

Thermodynamic and micellization properties of aqueous cetyltrimethylammonium bromide solution in presence of 1-butyl-2,3-dimethylimidazolium bromide



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ABSTRACT

Micellization behaviour of cetyltrimethylammonium bromide (CTAB) in the presence of ionic liquid (IL), 1-butyl-2,3-dimethylimidazolium bromide [bdmim][Br] in aqueous medium has been investigated by conductance, fluorescence, ¹H NMR, dynamic light scattering (DLS) and transmission electron microscopy (TEM) techniques. The temperature dependence of critical micelle concentration (cmc) obtained from conductivity measurements at different temperatures (298.15, 308.15, and 318.15) K has been used to calculate various thermodynamic parameters of micellization and the obtained parameters are further used to understand the surfactant-IL interactions for the studied (0–0.2) wt% of IL. Further fluorescence technique has been used to obtain the cmc and aggregation number from (0–30.0) wt% of added IL in the surfactant solution using different probes at 298 K. To understand the variation in micellar size at different wt% of IL, DLS and TEM techniques have been employed. Interestingly, due to presence of IL in surfactant solution in either low or high proportion, micellar size increases. IL effectively enhances the surface activity of surfactant solution until 2.0 wt% of added IL but above this wt% it starts increasing cmc. The crucial role of electrostatic interactions is clearly implied by ¹H NMR studies.

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1. Introduction

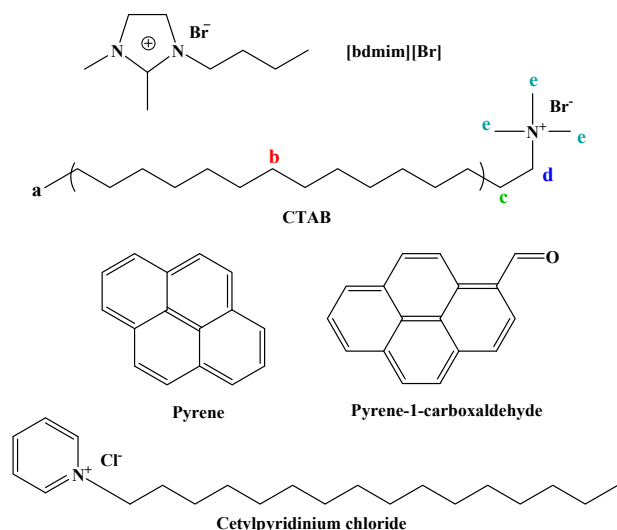
ILs have been grabbing the special attention of scientific community due to their impressive properties viz. minimal or no vapour pressure, non-flammability, high mechanical stability, high conductivity and excellent ability to solubilize various substances [1–4]. The above said versatile properties have made ILs useful for different synthesis processes [5–7]. They are widely used as catalysts owing to amphiphilic nature of some ILs which provide a micellar media for reactions [8,9]. Being ionic in nature, these constitute of a bulky organic cation and suitable anion, so used as electrolytes for batteries, solar and fuel cells [10,11]. Imidazolium based ILs consisting of 1-alkyl-3-methylimidazolium cation, [C_nmim]⁺[X][−] have been explored in the field of colloidal formulations [12–14]. The properties of ILs are

generally tailored by using different cations, anions and functional groups [15,16].

The use of ILs to modulate the aggregation properties of different type of surfactants had gain momentum during the past decade. Surfactants have made their place indispensable in manufacture of many conventional products in almost every chemical industry such as cosmetics, paints, dyestuffs, pharmaceuticals, agrochemicals, fibres, or plastics [17–19]. Javadian et al. studied the micellization behaviour of CTAB in ILs, N-butyl imidazolium chloride [bim][Cl], 1-butyl-3-methyl imidazolium chloride [bmim][Cl] and 1-hexyl-3-methyl imidazolium bromide [hmim][Br] in aqueous media [20]. The CTAB micellization is favourable in [bim][Cl]/water than that of [bmim][Cl]/water, pertaining to the crucial role of H-bonding in these systems. Pandey et al. investigated the role of IL in modifying the properties of CTAB in presence of IL 1-hexyl-3-methyl imidazolium bromide [hmim][Br] and a co-surfactant n-hexyltrimethylammonium bromide (HeTAB) where the dual nature of IL has been observed [21]. This work on IL-surfactant mixed systems is useful

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Scheme 1. Chemical structures of IL 1-butyl-2,3-dimethylimidazolium bromide [bdmim][Br], cationic surfactant cetyltrimethylammonium bromide (CTAB), fluorescence probes and quencher used in the study.

for various applications in different fields. ILs enhances surfactant properties which will help in better application of surfactant systems. The versatile properties of ILs also add to increased solubility of different organic and inorganic solutes which will aid in various chemical synthesis and reactions in surfactant micellar systems. The properties of surfactant micellar systems are highly relevant in the field of colloidal and interface applications.

In our previous investigations we have shown the modulating effect of IL 1-butyl-2,3-dimethylimidazolium chloride [bdmim][Cl] [22] and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bdmim][BF₄] [23] on micellization behaviour of sodium dodecylsulphate (SDS) in aqueous medium. The effect due to change of IL anion was clearly observed in these studies. Then we studied the effect of IL [bdmim][Cl] [24] on aggregation behaviour of dodecyltrimethylammonium bromide, DTAB to understand the change in behaviour of IL toward different kind of surfactants. There we clearly observed the change in IL behaviour towards different surfactants. Further we studied the effect of IL [bdmim][Br] [25] on the aggregation properties of tetradecyltrimethylammonium bromide, TTAB. Now in the cationic surfactant series the effect of IL [bdmim][Br] on CTAB micellization behaviour has been studied (Scheme 1). We want to observe the change in behaviour of IL towards same kind of surfactant but with longer tail region. Here distinct results have been obtained if compared to our previous investigations on cationic surfactants and those reported in literature in relation to the concentration of IL used as additive. We observed that the long chain surfactant CTAB in the series of these alkyltrimethylammonium bromides experiences a greater decrease in solvophobicity on addition of IL [bdmim][Br] if equated with TTAB. This IL behaved like an electrolyte in case of TTAB [25] even at a wt% as high as 20.0 while here it does so only up to 2.0 wt%. Most of the previous studies on CTAB had been confined to high concentration region of IL [20,21]. But we have studied very low as well as very high concentration of IL, thus very interesting results have been obtained.

2. Experimental section

2.1. Chemicals

1,2-Dimethylimidazole (98%), pyrene (99.9%) and pyrene-1-carboxaldehyde (99%) were obtained from Sigma–Aldrich. CTAB (99%, AR) has been obtained from Merck-Schuchardt and 1-bromobutane (>99%) from Acros Organics. Cetylpyridinium chloride (CPC) (99%) has been obtained from Loba Chemie. Deuterium oxide ($\geq 99.9\%$) was purchased from SD Fine Chemicals and methanol (99%) from Rankem. The origin and purity of IL, [bdmim][Br], is same as described in our previous communication [25]. The International Union of Pure and Applied Chemistry (IUPAC) relative atomic mass table is used to calculate the relevant atomic masses [26]. The details of chemicals used in this study are given in Table 1.

2.2. Instruments and methods

The chemicals were weighed using A&D Co. Ltd. electronic balance (Japan, model GR-202) with precision of ± 0.1 mg. The doubly distilled de-ionized water (conductivity $\leq 5 \mu\text{S cm}^{-1}$) obtained from a Millipore, Milli-Q Academic water purification system was used to perform the experiments. The average value obtained from three measurements for each experiment has been considered.

2.2.1. Conductance measurements

Conductance was measured using digital conductivity meter from Elico Ltd., India (model CM-183). It is provided with ATC probe and conductivity cell with platinized platinum electrode; it has EC-TDS analyser which is based on microprocessor. The detailed procedure and other specifications of conductivity measurements have been mentioned in our previous studies [22,23]. The level of uncertainty has been below 4% for conductance measurements.

2.2.2. Fluorescence measurements

A Shimadzu spectrofluorimeter (model RF-5301PC) was used to record the fluorescence spectra. This instrument works on a 150 W Xenon lamp and has blazed holographic grating excitation and emission monochromators. This instrument is computer controlled and uses an arbitrary scale from (0–1000) to detect the fluorescence signal. The probes used are pyrene and pyrene-1-carboxaldehyde (PyCHO), while quencher is CPC. The sample and stock solution preparation has been done as described in our previous study [22,25].

2.2.3. Dynamic light scattering

The size of surfactant aggregates present in solution has been obtained using dynamic light scattering. A Malvern Zetasizer Nano apparatus (Malvern, UK) was used to perform the experiments at 298 K. As light source a 4 mW power He–Ne laser has been used. IL-surfactant solutions of particular concentration were prepared for the measurements.

2.2.4. ¹H NMR measurements

The Bruker Avance III spectrometer (400 MHz) was used to obtain proton NMR chemical shifts δ (ppm). The solvent used was Deuterium oxide. Centre of the HDO signal (4.7 ppm) was used as the internal reference.

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