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Interfacial and aggregation behavior of dicationic and tricationic ionic liquid-based surfactants in aqueous solution

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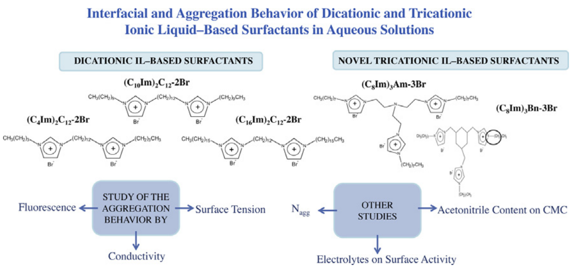
HIGHLIGHTS

- Two classes of tricationic IL-based surfactants were synthesized for the first time.
- Aggregation behavior of dicationic and tricationic IL-based surfactants was examined.
- Surfactant aggregation characterized by surface tension, conductivity, and fluorescence.
- Electrolytes enhanced the aggregation of IL-based surfactants at air/water interface.
- CMC values of tricationic surfactants were lower than linear trimeric analogs.

GRAPHICAL ABSTRACT



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ABSTRACT

The interfacial and aggregation behavior of three dicationic and two tricationic ionic liquid-based (IL) surfactants in aqueous solutions have been carried out. The studied dicationic IL-based surfactants were 1,12-di(3-butylimidazolium)dodecane bromide ($(C_4Im)_2C_{12}$-2Br), 1,12-di(3-decylimidazolium)dodecane bromide ($(C_{10}Im)_2C_{12}$-2Br), and 1,12-di(3-hexadecylimidazolium)dodecane bromide ($(C_{16}Im)_2C_{12}$-2Br). Two classes of trigonal tricationic surfactants containing triethylamine (Am) and 1,3,5-trimethylbenzene (Bn) cores were synthesized for first time and characterized, specifically, 3,3′,3″-octyl-1,1′,1″-(2-ethylamino) imidazolium bromide ($(C_8Im)_3$Am-3Br), and 3,3′,3″-octyl-1,1′,1″-(1,3,5)*tris*(methylene) benzene imidazolium bromide ($(C_8Im)_3$Bn-3Br). The critical micelle concentration (CMC) values and other aggregation parameters, including adsorption efficiency (pC_{20}), surface tension at the CMC (γ_{cmc}), degree of dissociation (α), and the degree of counterion binding in the micelle (β) were obtained using a variety of techniques including surface tension, conductivity, and fluorescence measurements. For the first time, the aggregation numbers (N_{agg}) were also obtained for this group of surfactants. A study into the influence of acetonitrile on the stability and aggregation behavior of dicationic and tricationic IL-based surfactants was also undertaken. The CMC values of the dicationic surfactants clearly decrease as a function of the side chain, when the same linker is maintained. The CMC values of the tricationic surfactants were lower

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than analogous linear trimeric surfactants. For the novel tricationic surfactants, the effect of sodium salts (C_6H_5COONa, NaBr, and NaI) on the surface activity was also investigated. It was also observed that the surface activity parameters (pC_{20} and CMC/C_{20}) of tricationic surfactants increased significantly in the presence of added electrolytes.

1. Introduction

Ionic liquids (ILs) are class of organic molten salts having low melting points (<100 °C), negligible vapor pressure, and high thermal stability. The physicochemical properties of ILs can be tailored for specific applications by structural modification of either the cation or anion [1]. Merrigan et al. [2] reported the synthesis of imidazolium-based fluorous ILs and examined the surface activity of these compounds in the solubilization of fluoroalkanes in conventional ILs. Anderson et al. [3] studied the aggregation phenomena of traditional surfactants in ILs using surface tension measurements. It was observed that the surface tension values of ILs were decreased due to solvatophobic interactions between the IL and traditional surfactants. It was also reported for first time that the solvation properties of micellar IL solutions were modified due to the formation of traditional surfactant micelles in ILs [3].

The first reports on the study of amphiphilic association structures of monocationic imidazolium-based IL surfactants in aqueous solutions was in 2004 [4,5]. The aggregation or micelle formation ability of ILs in aqueous solutions is due to the intrinsic amphiphilic nature of ILs [4–7]. Blesic et al. [8] studied the self-aggregation behavior of the 1-alkyl-3-methyl imidazolium C_nMIm^+ family of cations with various alkyl chain lengths and counter ions. It was observed that ILs possessing octyl and higher alkyl chain analogs exhibited self-aggregation, whereas lower alkyl chain length analogs did not show significant reduction in surface tension. Baltazar et al. [9] performed an extensive study on the surface activity of monocationic and dicationic imidazolium-based IL surfactants in aqueous solution by surface tensiometry measurements. It was shown that the critical micelle concentration (CMC) values of monocationic IL-based surfactants depended on the length of alkyl chain substituent attached to the head group. Freire et al. [10] also examined the effect of cation/anion, temperature, and water content on the surface activity of monocationic ILs containing the imidazolium head group. Recently, Bhargava and Klein [11] performed molecular dynamic simulation studies on dicationic IL-based surfactants in aqueous solutions. In their theoretical studies, it was observed that the hydrophobic tails of ILs were organized in a manner such that they possess minimum interaction with water molecules and anions of the IL. It was also observed that in comparison with anions, the cationic head groups of the ILs possessed weaker hydrogen bonding interaction with water molecules. Ao et al. [12] investigated the effect of spacer length on the surface activity of Gemini IL-based surfactants. It was observed that spacer groups containing lower number of carbon atoms possessed higher surface activity.

The surface activity of IL-based surfactants can be influenced by their molecular structure [13,14] and the presence of added electrolytes [15,16]. Recently, Jiao et al. [15] studied the effect of organic and inorganic salts on the aggregation of 1-butyl-3-methyl imidazolium dodecylsulfate in aqueous solutions. It was observed that the CMC values of the surfactants decreased with the increase in concentration of electrolyte. From their study, it was also observed that hydrophobicity and hydration ability of added electrolytes were crucial in promoting aggregation.

Trigonal tricationic ILs are new class of ILs comprised of three cationic moieties appended to a central core with various combinations of anions. Recently, Planellas et al. [17] studied palladium nanoparticle-catalyzed Suzuki cross-coupling reactions, wherein the stabilization of nanoparticles was improved by the application of tris-imidazolium-based tricationic ILs. The number of applications of tricationic imidazolium-based ILs within the literature is very small in comparison with monocationic and dicationic imidazolium-based ILs. Therefore, studying the self-assembly behavior of tricationic imidazolium-based ILs in aqueous solutions will provide significant fundamental understanding of these compounds which may extend their applications into different areas, including extraction solvents in aqueous biphasic systems (ABS), ion-pairing reagents in liquid chromatography, and as catalysts in organic synthesis.

In this study, the behavior of a group of dicationic IL-based surfactants is presented in an effort to increase the fundamental knowledge of these surfactant systems. In addition, this is the first study to examine the interfacial and aggregation properties of trigonal tricationic imidazolium-based ILs. The synthetic preparation of a novel group of tricationic IL-based surfactants and the overall characterization of their aggregation behavior is presented. The two classes of trigonal tricationic imidazolium-based ILs are comprised of two different cores, namely triethylamine (Am) and 1,3,5-trimethylbenzene (Bn) and were synthesized for the first time in this study. CMC values and surface activity parameters including adsorption efficiency (pC_{20}), CMC/C_{20}, and surface tension at the CMC (γ_{cmc}), micelle degree of dissociation (α), degree of counter-ion binding to the micelle (β), and the aggregation number (N_{agg}) were obtained using a number of techniques including conductivity, fluorescence, and surface tensiometry. The influence of the acetonitrile content was also addressed for the dicationic and tricationic IL-based surfactant micelles. In order to understand the effect of electrolytes on the aggregation of the novel tricationic surfactants in aqueous solutions, one organic and two inorganic salts were examined. Furthermore, the adsorption and aggregation phenomenon of tricationic IL-based surfactants was compared with traditional quaternary ammonium-based cationic surfactants.

2. Experimental

2.1. Reagents

The dicationic IL-based surfactants used in this study were 1,12-di(3-butylimidazolium)dodecane bromide ($(C_4Im)_2C_{12}$-2Br), 1,12-di(3-decylimidazolium)dodecane bromide ($(C_{10}Im)_2C_{12}$-2Br), and 1,12-di(3-hexadecylimidazolium)dodecane bromide ($(C_{16}Im)_2C_{12}$-2Br). These dicationic IL-based surfactants were synthetized and fully characterized according to the procedures described by Baltazar et al. [9].

The new tricationic IL-based surfactants prepared were 3,3′,3″-octyl-1,1′,1″-(2-ethylamino) imidazolium bromide ($(C_8Im)_3$Am-3Br) and 3,3′,3″-octyl-1,1′,1″-(1,3,5)*tris*(methylene) benzene imidazolium bromide ($(C_8Im)_3$Bn-3Br).

The structures of all surfactants utilized in this work are shown in Fig. S1.