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Synthesis and micellar properties of surface-active ionic liquids: 1-Alkyl-3-methylimidazolium chlorides

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Abstract

A series of surface-active ionic liquids, RMeImCl, has been synthesized by the reaction of purified 1-methylimidazole and 1-chloroalkanes, RCl, $R = C_{10}, C_{12}, C_{14}$, and C_{16}, respectively. Adsorption and aggregation of these surfactants in water have been studied by surface tension measurement. Additionally, solution conductivity, electromotive force, fluorescence quenching of micelle-solubilized pyrene, and static light scattering have been employed to investigate micelle formation. The following changes resulted from an increase in the length of R: an increase of micelle aggregation number; a decrease of: minimum area/surfactant molecule at solution/air interface; critical micelle concentration, and degree of counter-ion dissociation. Theoretically-calculated aggregation numbers and those based on quenching of pyrene are in good agreement. Gibbs free energies of adsorption at solution/air interface, ΔG^0_{ads}, and micelle formation in water, ΔG^0_{mic}, were calculated, and compared to those of three surfactant series, alkylpyridinium chlorides, RPyCl, alkylbenzyldimethylammonium chlorides, $RBzMe_2Cl$, and benzyl(3-acylaminoethyl)dimethylammonium chlorides, $R'AEtBzMe_2Cl$, respectively. Contributions to the above-mentioned Gibbs free energies from surfactant methylene groups (in the hydrophobic tail) and the head-group were calculated. For RMeImCl, the former energy is similar to that of other cationic surfactants. The corresponding free energy contribution of the head-group to ΔG^0_{mic} showed the following order: $RPyCl \approx RBzMe_2Cl > RMeImCl > R'AEtBzMe_2Cl$. The head-groups of the first two surfactant series are more hydrophobic than the imidazolium ring of RMeImCl, this should favor their aggregation. Micellization of RMeImCl, however, is driven by a relatively strong hydrogen-bonding between the chloride ion and the hydrogens in the imidazolium ring, in particular the relatively acidic H2. This interaction more than compensates for the relative hydrophilic character of the diazolium ring. As indicated by the corresponding ΔG^0_{mic}, micellization of $R'AEtBzMe_2Cl$ is more favorable than that of RMeImCl because the –CONH– group of the former surfactant series forms hydrogen bonds to both the counter-ion and the neighboring molecules in the micelle.

Keywords: Ionic liquids, surface active; Ionic liquids, micellar properties of; Imidazole-based cationic surfactants, synthesis of; Surface tension; Conductance; ISE; Fluorescence

1. Introduction

The amphiphilic nature of surfactants is responsible for their useful properties, hence applications: adsorption at interfaces (wetting, dispersion of solids, etc.), and aggregation in aqueous and non-aqueous solutions (detergency, emulsification, solubilization, preparation of nanoparticles, catalysis of chemical reactions, etc.) [1,2]. Therefore, the study of the relationship between structure of surfactants and their properties in solution will always be an important subject, both scientifically, and from the application point of view.

The structural variables include the length of the hydrophobic tail, the nature of the counter-ion, and the nature/charge of the head-group. The latter has been much less studied than the former ones; this is interesting, because: Many of the above-mentioned applications reflect substrate-head-group interactions; Electrostatic interactions make a large positive contribution to the free energy of micellization [1,3–9]. Rates of

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reactions that are sensitive to changes of solvent polarity (e.g., the spontaneous decarboxylation of the 6-nitrobenzisoxazole-3-carboxylate anion) or to desolvation of the attacking nucleophile (e.g., elimination by the E2 pathway; S_N2; and acyl transfers) are enhanced by an increase of the hydrophobic character of the head-group, e.g., upon going from trimethyl- to tri-n-butylammonium. The reason advanced is that large head-groups partially exclude water from the interface; this results in a less polar reaction environment [7,10].

Cationic surfactants are amenable to this line of study because the structure of the head-group can be changed, e.g., by increasing the length of the alkyl groups attached, while maintaining constant the nature of the head-ion, e.g., quaternary ammonium. This is not the case for anionic surfactants where a change in the structure of the head-group entails a corresponding change in its chemical nature, carboxylate, sulfate, phosphate, etc. An additional reason for interest in studying cationic surfactants is that they show antibacterial properties and are used as hair conditioners, fabric softeners, antistatic agents, and corrosion inhibitors [11–14].

Ionic liquids, ILs, are low-melting electrolytes, thus forming liquids that consist only of cations and anions. The current convention is that a salt melting below the boiling point of water is known as an IL. Of these, the compounds based on imidazole, e.g., RMeImX have received much attention because they constitute "green" substituents to classic (volatile) organic solvents. Here R, Me, Im, and X stand for alkyl group, methyl, imidazolium, and counter-ion, respectively; for simplicity we do not show the charges. Note that (R) and (Me) are usually attached to positions 1 and 3 of the imidazolium ring; typical (X) include simple and complex ions, e.g., Br^-, Cl^-, BF_4^-, PF_6^-, $(CN)_2N^-$, etc. In addition to extremely low vapor pressure, ILs are highly polar, chemically inert, noninflammable and thermally stable. A myriad of chemical reactions can be carried out in ILs; residual reagents, reaction products and catalysts are separated by suitable procedures (e.g., removal under reduced pressure or extraction) and the IL, in principle, can be recycled into the process indefinitely [15–19].

RMeImX with a long-chain (R) are expected to be surface active ionic liquids, SAILs. Indeed, conductimetric, potentiometric, surface tension and volumetric (from solution density) studies have indicated that C_{10}MeImBr aggregates in water and, at low concentrations, behaves as a classic cationic surfactant [20,21]; surface tension measurements have indicated a similar behavior of C_{16}MeImCl and $C_{16}MeImBF_4$ both in aqueous solution, and in the IL ethylammonium nitrate [22]. A few articles dealt with other physico-chemical properties of long-chain RMeImX, including their partition coefficients between n-octanol and water (RMeImCl, $R = C_8$, C_{10}, and C_{12}, respectively) [23]; solubility of C_{12}MeImCl in several alcohols [24] and dipolar aprotic solvents [25]. Additionally, the hydrated crystals of RMeImCl, $R = C_{12}$–C_{18}, were postulated to have a double-layer structure with stabilization derived from direct, or water mediated hydrogen-bonding between Cl^- and the hydrogens of the imidazolium moiety [26,27].

It is surprising that there has been no systematic study on the effects of the structure SAILs on the properties of their aqueous solutions. This lack of information, coupled with their potential applications has prompted us to synthesize and investigate the properties of a series of SAILs, RMeImCl, $R = C_{10}$, C_{12}, C_4 and C_{16}, respectively. Solution conductivity, surface tension, electromotive force, fluorescence of micelle-solubilized pyrene, and static light scattering have been employed to study their adsorption at solution/air interface and aggregation in aqueous solution. The data thus obtained was employed to calculate the following properties: Minimum area/surfactant at solution/air interface ($A_{\text{interface}}$); critical micelle concentrations (cmc); degrees of counter-ion dissociation (α_{mic}); aggregation numbers (N_{agg}), as well as contribution of the surfactant discrete segments to Gibbs free energies of adsorption (ΔG^0_{ads}) and micellization (ΔG^0_{mic}). In order to assess the effect of surfactant head-group on its adsorption and aggregation in water, we compare data of the present series with those of cationic surfactants with different head-groups, pyridinium; benzyldimethylammonium, and benzyldimethylammonium that carries an amide group, vide infra. This comparison shows that micellization of cationic surfactants is affected by head-group hydrophobicity and, where operative, hydrogen bonding in the interfacial region.

2. Experimental

2.1. Materials

The reagents were purchased from Acros and Apagão Química S.A. The solvents were purified as described elsewhere [28]; 1-methylimidazole was distilled from CaH_2; 1-chloroalkanes (C_{10}, C_{12}, C_{14}, and C_{16}, respectively) were repeatedly fractionally distilled in a 50 cm long Vigreux column, under reduced pressure. Gas chromatographic analysis showed that 1-methyimidazole, 1-chlorodecane, and 1-chlorododecane are chromatographically pure; satisfactory purity, >99.5%, was obtained for the remaining 1-chloroalkanes. Pyrene and 2,3,6,7-tetrahydro-9-(trifluoromethyl)-1H,5H,11H-[1]benzopyranpo [6,7,8-ij]quinolizin-11-one (coumarine 153, here after designated as "C153") were used as received.

2.2. Apparatus

Melting points were determined with IA 6304 apparatus (Electrothermal). Gas chromatographic analyses were carried out on Shimadzu 17A-2 chromatograph, equipped with a FID detector and Supelcowax 10 capillary column. NMR spectra were recorded with Varian Innova 300 spectrometer; elemental analyses were performed on Perkin-Elmer 2400 CHN apparatus at the Elemental Analyses laboratory of this Institute.

2.3. Surfactants

RMeImCl were prepared according to the general procedure, described elsewhere [29]. The reaction mixture was kept under dry, oxygen-free nitrogen atmosphere and was protected from light. To 1 mol of 1-methylimidazole, dissolved in 150 mL of