment of this compartmentalized system (depicted in Scheme-II.1) and are presented in Appendix A (Sec. A and B) and Figure-A.S1.

II.B.1.1. Thermodynamics of transfer of Pn (oil \rightarrow interface) (in absence or presence of IL)

In this section, analysis of the transfer of Pn from oil phase to the interface ($\text{Pn}_{\text{oil}} \rightarrow \text{Pn}_{\text{interface}}$) of water (IL)/Tween-20/Pn/Cy microemulsion system by employing the dilution method is presented from thermodynamic point of view, which is rarely reported.^{14,17} The details of the estimation have been given in Appendix A (Sec. A, Eqs. S1-S16).



Scheme-II.1. Schematic Representation showing possible interactions in microenvironment

II.B.1.2. Effect of [IL] and temperature on $\Delta G_{o \rightarrow i}^0$

$\Delta G_{o \rightarrow i}^0$ values are negative in absence or presence of IL, and hence, spontaneous formation of w/o microemulsions is suggested. Both similar and dissimilar values in this energetic parameter at comparable physicochemical conditions are reported.^{14,17-19} Both K_d and $\Delta G_{o \rightarrow i}^0$ show maxima in presence of 0.05 mol dm⁻³ of IL at each temperature (Figure-II.1 and inset B).

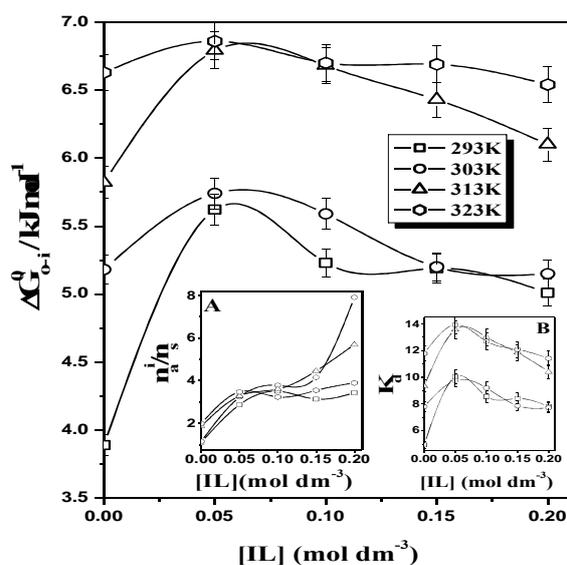


Figure-II.1. Plots of $\Delta G_{o \rightarrow i}^0$ as a function of [IL] for water/Tween-20/Pn/Cy microemulsion system at ω (= 30) with varying temperatures. Inset A: Plots of interfacial composition (n_a^i/n_s) as a function of [IL] for water/Tween-20/ Pn/Cy microemulsion system at ω (= 30) with varying temperatures. Inset B : Same plots for K_d

Though, the variations of K_d and $\Delta G_{o \rightarrow i}^0$ values between 0.05 mol dm⁻³ and 0.10 mol dm⁻³ may be small at higher temperatures (viz. 313 and 323 K), but both the values are still higher at 0.05 mol dm⁻³ compare to other concentrations of IL (Figure-II.1 and inset B, Table-A.S1) . This indicates that the transfer process of Pn from the oil phase to the interface is much favoured at 0.05 mol dm⁻³ of IL irrespective of temperature. Further, a low line secondary maximum in K_d or $\Delta G_{o \rightarrow i}^0$ values appears at 0.15 mol dm⁻³ of [IL] (Figure-II.1, including the error bars). A plausible explanation for this type of trend can be explained in view of the physicochemical (molecular) interactions

among the constituents involved in the transfer process of Pn (oil→interface).^{11,12,14,17} In this system, the interaction between nonionic surfactant (Tween-20) and alkanol (Pn) is of dipole-dipole or dipole-induced dipole or London dispersion type, because of the presence of uncharged or neutral hydroxyl groups (Pn) and POE chains (Tween-20), whereas, the interaction between [bpBzim]⁺ and Pn is possibly of ion-dipole type. Ion-dipole interaction is much stronger compared to dipole-dipole or dipole-induced dipole or London dispersion interactions.²⁰ Therefore, the association between Pn and Tween-20 becomes more favorable in presence of 0.05 mol dm⁻³ of [bpBzim][Br]. Consequently, the transfer process of Pn from the oil phase to the interface is much favoured at 0.05 mol dm⁻³ of [IL] irrespective of temperature. But at higher IL concentration (i.e., 0.10→0.20 mol dm⁻³), the addition of IL diminishes the interfacial area per polar head group of surfactant molecules by screening the steric repulsion between nonionic surfactants (herein, Tween-20), and this makes the interfacial layer more rigid and favors a greater curvature of the interface.^{14,17} As a result, the attractive interaction among the droplets decreases and subsequently, the transfer process of Pn (oil→interface) is also diminished. However, the appearance of a low line secondary maximum at [IL] equals to 0.15 mol dm⁻³ is likely to be originated from the non-ideality of the systems. Usually, different types of forces (viz. London dispersion forces, dipole-dipole forces, dipole-dipole induced forces etc.) act on real mixtures, making it difficult to predict the properties of such solutions. Non-ideal mixtures are identified by determining the strength and types (specifics) of the intermolecular forces (viz. intermolecular forces between the similar molecules and intermolecular forces between the dissimilar molecules) in that particular system.²¹ However, non-ideal behavior is not uncommon in multicomponent derived microemulsion systems.²²⁻

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Further, it has been observed that K_d or $\Delta G^0_{o \rightarrow i}$ gradually increases with the increase in temperature (Figure-II.1 and inset B) and this suggests that the transfer of Pn (oil→interface) is much favored at higher temperatures. The higher absolute values of $\Delta G^0_{o \rightarrow i}$ at higher temperatures indicate a comparatively stronger interaction between Tween-20 and Pn at the interface, which corroborates well with the interfacial composition (Figure-II.1, inset A). This trend corroborates well with the reports of Zhang et al.¹⁸ and Wang et al.¹⁴ for [bmim][BF₄]/CTAB/alkanol/toluene and [bmim][BF₄]/Brij-35/1-butanol/toluene w/o microemulsion systems, respectively. However, the overall scenario indicates towards formation of a more spontaneous w/o

microemulsion accompanied with 0.05 mol dm^{-3} of IL, as evident from K_d and $\Delta G^0_{o \rightarrow i}$ values at each temperature (Table-A.S1, Figure-II.1 and inset B).

Further, a significant difference in K_d or $\Delta G^0_{o \rightarrow i}$ values has been observed for 303K and 313K (Figure-II.1 and inset B). It may be due to the influence of temperature on the constituents (in particular to Tween-20 consisting of POE chains as polar head groups and IL as organic electrolyte, [bpBzim][Br]) and hence, two different mechanisms might be operative for the formation of microemulsions at lower temperature region (i.e., 293 and 303 K) as well as at higher temperature region (i.e., 313 and 323 K). The ordered structure formed from IL molecules around hydrophilic moiety (POE chains) of Tween-20, produced by ionic interaction instead of hydrogen bonding interaction, is considered to be an origin for the surfactant self-assembly²⁷ as represented in Scheme-II.1. It is obvious that Tween-20 molecules assemble to form reverse micelles in order to avoid the entropy loss due to ordered arrangement of IL molecules at low temperature region. On the other hand, at higher temperature region, the IL molecules participating in the ionic interaction with POE chains of Tween-20 may be less ordered (more disordered) due to their enhanced dehydration.^{27,28} Hence, it is imperative that the enthalpy loss for the release of solvated IL molecules would be overcome by the enthalpy gain for the contact of POE chains at higher temperature region. The reversal of entropy and enthalpy parameters might be occurred during transition from low temperature region (293 and 303 K) to high temperature region (313 and 323 K). This is why, a significant difference in $\Delta G^0_{o \rightarrow i}$ values has been observed for two sets of temperatures.

II.B.1.3. Effect of [IL] and temperature on $\Delta H^0_{o \rightarrow i}$ and $\Delta S^0_{o \rightarrow i}$

Due to nonlinear dependence of $(\Delta G^0_{o \rightarrow i}/T)$ on $(1/T)$ (the result fits a two degree polynomial equation (Figure-A.S2)), at each composition of surfactant (at $[\text{IL}] = 0.0 \rightarrow 0.20 \text{ mol dm}^{-3}$), four values of the standard enthalpy change, $\Delta H^0_{o \rightarrow i}$ and the standard entropy change ($\Delta S^0_{o \rightarrow i}$) of the Pn transfer process (oil \rightarrow interface) at four different temperatures have been evaluated according to Eqs. (S12) and (S15) and are presented Table-A.S1 and Figure-II.2. For pure Tween-20 system (i.e., in absence of IL), the overall transfer process is exothermic at all experimental temperatures with negative entropy change (more ordered) in Cy (Table-A.S1 and Figure-II.2). So, Pn causes release of heat during the transfer process. Consequently, the negative entropy

change may be due to more organization of the interface and its surroundings. Therefore, it may be argued that in the presence of Pn and Tween-20, the interface to some extent becomes ordered. Similar observation was also reported by Bardhan et al.¹² for water/Brij-35/Pn/IPM microemulsion systems. However, De et al.²⁹ and Kundu et al.¹¹ reported an opposite behavior (i.e., positive enthalpy and entropy changes) for Tween-20/Bu or Pn/Hp/water and Brij-58 or Brij-78/Pn/Hp or Dc/water microemulsion systems, respectively. Hence, difference in trends of $\Delta H^0_{o \rightarrow i}$ and $\Delta S^0_{o \rightarrow i}$ may be attributed to the differences in hydrophobic configuration and/or size of the polar head group of the nonionic surfactants vis-à-vis type of oil.

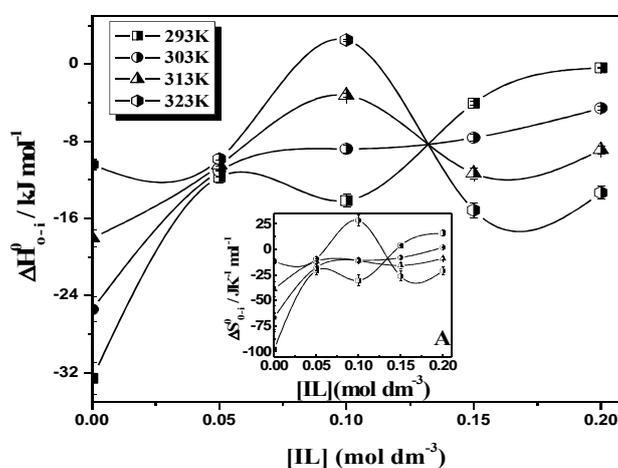


Figure-II.2. Plots of $\Delta H^0_{o \rightarrow i}$ as a function of $[IL]$ for water/Tween-20/Pn/Cy microemulsion system at $\omega (= 30)$ with varying temperatures. Inset A: Same plot for $\Delta S^0_{o \rightarrow i}$.

Further, it can be observed from Table-A.S1 and Figure-II.2 that, the overall transfer process is exothermic at all the experimental temperatures with negative entropy change (order) in Tween-20/Pn system in the presence of IL ($[IL] = 0.05 \rightarrow 0.20$ mol dm^{-3}). Such a negative enthalpy or entropy change was observed by Mukherjee et al.¹⁹ for triisobutyl (methyl) phosphoniumtosylate/IPM/trihexyl (tetradecyl) phosphoniumbis 2,4,4-(trimethylpentyl) phosphinate : isopropanol or butanol systems. It is quite likely that the negative contribution towards $\Delta H^0_{o \rightarrow i}$ is identified with the transfer of the surfactant tail from water to liquid hydrocarbon state in the interfacial layer and for restoring the hydrogen bonding structure of the water around the surfactant head group.³⁰ Further, it can be argued for negative entropy, $-\Delta S^0_{o \rightarrow i}$ as

follows: During formation of nano-droplets in w/o microemulsions, the penetration of water into the oil (Cy)/Tween-20/Pn (amphiphiles) continuum forming cavity and subsequently, organization of the amphiphiles at the droplet interface results in an increase in overall order with negative entropy of the multicomponent system.³¹ Further, $-\Delta S_{o \rightarrow i}^0$ suggests that both entropy as well as enthalpy are involved in the transfer process.³² Consequently, IL dependent microemulsion compositions with larger $-\Delta H_{o \rightarrow i}^0$ values (more exothermic) results in larger $-\Delta S_{o \rightarrow i}^0$ values (ordered) i.e., greater interaction between the constituents at the interface, leading to more ordered interface due to transfer of Pn (oil \rightarrow interface).³³

The variation of $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$ values with temperatures from Table S1 and Figure 2 indicates that the presence of IL influences the degree of exothermicity with orderliness of the transfer process (oil \rightarrow interface). Interestingly, the transfer process approaches towards less exothermic as well as less ordered with increase in temperature up to 0.10 mol dm⁻³ of IL, and thereafter, the degree of exothermicity and orderliness reverses in the vicinity of 0.136 mol dm⁻³. Subsequently, the process is more exothermic as well as more ordered with increase in temperature at [IL] equals to 0.15 and 0.20 mol dm⁻³ (Figure-II.2). This trend can be explained in the following way: The addition of IL to Tween-20 based microemulsions might have at least two effects. First, the partial reduction of the hydration of water around the polar head group of the non-associated surfactant molecule occurs with increase in temperature. As a result, a decrease in the energy needed for breaking down of this structure during the process of microemulsion formation and also to a decrease in the exothermic contribution i.e., decrease in the value of $\Delta H_{o \rightarrow i}^0$. The second consequence of the presence of higher IL concentrations appears to be related to the influence of counter ion binding on the structure of the microemulsions.³⁴ The reduction in disorder may be attributed to the effect of the liberation of surfactant hydration water molecules on microemulsification to be less important than the loss of freedom when monomers join each other to form reverse micelles.³⁵

Also, $\Delta S_{o \rightarrow i}^0$ values have been found to increase with temperatures up to 0.10 mol dm⁻³ of IL and thereafter, reversal of trend has been observed in the vicinity of 0.136 mol dm⁻³, as in case of $\Delta H_{o \rightarrow i}^0$ (Figure-II.2, inset A). This result is indeed interesting. It is quite likely that molecular interactions, arising from the tendency of the water molecules to regain their normal tetrahedral structure, and the attractive dispersion forces between hydrocarbon chains act cooperatively to remove the hydrocarbon

chains from the water cages, leading to the disorder of water and subsequently, increase in the entropy values.^{36,37} On the other hand, the decrease in entropy may be due to the breakdown of the normal hydrogen-bonded structure of water accompanied by the formation of water with different structures.^{36,37} The presence of higher concentration of hydrophilic species (herein, IL) promotes an ordering of water molecules in the vicinity of the hydrophilic head group of Tween.³⁶ However, no significant change in both thermodynamic parameters (i.e., $\Delta H^0_{o \rightarrow i}$ and $\Delta S^0_{o \rightarrow i}$) with temperature has been observed at certain IL concentration (i.e., at 0.05 and ~ 0.136 mol dm⁻³), leading to the formation of isoenthalpic and isoentropic microemulsion systems (Figure-II.2 and inset A). Similar observation was also reported earlier for mixed surfactant microemulsion systems comprising of cationic or anionic-nonionic.^{11,12,38}

II.B.1.4. Effect of [IL] on $(\Delta C^0_p)_{o \rightarrow i}$

Since $\Delta H^0_{o \rightarrow i}$ has become a function of temperature, the $(\Delta C^0_p)_{o \rightarrow i}$ values have also been evaluated for these systems (in absence or presence of IL) from the slope (= $\delta \Delta H^0_{o \rightarrow i} / \delta T$) of the plots of $\Delta H^0_{o \rightarrow i}$ vs. T (not illustrated) according to Eq. (S11).¹² All these values are presented in Table-A.S1. It can be observed from Table-A.S1 that, at $[IL] = 0.0 \rightarrow 0.10$ mol dm⁻³, $(\Delta C^0_p)_{o \rightarrow i} > 0$; whereas $(\Delta C^0_p)_{o \rightarrow i} < 0$ at $[IL] = 0.15$ and 0.20 mol dm⁻³. Negative values are usually observed for the self-association of amphiphiles and can be attributed to the removal of large areas of non-polar surface from contact with water on the formation of reverse micelles.³⁹ However, $(\Delta C^0_p)_{o \rightarrow i}$ tends to almost zero at $[IL] = 0.05$ and ~ 0.136 mol dm⁻³, which corroborates well with profile of $\Delta H^0_{o \rightarrow i}$ vs. $[IL]$ at different temperatures (Figure-II.2). This indicates the formation of temperature-insensitive microemulsions at $[IL]$ of 0.05 and ~ 0.136 mol dm⁻³. Similar observation [i.e., reversal of trend of $(\Delta C^0_p)_{o \rightarrow i}$ with concentration of methanol] was reported earlier by Perez-Casas et al.⁴⁰ for water/AOT/methanol/decane reverse micelles. Kunz et al.⁴¹ reported that formation of temperature-insensitive microemulsions are important for some practical purposes (e.g. for formulation of product).

II.B.2. Electrical Conductivity and Dynamic light scattering measurement

The electrical conductivity, size and size distribution of w/o microemulsion systems have been measured by conductometric and DLS, respectively for water/Tween-

20/Pn/Cy microemulsion system with the variation of [IL] ($= 0.0 \text{ mol dm}^{-3} \rightarrow 0.20 \text{ mol dm}^{-3}$) at a constant ω ($= 30$) and fixed temperature (303K). The results are depicted in Figure-A.S3. It can be observed from Figure-A.S3 that the electrical conductivity gradually increases with increase in [IL] in microemulsion. This trend may be attributed to high conducting nature of IL, as the blank experiment (similar concentration of IL in water) shows the identical trend with the variation of [IL] (Figure-A.S3, inset A). It can be observed that the conductance values in water-IL media range from 0.0016 to 8.2 mS cm^{-1} , whereas low values ($17.84 - 231.0 \text{ } \mu\text{S cm}^{-1}$) are obtained for IL in microemulsions at similar concentrations. The low value in microemulsion system can be justified as follows. In the present system, electrostatic interaction between imidazolium cation of IL and electronegative oxygen atoms of POE units of Tween-20 is quite likely to occur along with water-IL hydrogen bonding interaction (Scheme-II.1). However, the later part, i.e., water-IL hydrogen bonding interaction is present in bulk IL or water-IL media. The electrostatic interaction makes the palisade layer comprising Tween-20/Pn/IL more rigid⁴² and subsequently, decreases the conductance values. Hence, it can be concluded that the physicochemical properties of water molecules localized in the interior of the microemulsions are different from those of water-IL media.

Further, hydrodynamic diameter (D_h) of microemulsion droplet decreases from 3.90 nm to 2.31 nm with increase in [IL] ($0.0 \text{ mol dm}^{-3} \rightarrow 0.20 \text{ mol dm}^{-3}$) wherein about 3 fold increase of the droplet count rate has been observed under the prevailing condition (Figure-A.S3, inset B and C). The droplet count rate is directly proportional to the droplet number of the microemulsion system. Hence, the addition of IL shrinks the droplet size and thereby increases in droplet number. It was reported earlier that the curvature of the oil/water interface of a microemulsion can be adjusted by adding IL (a class of organic electrolyte)⁴³ or NaCl (inorganic electrolyte)⁴⁴ at different concentrations. The addition of electrolyte gives rise to a decrease in the repulsive interaction between the head groups of the nonionic surfactant, Tween-20, which further increases the packing parameter of surfactant molecules ($P = v/al$, where 'v' and 'l' are the volume and the length of hydrophobic chain, respectively and 'a' the area of polar head group of the surfactant) and decreases the droplet diameter. In addition, the presence of IL within the water pool weakens the hydrogen-bonding between water and POE chains of Tween-20 and thereby reduces hydration of POE chains, which results in the formation of smaller droplets due to decrease in swelling

of POE chains⁴⁵ In other words, when IL is solubilized in microemulsions, it decreases the average area occupied by each head group of surfactant (Tween-20), and subsequently, enhances the packing density and rigidity of the surfactant monolayer of the droplet, which may reduce the size of the droplets.⁴⁶ Typical values of polydispersity index (PDI) obtained here are in the range between 0.1–0.2, which indicates the monodispersity of the sample.^{12,13,38}

II.B.3. FTIR spectroscopy

Reports on the properties of the encapsulated water in a range of size and type of w/o microemulsions by studying the states of water organization using FT-IR measurement, are available in literature.^{13,37,41,47} The characteristics of the water molecules in confined environment of w/o microemulsion depend strongly on water content or the droplet size and the nature of the interface as well.^{47,48} As discussed in previous section that the values of hydrodynamic diameter of droplet (D_h) varies from 3.90 nm to 2.31 nm as a function of [IL] ($0.0 \text{ mol dm}^{-3} \rightarrow 0.20 \text{ mol dm}^{-3}$) at fixed ω (= 30) and temperature (= 303K) from DLS measurements. Further, the values of hydrodynamic diameter of droplet (D_h) are well comparable with microemulsion systems, wherein existence of different types/states of water species reported in confined environment using FTIR measurement.^{47,49} However, the influence of Pn (cosurfactant) on the O-H stretching vibration of the confined water needs to be underlined for the present system. To eliminate the effect of Pn on the O-H vibration of water, the spectra of Pn at same concentration is subtracted from the spectral intensity of O-H stretching band and the differential spectra have been analyzed. Different types of hydrogen bonded water molecules exist in reverse micelles which can broadly be classified into two major classes, namely, bound and bulk-like water molecules.^{13,37,41,50} The differential spectra obtained in the present study have been deconvoluted into two peaks at ~ 3500 and $\sim 3300 \text{ cm}^{-1}$, corresponding to the O-H stretching frequency of the bound and bulk-like water molecules, respectively (Figure-A.S4) and a representative result of deconvolution (relative abundance of different water species) is depicted in Figure-A.S5 . It reveals from Figure-A.S5 that the bound water proportion is the least in absence of IL. Whereas, the proportion of bound water increases with increase in [IL] in microemulsion. These results indicate a significant role of IL in determining the proportion of different water species (bound and bulk) in the confined environment of w/o microemulsion. However, this result is not very

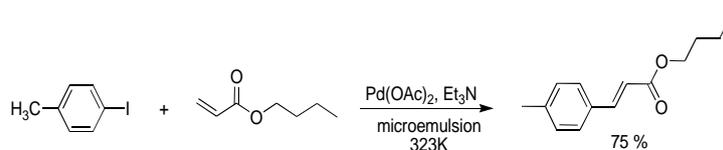
surprising if one considers possibility of interaction between IL and water molecules. With the increase in IL content, more bulk water molecules hydrate IL molecules and subsequently, increase the proportion of bound water molecules in microemulsion core.⁴² Further, it is evident from DLS measurements that the droplet size decreases with the increase in IL content. It is reported that as the droplet size decreases, the bound water proportion increases in the microemulsion and vice versa.^{47,50} Hence, DLS and FTIR results corroborate each other.

II.C. Study of C-C cross coupling (Heck) reaction in microemulsion

A model Heck reaction (Scheme-II.2) has been performed in the well characterized system (presented herein), to explore the properties of IL (additive) within the restricted geometry provided by microemulsions and the nature of interaction of the IL with the constituents of the interface and the subsequent changes of microenvironment during the reaction and the detection of most probable reaction site and yield of the Heck reaction. The progress of reaction was monitored by employing various instrumental techniques such as, conductance, FTIR, UV-Visible spectroscopy.

II.C.1. Standardization of Heck coupling reaction

The reaction has been performed in presence of different bases (inorganic and organic) to optimize the reaction at 323 K. It has been found that water soluble bases (potassium carbonate and tetramethyl ethelene diamine) produce almost comparable yield (30 % and 40%, respectively) of the desired product, whereas highest yield (75%) has been achieved using sparingly water soluble base, viz, triethyl amine (TEA) (Table-A.S2). Hence, the subsequent study on the Heck reaction in microemulsion media at varying [IL] ($0.0 \text{ mol dm}^{-3} \rightarrow 0.2 \text{ mol dm}^{-3}$) was performed in the presence of TEA as base and the standard mechanism of Heck coupling reaction is presented in Scheme-A.S1.



Scheme-II.2. Study of Heck reaction in microemulsion

In order to underline the effect of encapsulation or compartmentalization (provides with microemulsion), the Heck reaction has also been performed in bulk IL (water-IL media) containing [IL] similar to that of available in microemulsions and the results are presented in Table-II.1. The study showed (Table-II.1) that the yield of the desired product in water-IL media was very low in comparison with the microemulsion systems. The strong effect of confined environment of microemulsion, therefore, seems to play a vital role in studying this reaction.⁹ However, yields of the final product in microemulsion is not a direct function of IL concentration (Table-II.1). The reaction has also been critically monitored in the case of two different temperature-insensitive formulations at [IL] = 0.05 and 0.136 mol dm⁻³ (discussed in previous section, “Effect of [IL] on (ΔC_p^0)_{o→i}”, Figure-II.2). The yield of the final product has been found to be highest at lower range of [IL] (i.e., at 0.05 mol dm⁻³), at which highest spontaneity of Pn transfer process and temperature-insensitivity were exhibited (Figure-II.1 and 2). But at higher range of [IL] (i.e., at ~0.136 mol dm⁻³), the yield is least, where another temperature-insensitive formulation is obtained. Hence, it can be suggested that temperature insensitive composition is not the sole factor, rather than the highest spontaneity of Pn transfer (oil→interface) leads to highest yield of the product.

Table-II.1. Heck coupling reaction in both water and in microemulsion media (water/Tween-20/Pn/Cy) as a function of [IL] in presence of TEA at a fixed ω (= 30) and 323K.

Ionic liquid mol dm ⁻³)	Yield (%) in water-IL	Yield (%) in microemulsion
0.00	07.0	17
0.05	04.5	75
0.10	06.8	25
0.136	08.3	13
0.15	10.0	59
0.20	12.0	22

II.C.2. Conductance Study

Electrical conductance of w/o microemulsion system has been measured at regular interval during the course of reaction both in absence or presence of IL and the results are displayed in Figure-II.3. In both cases the trend of conductance curve is almost identical with smaller values in absence of IL. In absence of IL, the addition of palladium acetate [Pd(OAc)₂] results in a small increase in conductance due to the presence of charge carrier (viz. Pd(OAc)₂) and followed by decrease in conductivity, which may be due to the formation of the aqua palladium complex in the mixture.⁵¹

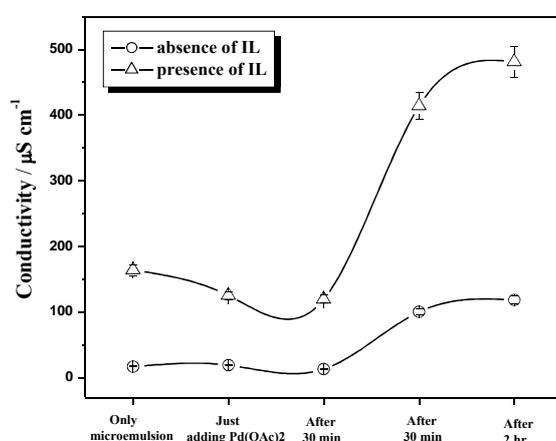


Figure-II.3. The conductivity of microemulsion in absence and presence of IL (= 0.05 mol dm⁻³) at regular interval during Heck reaction at 323K.

On the contrary, in presence of IL, the addition of Pd(OAc)₂ decreases the conductivity indicating the formation of palladium complex (Pd-NHC) with IL, the precursor of N-heterocyclic carbene (NHC).⁵² However, the process of Pd-NHC complexation is much faster in comparison with the palladium-aqua complexation which subsides the conducting properties of Pd(OAc)₂. However, a sharp increase in conductivity has been observed in both cases after addition of reagents (4-iodotoluene, triethylamine and butylacrylate) implying the progress of Heck reaction.

II.C.3. FTIR measurement

The observation FTIR studies during reaction (Figure-II.4) are very much supportive with the conductivity experiment. Addition of palladium acetate reduces the population of bound water indicates the formation of Pd-NHC complex which decreases the interaction with water molecules and the optimal decrease of bound

water implying the end point of complexation. Thereafter, a regular enhancement in population of bound water molecules have been observed with the addition of reagents (4-iodotoluene, triethylamine and butylacrylate) indicating the formation of the Heck coupled and the other possible side products (such as, halogen acid and corresponding amine salt). This trend is continued until the completion of reaction.

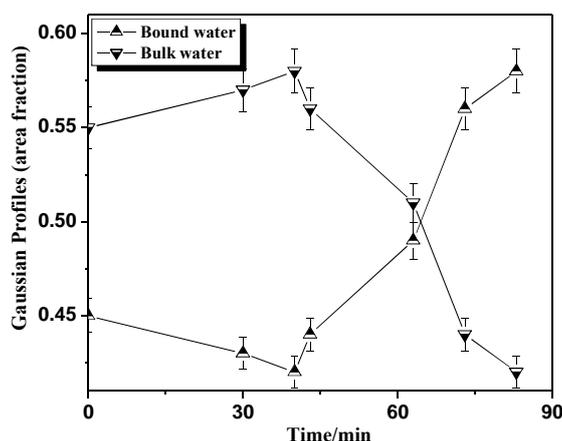


Figure-II.4. The variation of Gaussian profiles (area fraction) of the normalized spectra of different water species (bound water, bulk water) of IL containing (0.05 mol dm^{-3}) w/o microemulsion system with the reaction time.

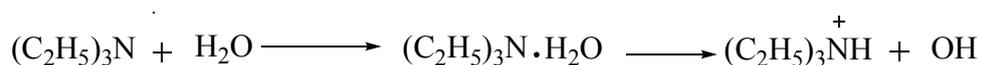
II.C.4. UV-Visible spectroscopy

Comparing the UV-Visible spectra of individual components and the spectra recorded during the course of reaction at regular interval of time, a single absorption peak at 271 nm has been observed after 10 minutes of the reaction (Figure-A.S6). The λ_{max} of the product is reported to be 274 nm.⁵³ The little decrease in λ_{max} of the product from that of the literature value may be due to H-bonding between ester group of the product and medium of the reaction. The absorption became more intense after 40 minutes of reaction. The increase in intensity of the spectral band increases with the progress of reaction indicating increase in concentration of the product with the progress of time.

II.D. Comprehension of the Results

The Heck reaction was carried out in w/o microemulsion with varying amount of IL ($0.0 \rightarrow 0.20 \text{ mol dm}^{-3}$) and the corresponding results are presented in Table-II.1. The optimal concentration of IL required for effective Heck reaction is 0.05 mol dm^{-3} in the present system. Further, it is evident from the dilution method that the spontaneity of formation with maximization in stability of the microemulsion system can be achieved with 0.05 mol dm^{-3} of IL (Table-A.S1 and Figure-II.1). It is obvious that IL with 0.05 mol dm^{-3} facilitates the Pn transfer process (oil \rightarrow interface) due to favorable organization of the constituents at the interface, and thereby, results in achieving more stability, which leads to better performance of the Heck reaction in microemulsion medium. The decrease in the conductance with the addition of palladium acetate [$\text{Pd}(\text{OAc})_2$] indicates the formation of palladium complex (Pd-NHC) with IL (Figure-II.3). FTIR study also supported the formation of Pd-NHC complex which reduces the number of IL molecules inside the water pool and thereby decreases the bound water population (Figure-II.4). The ratio between bound and bulk water populations indicates that no interaction persists between water and newly formed Pd-NHC complex. However, it can be concluded that the availability of Pd-NHC complex inside the water pool is least. In bulk IL i.e, water-IL media, the possibility of Pd-NHC complex formation is negligible, because of the instability of N-heterocyclic carbenes in water, and subsequently, reducing the rate of the forward reaction. It can be inferred from the low yield of the desired product in water-IL media indicates that formation of stable Pd-NHC complex during the performance of Heck reaction in compartmentalized systems plays a pivotal role, which leads to higher yields compare to corresponding bulk [IL] (Table-II.1). In addition, use of water soluble bases (viz., K_2CO_3 and TMEDA) which are quite likely to be located in the water pool of microemulsion, results in low yield of the desire product. Whereas TEA preferentially soluble in Pn, as reveals from solubility analysis, ends up with best results (75% yield of the product) (entry 2, Table-A.S2). A plausible explanation emerges from the increase in population of Pn at the interfacial region vis-à-vis its interaction with TEA, which rationalizes the availability of all constituents involved in this reaction. It can be inferred that apart from the molecular interactions of the constituents involved in formation of microemulsion as template (discussed in Appendix A (Sec. B)), two types of interactions are likely to occur at the oil/water interface or in the palisade

layer of the microemulsion at one hand. On the other hand, bound water in the confined environment. For example, (i) dipole-dipole interaction between Pn and TEA, which enhances the availability of TEA at the interfacial region with increasing population of Pn at the interface, and (ii) water binds to TEA to form a surrounding OH⁻ base in the following fashion [Eq.(1)].⁵⁴



Hence, small amounts of the OH⁻ are likely to be entered the palisade layer of microemulsion and subsequently, basic environment develops in the peripheral region of the interface, which is essentially required for Heck reaction (Scheme-II.2 and Scheme-A.S1) and a good yield of the product is achieved. However, the correlation between [IL] and reaction yield is not straightforward. After getting the utmost yield of 75% at [IL] (= 0.05 mol dm⁻³), the reaction yield decreases to 25% at [IL] (= 0.10 mol dm⁻³) and shows further increase (59%) at [IL] (= 0.15 mol dm⁻³). As stated earlier, a low line secondary maxima in K_d and ΔG⁰_{o->i} values appear at 0.15 mol dm⁻³ of [IL] after achieving the highest values at 0.05 mol dm⁻³ of [IL] (Figure-II.1) and the second highest yield of Heck product has been found at the same IL concentration (=0.15 mol dm⁻³) (Table-II.1). K_d and ΔG⁰_{o->i} values actually signify the spontaneity of Pn transfer process from bulk to interface. Hence, it is probable that accumulation of Pn at the interface governs the availability of TEA and OH⁻ in the vicinity of the interface as well as tunes the interfacial characteristics with different degrees by interaction with IL (of different contents) which influences the yield of desired Heck product. Gayet et al.⁹ reported that the IL content affects the yields of Matsuda-Heck reaction in reverse microemulsions. All these observations together sensing that the most plausible location or site of the Heck reaction in the studied microheterogeneous system is the interfacial region. However, the present report is not comprehensive from the view point of the direct correlation between the content of IL and the reaction yield (herein, the Heck couple product). However, this is trivial as because a maximum in both K_d and ΔG⁰_{o->i} values was obtained at 0.05 mol dm⁻³ and we concern on the maximum values of physicochemical parameters (K_d and ΔG⁰_{o->i}) with that of highest yield in Heck product at same concentration of [IL]. Several factors, such as, changes in molecular interactions between the constituents at the interface,

microstructure, polarity due to the presence of phenyl group in IL with the variation in [IL], might be responsible for overall yield of the final product. Further studies in this direction by employing SANS, ¹H NMR along with two-dimensional rotating frame nuclear Overhauser effect (NOE) experiments (ROESY) are warranted.

II.E. Experimental

II.E.1. Materials and methods

Polyoxyethylenesorbitanmonolaurate (Tween-20, $\geq 99\%$), palladium acetate [Pd(OAc)₂, $\geq 99.98\%$] and 4-iodo-toluene (CH₃C₆H₄I, $\geq 99\%$) were purchased from Sigma Aldrich, USA. 1-Pentanol (Pn, $\geq 99\%$) and cyclohexane (Cy, $\geq 98\%$) were the products of Fluka, Switzerland. Triethyl amine (TEA, $\geq 99.5\%$) and n-butyl acrylate were purchased from Merck, Germany. All these chemicals were used without further purification. The IL, 1-butyl-3-propylbenzimidazolium bromide ([bpBzim]Br) was synthesized in accordance our reported method.⁴ Doubly distilled water of conductivity less than 3 μ S cm⁻¹ was used in the experiments.

The dilution experiment was performed to investigate the interfacial composition of Tween-20 based microemulsion in different physicochemical conditions, as described earlier^{11-14,17} using spectrophotometric technique⁵⁵ to measure the change in sample turbidity produced by Pn addition (Figure-A.S7). The detail of the spectrophotometric technique was provided in our previous report.¹² Basics of the dilution method and thermodynamics of the transfer of cosurfactant from oil to the interface has been dealt in Appendix A (Sec. A).

Conductivity measurements were performed using Mettler Toledo (Switzerland) Conductivity Bridge. The instrument was calibrated with standard KCl solution. The uncertainty in conductance measurement was within $\pm 1\%$.

DLS measurements were carried out using Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd, U.K.). He-Ne laser of 632.8 nm wavelength was used and the measurements were made at a scattering angle of 90⁰. Details of the measurement have been provided in our previous report.^{12,13}

FTIR absorption spectra were recorded in the range of 400-4000 cm⁻¹ with a Shimadzu 83000 spectrometer (Japan) using a CaF₂-IR crystal window (Sigma-Aldrich) equipped with Press lock holder with 100 number scans and spectral resolution of 4 cm⁻¹. Deconvolution of spectra has been made using Origin software.

3 ml microemulsion (water/Tween-20/Pn/Cy) containing IL ($0-0.20 \text{ mol dm}^{-3}$) at ω (= 30) and 4.48 mg (0.02 mmol, 4 mol %) Pd(OAc)₂ were taken in a 25 ml round bottom flask and the mixture was placed in a preheated oil bath at 323 K for 30 minutes with constant stirring. Thereafter, 109 mg (0.5 mmol) of 4-iodotoluene, 76.8 mg (0.6 mmol) of n-butylacrylate and 101.12 mg (1 mmol) of triethylamine (TEA) were introduced into it and the resulting mixture was heated at 323K for 45 minutes. The resulting multicomponent solution shows no instability towards temperature or otherwise. The progress of the reaction was monitored by silica gel thin layer chromatography (TLC). In addition, conductance, FTIR, and UV-Vis spectroscopy were employed to characterize the microenvironment of microemulsion with the progress of reaction. Yield of Heck coupled product was determined by HPLC. Finally, the product was characterized by ¹H-NMR and ¹³C-NMR (Appendix A, Sec. 2). Similar experiment was performed in water-IL media (bulk IL) at the corresponding [IL] as used in microemulsion system.

II.F. Summary

Present study is focused on the characterization of a quaternary water-in-oil microemulsions comprising of Tween-20, Pn and Cy in absence and presence of IL, 1-butyl-3-propylbenzimidazolium bromide ([bpBzim]Br) with a detailed description of the interfacial composition as a function of transfer of Pn from bulk oil phase to the interface on the system composition. Synergism in distribution constant (K_d) and $-\Delta G^0_{o \rightarrow i}$ have been observed in the vicinity of 0.05 mol dm^{-3} of IL at each temperature (293, 303, 313 and 323K). This indicates that the transfer process of Pn from oil phase to the interface is more favoured at 0.05 mol dm^{-3} of IL irrespective of temperature. The standard enthalpy change ($\Delta H^0_{o \rightarrow i}$) and the standard entropy change ($\Delta S^0_{o \rightarrow i}$) of the transfer process have been found to be negative [i.e., exothermic process with less disordered (organized)] in absence or presence of IL at all the experimental temperatures. Further, temperature-insensitive microemulsion has been formed at [IL] of 0.05 and $\sim 0.136 \text{ mol dm}^{-3}$. FTIR study reveals an increase in the proportion of bound water molecules with increasing [IL]. This shows the significant role of IL in determining the states of different water species (bound and bulk) in the confined environment of w/o microemulsion.

Additionally, an in-depth characterization of microenvironment of w/o microemulsion in presence of IL has been made during the performance of the model C-C cross

coupling (Heck) reaction. The reaction ends up with the highest yield in presence of 0.05 mol dm^{-3} of IL, wherein Pn transfer process reported to be most spontaneous as evident from the physicochemical and thermodynamic parameters obtained by the dilution method. All findings of the present investigation, starting from simple titrimetric method to sophisticated instrumentations, lead to the conclusion that the most plausible reaction location/site is the interfacial region of w/o microemulsion, where the population of all active ingredients of both template and the Heck reaction are impart stability to the system. The confinement of IL (as additive) improved the reactivity of Heck reaction, which can be used in various domains, such as biocatalysts or nanomaterial synthesis.⁹ The understanding of physicochemical parameters and interactions during the progress of the organic reaction in w/o microemulsion has implications for designing of suitable reaction media for organic synthesis.

II.G. References

References are given in BIBLIOGRAPHY under Chapter-II (pp. 105-108).