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Conductometric and spectroscopic study of interaction of cationic surfactants with 3-methyl-1-pentylimidazolium hexafluorophosphate

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This paper outlines the effect on micellar behavior of aqueous solutions of cationic surfactants viz. cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC) upon addition of ionic liquid 3-methyl-1-pentylimidazolium hexafluorophosphate [C_5mim][PF_6]. Important physicochemical properties such as conductance, critical micelle concentration (cmc) and aggregation number (N_{agg}) are observed to change as [C_5mim][PF_6] is added to aqueous CTAB/CTAC. The conductivity/concentration data of aqueous solutions of CTAB/CTAC with [C_5mim][PF_6] were determined in the temperature range 298.15, 308.15, 318.15 K. These data were used to determine cmc as a function of temperature and concentration and to evaluate degree of ionization. Using temperature dependence of cmc, various thermodynamic parameters have been evaluated. Behavior of fluorescence probe, pyrene, confirms the interaction between [C_5mim][PF_6] and cationic micellar surface. Further, ^{1}H NMR studies in micelle solutions containing [C_5mim][PF_6] have also been carried out in order to interpret the preferential solubilization site of [C_5mim][PF_6] on the studied micellar systems.

1. Introduction

Aqueous surfactant solutions have enormous prospective applications in routine life [1]. The surfactant organized assemblies have multi-fold technological applications such as flow field regulators, solubilizing and emulsifying agents, membrane mimetic media, nanoreactors for enzymatic reactions, in cosmetics and personal care products [2,3]. Properties of micelles and the values of cmc are often tailored in function of given application. Modulation of the cmc of surfactants can be achieved by varying temperature and pressure, nature of surfactant, the net charge of surfactant, or by using external additives [4–7]. The interaction between ionic surfactants and ILs is attracting widespread attention because of the multifaceted practical uses of such systems and the inherently interesting properties of ILs as additives in modifying properties of aqueous surfactant systems. In our recent investigations we have clearly demonstrated the uniqueness of ILs in altering the key physicochemical properties of aqueous ionic surfactant system [8,9]. Interaction between the anionic headgroup of SDS and IL cation was proposed to be responsible for changed physicochemical properties. In present communication, the surfactants chosen for the investigation are cationic surfactants, cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC). They have widespread applications in biochemical, pharmaceutical, chemical and industrial fields.

The present paper deals with conductometric and spectroscopic studies of CTAB/CTAC in hydrophobic IL, 3-methy-1-pentylimidazolium hexafluorophosphate [C_5mim][PF_6] to predict the thermodynamics and to elucidate the hydrophobic and electrostatic contributions for the building up of the micellar aggregates. Their chemical structures are presented in Scheme 1.

2. Materials

CTAB of purity 98% was purchased from SD Fine chemicals, CTAC was procured from Sigma-Aldrich and were used as received. CTAB was dried under vacuum and stored over P_2O_5 in vacuum desiccators. IL [C_5mim][PF_6] was prepared in our laboratory as described previously [8]. Deuterium oxide (SD Fine Chemicals) having isotopic purity ≥ 99.9% was used as solvent in ^{1}H-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 [10].

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. Deionized, double distilled water of conductance 1×10^{-5} S cm^{-1} at 298.15 K was used for all the measurements.

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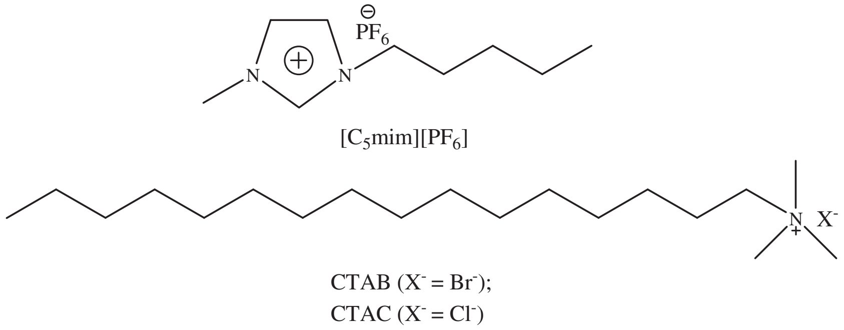

Scheme 1. Chemical structure of ionic liquid 3-methyl-1-pentylimidazolium hexafluorophosphate [C_5mim][PF_6] and surfactants cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC).

3.1. Conductometry

Electrical conductivities were measured at different temperatures (298.15 to 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 4%.

3.2. 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. Details have been given in our previous communication [8,9].

3.3. Spectral analysis

The NMR chemical shifts for ^{1}H were observed with a Bruker FT-NMR spectrometer operating at 300 MHz. In order to determine chemical shift δ for [C_5mim][PF_6]-CTAB/CTAC solution, D_2O was used as solvent instead of water to weaken the water signal for all the solutions studied. ^{1}H spectra of 0.1 M surfactant solutions were obtained in the absence and presence of studied IL. The chemical shift differences were only considered in this study. The chemical shift measurements of various resonance peaks of CTAB/CTAC are given on the δ scale in parts per million (ppm). All data analysis performed using Microsoft Excel and Origin 6.1 softwares.

4. Results and discussion

4.1. Conductometric studies

Plots of specific conductivity, κ, of surfactant–IL solutions against CTAB/CTAC concentration were obtained for a series of temperature and are reported in Fig. 1(A), (B) and Fig. 2(A), (B). For each temperature, the electrical conductivity increases with concentration with a gradual decrease in slope. The break in plot instigates from the onset of micellization. The cmc values of surfactant–IL mixtures along with the degree of counterion dissociation (α) at different temperatures and compositions are presented in Table 1. The cmc values of pure surfactants agree well with literature values [11,12]. Results reported in Table 1 show that the presence of the IL significantly increases the value of cmc. The higher cmc is either due to the increasing concentration of counterions or to the formation of mixed micelles (cation of surfactant + cation of IL). For each temperature, an increase in electrical conductivity with concentration of surfactant is seen with a gradual decrease in slope. The slope change at cmc is due to an effective loss of ionic charges because a fraction of the counterions are believed to be confined to the micellar surface. The slope change is evident in aqueous CTAB/CTAC solutions as well as that in presence of

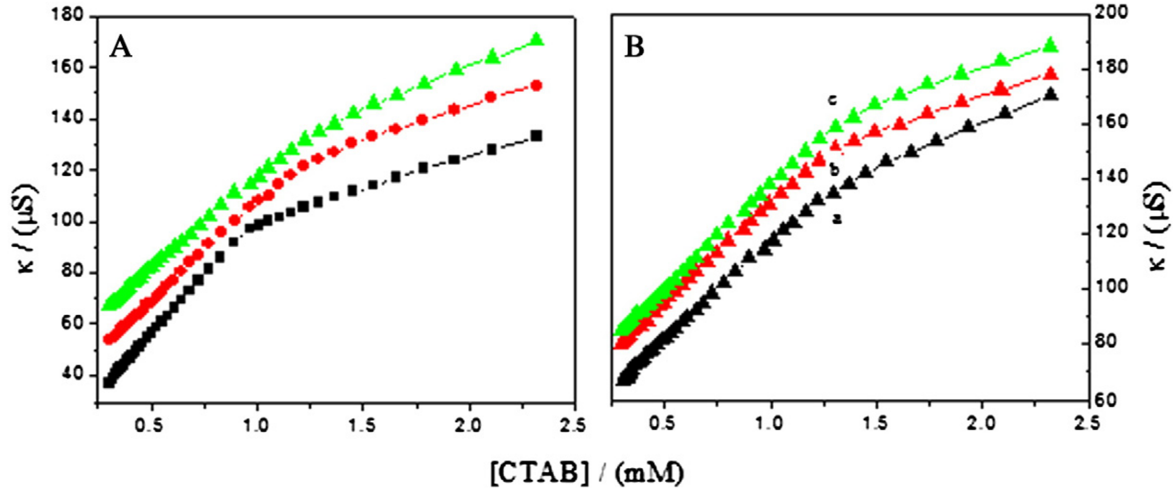

Fig. 1. (A) Specific conductance showing variation in cmc of aqueous CTAB in absence (■) and in presence of 0.025 wt.% (●), 0.05 wt.% (▲) IL [C_5mim][PF_6] at 298.15 K. (B) Temperature dependence of specific conductance showing gradual rise in cmc with 0.05 wt.% of IL at 298.15 K (a), 308.15 K (b) and 318.15 K (c).