Self-aggregation of cationic dimeric surfactants in water–ionic liquid binary mixtures

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ABSTRACT

The micellization of four dimeric cationic surfactants ("gemini surfactants") derived from N-dodecyl-N,N,N-trimethylammonium chloride was studied in pure water and in water–ionic liquid (IL) solutions by a wide range of techniques. The dimeric surfactants are distinguished by their rigid spacer groups separating the two surfactant motifs, which range from C_3 to C_5 in length. In order to minimize organic ion pairing effects as well as the role of the ionic liquids as potential co-surfactants, ILs with inorganic hydrophilic anions and organic cations of limited hydrophobicity were chosen, namely ethyl, butyl, and hexyl-3-imidazolium chlorides. ^{1}H NMR two-dimensional, 2D, rotating frame nuclear Overhauser effect spectroscopy measurements, ROESY, supported this premise. The spacer nature hardly affects the micellization process, neither in water nor in water–IL solutions. However, it does influence the tendency of the dimeric surfactants to form elongated micelles when surfactant concentration increases. In order to have a better understanding of the ternary water–IL surfactant systems, the micellization of the surfactants was also studied in aqueous NaCl solutions, in water–ethylene glycol and in water–formamide binary mixtures. The combined results show that the ionic liquids play a double role in the mixed systems, operating simultaneously as background electrolytes and as polar organic solvents. The IL role as organic cosolvent becomes more dominant when its concentration increases, and when the IL alkyl chain length augments.

1. Introduction

Dimeric surfactants are amphiphilic molecules that contain two hydrophobic tails and two head groups connected at the level of the head groups by a spacer that may be hydrophilic, hydrophobic, flexible or rigid [1,2]. Their structure confers them superior properties compared to the corresponding conventional (single-chain) surfactants. They have lower cmc, stronger efficiency in reducing the surface tension of water, better wetting power, better solubility power, better foaming, etc. [1–3]. All these advantages make them of special interest for biomedical and technological applications, where they have been investigated as drug delivery systems, DNA carriers, nanoreactors for enzymatic reactions, emulsifying agents, detergents, etc. [3–12].

The solution properties of surfactants can be modulated by controlling temperature, pressure and/or by addition of different modifiers (e.g. cosolvents, cosurfactants, electrolytes, etc.) [13,14]. Ionic liquids, ILs, are a class of organic electrolytes, which are composed of an organic cation and an inorganic or organic anion, that melt at temperature lower than 100 °C [15]. An advantage of ILs is that by combining organic cations with suitable anions it is possible to tailor their physical and chemical properties. In general ILs are considered environmentally friendly compounds because mostly they are non-flammable and non-volatile. Besides, many ILs have an excellent chemical and thermal stability, wide liquid temperature ranges and wide electrochemical windows. Therefore ILs have been widely used in organic synthesis, catalysis, nanomaterial separation, chemical separation, etc. [16–20]. For the application of ILs in such fields, they are frequently used with water, whose presence can strongly affect their physical and chemical properties of ILs [21–23]. The surfactant–water–IL three component systems are particularly interesting because ILs can behave not only as co-solvents, but also as background electrolytes and as co-surfactants, their main role depending on the IL structure [24–29]. This gives the opportunity of tuning the physicochemical properties of the surfactant aggregates formed

in water–IL binary mixtures, which is of interest for potential applications. Bearing this in mind, we investigated the effects of the addition of ethyl-3-methylimidazolium chloride, C_2mimCl, butyl-3-methylimidazolium chloride, C_4mimCl, and hexyl-3-methylimidazolium chloride, C_6mimCl, on the aggregation of various cationic dimeric surfactants (see Scheme 1) in aqueous solutions at 303 K. Since the dimeric surfactants studied contain chloride as common counterion, ILs with the same anion were chosen, while the hydrophobic substituents on their organic cations were confined to short or medium alkyl chains in order to minimize their possible role as co-surfactants [30]. The dimeric surfactants investigated have all dodecyl hydrophobic chains, but different rigid spacers, namely two isomeric pairs of butylidene and xylidine moieties that separate the ammonium groups by three to five carbon atoms. Therefore, the results obtained in this work will give relevant information about the influence of the dimeric surfactant spacer nature, with respect to either its length for a given hydrophobicity, or to its hydrophobicity for a given length, on the micellization in water–IL solutions. The studies were also aimed at a deeper understanding of the role played by the ionic liquids on micellization, and of the dependence of this role on the IL alkyl chain length. The results will provide useful information on how to tune the physicochemical properties of the surfactant aggregates in aqueous solution by adding ILs.

Before studying the surfactants in water–IL solutions, the aqueous dimeric surfactants solutions were thoroughly characterized at 303 K. This characterization includes the study of changes in the size and shape of the micelles caused by an increase in surfactant concentration and their dependence on the dimeric surfactant spacer group.

2. Experimental

2.1. Materials

The dimeric surfactants were synthesized as described previously [31]. The ILs were from Fluka, of the highest purity available, and were used as received. Pyrene-3-carboxaldehyde, P3C, and NaCl were from Aldrich. Pyrene was from Aldrich and it was purified before use by methods reported in the literature [32]. N-Hexadecylpyridinium chloride (cetylpyridinium chloride, CpyCl), methyl 4-nitrobenzenesulfonate and dodecyltrimethylammonium

chloride were purchased from Fluka. 6-Methoxy-N-(3-sulfopropyl)quinolinium, SPQ, was from Molecular Probes, Inc. and used as received.

All solutions were prepared in double-distilled water (resistivity >18 MΩ cm).

2.2. Conductivity measurements

Conductivity was measured with a Crison GLP31 conductimeter as described in Ref. [33].

2.3. Fluorescence measurements

Fluorescence measurements were performed by using a Hitachi F-2500 fluorescence spectrophotometer. The temperature was kept at 303 K by a water flow cryostat connected to the cell compartment.

2.3.1. cmc's determination by using pyrene as probe

The 1×10^{-6} M pyrene surfactant solutions were prepared as is described in Ref. [34]. The excitation wavelength was 335 nm and the fluorescence intensities were measured at 373 nm (band 1) and 384 nm (band 3). Excitation and emission slits were 2.5 nm and a scan speed of 60 nm/min was used. The intensity ratio of the vibronic bands (1:3) is called the pyrene 1:3 ratio [35].

2.3.2. Second critical micelle concentration, C^*, determination

The SPQ concentration in the surfactant solutions was 1×10^{-6} M. The excitation wavelength was 346 nm and the fluorescence intensity was measured at 443 nm, as indicated in Ref. [36]. Excitation and emission slits were 5 and 10 nm, respectively, and a scan speed of 60 nm/s was used. Surfactant concentrations were well above the cmc.

#### 2.3.3. Average micellar aggregation number determination

Pyrene (1×10^{-6} M) micellar solutions were prepared as in Ref. [34]. The fluorescence quenching of pyrene by cetylpyridinium chloride, CPyCl, was studied by exciting the pyrene at 335 nm, and recording its emission at 374 nm, with the use of excitation and emission slits of 2.5 and 2.5 nm, respectively. A scan speed of 60 nm/min was used. The low pyrene concentration avoided excimer formation, and the CPyCl concentration was varied in such a way that [pyrene]/[micelles] and [quencher]/[micelles] ratios were low enough to ensure a Poisson distribution [37,38].

2.3.4. Study of the polarity of the micellar interfacial region

The 10^{-5} M pyrene-3-carboxaldehyde, P3C, micellar solutions were prepared as in Ref. [34]. P3C was excited at 356 nm and fluorescence spectra were recorded from 380 to 600 nm. A scan speed of 60 nm/min was used and the excitation and emission slits were 5 nm and 10 nm, respectively. In order to check the reliability of our data, the fluorescence emission spectrum of P3C in a 0.1 M aqueous dodecyltrimethylammonium bromide, DTAB, micellar solution was recorded. The fluorescence maximum was 446 nm, in good agreement with literature data [35]. The precision in the measurements was ±1 nm.

2.4. Surface tension measurements

Surface tension was measured by a du Noüy ring method using a KSV 703 digital tensiometer (Finland) as described in Ref. [33]. The precision in the measurements was $\pm(1 \times 10^{-3})$ N m^{-1}. Care has to be taken in using the du Noüy ring method to deduce surfactant properties, because the surfactant adsorption kinetics can influence the results [39]. In our experiments the ring rising velocity was chosen low enough to allow the surfactant adsorption to
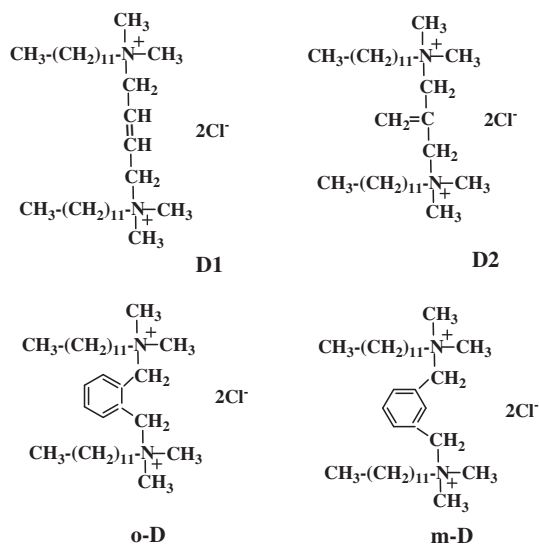
Scheme 1. Structure of the dimeric surfactants investigated in this work.