



# Investigations of interactions between surface active ionic liquid 1-butyl-3-methyl imidazolium dodecylbenzenesulfonate and cationic polyelectrolyte poly(diallyldimethylammonium chloride) in aqueous solution

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## ABSTRACT

In the present study, we have reported a comprehensive assessment of interactional behavior between the surface active ionic liquid (SAIL) 1-butyl-3-methylimidazolium dodecylbenzene sulfonate [C<sub>4</sub>mim][DBS] and cationic polyelectrolyte poly(diallyldimethylammonium chloride) [PDADMAC] solution in aqueous solution. Various techniques such as surface tension, isothermal titration calorimetry (ITC), conductivity, dynamic light scattering (DLS) and turbidity have been employed to get insight into interactions among [C<sub>4</sub>mim][DBS] and polyelectrolyte in the interfacial region. Then surface parameters such as surface excess concentration ( $\Gamma_{cmc}$ ), surface pressure at interface ( $\Pi_{cmc}$ ), minimum area occupied by one molecule of SAIL at air-solvent interface ( $A_{min}$ ), adsorption efficiency ( $pC_{20}$ ) and surface tension at critical micelle concentration (cmc) ( $\gamma_{cmc}$ ) have been calculated from tensiometric measurements. The values of cmc decrease with increase in concentration of polyelectrolyte indicating towards the predominance of electrostatic interactions except at intermediate concentration (0.01 g/L PDADMAC) for which hydrophobic interactions can be held responsible. The standard enthalpy of micellization ( $\Delta H_m^\circ$ ) has been obtained from ITC measurements. Further, thermodynamic parameters i.e. standard free energy of micellization ( $\Delta G_m^\circ$ ) and standard entropy of micellization ( $\Delta S_m^\circ$ ) have been evaluated from conductivity measurements. The size of complexes formed among [C<sub>4</sub>mim][DBS] and polyelectrolyte have been characterized using DLS and turbidity measurements. Overall, the electrostatic interactions play a major role among SAIL and polyelectrolyte which is generally expected from oppositely charged systems. The process of micellization has been found to be exothermic and spontaneous thermodynamically in presence of PDADMAC supported by gain in entropy.

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## 1. Introduction

Systems comprising amphiphilic surfactant and oppositely charged polyelectrolytes are well established discipline from scientific and industrial standpoint [1–7]. These systems display a complex associative mechanism upon mixing these charged species in aqueous solution resulting into organized dynamic aggregates called surfactant-polyelectrolyte complexes which embrace great technological importance [8–20]. The associative mechanism among polyelectrolytes/polymers and surfactants has been substantially justified as a competition among hydrophobic and electrostatic interactions [21,22]. However, in case of oppositely charged polyelectrolytes and surfactants, electrostatic interactions are dominant and hydrophobicity gives a judgement for

the interactions between non-ionic polyelectrolytes/polymers and ionic surfactants [23,24]. The surfactant-polymer interactions depend upon several factors such as the nature of surfactant head group, polar groups embedded in the polymer backbone, polymer hydrophobicity, and flexibility.

Several dedicated efforts have been made to study the interactions existing among oppositely charged surfactants and polyelectrolytes. Also, micellization appears to be the weightiest attribute while discussing surfactant solutions. So the comprehension of driving forces accountable for micelle formation becomes quite imperative and for this sake, parameters such as free energy, enthalpy and entropy of micellization have been calculated by utilizing the laws of thermodynamics. There is an ongoing committed effort to look out for better alternatives for specific applications by altering the molecular structure of ionic liquid. The various applications of SAILs in aqueous polyelectrolyte solutions rest upon the understanding of the manifold synergic mechanisms between SAILs and polyelectrolytes.

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The halogen free ILs soon became appreciated as greener alternative to halogen containing ILs and various halogen free ILs with sulfate [25], nitrite [25], nitrate [25], benzenesulfonate [26], toluenesulfonate anions [27] and dodecylbenzenesulfonate [28] have been synthesized. Interactions between sodium dodecylbenzenesulfonate and polymers have been investigated for long and have been extensively documented [29–36]. But imidazolium based surface active ionic liquid having dodecylbenzenesulfonate as anion in aqueous solution has been rarely investigated [28]. Conventionally, alkylbenzenesulfonates enjoy the status of workhorse in the synthetic detergent industry.

Our group has also investigated the interactional behavior of cationic surfactant lauryl isoquinolinium bromide [C<sub>12</sub>iQuin][Br] and oppositely charged polyelectrolytes, poly (acrylic acid sodium salt) (NaPAA) in aqueous solution [37]. It has been established that the increase in cmc with increase in polyelectrolyte concentrations was due to the dominance of hydrophobic interactions. Here, a systematic study dedicated to understand the interactional behavior of synthesized anionic surfactant [C<sub>4</sub>mim][DBS] with an oppositely charged polyelectrolyte poly (diallyldimethylammonium chloride) [PDADMAC] in aqueous solution has been reported for the first time by using surface tension, isothermal titration calorimetry, electrical conductivity, dynamic light scattering and turbidity measurements. There is no such report available on the interplay of SAIL such as [C<sub>4</sub>mim][DBS] and [PDADMAC] in aqueous media. Altogether, this information provides an understanding of various interactions prevailing into our systems. The documentation of aggregation properties of these novel SAILS may generate interest in their uses as novel reaction media and in electrochemistry as well as promising alternatives to conventional surfactants in various multi-ton-scale technical applications. The schematic of the present work has been presented into Scheme 1.

## 2. Experimental

### 2.1. Materials

1-Bromododecane (>98%), poly(diallyldimethylammonium chloride) solution PDADMAC, were purchased from Sigma-Aldrich. Methanol (99%) was bought from Rankem. 1-Methylimidazole (99%) was obtained from Acros Organics. All aqueous solutions have been

prepared using Millipore grade water. The specific conductivity and surface tension of millipore grade water were measured as 3  $\mu\text{S cm}^{-1}$  and as 71  $\text{mN m}^{-1}$  at 298.15 K respectively. The ionic liquid, 1-butyl-3-methylimidazolium dodecylbenzenesulfonate [C<sub>4</sub>mim][DBS] has been synthesized and purified into laboratory followed by drying under reduced pressure. <sup>1</sup>H NMR technique has been used to verify the purity of [C<sub>4</sub>mim][DBS]. The detailed information of chemicals used in the present study has been provided into Table 1.

### 2.2. Synthesis of 1-butyl-3-methylimidazolium dodecylbenzenesulfonate [C<sub>4</sub>mim][DBS]

Equimolar mixture of 1-butyl-3-methyl imidazolium bromide [C<sub>4</sub>mim][Br] and sodium dodecylbenzenesulfonate (SDBS) were dissolved in dichloromethane (DCM) in a round bottomed flask and stirred for 24 h. At the end of the reaction, salt NaBr precipitated at the bottom of flask was filtered with Whatmann filter paper and DCM layer containing ionic liquid was washed several times with water up to the point where the aqueous layer started giving negative result with 1 M AgNO<sub>3</sub> solution which showed that there are no Br-ions present followed by drying of DCM layer over Na<sub>2</sub>SO<sub>4</sub>. The ionic liquid was dried under vacuum. The structure of [C<sub>4</sub>mim][DBS] was confirmed by analyzing its <sup>1</sup>H NMR spectra.

The NMR details of corresponding protons for [C<sub>4</sub>mim][DBS] are given below:

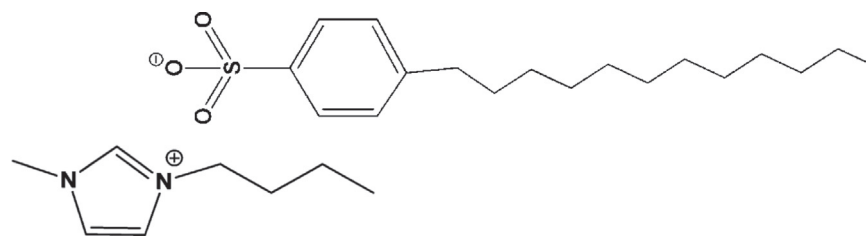
<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>,  $\delta_{\text{H}}$ ): 9.74 (s, 1H, 2-H), 7.74 (d, 2H, 2' & 6'-H,  $J_{\text{O}} = 8.0$  Hz), 7.48 (s, 1H, 4-H), 7.37 (s, 1H, 5-H), 7.09 (d, 2H, 3' & 5'-H,  $J_{\text{O}} = 8.0$  Hz), 4.15 (t, 2H, N-CH<sub>2</sub>), 3.95 (s, 3H, 1-CH<sub>3</sub>), 1.71–1.78 (m, 2H, 4'-CH<sub>2</sub>), 0.81–1.27 (m, 32H, CH<sub>2</sub>, CH<sub>3</sub> groups).

### 2.3. Instruments and methods

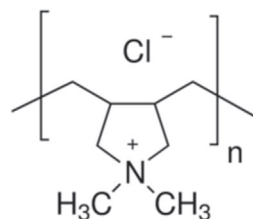
All aqueous solutions have been prepared with Millipore grade water. A & D co limited electronic balance (Japan, model GR-202) has been used to weigh the chemicals and it has an accuracy of 0.01 mg.

#### 2.3.1. Tensiometry

Surface tension measurements were performed out at 298.15 K by a Data Physics, Model DCAT-II automated tensiometer which employs the



1-Butyl-3-methyl imidazolium dodecylbenzenesulfonate



Poly(diallyldimethylammonium chloride)

**Scheme 1.** Chemical structure of ionic liquid 1-butyl-3-methylimidazolium dodecylbenzene sulfonate [C<sub>4</sub>mim][DBS] and polyelectrolyte poly(diallyldimethylammonium chloride) solution (PDADMAC).

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