SHORT COMMUNICATION



Mixed Micelles of Surface Active Ionic Liquid (SAIL)– Octylphenol Ethoxylate: A Novel Reaction Medium for Selective Oxidation of Toluene to Benzaldehyde

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Abstract Ionic liquids have been found to be suitable alternatives to volatile organic solvents in chemical transformation. Through a proper choice of cations and anions, the properties of an ionic liquid can be tuned so that it resembles an amphiphile. Such specially designed molecules are known as surface-active ionic liquids (SAIL). Like conventional surfactants, SAIL also form aggregates in an aqueous medium. Studies show that the mixing of SAIL with conventional surfactants leads to synergistic micellization. However, very few reports are available on the application of such systems as reaction media. Present study focuses on the application of mixed micelles of 1tetradecyl-3-methylimidazol-1-ium bromide, ([C₁₄mim]Br) with nonionic surfactant, Octylphenol ethoxylate with 10 moles of ethylene oxide (OPE-10). Enhanced solubilization and selective catalytic oxidation of toluene using hydrogen peroxide as an oxidant and tungstic acid as a catalyst have been studied in detail using this system.

Keywords Surface-active ionic liquid \cdot Mixed micelles \cdot Molar solubilization ratio \cdot Partition coefficient \cdot Catalytic oxidation of toluene \cdot Micellar catalysis

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Supporting information Additional supporting information may be found online in the Supporting Information section at the end of the article.

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Introduction

Liquid phase oxidation of organic compounds is a wellestablished method for the production of intermediates and specialty chemicals (Clerici and Kholdeeva, 2013). Oxidation of butane to acetic acid, cumene to phenol, cyclohexane to adipic acid, p-xylene to terephthalic acid are some of the important liquid phase oxidation processes which have industrial relevance (Suresh et al., 2000). Liquid phase selective oxidation of toluene to benzaldehyde is a challenge as oxidation of C-H bonds requires high pressure, high temperature, and/or oxidants with additives, which have tendency to produce a reactive oxygen species (Guajardo et al., 2015). A wide variety of oxidants are available to the synthetic chemist ranging from molecular oxygen, hydrogen peroxide, tert-butyl hydroperoxide (TBHP) to organic peroxides, peroxy acids, and iodosobenzene (Kholdeeva and Zalomaeva, 2016). Use of molecular oxygen (O_2) or hydrogen peroxide (H_2O_2) is encouraged as they produce nonhazardous by-products. Though inexpensive, molecular oxygen requires high pressure to get homogenized in liquid phase reaction medium (Hone and Kappe, 2018). Hydrogen peroxide is a promising alternative as it produces only water as by-product and is easy to handle (Noyori et al., 2003). However, H₂O₂ is a water-soluble oxidant and hence, while using it as an oxidant for the oxidation of organic compounds that have limited or no solubility in water, a solubilization mechanism becomes necessary.

Surfactants can form organized molecular system within the water, popularly known as micelles, thus generating a dispersed phase (Rosen and Kunjappu, 2012). These micellar aggregates are of different types such as normal spherical micelles, cylindrical micelles, vesicles *etc*. (Ghosh

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et al., 2014; Saha, et al., 2013a, Saha, et al., 2013b). In normal micelles, the interior hydrophobic part is composed of the hydrocarbon chain, the first few methylene groups being known as palisade layer, whereas the surface of the polar heads faces water. A concentric shell of hydrophilic head groups with $(1 - \alpha)N$ counter ions, where α is the degree of ionization and N is the aggregation number (number of molecules in micelles), is called Stern layer (Acharjee et al., 2019a, b; Saha et al., 2014). The dielectric constant of the micellar phase is generally much lower than that of water and hence this medium can solubilize many organic compounds, which have limited solubility in water (Dwars et al., 2005). Solubilization can occur with or without interactions of the surfactant molecules with the solute. Nonionic surfactants which have lower critical micelle concentration (CMC) form larger aggregates and thus solubilization results in a considerably high concentration of the organic solute in the micellar medium (Ullah et al., 2019). Ionic surfactants on the other hand, form smaller micellar aggregates, and also exhibit some sort of interaction with polar solutes. This interaction further enhances solubilization, which plays a vital role in micellar catalysis (Mirgorodskaya et al., 2018; Pillai et al., 2018).

If two or more surfactants are mixed, their binary or ternary mixture shows either synergism or antagonism and, due to this property, mixed surfactant systems have been found to be superior to single surfactant systems in many applications (Agneta et al., 2019; Paria, 2008). The structure of micelles formed by the mixture of surfactants can be substantially different from those of individual surfactants (Varade and Bahadur, 2005).

In the last few decades, ionic liquids have been extensively studied due to their unique physicochemical properties (Welton, 2018). Use of ionic liquids as reaction media is well known and in many cases the ionic liquids not only act as solvents but also actively participate in the formation or stabilization of intermediates (Pârvulescu and Hardacre, 2007). However, the high cost and viscosity of ionic liquids are major constraints in their application as reaction medium.

Ionic liquids that contain a hydrophobic chain of suitable length exhibit surfactant-like behavior and hence are termed as surface-active ionic liquids (SAIL). Like conventional surfactants, they also form aggregates in water and hence function as solubilizing agents (Gehlot et al., 2018; Shaheen et al., 2019).

In the present study, 1-tetradecyl-3-methylimidazol-1ium bromide $[C_{14}mim]Br$, a SAIL, was synthesized and mixed with a nonionic surfactant, Octylphenol ethoxylate with 10 moles of ethylene oxide (OPE-10). Solubilization of toluene in this mixed surfactant system was determined by molar solubilization ratio (MSR) and partition coefficient values. The solubilized toluene was then subjected to selective oxidation to benzaldehyde using hydrogen peroxide as a green oxidant and tungstic acid as a catalyst.

[C₁₄mim]Br was synthesized by a reported method (Liu et al., 2019) in which equimolar quantities of 1methyl imidazole and 1-bromotetradecane were mixed in methanol and refluxed for 24 h under nitrogen atmosphere. Diethyl ether was added to the viscous semisolid obtained after removing the solvent by rotary evaporator. The mixture was kept aside for 72 h in a refrigerator. The white solid obtained was filtered and characterized by FTIR, and ¹H NMR techniques. CMC of the individual surfactants and their mixtures were determined by surface tension, specific conductivity, and dye solubilization methods (Supporting information). Average CMC obtained by these three techniques are given in Table 1.

The CMC obtained are close to those reported earlier (Sun et al., 2013). CMC of $[C_{14}mim]Br$ decreases with the addition of OPE-10. This may be due to the decrease in the mutual repulsion among the $[C_{14}mim]^+$ ions by the insertion of OPE-10. Possible hydrogen bonding between the ionic liquid and OPE-10 can be another reason for the

Table 1 CMC of individual surfactants ([C14mim]Br and OPE-10) and their mixtures (25 °C)

Sr. No.	$\alpha([C_{14}mim]Br)$	CMC (mM)					
		Surface tension method	Specific conductivity method	Dye solubilization method	Average		
1	1	2.31	2.33	2.0	2.21		
2	0.8	0.68	0.67	0.59	0.64		
3	0.6	0.29	0.26	0.21	0.25		
4	0.4	0.26	0.25	0.20	0.23		
5	0.2	0.19	0.17	0.14	0.16		
6	0	0.23	_	0.18	0.21		

Note: Where α is the mole fraction of [C₁₄mim]Br.



Fig 1 Solubility of toluene in pure surfactant (a) OPE-10, (b) [C₁₄mim]Br and their mixtures by varying mole fraction of [C₁₄mim]Br (c) $\alpha = 0.8$ (d) $\alpha = 0.6$ (e) $\alpha = 0.4$ (f) $\alpha = 0.2$

lower CMC of the mixed surfactants as compared to that of the SAIL (Sen et al., 2019; Wang et al., 2017).

The solubilization capacity for toluene was determined using various compositions of the two surfactants. Tenmillilter of five different concentrations of each surfactant was prepared and mixed accordingly to get a constant composition of mole fraction in each set. Constant volume of toluene (1 mL) was added in each flask and the flasks were kept in a shaker for 24 h to attain equilibrium. The phases were separated using a separating funnel and water was added to the aqueous phase to bring the concentration below CMC. Toluene was then extracted by petroleum ether from the aqueous phase and the amount of toluene present was analyzed by gas chromatography.

The MSR and partition of solute in micelles—water (partition coefficient, K_M) are two important parameters to

Sr. No.	$\alpha([C_{14}MIM]Br)$	MSR _{ideal}	MSR _{exp}	$R = MSR_{exp} / MSR_{ideal}$	K_M	$\ln K_M$
1	1	_	0.22	_	1746.86	7.46
2	0.8	0.25	0.28	1.13	2144.97	7.67
3	0.6	0.28	0.41	1.33	2851.47	7.95
4	0.4	0.31	0.43	1.38	2948.53	7.98
5	0.2	0.34	0.49	1.41	3224.66	8.07
6	0	_	0.38	_	2700.09	7.90

Table 2 MSR and partition coefficient of toluene in SAIL and its mixture with OPE-10

measure the effectiveness of micelles toward solubilization. MSR depicts the number of moles of solute that can be solubilized per mole of surfactant while K_M is the distribution of solute between water and micelles in terms of moles.

MSR is expressed by Eq. (1) (Maswal et al., 2015)

$$MSR = \frac{[S_T] - [S_M]}{[C] - CMC}$$
(1)

where S_T and S_M are the apparent solubilities of the solute in water and micelles, respectively. *C* is the concentration of surfactant taken and CMC its critical micelle concentration. The surfactant concentrations used for determining MSR are higher than the CMC (*C* >> CMC). The slope of the plot of concentration of solute present in the solution *versus* concentration of surfactant gives the MSR (Fig. 1).

The partition coefficient is given by Eqs (2) and (3)

$$K_M = \frac{X_m}{X_a}.$$
 (2)

where

 X_m = mole fraction of solute in micelles = $\frac{MSR}{(1 + MSR)}$ and

 X_a = mole fraction of solute in aqueous phase = $[S_T]$. V_w

Equation (2) can be rearranged as

$$K_M = \frac{\text{MSR}}{S_T \cdot V_W \cdot (1 + \text{MSR})} \tag{3}$$

The MSR and K_M of toluene in individual and mixed surfactants system are given in Table 2.

The MSR and K_M values reveal enhanced solubilization of toluene in the mixed surfactant system. In the case of SAIL, solubilization may occur with additional π - π interaction between the solute and the imidazolium head group (Łuczak et al., 2013). The higher values of MSR and K_M obtained with mixed surfactants support synergism.

Ideal value of MSR is given by Eq. (4) as (Rao and Paria, 2009)

$$MSR_{ideal} = \alpha_1 MSR_1 + \alpha_2 MSR_2$$
(4)

In the present study, MSR $_{experimental}/MSR_{ideal} > 1.0$, indicating better solubilization of toluene in the mixed surfactant system.



Scheme 1 Oxidation of toluene



Scheme 2 Bromination of toluene

Table 3 Conversion and selectivity for the oxidation of toluene

Entry	Catalyst	Conversion	Selectivity (%)		
		(%)	Benzaldehyde	Benzoic acid	
1	Sodium tungstate	Trace	—	—	
2	Ammonium molybdate	Trace	—	—	
3	Tungstic acid	30	80	20	
4	Molybdic acid	10	75	25	
5	Ferric chloride	Trace	—	_	

The solubilized toluene was then subjected to liquid phase catalytic oxidation (Scheme 1). For this study, 5 mL solution of $[C_{14}mim]Br$ ($\alpha = 0.6$) and OPE-10 were taken in a round bottom flask to which 0.5 mmol of toluene and 0.1 mol% of the catalyst were added and the reaction mixture was kept in an ice bath. The oxidant H₂O₂ in appropriate mole ratio was then added dropwise. The reaction was carried out at various temperatures. The progress of

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Fig 2 Effect of temperature on conversion and selectivity



Fig 3 Effect of mole ratio of H_2O_2 on conversion and selectivity

reaction was monitored by gas chromatography using biphenyl as an internal standard.

It was confirmed both surfactants did not have any catalytic activity for the chosen reaction (Supporting information, Table 1 entry 1, 2, and 3). Sodium molybdate, sodium tungstate, tungstic acid, molybdic acid, and ferric chloride were tested as catalysts for the oxidation of toluene and the results are summarized in Table 3. The tungstic acid catalyzed system gives the highest conversion (30%) as well as selectivity to benzaldehyde (80%).

Effect of mole ratio of hydrogen peroxide to toluene and the effect of temperature on conversion and selectivity was also studied (Fig. 2).

When the temperature was increased from 40 to 80 $^{\circ}$ C, conversion of toluene increased from 10% to 80%. However, at 80 $^{\circ}$ C, selectivity toward benzaldehyde decreases to 40%. It is possible that at this temperature, complete oxidation occurs as a parallel reaction.

The effect of mole ratio of H_2O_2 was studied at 60 °C (Fig. 3). At 1:1 and 1:2 mol ratios, selectivity for the formation of benzaldehyde was higher but when the mole ratio

was changed to 1:3, benzoic acid was observed as the major product indicating a decreased selectivity toward benzaldehyde.

As it is well known that the oxidizing efficiency of peroxotungstate may increase in acidic solutions (Ishimoto et al., 2012), pH of the reaction mixture in the present study was decreased to about 4.0 by the addition of Conc.H₂SO₄. Surprisingly under such acidic conditions, bromo toluene was obtained as reaction product confirmed by Gas Chromatography–MS results (Scheme 2). This can be due to the reaction of the counterion of the SAIL with toluene under acidic conditions.

In conclusion, MSR and partition coefficient values indicate enhanced solubilization of toluene in the mixed micellar system. The solubilized toluene can successfully be oxidized by tungstic acid to benzaldehyde at 60 °C.

Considering the high cost of ionic liquids, use of mixed systems of SAIL and a conventional surfactant system can be a cost effective alternative. This new class of reaction medium can be extensively explored for a gamut of organic reactions.

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Conflict of Interest The authors declare that they have no conflict of interest.

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