

# Modulating effect of ionic liquid 1-butyl-2,3-dimethylimidazolium chloride on micellization behaviour of cationic surfactant dodecyltrimethylammonium bromide in aqueous media



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## ABSTRACT

The micellization behaviour of cationic surfactant dodecyltrimethylammonium bromide (DTAB) has been studied upon addition of 1-butyl-2,3-dimethylimidazolium chloride, [bdmim][Cl], a trisubstituted imidazolium based ionic liquid (IL) in aqueous media. The critical micelle concentration (cmc) and degree of dissociation ( $\alpha$ ) for the micelles were determined from conductance measurements for a temperature range of 298.15–318.15 K at different wt% of IL in the medium. The thermodynamic parameters ( $\Delta G_m^\circ$ ,  $\Delta H_m^\circ$  and  $\Delta S_m^\circ$ ) of micellization were evaluated by applying the charged pseudo-phase separation model for the micellar systems. Further fluorescence probe analysis has been utilized to obtain cmc value as a complementary to conductivity in order to validate the cmc values obtained from conductivity measurements. A continuous decrease in cmc was observed with addition of 10.0 wt% of IL but further addition of IL causes an increase in cmc of the surfactant solution. The aggregation number,  $N_{agg}$  and size of aggregates in aqueous DTAB solutions at different wt% of IL were determined by fluorescence quenching of pyrene and dynamic light scattering (DLS) studies, respectively. <sup>1</sup>H NMR measurements of post-micellar solution at lower wt% of IL have been done to understand the different inter-molecular interactions of surfactant molecules with [bdmim][Cl].

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## 1. Introduction

The self-assembly of amphiphiles into different structures allows their utilization in a number of fields such as drug delivery, flow field regulators, membrane mimetics media, nano-reactors for enzymatic reactions, solubilizing and emulsifying agents, and other dispersant technologies [1–3]. The properties of amphiphiles like surfactants significantly changes at critical micelle concentration due to aggregation of surfactant molecules. After aggregation micelles provide a medium which is entirely different from the surrounding environment. This forms the basis for a variety of technological applications of surfactant systems. Their aggregation properties can be modified due to change in temperature and pressure or with addition of some external additives such as co-solvents, co-surfactants, electrolytes, polar and non-polar organics etc. under similar conditions [4–7].

Nowadays different types of ILs have been employed to modulate the aggregation properties of surfactant systems. Due

to their environmentally benign nature ILs are receiving huge attention from scientific community. These possess interesting and useful properties such as negligible vapor pressure, large liquid range, high thermal stability, excellent dissolution capacity, non-flammability and high electrical conductivity [8–10]. So these have been found tremendous applications in the field of catalysis, solvation, separation, chemical synthesis and electrochemical processes etc. [11–13]. ILs generally composed of a bulky organic cation and appropriate organic or inorganic anion and have melting point less than 373 K. Their high stability and easy recyclability makes them potential substitutes to their organic analogues [14]. The properties of ILs have been usually modified for desired applications by introducing different functional groups or alkyl chains in their structure thus to obtain ‘task specific ILs’.

From the past decade many research groups have invested efforts to utilize ILs to modify the properties of various surfactants [15–18]. 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 behaviour of sodium dodecyl sulphate, (SDS), [19] cetyltrimethylammonium bromide, (CTAB) and cetyltrimethylammonium chloride, (CTAC) [20]. We have reported that surfactant micellization in [pmim][PF<sub>6</sub>] is primarily

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governed by the combination of cation–anion interactions with solvophobic effect 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. Pandey et al. have shown the effect of ILs on aggregation behaviour of different type of surfactants [21–23]. Furthermore, Inoue's group has also highly explored the effect of ILs on aggregation of polyoxyethylene (POE)-type non-ionic surfactants [24,25]. In all these previous studies effect of mainly disubstituted 1,3-dialkylimidazolium salts have been studied, addition of extra alkyl group on IL can differently modulate the surfactant properties.

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 [26,27]. Therein we have clearly shown the effect due to change in anion of IL on surfactant properties. Further it will be interesting to study the effect of these 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 dodecyltrimethylammonium bromide (DTAB) (Scheme 1) upon addition of IL 1-butyl-2,3-dimethylimidazolium chloride, [bdmim][Cl] (Scheme 1). Conductivity and fluorescence measurements have been used to obtain the cmc value for surfactant-IL solutions. Further thermodynamic parameters have been analysed to understand the driving force of micellization. It was possible to obtain the cmc values from both conductometry and fluoremetry up to 1.0wt% of added IL, after it cmc determination has been done through fluorescence only. The aggregation number and size of micelles has been determined through fluorescence quenching and DLS studies, respectively. <sup>1</sup>H NMR measurements have been done to understand the preferential site of interactions between IL and surfactant molecules. Here due to addition of IL [bdmim][Cl], contrasting results have been obtained from our previous investigations [26,27].

## 2. Experimental

### 2.1. Materials

DTAB (99%, AR) was obtained from Acros Organics and pyrene (99.9%) was procured from Sigma–Aldrich. 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 1-butyl-2,3-dimethylimidazolium chloride used in the present study is of the

same origin and purity as used in earlier study [26]. Water content in the IL was estimated to be less than 300 ppm using Karl–Fisher 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 [28]. The details of chemicals used in the present work are given in Table 1.

### 2.2. 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.

#### 2.2.1. Conductance measurements

The electrical conductivities were measured at different temperatures 298.15–318.15 K with an uncertainty of  $\pm 0.01$  K in a water jacketed flow dilution cell. A digital conductivity meter CM-183 microprocessor based EC-TDS analyser with ATC probe and conductivity cell with platinized platinum electrodes purchased from Elico Ltd., India was used for conductance measurements. This instrument works on the power supply of 90–260 V alternating current and at frequency of 50–60 Hz. Before the measurements, the conductivity cell was calibrated with the standard aqueous potassium chloride solutions in the concentration range of 0.01–1.0 mol kg<sup>-1</sup> of known specific conductance and 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%.

#### 2.2.2. Fluorescence measurements

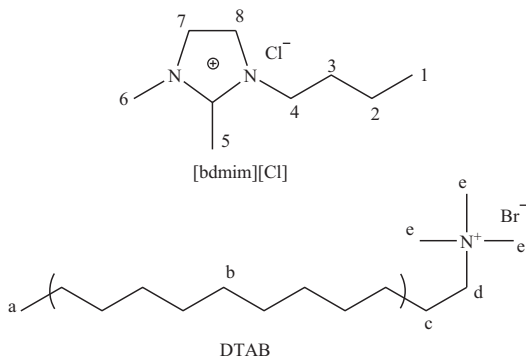
Fluorescence spectra were taken on model RF-5301PC with blazed holographic grating excitation and emission monochromators fitted with a 150 W Xenon lamp purchased from Shimadzu and using quartz cuvette. Pyrene and cetylpyridinium chloride were used as fluorescence probe and quencher, respectively. Stock solution of pyrene (1  $\mu\text{M}$ ) was prepared in methanol. DTAB and IL solutions at various concentrations were freshly prepared in doubly distilled de-ionized degassed water and stirred for 12 h. After 12 h stirring, these solutions were allowed to stabilize for half an hour to record the spectra. The fluorescence spectra 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 ratio ' $I_1/I_3$ ' of the fluorescence intensities of the first and third vibronic peaks was calculated for data analysis.

#### 2.2.3. 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.

#### 2.2.4. <sup>1</sup>H NMR measurements

The NMR chemical shifts for various protons were observed with a Brüker FT-NMR spectrometer operating at 300 MHz. In order to determine chemical shift  $\delta$  for [bdmim][Cl]+DTAB solution in aqueous media, deuterium oxide (D<sub>2</sub>O) was used as solvent for all the NMR measurements. The chemical shifts are



**Scheme 1.** The chemical structures of IL, 1-butyl-2,3-dimethylimidazolium chloride [bdmim][Cl] and cationic surfactant dodecyltrimethylammonium bromide (DTAB).

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