Metal-based surface active ionic liquids: Self-assembling characteristics and C-C bond functionalization of tertiary amines with TMSCN in aqueous micellar solutions



Akshay Kulshrestha, Gaurav Kumar, N.H. Khan, Arvind Kumar

PII:	80167-7322(19)35335-8
DOI:	https://doi.org/10.1016/j.molliq.2019.112157
Reference:	MOLLIQ 112157
To appear in:	Journal of Molecular Liquids
Received date:	25 September 2019
Revised date:	11 November 2019
Accepted date:	16 November 2019

Please cite this article as: A. Kulshrestha, G. Kumar, N.H. Khan, et al., Metal-based surface active ionic liquids: Self-assembling characteristics and C-C bond functionalization of tertiary amines with TMSCN in aqueous micellar solutions, *Journal of Molecular Liquids*(2019), https://doi.org/10.1016/j.molliq.2019.112157

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier.

Metal-based Surface Active Ionic Liquids: Self-Assembling Characteristics and C-C Bond Functionalization of Tertiary Amines with TMSCN in Aqueous Micellar Solutions

Akshay Kulshrestha,<sup>ab</sup> Gaurav Kumar,<sup>ac</sup> N.H. Khan,<sup>ac</sup> and Arvind Kumar<sup>a,b,</sup>\*

<sup>a</sup>Academy of Scientific and Innovative Research (AcSIR)-Central Salt and Marine Chemicals Research

Institute, Council of Scientific and Industrial Research (CSIR), G. B. Marg, Bhavnagar, 364002, Gujarat

India.

<sup>b</sup>Salt and Marine Chemicals Division, CSIR-Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research, G. B. Marg, Bhavnagar, 364002, Gujarat India

<sup>c</sup>Inorganic Materials and Catalysis Division, CSIR-Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research, G. B. Marg, Bhavnagar, 364002, Gujarat India

\*To whom correspondence should be addressed: e-mail: <u>mailme\_arvind@yahoo.com</u>; <u>arvind@csmcri.org</u>; Tel: +91-278-2567039; Fax: +91-278-2567562.

Abstract

Metal-based surface active ionic liquids (MSAILs), 1-alkyl-3-methyl imidazoliumtetrachloromanganate  $[C_n mim][MnCl_4]^{2-}$  (n=8,10,12) have been synthesized and characterized for self-assembling behavior in aqueous solution using tensiometry, fluorescence, conductivity, dynamic light scattering (DLS) and transmission electron microscopy (TEM) techniques. MSAILs have exhibited 4 to 5 fold higher surface activity as compared to the non-metal based surface active ionic liquids. MSAILs micellar solutions have been successfully used for C(sp<sup>3</sup>)-H functionalized oxidative cyanation of the tertiary amines. Oxidative Strecker reaction was carried out with different concentrations of the MSAILs, cyanide source (TMSCN) and substrate, and moderate to very high yields (up to 95%) could be achieved in 3-4 h. Usually, cyanation of tertiary amines is carried out in organic solvents under harsh conditions without recycling of the catalyst. Herein aqueous MSAILs micellar solutions have been used as a solvent, catalyst as well as template with a good recycling ability, thus making the approach simpler, greener, and sustainable.

Keywords: Metal-based surface active ionic liquids, micellar catalysis, cyanation, tertiary amines.

#### 1. Introduction

lonic liquids (ILs) are molten organic salts with wide liquidus range (up to 100oC). Due to negligible vapor pressure and other suitable physicochemical properties, ILs are considered as comparatively greener solvents.[1,2] Recently, ILs have been widely used in colloidal science as medium or surfactants because of their tunable properties and insignificant vapor pressure, which avoids the environment pollution.[3] ILs which exhibit surface active properties are synthesized by introducing the amphiphilic character into the ILs and have been termed as surface active ionic liquids (SAILs). Many of such SAILs have some superior surface activity in solvent media as compared to the conventional surfactants.[4] The self-assembly of SAILs leads to the formation of micelles, wormshaped micelles, vesicles, rod-like micelles, reverse vesicles, reverse micelles.[5-10] ILs have also found applications in several organic transformations as both catalyst and solvent. Due to the multiple advantages of the ILs, we performed organic transformations via micellar route by using ILs

as a catalyst and an emulsifying agent. Literature survey on SAILs has shown a variety of applications such as drug screening,[11] micellar catalysis,[12] micellar extraction,[13] biochemical reaction, detergents, pharmaceutical and their biochemical demand like gene transfection, DNA binding, drug delivery, interaction with biomolecules.[14-16]

The use of surfactants under micellar conditions represents one of the simplest methods to achieve catalysis in water. Micellar Catalysis has been used to perform the synthesis of the organic molecules, and conventional materials in the surfactant aggregate.[17] The micellar solution provides the hydrophobic and ionic environment to perform the reaction, and the product can be separated by an aqueous biphasic system. [18-20] ILs can dissolve the series of the transition metals.[21] Therefore, the metal-based ionic liquids can be used as a catalyst as well as solvent in organic transformations in an eco-friendly way. Previously, conventional surfactants (SDS, Triton X-100, Brij-36) have been used for organic transformation. [22-29] The micellar aqueous solutions have been used in the dehydration reaction, [22] C-C bond forming reaction, [23] Oxidation reaction, [24] metal catalyzed reaction, [25,26] cross-coupling reaction (Suzuki, Sonoghasira, Negishi) [27-29] or Carbon-heteroatom coupling reaction[30] with the better yield and selectivity. In another case, the metal nanoparticle can be stabilized in the micelles, which can be cross contact between the micellar and heterogeneous catalysis. [10,31] Many groups have rooted their work on the micellar catalysis by SAILs, to increase the rate of the reaction and to perform the reactions in aqueous media. The work of Bica and co-workers, [32-34] shows the enhancement in the rate of the Diels Alder Reaction by the micellar solution of the 1-dodecyl-3- methyl imidazolium chloride and replacement of traditional organic solvent with water. Effect of the nucleophile (Cl, Br, I, OTs, OTf, Ms) on the rate of the reaction for the degradation of the organophosphorus compounds and palladium catalyzed micellar catalysis with  $[C_n mim][X]$  for the cross-coupling reaction has also been investigated. Xie et al. performed Ugi-type reaction by the copper-catalyzed in surfactant medium[35] whereas Klumphu et al. showed the cycloisomerization conversion of the allenes into the heterocyclic product in the

presence of gold (ppm) in micellar media.[36] The Nitrile group is an essential and handy purposeful assembly in organic synthesis. It is also a needy backbone for various drug compounds[37] as it is easily converted to further valuable functional groups.[38] Consequently, the cyano group as a primer into an organic framework at C1 position has been well studied.[39] Amongst the wide-ranging bioactive molecules and synthetic intermediates of alpha-amino carbonyl compounds and 1,2-diamines, alpha-amino nitrile derivatives are the primary representative of substructure.[40] The most legendary Strecker reaction is the reliable paramount method for synthesis of alpha-amino nitrile derivatives, i.e., the addition of a cyanide anion to an imine.[41]

In new existences, C–C bond formations are always high in demand, and it can be readily synthesized via C–H bond activation, which is a most favorable synthetic tool.[42] The oxidative cyanation reaction is leading age route C–C bond formations through C–H bond activation, which is considered to be an environmentally sustainable and atom-efficient procedure for a sustainable development perspective. Oxidative cyanation of tertiary amines compounds has been actively examined in many reports. Since 2003, many groups like as Murahashi,[43] Li's,[44] and others reported the groundbreaking work of C–H cyanation of N, N dialkyl aniline.[45]Also, other recipes of oxidants and cyanide cradles were similarly relevant to oxidative C–H cyanation.[46] Contemporary advancement of photo-redox catalysis assists direct C–H bonds functionalization.[47-48] Commonly, oxidative cyanation reactions are dependent on the use of transition metal catalysts like ruthenium,[43] manganese[49] and iron[50] besides various oxidants, such as H<sub>2</sub>O<sub>2</sub>,[51] O<sub>2</sub>,[52] tert-butylhydroperoxide,[53] and 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ).[54]

In this report, we have synthesized a series of manganese-based SAILs using the 1-alkyl-3imidazolium chloride and Manganese Chloride and characterized using Raman Spectra, UV spectra, and EPR spectra. The thermal behavior has been analyzed using TGA, and DTG Micellar solutions of imidazolium-type of amphiphilic ILs have been reported to increase the solubility organic

compounds,[55]therefore, we have utilized the synthesized MSAILs micellar solutions as a solvent system and catalyst for the chemical transformation of tertiary amine to the cyanated product.

#### 2. Materials and methods

**2.1 Material:** Methyl imidazole (>98% purity), 1-Chlorodecane (>98% purity), 1-Chlorododecane (>98% purity) were purchased from TCI Chemical (India) Pvt. Ltd. 1-Octyl-3-methyl imidazolium chloride (>97% purity), manganese (II) chloride tetrahydrate and TBHP were purchased from Sigma-Aldrich. N, N-dimethyl aniline, TMSCN was obtained from Spectrochem. The Hydrogen Peroxide solution 50% was purchased from Qualigens fine chem. Ltd. The solvent-like methanol, ethyl acetate, and n-hexane of AR grade were purchased from Loba Chemie Ltd., India.



Scheme 1. Chemical structure of investigated MSAILs

**2.2 Synthesis and Characterization:** Details of synthesis and characterization of MSAILs are provided in supporting information (ESI<sup>†</sup>). In brief, 1- Chlorododecane and 1-chlorodecane was added (1.1: 1 mole eq.) dropwise in a solution of 1-methylimidazole in the acetonitrile at 90°C under reflux conditions for 48 h. [C<sub>n</sub>mim]Cl (n =8,10,12) and manganese(II) chloride tetrahydrate were taken in methanol solvent, and reaction mixtures were kept for reflux for 24 hours. The product was washed with ethyl acetate and hexane, dried and stored in a desiccator. Synthetic scheme is shown in Figure S1, and the molecular structures of synthesized MSAILs are shown in Scheme 1. Materials were characterized using <sup>1</sup>H NMR, Raman, UV, and EPR spectra. Confirmation of Mn-Cl bond and tetrahedral manganese complex formation in the  $(MnCl_4)^{2^2}$ counterion of MSAILs was obtained from Raman and UV spectra (Figure S2) whereas the oxidation number of Mn(II) in  $(MnCl_4)^{2^2}$  of the MSAILs was obtained from EPR spectra (Figure S3). C, H, N, and ICP measurements were done for elemental analysis (Table S1). Thermal stability of the MSAILs was investigated by the thermogravimetric analysis (TGA) experiment (Figure S4).

#### 2.3 Methods:

*2.3.1. Spectroscopy*. LabRAM HR Evolution Horiba Jobin, Yvon Raman spectrometer, was used to identify the characteristic peak of Mn-Cl bond of the complex [MnCl<sub>4</sub>]<sup>2-</sup>at 298.15 K of the sample. UV spectra of MSAILs solutions prepared in acetonitrile were recorded by the JobinYvon UV–VIS spectrophotometer. For EPR spectra of the investigated MSAILs solutions were prepared in acetonitrile solvent, and the spectra were recorded by using EPR benchtop instrument (Freiberg Instruments, Germany). Characteristic parameters were: magnetic field range 300 to 400 mT, frequency 100 kHz, sweep time 60s, and the modulation 0.20 mT.

2.3.2.Tensiometry, Conductivity, and Fluorimetry. Attention Force Sigma 700 tensiometer with Du Nouy ring method was used for the surface tension measurements. Triplicate measurements were done, and the average value was considered as surface tension value. CMC and other surface parameters were determined from measured surface tension values. Conductivity measurement was done on digital Eutech auto temperature conductivity meter model PC 2700 assembled with a conductivity cell and temperature probe. Solution temperature was maintained by using a Julabo thermostat at 25°C (with  $\pm$  0.1°C). The conductivity was measured after each addition of the MSAILs in the solution. Conductivity value was used to find out the CMC, degree of counterion binding ( $\beta$ ), and standard free energy of micellization. The Fluorescence of pyrene was measured at different concentrations of MSAILs by Fluorolog (Horiba Jobin Yvon) spectrometer. The excitation/emission wavelength is 334/365nm (slit width 1.2nm). Measurements were done in a quartz cuvette of 1 cm path length.

2.3.3. Transmission electron microscopy and Dynamic Light Scattering (DLS). TEM images were recorded by JEOL JEM-2100 electron microscope at aworking voltage of 80kv. The MSAILs samples were prepared by putting a drop of MSAIL solutions on the carbon-coated copper grid (300 mesh), and the samples were dried under vacuum desiccator. Dynamic light scattering measurements were

performed at a 90° angle with a He-Ne laser (660-670 nm, 4mW) by using NaBiTec Spectro-Size300 light scattering apparatus (NaBiTec, Germany).

2.3.4. Gas chromatography (GC). Gas chromatography was carried out on the Shimadzu GC-2010. The column oven temperature was at 110°C, FID 200°C, and the pressure of GC was 110kPa. All the samples were prepared in methanol, and dodecane as a standard solution was used.

#### 3. Result and discussion

*3.1. Surface tension:* The surface activity of the investigated MSAILs was determined by surface tension measurements. The adsorption isotherms determined from surface tension ( $\gamma$ ) measurements at 298.15 K are shown in Figure 1A. The surface tension of aqueous-MSAILs solutions decreased in a polynomial manner with the logarithm of concentration because of adsorption of MSAILs molecules at the air/water interface and attained a critical micelle concentration (*cmc*) value, above which a nearly constant value of surface tension ( $\gamma_{cmc}$ ) is observed. The *cmc* values decreased with increase in the length of the alkyl chain of MSAIL i.e. [ $C_8mim$ ]<sub>2</sub>[MnCl<sub>4</sub>] (51.18 mM), [ $C_{10}mim$ ]<sub>2</sub>[MnCl<sub>4</sub>] (5.6 mM) and [ $C_{12}mim$ ]<sub>2</sub>[MnCl<sub>4</sub>] (2.05mM). The *cmc* values of the are 4 to 5 folds lower than the previously reported *cmc* values for the SAILs, [ $C_nmim$ ][X],[56] [ $C_nPy$ ][X][57,58] (where n = 8,10,12; X = Br and Cl), or functionalized SAILs.[59] Lower *cmc* values are due to higher hydrophobicity of tetrahedral [MnCl<sub>4</sub>]<sup>2-</sup> metal counterion.

The surface activity and related parameters at air/solution interface, i.e. adsorption efficiency ( $\pi_{cmc}$ ), effectiveness reduction in surface tension ( $pC_{20}$ ), surface excess concentration ( $\Gamma_{max}$ ), covered area by single-molecule ( $A_{min}$ ) and packing parameter (P) were derived from documented equations [60] and are provided in Table 1. The Amin value of the MSAILs is higher than the conventional surfactants. The Amin follows the order:  $[C_8mim]_2[MnCl_4] < [C_{10}mim]_2[MnCl_4] < [C_{10}mim]_2[MnCl_4]$  whereas  $\Gamma_{max}$  values follow a reverse order indicating that the molecules are assembling more compactly at air-water interface with the increase in the chain length.

3.2. Conductivity: The conductivity measurements are used for the determination of the *cmc* as well as the degree of counterion binding ( $\beta$ ). The specific conductivity ( $\kappa$ , m.Scm<sup>-1</sup>) was measured as a function of MSAILs concentration (mmol.L<sup>-1</sup>) in the aqueous solution. Figure 5 shows  $\kappa$  vs. C profile of a representative MSAIL, [C<sub>12</sub>mim]<sub>2</sub>[MnCl4] (profiles for other MSAILs are provided in supporting information, Figure S5). The  $\kappa$  vs. C profiles were used to determine *cmc* values. Similar to the surface tension behavior, the observed *cmc* value of MSAILs from conductivity measurements follow the order is [C<sub>8</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>] > [C<sub>10</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>] > [C<sub>12</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>](Fig. S5,ESI<sup>+</sup>). The  $\beta$  value is obtained from the formula ( $\beta$  =1- $\alpha$ ) where the  $\alpha$  is the degree of counterion dissociation which is obtained by the ratio of the slope post micellar region and the pre micellar region (S<sub>2</sub>/S<sub>1</sub>) were used to derive the value of standard free energy of micellization from the equation:[61]

$$\Delta G_{mic}^{o} = (1 + \beta) RT \ln X_{cmc}$$

Where  $X_{cmc}$  is the *cmc* in mole fraction, T is the temperature in Kelvin (K), and R is the gas constant. The negative value of the standard free energy of micellization shows the spontaneous formation of the micelles. The standard free energy of micellization and  $\beta$  values is provided in Table 1.

*3.3. Steady State Fluorescence measurement*: Fluorescent probe pyrene is very sensitive to the polarity of the cybotactic region and used to identify the *cmc* of amphiphilic molecules in the aqueous solution.[61,62] The pyrene fluorescent probe shows the five emission bands. The first vibronic peak I<sub>1</sub> is sensitive to the polarity, which shows a decrease in the intensity with the addition of the amphiphilic molecules, whereas the third vibronic peak I<sub>3</sub> is not sensitive to the polarity. Therefore, the ratio I<sub>1</sub>/I<sub>3</sub> is a good indicator of pyrene environment in the solution and can be used for determination of *cmc*. The plot of I<sub>1</sub>/I<sub>3</sub> vs. concentration of a representative MSAIL,  $[C_{12}mim]_2[MnCI_4]$  is provided in Fig. 1C. (profiles for other MSAILs are provided in supporting information, Fig. S6 ESI<sup>+</sup>). The observed order of cmc of MSAILs by fluorescence measurements is

similar to that determined from the surface tension and conductivity measurements, i.e.[C<sub>8</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>]>[C<sub>10</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>]> [C<sub>12</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>] (Fig. S6, ESI<sup>+</sup>).



**Fig. 1** (a) The surface tension vs. concentration plot of the various MSAILs, (b, c) Conductivity plot and  $I_1/I_3$  intensity ratio of a representative MSAIL,  $[C_{12}mim]_2[MnCl_4]$ , and (d)Intensity vs.  $\lambda$  graph on increasing the concentration,  $C_q$  of  $[C_{12}mim]_2[MnCl_4]$ .

*3.4. Size and shape of the aggregates*: DLS and TEM imaging were performed to determine the size and the shape of the aggregated structure of MSAILs in the aqueous solution. Fig. 2A shows the graph between the hydrodynamic diameter (nm) and the intensity count per second distribution profile of the micellar aqueous solution of the MSAILs. The autocorrelation diagram is provided in supporting information (Fig. S7, ESI<sup>†</sup>). The DLS profiles of  $[C_8mim]_2[MnCl_4]$  and  $[C_{10}mim]_2[MnCl_4]$ show two peaks centered at around 3 nm and 10 nm indicating co-existence of smaller size micelles along with bigger aggregates. DLS profiles of  $[C_{12}mim]_2[MnCl_4]$  shows only a single peak around 3 nm

indicating the formation only smaller micelles. TEM images (Fig. 2b-d) also confirms formation of micellar structures of similar sizes by MSAILs.



**Fig. 2** (a) DLS plot of MSAILs with different alkyl chain length. (b-d) shows the TEM images of  $[C_{12}mim]_2[MnCl_4]$ ,  $[C_{10}mim]_2[MnCl_4]$ , and  $[C_8mim]_2[MnCl_4]$  MSAILS.

## 3.5. Micellar Catalysis

*Functionalized Oxidative Cyanation using MSAILs micellar solutions:* Insights into the influence of structural features of metal-based surface active ionic liquids on the oxidative cyanation of tertiary amines with trimethylsilyl cyanide have been obtained as per Scheme 2.



Scheme 2. Cyanation of tertiary amines in micellar solutions

Preliminary trials on the oxidative cyanation reaction were accomplished by using 100 mM concentration of various MSAILs, which is quite higher than the cmc of MSAILs in aqueous solution. The reaction of N, N-dimethyl aniline and TMSCN using the micellar solution was achieved at 40°C (Table 2). At 100 mM MSAILs concentration moderate yields were obtained (Table 2, entry 1-3). Further investigations revealed a marked influence of concentration of the surface-active ionic liquids. Therefore, to further enhance the yield of the products we carried out reactions at different concentrations of MSAILs, i.e. 70, 25, 15, 5 mM, apart from varying other parameters. (Table 2, entry 4-15). An exceptional behavior was seen when the concentration was decreased to 25 mM. In the case of  $[C_{12}mim]_2[MnCl_4]$ , the yield increased to 95% (Table 2, entry 7). Similar behavior was also observed for other MSAILs, albeit with lesser yield as compared to [C<sub>12</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>]. Higher yields with longer alkyl chain length MAIL, i.e. [C<sub>12</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>] is likely due to the formation of compact micellar structure, which is providing more surface area for substrates to react. Further, by varying the other parameters like as oxidant, cyanide source, with optimized [C<sub>12</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>] concentration i.e., 25 mM, there was no further improvement of the yield of the desired products even by using nascent oxygen or TBHP as an oxidant (Table 2, entry 16, 17). We also checked the reaction parameters by without using oxidant wherein no reaction was observed (Table 2, entry 18). Oxidant hydrogen peroxide was also optimized for the reaction. Finally, we varied the cyanide source (Table 2, entry 19 and 20) and used sodium cyanide and potassium cyanide. Conventional non-metal ionic liquid and manganese chloride were also tested (Table 2, entry 21, 22). The consequences give a clear path that conventional ionic liquid as well MnCl<sub>2</sub> are not sufficient separately to effectively catalyze the reaction. Therefore, the use of MSAILs provides an effective procedure for C-H functionalization of tertiary amines under aerobic conditions as a consequence of the hydrophobic and ionic environment. Under optimized conditions of [C<sub>12</sub>mim]<sub>2</sub>[MnCl<sub>4</sub>] (25 mM) cyanation of various tertiary amines was carried out efficiently (Table 3). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the cyanation products are provided in supporting information (ESI<sup>+</sup>).

*Reaction mechanism:* A conceivable reaction pathway has been projected for the sp<sup>3</sup> C-H oxidative cyanation of tertiary amines in the self-assembled structure of MSAIL in water with TMSCN. As shown in Scheme 3, primarily Mn(II) containing micellar aqueous solution, reacts with  $H_2O_2$  leading to the formation of reactive oxo-complex species, which consequently reacts with the amine to give an iminium ion. A conceivable reaction pathway has been projected for the sp<sup>3</sup> C-H oxidative cyanation of tertiary amines where the reaction trails an oxidative and reductive path. This intermediate reacts with in-situ generated -CN and delivers the corresponding  $\alpha$ -aminonitrile

(Scheme 3). The detailed reaction mechanism of the reaction has been provided in supplementary Information (Figure S8).



**Scheme3.** Plausible reaction mechanism for the Manganese based surface active ionic liquids (MSAILs) catalyzed C-H activation of tertiary amines with hydrogen peroxide.

#### 4. Conclusion

The manganese-based imidazolium type surface active ionic liquids with varying chain length have been synthesized and characterized for their thermal stability and surface activity. MSAILs have been found more stable than the conventional imidazolium SAILs and form well organized self-assembled micellar structures spontaneously in aqueous medium as suggested by various techniques viz. tensiometry, fluorometry, and conductivity. The formation of micelles is confirmed using TEM images and DLS profiles. The various surface parameters indicate that MSAILs are more surface active than the conventional SAILs due to the incorporation of hydrophobic metal counterion. The micellar solutions of MSAILs have been successfully used as catalyst, template as well solvent for cyanation of tertiary amines using TMSCN as cyanide source in the presence of hydrogen peroxide as the oxidant. Longer chain MSAILs have been found more efficient for catalytic activity due to the formation of compact micellar structures, and yield as high as 95% could be achieved under optimized conditions. The devised methodology of C-C bond functionalization of tertiary amines

with TMSCN in aqueous MSAILs micellar solutions is more eco-friendly and follows more simple protocols, and can be generalized for other chemical transformations in water.

#### Acknowledgement

The authors are grateful for the financial support from the Department of Science and Technology, India(EMR/2016/004747). Authors thank Krishnaiah Damarla and P.S. Gehlot for the helpful suggestions. We also thank the centralized Instrumental Facility of our Institute for assistance.

#### References

[1] A.-O. Diallo, G. Fayet, C. Len and G. Marlair, Evaluation of Heats of Combustion of Ionic Liquids through Use of Existing and Purpose-Built Models, Ind. End. Chem. Res. 51 (2012) 3149–3156. https://doi.org/10.1021/ie2023788.

 [2] A. Bado-Nilles, A.-O. Diallo, G. Marlair, P. Pandard, L. Chabot, A. Geffard, C. Len, J.-M. Porcher and W. Sanchez, J. Hazard. Mater. 283 (2015) 202–210. https://doi.org/10.1016/j.jhazmat.2014.09.023

[3] T.Welton, Room-Temperature Ionic Liquids, Solvents for Synthesis and Catalysis. Chem. Rev. 99 (1999) 2071–2084. https://doi.org/10.1021/cr980032t.

[4] B.Dong, N. Li, L. Zheng, L.Yu and T. Inoue, Surface Adsorption and Micelle Formation of Surface
 Active Ionic Liquids in Aqueous Solution, Langmuir 23 (2007) 4178–4182.
 https://doi.org/10.1021/la0633029.

[5] K. D. Danov, P. A. Kralchevsky, S. D. Stoyanov, J. L. Cook, I. P. Stott and E. G. Pelan, Growth of wormlike micelles in nonionic surfactant solutions: Quantitative theory vs. experiment, Adv. Colloid Interface Sci. 256 (2018) 1–22. https://doi.org/10.1016/j.cis.2018.05.006.

[6] K.S Rao, S. So and A. Kumar, Vesicles and reverse vesicles of an ionic liquid in ionic liquids, ChemComm 49 (2013) 8111-8113. https://doi.org/10.1039/C3CC44462G.

[7] X. Liu, G. Zhou, H. He, X. Zhang, J. Wang and S. Zhang, Rodlike Micelle Structure and Formation of Ionic liquid in Aqueous Solution by Molecular Simulation, Ind. Eng. Chem. Res. 54 (2015) 1681–1688. https://doi.org/10.1021/ie503109z.

[8] D. Blach, M. Pessêgo, J. J. Silber, N. M. Correa, L. García-Río and R. D. Falcone, Ionic liquids entrapped in reverse micelles as nanoreactors for bimolecular nucleophilic substitution reaction.

Effect of the confinement on the chloride ion availability, Langmuir 30 (2014) 12130-12137. https://doi.org/10.1021/la501496a.

[9] K. Damarla, P. Bharmoria, K. S. Rao, P. S. Gehlot and A. Kumar, Illuminating microemulsions: ionic liquid–CdS quantum dots hybrid materials as potential white light harvesting systems, ChemComm. 52 (2016) 6320–6323. https://doi.org/10.1039/C6CC02133F.

[10] K.S.Rao, T.J. Trivedi and A. Kumar, Aqueous-Biamphiphilic Ionic Liquid Systems: Self-Assembly and Synthesis of Gold Nanocrystals/Microplates, *J. Phys. Chem. B* 116 (2012) 14363–14374. https://doi.org/10.1021/jp309717n.

[11] S. Mahajan, R. Sharma and R. K. J. Mahajan, An investigation of drug binding ability of a surface active ionic liquid: micellization, electrochemical, and spectroscopic studies, Langmuir 28 (2012) 17238-17246. https://doi.org/10.1021/la303193n.

[12] G. L.Sorella, G. Strukul and A. Scarso, Recent Advances in Catalysis in Micellar Media, Green Chem. 17 (2015) 644-683. https://doi.org/10.1039/C4GC01368A.

[13] H. R. Rabie and J.H. Vera, A simple model for reverse micellar extraction of proteins. Sep. Sci. Technol.(1998). https://doi.org/10.1080/01496399808545248.

[14] M. Jones, Surfactant interactions with biomembranes and proteins, Chem. Soc. Rev, 21 (1992) 127-136. https://doi.org/10.1039/CS9922100127.

[15] E. D. Goddard, K. P. Ananthapadmanabhan, Interactions of surfactants with polymers and proteins, CRC Press: Boca Raton, (1993).

[16] Sjöblom Johan. Emulsions and emulsion stability; Taylor & Francis: Boca Raton, (2006).

[17] (a)M. a. d. M. Graciani, A. Rodríguez, V. I. Martín, G. Fernández and M. a. L. Moyá, Concentration and medium micellar kinetic effects caused by morphological transitions, Langmuir 26 (2010) 18659-18668. https://doi.org/10.1021/la102857d.

[18] 18. J. Baumrucker, M. Calzadilla and E. H. Cordes, Micellar Catalysis for Carbonium Ion Reactions, Reaction Kinetics in Micelles (1973) 25–51.

[19] . S. Naskar, P. Saha, R. Paira, A. Hazra, P. Paira, S. Mondal, A. Maity, K. B. Sahu, S. Banerjee and N. B. Mondal, Synthesis of polycyclic fused 2-quinolones in aqueous micellar system,Tetrahedron Lett. 51 (2010) 1437-1440. https://doi.org/10.1016/j.tetlet.2010.01.030.

[20] B. S. Kitawat, M. Singh and R. K. Kale, Robust Cationic Quaternary Ammonium Surfactant-Catalyzed Condensation Reaction for (E)-3-Aryl-1-(3-alkyl-2-pyrazinyl)-2-propenone synthesis in water at room temperature,ACS Sustain. Chem. Eng. 1 (2013) 1040-1044. https://doi.org/10.1021/sc400102e.

[21] . A. G. Zazybin, K. Rafikova, V. Yu, D. Zolotareva, V. M. Dembitsky and T. Sasaki, Metalcontaining ionic liquids: current paradigm and applications, Russ.Chem.Rev. 86 (2017) 1254. https://doi.org/10.1070/RCR4743.

[22] K. Manabe, S. Iimura, X. M. Sun and S. Kobayashi, Dehydration Reactions in Water. Broensted Acid—Surfactant-Combined Catalyst for Ester, Ether, Thioether, and Dithioacetal Formation in Water, J. Am. Chem. Soc.124 (2002) 12411971-11978. https://doi.org/10.1021/ja026241j.

[23] K. R. Reddy, K. Rajanna ands K. Uppalaiah, Environmentally benign contemporary Friedel–Crafts acylation of 1-halo-2-methoxynaphthalenes and its related compounds under conventional and nonconventional conditions, Tetrahedron Lett. 54 (2013) 3431-3436. https://doi.org/10.1016/j.tetlet.2013.04.075.

[24] K. Bahrami, M. M. Khodaei and J. Abbasi, Synthesis of Sulfonyl Chlorides and Sulfonic Acids in SDS Micelles, Synthesis 44 (2012) 316-322. https://doi.org/10.1055/s-0031-1289628.

[25] A. Kumar, D. Saxena and M. K. Gupta, Nanoparticle catalyzed reaction (NPCR): ZnO-NP catalyzed Ugi-reaction in aqueous medium, Green Chem. 15 (2013) 2699-2703. https://doi.org/10.1039/C3GC41101J.

[26] F.Szabó, B. Pethő, Z. Gonda and Z. Novák, Iron–surfactant nanocomposite-catalyzed benzylic oxidation in water, RSC Adv. 3 (2013) 4903-4908. https://doi.org/10.1039/C3RA22856H.

[27] . B. H. Lipshutz and A. R. Abela, Micellar catalysis of Suzuki– Miyaura cross-couplings with heteroaromatics in water, Org. Lett. 10 (2008) 5329-5332. https://doi.org/10.1021/ol801712e.

[28] B. H. Lipshutz, D. W. Chung and B. Rich, Sonogashira couplings of aryl bromides: room temperature, water only, no copper, Org. Lett. 10 (2008) 3793-3796. https://doi.org/10.1021/ol801471f.

[29] A. Krasovskiy, I. Thomé, J. Graff, V. Krasovskaya, P. Konopelski, C. Duplais, and B. H. Lipshutz, Cross-couplings of alkyl halides with heteroaromatic halides, in water at room temperature, Tetrahedron Lett. 52 (2011) 2203-2205. https://doi.org/10.1016/j.tetlet.2010.11.160.

[30] X. Ge, S. Zhang, X. Chen, X. Liu and C. Qian, A designed bi-functional sugar-based surfactant:micellar catalysis for C–X coupling reaction in water, Green Chem. 21 (2019) 21 2771-2776. https://doi.org/10.1039/C9GC00964G.

[31] A. Kraynov and T. E. Muller, Concepts for the Stabilization of Metal Nanoparticles in Ionic Liquids, Applications of Ionic Liquids in Science and Technology (2011).

[32] K. Bica, P. Gaertner, P. J. Gritsch, A. K. Ressmann, C. Schröder and R. Zirbs, Micellar catalysis in aqueous–ionic liquid systems, ChemComm. 48 (2012) 5013-5015.
https://doi.org/10.1039/C2CC31503C.

[33] A. Cognigni, P. Gaertner, R. Zirbs, H. Peterlik, K. Prochazka, C. Schröder and K. Bica, Surfaceactive ionic liquids in micellar catalysis: impact of anion selection on reaction rates in nucleophilic substitutions, Phys. Chem. Chem. Phys. 18 (2016) 13375-13384. https://doi.org/10.1039/C6CP00493H.

[34] M. Taskin, A. Cognigni, R. Zirbs, E. Reimhult and K. Bica, Surface-active ionic liquids for palladium-catalysed cross coupling in water: effect of ionic liquid concentration on the catalytically active species, RSC Adv. 7 (2017) 41144-41151. https://doi.org/10.1039/C7RA07757B.

[35] C. Xie and L.Han, Development of aqueous oxidative Ugi-type reactions by copper-catalyzed surfactant-promoted C (sp3)–H direct functionalization in water, Tetrahedron Lett. 55 (2014) 240-243. https://doi.org/10.1016/j.tetlet.2013.11.006.

[36] . P. Klumphu, C. Desfeux, Y. Zhang, S. Handa, F. Gallou and B. H. Lipshutz, Micellar catalysisenabled sustainable ppm Au-catalyzed reactions in water at room temperature, Chem. Sci. 8 (2017) 6354-6358.https://doi.org/10.1039/C7SC02405C.

[37] J.C. K. Chu and T. Rovis, Complementary Strategies for Directed C(sp3)-H Functionalization: A Comparison of Transition-Metal-Catalyzed Activation, Hydrogen Atom Transfer, and Carbene/Nitrene Transfer, Angew. Chem. 57 (2018) 62–1. https://doi.org/10.1002/anie.201703743.

[38] . Y. Ping, Q. Ding and Y. Peng, Advances in C–CN Bond Formation via C–H Bond Activation, ACS Catal. 6 (2016) 5989–6005. https://doi.org/10.1021/acscatal.6b01632.

[39] S.-I. Murahashi, N. Komiya, H. Terai and T. Nakae, Aerobic Ruthenium-Catalyzed Oxidative Cyanation of Tertiary Amines with Sodium Cyanide, J. Am. Chem. Soc. 125 (2003) 15312–15313. https://doi.org/10.1021/ja0390303.

[40] H.E. Ho, Y. Ishikawa, N. Asao, Y. Yamamoto and T. Ji,Highly efficient heterogeneous aerobic cross-dehydrogenative coupling via C–H functionalization of tertiary amines using a nanoporous gold skeleton catalyst, ChemComm. 51 (2015) 12764–12767. https://doi.org/10.1039/C5CC04856G.

[41] M. Rueping, J. Zoller, D.C. Fabry, K. Poscharny, R.M. Koenigs, T.E. Weirich and J. Mayer, Light-Mediated Heterogeneous Cross Dehydrogenative Coupling Reactions: Metal Oxides as Efficient, Recyclable, Photoredox Catalysts in C-C Bond-Forming Reactions, Chem. Euro J. 18 (2012) 3478– 3481. https://doi.org/10.1002/chem.201103242.

[42] R. Shang, L. Ilies and E.Nakamura Iron-Catalyzed C–H Bond Activation, Chem. Rev. 13 (2017) 9086-9139. https://doi.org/10.1021/acs.chemrev.6b00772.

[43] S.-I. Murahashi, T. Nakae, H. Terai and N. Komiya, Ruthenium-Catalyzed Oxidative Cyanation of Tertiary Amines with Molecular Oxygen or Hydrogen Peroxide and Sodium Cyanide: sp3 C–H Bond Activation and Carbon–Carbon Bond Formation, J. Am. Chem. Soc. 130 (2008) 11005–11012. https://doi.org/10.1021/ja8017362

[44] M. Rueping, S. Zhu and R. M. Koenigs, Visible-light photoredox catalyzed oxidative Strecker reaction, ChemComm.47 (2011) 12709. https://doi.org/10.1039/C1CC15643H.

[45] M.-X. Sun, Y.-F. Wang, B.-H. Xu, X.-Q. Ma and S.-J. Zhang, A metal-free direct C (sp3)–H cyanation reaction with cyanobenziodoxolones, Org. Biomol. Chem. 16 (2018) 1971–1975. https://doi.org/10.1039/C8OB00173A.

[46] H. P. Kim, H. Yu, H. Kim, S. –H. Kim and D. Lee, DDQ-Promoted Mild and Efficient Metal-Free Oxidative  $\alpha$ -Cyanation of N-Acyl/Sulfonyl 1,2,3,4-Tetrahydroisoquinolines, Molecules 23 (2018) 3223. https://doi.org/10.3390/molecules23123223.

[47] G. Kumar, S. Verma, A. Ansari, N. H. Khan and R. I. Kureshy, Enantioselective cross dehydrogenative coupling reaction catalyzed by Rose Bengal incorporated-Cu (I)-dimeric chiral complexes, Catal. Comm 99 (2017) 94-99. https://doi.org/10.1016/j.catcom.2017.05.026.

[48] G. Kumar, P. Solanki, Md.Nazish, S. Neogi, R.I.Kureshy and N. H. Khan, Covalentyl hooked EOSIN-Y in a Zr(IV) framework as visible-light mediated, heterogeneous photocatalyst for efficient C-H functionalization of tertiary amines, Journal of catalysis 371 (2019) 298-304. https://doi.org/10.1016/j.jcat.2019.02.011.

[49] K. Yamaguchi, Y. Wang and N. Mizuno, A Widely Applicable Regioselective Aerobic α-Cyanation of Tertiary Amines Heterogeneously Catalyzed by Manganese Oxides, ChemCatChem 5 (2013) 2835–2838. https://doi.org/10.1002/cctc.201300477.

[50] V. Panwar, P. Kumar, A. Bansal, S. S. Ray,and S. L. Jain,PEGylated magnetic nanoparticles (PEG@Fe 3 O 4 ) as cost-effective alternative for oxidative cyanation of tertiary amines via C-H activation, Appl. Catal., A. 498 (2015) 25–31. https://doi.org/10.1016/j.apcata.2015.03.018.

[51] S. Verma, S. L. Jain and B. Sain, Starch Immobilized Ruthenium Trichloride Catalyzed Oxidative Cyanation of Tertiary Amines with Hydrogen Peroxide, ChemCatChem 3 (2011) 1329–1332. https://doi.org/10.1002/cctc.201100111.

[52] L. Zhang, X. Gu, P. Lu and Y. Wang, Synthesis of α-aminonitriles via a FeSO4-mediated oxidative cyanation of tertiary amines with benzoyl cyanide and molecular oxygen or TBHP, Tetrahedron (72) 2016 2359–2363. https://doi.org/10.1016/j.tet.2016.03.061.

[53] F. Zhang, P. Du, J. Chen, H. Wang, Q. Luo and X. Wan, Co-Catalyzed Synthesis of 1,4-Dicarbonyl Compounds Using TBHP Oxidant, Org. Lett. 16 (2014) 1932–1935.
https://doi.org/10.1021/ol5004687.

[54] H. P. Kim, H. Yu, H. Kim, S. –H. Kim and D. Lee, DDQ-Promoted Mild and Efficient Metal-Free Oxidative  $\alpha$ -Cyanation of N-Acyl/Sulfonyl 1,2,3,4-Tetrahydroisoquinolines, Molecules 23 (2018) 3223. https://doi.org/10.3390/molecules23123223.

[55] J. Łuczak, C. Jungnickel, M. Markiewicz and J. Hupka, Solubilization of Benzene, Toluene, and Xylene (BTX) in Aqueous Micellar Solutions of Amphiphilic Imidazolium Ionic Liquids, J. Phys. Chem. B 117 (2013) 5653-5658. https://doi.org/10.1021/jp3112205.

[56] . J. Łuczak, J. Hupka, J. Thöming, C. Jungnickel, Self-organization of imidazolium ionic liquids in aqueous solution, Colloids and Surfaces A: Physicochemical and Engineering Aspects 329 (2008) 125–133. https://doi.org/10.1016/j.colsurfa.2008.07.012.

[57] A.Cornellas, L. Perez, F. Comelles, I. Ribosa, A. Manresa, M.T.Garcia, Self-aggregation and antimicrobial activity of imidazolium and pyridinium based ionic liquids in aqueous solution, Journal of Colloid and Interface Science 355 (2011) 164-171. https://doi.org/10.1016/j.jcis.2010.11.063.

[58] P.Quagliotto, N. Barbero, C. Barolo, E.Artuso, C. Compari, E. Fisicaro, G. Viscardi, Synthesis and properties of cationic surfactants with tuned hydrophylicity, Journal of Colloid and Interface Science 340 (2009) 269-275. https://doi.org/10.1016/j.jcis.2009.09.009.

[59] . M. T Garcia, I. Ribosa, L. Perez, A. Manresa, F. Comelles, Aggregation behavior and antimicrobial activity of ester-functionalized imidazolium-and pyridinium-based ionic liquids in aqueous solution, Langmuir 29 (2013) 2536-2545.

[60] M. J. Rosen, J.H. Mathias, L.Davenport, Aberrant aggregation behavior in cationic gemini surfactants investigated by surface tension, interfacial tension, and fluorescence methods, Langmuir 15 (1999) 7340-7346.https://doi.org/10.1021/la304752e.

[61] T. Singh, A. Kumar, Aggregation Behavior of Ionic Liquids in Aqueous Solutions: Effect of Alkyl Chain Length, Cations, and Anions, The Journal of Physical Chemistry B 111 (2007) 7843–7851. https://doi.org/10.1021/jp0726889.

[62] K. Kalyanasundaram, J. K. Thomas, Environmental Effects on Vibronic Band Intensities in Pyrene Monomer Fluorescence and Their Application in Studies of Micellar Systems, J. Am. Chem. Soc. 99 (1977) 2039-2044. https://doi.org/10.1021/ja00449a004.

Table 1: Critical aggregation concentration (CAC), surface tension at CMC with ±0.1mN.m<sup>-1</sup> accuracy ( $\gamma_{CAC}$ ), effective surface tension reduction with ±0.1mN.m<sup>-1</sup> accuracy ( $\pi_{CMC}$ ), adsorption efficiency ( $pC_{20}$ ), maximum surface excess concentration ( $\Gamma_{max}^{tot}$ ), and minimum area occupied by a single molecule at the air-water interface ( $A_{min}$ ), degree of counterion binding ( $\theta$ ) and standard free energy of micellization  $\Delta G_m^o$  of MSAILs in aqueous medium at 298.15K.

MSAILs		стс			Surface parameter from ST and conductivity measurements						
	ST	Cond.	flr.	Ycmc	π <sub>cmc</sub>	pC <sub>20</sub>	Γ <sub>max</sub>	A <sub>min</sub>	β	$\Delta G_m^0$	
	(mM)	(mM)	(mM)	(mNm⁻¹)	(mNm⁻¹)		(µmolm⁻²)	(Å <sup>2</sup> )		(kJ mol <sup>-1</sup> )	
[C <sub>8</sub> mim] <sub>2</sub> [MnCl <sub>4</sub> ]	52.8	50.8	45.5	30.51	38.85	2.69	1.19	139.8	0.32	-22.90	
[C <sub>10</sub> mim] <sub>2</sub> [MnCl <sub>4</sub> ]	4.46	5.44	4.72	26.12	43.12	4.22	1.08	153.9	0.16	-27.08	
[C <sub>12</sub> mim] <sub>2</sub> [MnCl <sub>4</sub> ]	1.94	2.40	1.70	30.59	40.07	3.67	1.00	165.7	0.20	-30.60	

Entry	Surfactant	Conc. (mM)	Oxidant	Yield (%)
1	$[C_{12}mim]_2[MnCl_4]$	100	H <sub>2</sub> O <sub>2</sub>	75
2	$[C_{10}mim]_2[MnCl_4]$	100	$H_2O_2$	65
3	$[C_8mim]_2[MnCl_4]$	100	$H_2O_2$	60
4	$[C_{12}mim]_2[MnCl_4]$	70	$H_2O_2$	78
5	$[C_{10}mim]_2[MnCl_4]$	70	$H_2O_2$	65
6	$[C_8mim]_2[MnCl_4]$	70	H <sub>2</sub> O <sub>2</sub>	60
7	$[C_{12}mim]_2[MnCl_4]$	25	$H_2O_2$	95
8	$[C_{10}mim]_2[MnCl_4]$	25	$H_2O_2$	90
9	$[C_8 mim]_2[MnCl_4]$	25	$H_2O_2$	85
10	$[C_{12}mim]_2[MnCl_4]$	15	$H_2O_2$	50
11	$[C_{10}mim]_2[MnCl_4]$	15	$H_2O_2$	45
12	[C <sub>8</sub> mim] <sub>2</sub> [MnCl <sub>4</sub> ]	15	$H_2O_2$	40
13	$[C_{12}mim]_2[MnCl_4]$	5	$H_2O_2$	34
14	[C <sub>10</sub> mim] <sub>2</sub> [MnCl <sub>4</sub> ]	5	$H_2O_2$	32
15	[C <sub>8</sub> mim]₂[MnCl₄]	5	$H_2O_2$	30
16	$[C_{12}mim]_2[MnCl_4]$	25	O <sub>2</sub>	70
17	$[C_{12}mim]_2[MnCl_4]$	25	ТВНР	88
18	$[C_{12}mim]_2[MnCl_4]$	25	-	N.R.
19 <sup>b</sup>	$[C_{12}mim]_2[MnCl_4]$	25	$H_2O_2$	80
20 <sup>c</sup>	$[C_{12}mim]_2[MnCl_4]$	25	$H_2O_2$	85
21 <sup>d</sup>	MnCl <sub>2</sub>	-	$H_2O_2$	55
22 <sup>e</sup>	IL, [ C <sub>8</sub> mim][Cl]	-	$H_2O_2$	10

 Table 2: Optimization of reaction conditions for Effect of MSAILs concentration with manganese catalysed oxidative cyanation of tertiary amines with cyanide source.

<sup>a</sup> Reaction conditions: 1 equivalent mmol of N, N-dimethyl aniline, 1.5 equivalent of TMSCN, 1.5 equivalent of  $H_2O_2$  in 0.5 ml of MSAIL for 4 h. <sup>b</sup>NaCN 1.5 equivalent and <sup>c</sup>KCN 1.5 equivalent, <sup>d</sup>using 10 mol % in water, <sup>e</sup> 0.5 ml of IL,[C<sub>8</sub>mim][Cl] was used.

# Table 3: Substrate Scope for the oxidative cyanation of tertiary amines in micellar solution.<sup>a</sup>



Southand



## Table of contents

Graphical abstract

### Highlights

- □ Synthesis of Metal-based surface active ionic liquids.
- □ Higher surface activity than conventional surfactants.
- $\Box$  Micellar catalysis of the tertiary amines with very high yields.



Figure 1

