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Journal of Colloid and Interface Science 307 (2007) 235–245
Journal of Colloid and Interface Science
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Effect of added ionic liquid on aqueous Triton X-100 micelles

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Received 29 September 2006; accepted 6 November 2006

Available online 20 December 2006

Abstract

Addition of ionic liquids to aqueous surfactant solutions can alter/modify physicochemical properties of such systems in favorable manner. Changes in the properties of aqueous solutions of a useful nonionic surfactant Triton X-100 (TX-100) are assessed upon addition of 2.1 wt% of a common and popular ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$). It is shown that the solubility of 'hydrophobic' $bmimPF_6$ in aqueous TX-100 increases with TX-100 concentration. This observation combined with the conductivity data strongly indicates partitioning of $bmimPF_6$ into TX-100 micellar phase. Behavior of a variety of molecular absorbance [methyl orange, phenol blue, and *N*,*N*-diethyl-4-nitroaniline] and fluorescence [phenyl on the TX-100, pyrene, pyrene-1-carboxaldehyde, 2-(*p*-toluidino)naphthalene-6-sulfonate, and 1,3-*bis*-(1-pyrenyl)propane] probes further confirm this observation. Statistically insignificant increase in critical micelle concentration (cmc) and decrease in aggregation number (N_{agg}) of TX-100 micelles are observed upon addition of 2.1 wt% $bmimPF_6$. Based on the overall data, it is inferred that ionic liquid $bmimPF_6$ partitions into the TX-100 micellar phase; presence of $bmimPF_6$ both close to the core as well as in the palisade layer of TX-100 micelles is suggested. Presence of favorable interactions (e.g., H-bonding, dipole-induced dipole, among others) between $bmimPF_6$ and TX-100 is proposed to be the reason for these observations.

Keywords: Ionic liquids; TX-100; Nonionic surfactants; $bmimPF_6$; Fluorescence probes

1. Introduction

Due to their unusual properties, room temperature ionic liquids (ILs) are receiving increased attention from both academic and industrial research communities [1–10]. Many chemical reactions have been reported in ILs [11–13]. Novel as well as routine analytical applications of ILs are emerging everyday [14–19]. Apart from the fact that ILs are constituted of cations/anions and are still in the liquid state at the ambient, most of the recent investigations with ILs are driven by the possibility of their *potential* environmentally-benign nature; they possess almost negligible vapor pressure and can be recycled easily. As a consequence, it is logical to employ these ILs in concert with other environmentally-friendly systems such as, supercritical fluids [20–26], aqueous [27–34] and polymer [35–39] solutions, surfactant-based systems [40–51], etc.

The aqueous surfactant solutions comprising of micelles are very-well studied and are used as media in a variety of chemical analysis and synthesis [52–57]. Micellar systems have immense technological applications such as flow field regulators, solubilizing and emulsifying agents, membrane mimetic media, nanoreactors for enzymatic reactions, to name just a few [52–57]. Although efforts have been invested by many research groups including our own to study surfactant behavior and possibility of surfactant self-assembly within ILs [40–51], utilization of ILs to effectively and favorably alter/modify properties of dilute aqueous surfactant solutions is an appealing concept from both environmental and application points-of-view which is still unexplored [58].

In this paper, we report the alterations/modifications in the properties of dilute aqueous micellar solutions of a common nonionic surfactant Triton X-100 (TX-100, see structure in Scheme 1) upon addition of a popular 'hydrophobic' IL 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$, Scheme 1). Favorable modifications in the physicochemical properties of dilute aqueous micellar solutions upon addition

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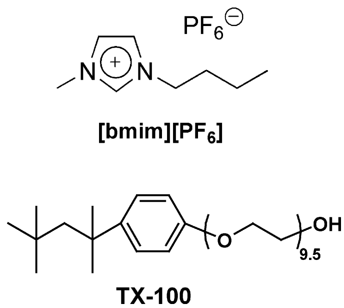
0021-9797/$ – see front matter
doi:10.1016/j.jcis.2006.11.009



Scheme 1. Structures of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) and surfactant Triton X-100 (TX-100).

of ILs will expand and enhance the overall capabilities and applications of aqueous surfactant solutions; utilization potential of ILs will increase as well.

2. Experimental

2.1. Materials

TX-100 [polyoxyethylene(10)octylphenyl ether, scintillation grade] was obtained from SISCO Research Laboratories and was used as received. IL $bmimPF_6$ (Merck, ultra pure, halide content <10 ppm, water content <10 ppm) was used as received. Doubly-distilled deionized water was obtained from a Millipore, Milli-Q Academic water purification system having ⩾18 MΩ cm resistivity. Following materials were used as received: methyl orange (MO, 4-[4-(dimethylamino)phenylazo]benzene sulfonic acid, sodium salt), pyrene (Py), and pyrene-1-carboxaldehyde (PyCHO) from Sigma-Aldrich, phenol blue (PB, *N*,*N*-dimethylindoaniline) and 2-(*p*-toluidino)naphthalene-6-sulfonate (TNS) from Acros Organics, *N*,*N*-diethyl-4-nitroaniline (DENA) from Frinton Laboratories, 6-propionyl-2-(dimethylamino)naphthalene (PRODAN) from Fluka, and 1,3-*bis*-(1-pyrenyl)propane from Molecular Probes. Ethanol (99.9%) was obtained from sd finechem. Ltd.

2.2. Methods

Required amounts of materials were weighed using Mettler Toledo AB104-S balance with a precision of ±0.1 mg. Stock solutions of the absorbance and fluorescence probes were prepared in ethanol and stored in precleaned amber glass vials at ∼4 °C. TX-100 solutions were freshly prepared in doubly-distilled deionized water. Aqueous TX-100 solutions of the probes were prepared taking appropriate aliquots of the probes from the stock and evaporating ethanol using a gentle stream of high purity nitrogen gas. Aqueous TX-100 of desirable concentration was added to achieve required final probe concentration. Precalculated amount of IL $bmimPF_6$ was directly added to the aqueous TX-100 solutions.

Fluorescence spectra were acquired on model FL 3-11, Fluorolog-3 modular spectrofluorometer with single Czerny–Turner grating excitation and emission monochromators having 450 W Xe arc lamp as the excitation source and PMT as the detector purchased from Horiba-Jobin Yvon, Inc. A Perkin-Elmer Lambdabio 20 double beam spectrophotometer with variable band width was used for acquisition of the UV–vis molecular absorbance data. All the data were acquired using 1-cm^2 path length quartz cuvettes. Spectral response from appropriate blanks was subtracted before data analysis. All the measurements were taken in triplicate and averaged. Conductivity measurements were carried out on a CM-183 µp-based EC-TDS analyzer with ATC probe and conductivity cell (CC-03B) purchased from Elico Ltd., India. Solubility of $bmimPF_6$ in aqueous TX-100 was first ascertained from visual inspection followed by verification using UV–vis absorbance. All data analysis was performed using Microsoft Excel and SigmaPlot 8.0 software.

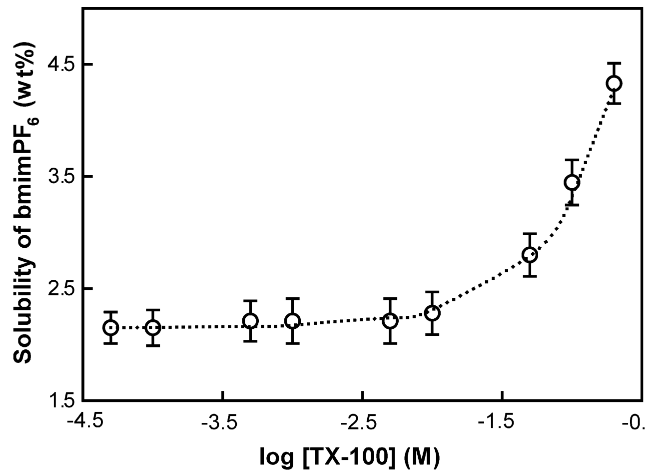


Fig. 1. Solubility of $bmimPF_6$ in aqueous TX-100 at ambient conditions.

3. Results and discussion

3.1. Solubility of $bmimPF_6$ in aqueous TX-100

$bmimPF_6$ is generally considered a 'hydrophobic' IL with limited solubility in water (at ambient conditions, solubility of $bmimPF_6$ in water is ca. 2.1 wt%) [59–62]. This poses obvious restrictions on utilization of aqueous $bmimPF_6$ and, in turn, limits the potential applications of aqueous $bmimPF_6$. The presence of TX-100 in water may alter the solubility of $bmimPF_6$. The solubility of $bmimPF_6$ in aqueous TX-100 at ambient conditions is presented in Fig. 1. Interestingly, solubility of $bmimPF_6$ does not change significantly at lower [TX-100] ($<1 \times 10^{-4}$ M); in the range 1×10^{-4}–0.20 M however, the solubility (S) of $bmimPF_6$ in TX-100 can be predicted by a simple linear relation: $S = 11.1(\pm 0.5)[\text{TX-100}] + 2.2(\pm 0.1)$, $r^2 = 0.9923$. The solubility of $bmimPF_6$ in the complete range of [TX-100] fits to a rather simple mathematical relation with three parameters: $S = 2.15(\pm 0.05) + 8.62(\pm 0.69)\exp[X/0.51(\pm 0.03)]$, where $X = \log[\text{TX-100}]$.

The increase in solubility of $bmimPF_6$ in the presence of TX-100 in water may be attributed to the following two factors. Cations and/or anions of IL $bmimPF_6$ may be associating with TX-100 (perhaps through ion–dipole interactions) or $bmimPF_6$