Fluid Phase Equilibria 375 (2014) 23–29

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Modulating the aggregation behavior of aqueous sodium dodecylsulphate (SDS) with addition of trisubstituted imidazolium based ionic liquid 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bdmim][BF_4]

Amalendu Pal*, Ankita Pillania

Department of Chemistry, Kurukshetra University, Kurukshetra 136119, India

ARTICLE INFO

Article history:
Received 24 January 2014
Received in revised form 17 April 2014
Accepted 25 April 2014
Available online 5 May 2014

Keywords:
Anionic surfactant
Critical micelle concentration
Conductance
^{1}H NMR
Aggregation number

ABSTRACT

The aggregation behavior of an anionic surfactant sodium dodecylsulphate (SDS) in aqueous system in the presence of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bdmim][BF_4], a trisubstituted ionic liquid (IL) has been studied. Critical micelle concentrations (cmcs) were determined from conductance measurements at a temperature range of 298.15–318.15 K and using fluorescence probe at different wt% of IL. Results obtained from these methods are in good agreement with each other. An increase in cmc was observed for all the studied systems with increase in temperature as well as with increase in wt% of IL. Further the degree of dissociation, α and thermodynamic parameters viz. free energy of micellization, ΔG^o_m and entropy of micellization, ΔS^o_m has been evaluated. The aggregation number, N_{agg} of aqueous SDS micelles in the absence and presence of different wt% of [bdmim][BF_4] is determined by fluorescence quenching of pyrene. ^{1}H NMR measurements of post-micellar solutions have also been done to understand the different inter-molecular interactions of surfactant molecules in [bdmim][BF_4].

1. Introduction

Surfactant solutions having micelles are used as medium for various chemical and industrial processes and synthesis [1]. Micelles get formed inside the solution of an amphiphile at a narrow concentration range which is called cmc. This narrow range is highly studied for surfactant systems as, at this, there is an abrupt change in the physicochemical properties due to surfactant aggregation. Surfactants aqueous systems are highly explored due to their environment friendly nature. Micellar systems possess numerous applications such as nano-reactors for reactions, flow field regulators, membrane mimetic media, solubilizing and emulsifying agents, drug delivery and other dispersant technologies [2–5]. Properties of a surfactant solution depend entirely on surfactant itself. Although recently a number of external additives are used to modify the properties of surfactant systems for desired applications. These additives can be co-surfactants, co-solvents, electrolytes, polar organics etc. under similar conditions [6,7].

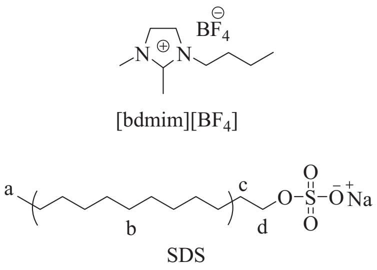
From the past decade room temperature ILs has been receiving immense attention from the scientific community to alter the physicochemical properties of surfactant systems. This is due to the inherent unusual properties of ILs such as negligible vapor pressure, large liquid range, high thermal stability, excellent dissolution capacity, non-flammability and high electrical conductivity [8–10]. Their physicochemical properties can be easily modified by introducing different functional groups as part of *N*-alkyl chains to obtain ‘task-specific’ ILs. They have found tremendous applications in a number of fields such as catalysis, solvation, separation, chemical synthesis and electrochemical processes [11–13]. Recently ILs has been studied for the absorption of greenhouse gases such as carbon dioxide and very promising outcomes obtained for the possibility of using ILs for carbon dioxide emission reduction [14]. ILs constitutes a class of salts composed of bulky organic cation and appropriate anion and exists in liquid state; enhanced investigations on these are due to their environmentally benign nature. Imidazolium based ILs having anions like $[Cl]^-$, $[Br]^-$, $[BF_4]^-$, $[PF_6]^-$, $[N(CF_3SO_2)_2]^-$, $[CF_3SO_3]^-$, $[MeSO_4]^-$ and $[SCN]^-$ have been highly explored for various purposes [15–17].

Efforts have been invested by many research groups including our own to study the surfactant aggregation within ILs. Reddy’s group is the first to demonstrate the effect of various ILs on

---

* Corresponding author. Tel.: +91 1744 239765; fax: +91 1744 238277.
E-mail address: palchem@sify.com (A. Pal).

http://dx.doi.org/10.1016/j.fluid.2014.04.027
0378-3812/



Scheme 1. Chemical structures of IL 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bdmim][BF_4] and anionic surfactant sodium dodecyl sulphate (SDS).

the properties of a surfactant system [18]. Then Pandey's group have systematically investigated the effect of ILs in altering the physicochemical properties of anionic, cationic, non-ionic and zwitterionic surfactants [19–21]. Inoue's group have shown the role of imidazolium based ILs in modifying the properties of non-ionic surfactants [22,23]. Our own group have studied the effect of pentyl odd chain substituted ILs on the properties of anionic and cationic surfactants [24,25]. Till date most of the research on IL induced changes in aggregation behavior of surfactants is confined to disubstituted 1,3-dialkyimidazolium salts, which limits these studies. Imparting functional groups or side chains in the structure of ILs can further modulate the properties of surfactant systems in a different way. The extent of alteration in the properties of a surfactant system depends upon: (1) structure of cation and anion of IL involved in the study, and (2) various interactions it undergoes with the surfactant head and tail groups [26,27].

In our previous investigation, we have effectively demonstrated the role of IL, 1-butyl-2,3-dimethylimidazolium chloride, [bdmim][Cl] in altering the physicochemical properties of aqueous SDS [28]. In continuation to our previous work, herein we are reporting the modulations in the properties of dilute aqueous micellar solutions of a common anionic surfactant SDS (Scheme 1) upon addition of IL 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, [bdmim][BF_4] (Scheme 1). The outcome of the results have been compared with the behavior of [bmim][BF_4] and [bdmim][Cl] with SDS, where effect of an additional methyl group and change due to anion has been studied [20,28]. The cmc values were obtained at different temperatures in the absence and presence of IL. From the temperature dependence of cmc various thermodynamic parameters have been calculated. These parameters have been examined to understand the various interactions present among hydrophobic and hydrophilic regions of the surfactant and IL. The present work demonstrates that the presence of IL delays the process of micellization. IL [bdmim][BF_4] is more effective than [bmim][BF_4] in delaying the micellization process but less effective than [bdmim][Cl], the extent of hydrophobic interactions seems to be the possible reasons behind these observations. This investigation will help in better understanding the effect of ILs in modifying the properties of aqueous surfactant systems.

2. Experimental

2.1. Chemicals

SDS (99%, AR) was obtained from Himedia 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 (≥99.9%) was obtained from SD Fine Chemicals. IL 1-butyl-2,3-dimethylimidazolium tetrafluoroborate used in the present study is of the same origin and purity as used in earlier study [29]. Water content in the IL was estimated to be less than 250 ppm using Karl–Fisher analysis. This was flushed with N_2 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 [30]. The details of chemicals used in the present work are given in Table 1.

Table 1
Specification of chemicals.

Chemical name	Provenance	Mass fraction purity (%)
Sodium dodecylsulphate	Himedia, India	≥99.0
1-Butyl-2,3-dimethylimidazolium tetrafluoroborate	Sigma-Aldrich, USA	≥99.8
Deuterium Oxide	SD Fine Chemicals, India	≥99.9
Pyrene	Sigma-Aldrich, USA	≥99.9
Cetylpyridinium chloride	Loba Chemie, India	≥99.0
Methanol	Rankem, India	≥99.0

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 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 conductance $\leq 5\ \mu S\ cm^{-1}$.

2.2.1. Conductance measurements

The electrical conductivities were measured at different temperatures 298.15 to 318.15 K with an uncertainty of ± 0.01 K in a water jacketed flow dilution cell. 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 was used for conductance measurements. 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^{-1} of known specific conductance. The cell constant which is a ratio of known specific conductance of the standard potassium chloride solution and the measured specific conductance of the same solution was determined to be 1.0021 cm^{-1}. At least five measurements were made for each concentration and only the mean values were taken into consideration. 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.

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. SDS and IL solutions at various mole fractions in water were freshly prepared in doubly distilled de-ionized degassed water. Pyrene and cetylpyridinium chloride were used as fluorescence probe and quencher, respectively. Stock solution of pyrene was prepared in methanol and stored in pre-cleaned amber glass vial. Aqueous SDS solutions of the probe were prepared taking appropriate amount of the probe from the stock and evaporating methanol using a gentle stream of high purity nitrogen gas. Aqueous SDS of desirable concentration was added to achieve required final concentration. Then calculated amount of IL was directly added to the aqueous SDS solution and stirred for 12 h. The emission spectra of pyrene 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_I/I_{III}' of the fluorescence intensities of the first and third