

## Ionic liquid induced alterations in the physicochemical properties of aqueous solutions of sodium dodecylsulfate (SDS)



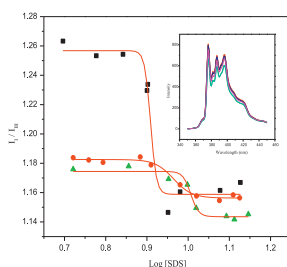
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### HIGHLIGHTS

- Micellization behaviour of anionic surfactant in presence of pentyl appended imidazolium based ionic liquid has been investigated systematically.
- Various thermodynamics parameters have been evaluated using conductivity data.
- An increase in *cmc* on addition of ionic liquid has been observed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Changes in the micellization behavior of an anionic surfactant sodium dodecylsulfate (SDS) in aqueous solutions have been investigated at varying concentration of hydrophobic ionic liquid 3-methyl-1-pentylimidazolium hexafluorophosphate  $[C_5mim][PF_6]$  using techniques like conductometry, densimetry and speed of sound at a temperature range of 298.15–318.15 K. Critical micelle concentration (*cmc*) of SDS increases upon addition of  $[C_5mim][PF_6]$ , which is also evidenced from fluorescence spectra of pyrene probe. Presence of solvophobic interactions is proposed to be the reason for these observations.

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### 1. Introduction.

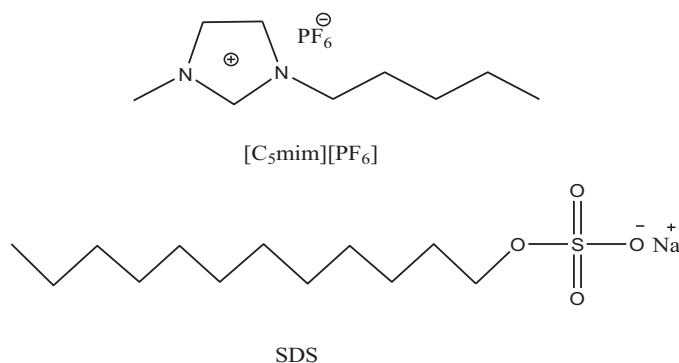
Favorable alterations of the physicochemical properties of aqueous micellar solutions of surfactants are important due to their applications in colloidal formulation. Ionic liquids (ILs) have emerged as one of the most interesting chemical both in fundamental and applicative research during last three decades [1–6]. ILs are special because of their properties such as low vapor pressure, tuneability [7], large liquid ranges and unique solvating ability which can be utilized in synthesis, catalysis and extraction

processes for the reduction of the amount of volatile organic solvents (VOSs) used in industry [8]. Disubstituted imidazolium cation based ionic liquids have been the most extensively studied in the open literature with anions like  $[BF_4]^-$ ,  $[PF_6]^-$ ,  $[N(CF_3SO_2)_2]^-$ ,  $[Br]^-$ ,  $[Cl]^-$ ,  $[CF_3SO_3]^-$ ,  $[MeSO_4]^-$ ,  $[SCN]^-$ ,  $[MDEGSO_4]^-$ ,  $[FeCl_4]^-$  and  $[CoBr_4]^-$  for various applications [9–33].

The utilization of ILs to alter the solution properties of surfactant solutions is an interesting and appealing concept both from environmental and applicative point of view. Armstrong et al. and Fletcher and Pandey have demonstrated the effectiveness of ILs in altering the key physicochemical properties of the aqueous solution of zwitterionic, nonionic and anionic surfactants [33–40]. The ability of IL in changing the properties of aqueous solution of surfactant is dependent on extent of interactions between the cation/anion of

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**Scheme 1.** Chemical structure of ionic liquid 3-methyl-1-pentylimidazolium hexafluorophosphate  $[C_5mim][PF_6]$  and surfactant sodium dodecylsulfate (SDS).

the IL and surfactant head group. Most of these investigations are based on the formation of IL aggregates in a variety of surfactants with imidazolium cation appended with even number of carbon atoms in alkyl chains [34,36,40–43]. It is well reported in literature that *cmc* of ionic surfactants in aqueous solutions decreases with the increase in ionic strength of the solution [44]. The presence of salt in water screens the electrostatic repulsion between charged head groups facilitating aggregation between surfactants and thereby lowering the *cmc*. Considering the lesser hydrophilic nature of IL ions compared to common inorganic ions the *cmc* of ionic surfactants is expected to be less because of better counter ion binding as water produces lesser resistance to the IL ions [34,35]. There are reports in literature that *cmc* of the surfactants is higher in ILs compared to pure water which is attributed to lower solvophobicity of the surfactant in ionic liquids [45].

Herein we report the changes occurring in micellar behavior of anionic surfactant sodium dodecylsulfate (SDS) with the addition of hydrophobic ionic liquid 3-methyl-1-pentylimidazolium hexafluorophosphate  $[C_5mim][PF_6]$ . Due to the solubility problems of  $[C_5mim][PF_6]$  in aqueous media the present study is limited only up to lower concentration. The outcomes of the results have been compared with interaction behavior of 1-butyl-3-methylimidazolium hexafluorophosphate with the surfactant solution [39]. There has been no report so far regarding the micelles formed by ions having pentyl side chain. Since there is always continued search for formulations with specific properties for various applications, the present results will be useful in designing formulations consisting of SDS and ionic liquid. The present study can prove to be useful from both practical and academic points of view.

Chemical structures of the IL  $[C_5mim][PF_6]$  and sodium dodecylsulfate (SDS) studied in this system are presented in Scheme 1.

## 2. Materials

SDS (purity 99%, AR) was obtained from Himedia and was used as received. IL  $[C_5mim][PF_6]$  was prepared in our laboratory and structure was confirmed by IR and NMR technique. IL was dried under reduced pressure prior to the experiment and moisture content was checked by using Karl Fischer analysis. Deuterium oxide (SD Fine Chemicals) having isotopic purity  $\geq 99.9\%$  was used as solvent in  $^1H$  NMR studies. Pyrene (purity 99.9%) from Sigma–Aldrich, cetylpyridinium chloride (purity 99%) from Loba Chemie and methanol (99%) from Rankem were used as received. All molar quantities were based on the International Union of Pure and Applied Chemistry (IUPAC) relative atomic mass table [46].

### 2.1. Synthesis of $[C_5mim][PF_6]$

1-Bromopentane added dropwise to 1-methylimidazole in a round bottom flask. The solution heated to reflux around 70–80 °C

for 24 h under nitrogen, and then cooled to room temperature for 12 h. The resulting compound was washed with ether several times to yield a viscous liquid, which was dried in vacuo to give 3-methyl-1-pentylimidazolium bromide ( $[C_5mim][Br]$ ) with a yield of approximately 82%.  $KPF_6$  was added to a solution of  $[C_5mim][Br]$  in dichloromethane and stirred for 24 h. The suspension was filtered to remove the precipitated bromide salt. The organic phase was repeatedly washed with distilled water ( $4 \times 30$  mL) until no precipitation of AgBr occurred in the aqueous phase upon the addition of a concentrated  $AgNO_3$  solution. The organic phase then washed two more times with water to ensure the complete removal of the bromide salt, dried over  $MgSO_4$ . The solvent removed in vacuo and the resulting IL stirred with activated charcoal for 12 h. The IL was then passed through a short alumina column(s) (acidic and/or neutral) to give a colorless IL, which was dried at 100 °C in vacuo for 24 h or until no visible signs of water were present in the IR spectrum (ABB MB3000) [47]. Yield: 80%. Karl Fischer coulometric titration (Metrohm) was used to measure the residual water content. The analysis was conducted as a function of time over 3 days, under ambient conditions, until no more water was detected.

$^1H$  NMR ( $D_2O$ , 300 MHz):  $\delta = 0.95(3H,t)$ ,  $1.31(2H,m)$ ,  $3.72(2H,t)$ ,  $2.46(1H,d)$ ,  $3.11(1H,s)$ ,  $1.96(3H,s)$ ,  $1.74(2H,m)$

## 3. Methods

Required amounts of materials were weighed using an A&D Co. limited electronic balance (Japan, model GR-202) with a precision of  $\pm 1 \times 10^{-2}$  mg. All the experiments were carried out in doubly distilled de-ionized water obtained from a Millipore, Milli-Q Academic water purification system having resistivity  $\geq 18$  M $\Omega$  cm.

### 3.1. Density and speed of sound measurements

Densities and speeds of sound were measured with an Anton Paar DSA 5000 (oscillating U-tube density and speed of sound analyzer) instrument and the temperature was controlled to  $\pm 1 \times 10^{-2}$  K by a built-in solid-state thermostat. Before each series of measurements, the densimeter was calibrated with doubly distilled, degassed water and with dry air at atmospheric pressure. The maximal error in the measurements of density and speed of sound relative to water ( $997.050$  kg  $m^{-3}$  and  $1496.687$  m  $s^{-1}$ ) [48,49] is estimated to be less than  $5 \times 10^{-3}$  kg  $m^{-3}$  and  $5 \times 10^{-2}$  m  $s^{-1}$ .

### 3.2. Conductometry

Electrical conductivities were measured at different temperatures (298.15–318.15 K) with an uncertainty of  $\pm 1 \times 10^{-2}$  K in a water jacketed flow dilution cell, by using a digital conductivity meter CM-183 microprocessor based EC-TDS analyzer with ATC probe and conductivity cell with platinized platinum electrodes purchased from Elico Ltd., India. Prior to measurements, cell was calibrated with the aqueous KCl solutions in the concentration range of 0.01–1.0 mol  $kg^{-1}$ . At least five measurements made for each concentration and only the mean values were taken into consideration. Uncertainty of the measurements was less than 0.3%.

### 3.3. Fluorescence measurements

Fluorescence spectra were taken on model RF-5301PC with blazed holographic grating excitation and emission monochromators having 150 W xenon lamp purchased from Shimadzu. SDS and IL solutions at various mole fractions in water were freshly prepared in doubly distilled de-ionized degassed water. Stock solution of fluorescence probe, pyrene was prepared in methanol and stored in pre-cleaned amber glass vial. Aqueous SDS solutions

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