



# The effect of hydrophilic ionic liquid 1-butyl-2,3-dimethylimidazolium bromide on the aggregation behavior of tetradecyltrimethylammonium bromide in aqueous media

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## ABSTRACT

The aggregation behavior of a conventional cationic surfactant, tetradecyltrimethylammonium bromide (TTAB), in a trisubstituted imidazolium based hydrophilic ionic liquid (IL), 1-butyl-2,3-dimethylimidazolium bromide [bdmim][Br]/water systems was investigated by conductance, fluorescence, <sup>1</sup>H NMR spectroscopy and dynamic light scattering (DLS). Different physicochemical properties such as the critical micelle concentration (cmc), degree of dissociation ( $\alpha$ ), thermodynamic parameters ( $\Delta G_m^\circ$ ,  $\Delta H_m^\circ$  and  $\Delta S_m^\circ$ ) of micellization, aggregation number ( $N_{agg}$ ) and aggregate size were determined. The micelles formed just like in aqueous medium and cmc values were found to be smaller at different wt.% of IL than in water. The cmc value of TTAB gets lowered until 20.0 wt.% of IL in the medium. At significantly higher wt.% of IL in the system cmc becomes higher. The variation of chemical shifts of surfactant protons in the presence of IL revealed that the electrostatic interaction has a prominent influence on the cmc and other thermodynamic properties of surfactant. It is demonstrated that [bdmim][Br] can be judiciously utilized at different wt.% for enhancing the surface activity and altering the physicochemical properties of TTAB.

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## 1. Introduction

ILs are a class of organic compounds which generally composed of a bulky organic cation and appropriate organic or inorganic anion and have melting points less than 373 K. Their interesting properties such as negligible vapor pressure, large liquid range, high thermal stability, excellent dissolution capacity, non-flammability and high electrical conductivity made them very useful green solvents [1–3]. Due to their environmentally benign nature ILs are receiving huge attention from scientific community. These have been found tremendous applications in the field of catalysis, solvation, separation, chemical synthesis and electrochemical processes [4–6]. Their high stability and easy recyclability make them potential substitutes to their organic analogues [7]. The physical and chemical properties of ILs depend on their molecular structure. These have been highly modified for desired applications by introducing different functional groups or alkyl chains in their structure thus to obtain ‘task specific ILs’. Their amphiphilic properties have attracted the interest of researchers in the past few years in investigating their self-aggregation in aqueous and other media [8–10]. Nowadays, different types of ILs have also been employed to modulate the aggregation properties of other amphiphiles such as surfactants, lipids and block copolymers [11].

The self-assembly of surfactant molecules into different structures allow their utilization in a number of fields such as drug delivery, flow field regulators, membrane mimetic media, nano-reactors for enzymatic reactions, solubilizing and emulsifying agents, and other dispersant technologies [12–14]. The surfactant properties significantly changes at their critical micelle concentration. As upon aggregation a different medium becomes available which is entirely different from the surrounding environment. This forms the basis for the variety of technological applications of surfactant systems. Their aggregation properties can be judiciously modified due to the change in temperature and pressure or with addition of some external additives such as co-solvents, co-surfactants, electrolytes, and polar and non-polar organics under similar conditions [15–18].

From the past decade many research groups have invested efforts to utilize ILs to modify the properties of various surfactants [19–22]. Pandey et al. have shown the effect of ILs on the aggregation behavior of different types of surfactants [23–25]. Inoue's group has highly explored the effect of ILs on aggregation of polyoxyethylene (POE)-type non-ionic surfactants [26,27]. In this regard, recently our own group had reported the effect of IL, 3-methyl-1-pentylimidazolium hexafluorophosphate, [pmim][PF<sub>6</sub>] on aggregation behavior of sodium dodecyl sulfate (SDS) [28], cetyltrimethylammonium bromide (CTAB), and cetyltrimethylammonium chloride (CTAC) [29]. We have reported that surfactant micellization in [pmim][PF<sub>6</sub>] is primarily governed by the combination of cation–anion interactions with solvophobic effect

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which results in an increase in cmc of the studied surfactants. Other properties such as  $N_{agg}$  and  $\delta$  values of surfactant protons also varied significantly in the presence of IL.

In our previous work, we have successfully demonstrated the effect of trisubstituted imidazolium based ILs, 1-butyl-2,3-dimethylimidazolium chloride [bdmim][Cl], and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bdmim][BF<sub>4</sub>] in altering the micellization properties of anionic surfactant SDS in aqueous media [30,31]. Therein we have clearly shown the effect due to change in anion of IL on surfactant properties. It can be concluded there that due to the solvophobicity of the IL/water system the cmc of aqueous SDS solution increases and the aggregation number decreases. Further it will be interesting to study the effect of this kind of ILs on a cationic surfactant, where change due to head group will be observed. Therefore, in continuation to our previous work, herein we are reporting the modulations in the aggregation properties of aqueous solutions of a cationic surfactant tetradecyltrimethylammonium bromide (TTAB) (Scheme 1) upon addition of IL 1-butyl-2,3-dimethylimidazolium bromide, [bdmim][Br] (Scheme 1) using conductance, fluorescence, <sup>1</sup>H NMR spectroscopy and dynamic light scattering (DLS). This investigation will help in better understanding the effect of ILs in modifying the properties of aqueous surfactant systems.

## 2. Experimental section

### 2.1. Chemicals

1,2-Dimethylimidazole (98%), pyrene (99.9%) and pyrene-1-carboxaldehyde (99%) were procured from Sigma-Aldrich. TTAB (98%, AR) was obtained from Merck-Schuchardt and 1-bromobutane (>99%) from Acros Organics. Cetylpyridinium chloride (99%) was purchased from Loba Chemie and methanol (99%) from Rankem. Deuterium oxide having isotopic purity ( $\geq 99.9\%$ ) was obtained from SD Fine Chemicals. IL, [bdmim][Br], was synthesized in our laboratory and its structure was determined by IR and NMR technique. IL was dried under reduced pressure prior to the experiment and water content was checked by using Karl Fischer analysis. This was flushed with N<sub>2</sub> and stored in a dry place before use. All molar quantities were based on the International Union of Pure and Applied Chemistry (IUPAC) relative atomic mass table [32].

### 2.2. Synthesis of 1-butyl-2,3-dimethylimidazolium bromide [bdmim][Br]

For the synthesis of 1-butyl-2,3-dimethylimidazolium bromide [bdmim][Br], initially a slight excess of 1-bromobutane (14.8 g, 108 mmol) was added drop wise to 1,2-dimethylimidazole (10 g, 104 mmol) in a round bottom flask followed by refluxing the solution at about 60–70 °C for 24 h under N<sub>2</sub> atmosphere and then cooled to room temperature for 12 h. The resultant compound was washed with ether several times to get a white solid, which was dried in vacuum to

get 1-butyl-2,3-dimethylimidazolium bromide [bdmim][Br], with 89% yield. Karl–Fisher examination of the IL indicated that the water content reduced to less than 250 ppm. The product obtained was flushed with N<sub>2</sub> and stored in a dry place before use.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ -ppm): 0.847 (t, 3H), 1.267 (m, 2H), 1.708 (m, 2H), 2.507 (s, 3H), 3.588 (s, 3H), 4.029 (t, 2H), 7.233 (d, 1H), 7.267 (d, 1H).

### 2.3. Instruments and methods

Required amounts of materials were weighed using an A&D Co. Ltd. electronic balance (Japan, model GR-202) with a precision of  $\pm 0.1$  mg. All the experiments have been carried out in doubly distilled de-ionized water obtained from a Millipore, Milli-Q Academic water purification system having conductivity  $\leq 5 \mu\text{S cm}^{-1}$ . All experiments were performed in triplicate and obtained values were averaged.

#### 2.3.1. Conductance measurements

The electrical conductivities were measured at different temperatures, 298.15 to 318.15 K, with an uncertainty of  $\pm 0.01$  K in a water jacketed flow dilution cell. A digital conductivity meter CM-183 micro-processor based EC-TDS analyzer with ATC probe and conductivity cell with platinized platinum electrodes purchased from Elico Ltd., India was used for conductance measurements. Before the measurements, the conductivity cell was calibrated with the aqueous KCl solutions in the concentration range of 0.01–1.0 mol kg<sup>-1</sup>. The cell constant was determined to be 1.0021 cm<sup>-1</sup>. The small conductance due to water was subtracted from the measured data. Uncertainty of the measurements was less than 4%. The conductance measurements were taken after stirring the solution with each addition for the homogeneous mixing of the solution.

#### 2.3.2. Fluorescence measurements

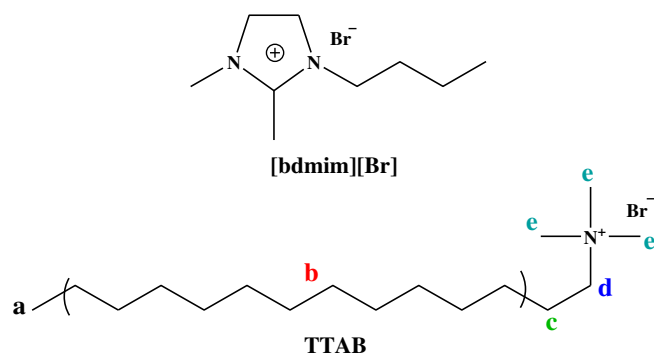
Fluorescence spectra were taken on model RF-5301PC with blazed holographic grating excitation and emission monochromators fitted with a 150 W Xenon lamp purchased from Shimadzu and using quartz cuvettes. TTAB and IL solutions at various concentrations were freshly prepared in aqueous media. Pyrene (Py) and pyrene-1-carboxaldehyde (PyCHO) were used as fluorescence probes and cetylpyridinium chloride as fluorescence quencher. Stock solution of Py (1  $\mu\text{M}$ ) and PyCHO (1  $\mu\text{M}$ ) was prepared in methanol. Aqueous TTAB-IL solutions were prepared by taking the appropriate amount of probe from the stock. The requisite amount of aqueous TTAB of desirable concentration was added to achieve required final concentration. Then calculated amount of IL was directly added to the aqueous TTAB solution and stirred for 12 h. The emission spectra of Py were recorded in the wavelength region 350–600 nm at an excitation wavelength of 334 nm using the slit width of excitation and emission, 3 and 1.5 nm respectively. The excitation wavelength for the PyCHO was 365 nm, while the emission spectra were recorded between 375 and 600 nm using the slit width of excitation and emission, 3 and 3 nm respectively.

#### 2.3.3. Dynamic light scattering

The size of aggregates present in the surfactant solution was measured by means of dynamic light scattering (DLS) method. DLS measurements were performed with a Malvern Zetasizer Nano apparatus (Malvern, UK) at 298 K. A He–Ne laser with a power of 4 mW was used as a light source. IL-surfactant solutions of particular concentration were prepared for the measurements.

#### 2.3.4. NMR measurements

The NMR chemical shifts for various protons were observed with a Bruker Avance III spectrometer operating at 400 MHz. In order to determine chemical shift  $\delta$  for [bdmim][Br] + TTAB solution in water, deuterium oxide (D<sub>2</sub>O) was used as a solvent for all the NMR measurements.



**Scheme 1.** Chemical structures of IL 1-butyl-2,3-dimethylimidazolium bromide [bdmim][Br] and cationic surfactant tetradecyltrimethylammonium bromide (TTAB).

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