Journal of Colloid and Interface Science 340 (2009) 269–275

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Synthesis and properties of cationic surfactants with tuned hydrophylicity

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ARTICLE INFO

Article history:
Received 30 June 2009
Accepted 4 September 2009
Available online 10 September 2009

Keywords:
Cationic surfactants
Pyridinium
Surface tension
Conductivity
Amphiphilic properties
Gibbs paradox

ABSTRACT

A series of pyridinium-based cationic surfactants has been synthesised and their amphiphilic properties have been studied by conductivity and surface tension measurements. The modification of the substitution pattern on the pyridinium ring by hydrophobic moieties (methyl vs. hydrogen and presence or not of condensed benzene ring) gave the opportunity to investigate structure–activity relationships. Characterization by conductivity and surface tension measurements shed light on the behaviour at the air/water interface and in the micellar environment. In particular, the tendency to form ion pairs at very low concentration was evidenced for all the surfactants substituted on the ring, but not for the simple pyridinium ones. The formation of ion pairs affects both the conductivity and the surface tension plots, showing that a series of steps is involved during the adsorption to the air/water surface. An attempt was made to qualify the single steps in the adsorption at the surface layer. Those steps were attributed to different chemical species (free surfactant ions or ion pairs) and to different arrangements of the surfactant. This work also represents a contribution of investigation at very low surfactant concentrations and high surface tension values.

1. Introduction

Cationic surfactants have attracted the attention of chemists for a long time, due to their general simple synthesis and their broad application in several fields. Pyridinium surfactants [1], in particular, are important as ingredients of cosmetic products [2], and are also used as corrosion inhibitors [3], in emulsion polymerization [4] and textile processing [5]. Within biological applications, they show a good antimicrobial activity [6] and can be used as drugs [7], gene delivery agents [8] or in DNA extraction methods [9]. Quite recently, cationic pyridinium surfactants have found applications in the synthesis of TiO_2 nanoparticles [10], in ionic liquids synthesis [11] or as electrolytes for dye-sensitized solar cells [12].

The aim of the present work was the synthesis and the characterization of a series of cationic pyridinium and quinolinium surfactants. The investigation of their behaviour was performed by conductivity and surface tension measurements trying to evaluate the influence of the modification of the headgroup polarity on the aggregation properties. The obtained results can be helpful for their use in a wide range of applications.

2. Materials and methods

2.1. Materials

All the chemicals were purchased from Sigma Aldrich, and were normally freshly distilled before use. The glassware used for synthesis was heated overnight in an oven at 150 °C and assembled in the oven, then cooled under Ar flux before starting the reactions.

Melting points were taken on a hot plate equipped with a microscope and are uncorrected.

^{1}H NMR (400 MHz) spectra were recorded on a Jeol EX400 NMR spectrometer in DMSO-d_6 using the DMSO signal as a reference. NMR signals are described by use of s for singlet, d for doublet, t for triplet, m for multiplet.

FT-IR spectra were recorded in KBr on a Shimadzu FT-IR Spectrometer.

UV spectra were recorded on a Shimadzu UV-1700 spectrometer. For the evaluation of the surfactants concentration after their purification, several solutions at different concentration were used as standards in order to build a regression plot.

ESI-MS spectra (positive ions) were recorded using a LCQ Deca XP plus spectrometer (Thermo), with electrospray interface and ion trap as mass analyzer. The flow injection effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas.

TLC were performed on silica gel 60 F_{254} or basic alumina plates using BAW (Butanol:Acetic Acid:Water 4:1:5, organic phase) as eluents.

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doi:10.1016/j.jcis.2009.09.009

2.2. General procedures

The synthesis of N-(*n*-Dodecyl)-4-methylpyridinium bromide (**2b**) and N-(*n*-Dodecyl)-4-methylquinolinium bromide (**3b**) were already reported [6].

2.2.1. N-(n-Dodecyl)-4-methylquinolinium iodide (*3c*)

Four grams of 4-methylquinoline (0.028 mol) and 10.7 g of iododododecane were introduced under nitrogen in a round bottom flask. Dry toluene was added and the reaction was stirred and warmed at 120 °C for 6 h. The resulting mixture was cooled to room temperature and washed repeatedly with diethyl ether to remove both iododododecane and toluene. The residue was dissolved in methyl ethyl ketone and evaporated under reduced pressure. The resulting viscous paste was warmed with water, giving a yellow solid that was filtered on a Hirsch funnel. The product was recrystallized in warm ethanol and cooled in a refrigerator, giving yellow-greenish crystals. Yield 80%, after crystallization 65%. M.p. 43–45 °C. UV (ethanol) λ_{max} 221, 317 nm, log ε = 4.10, 3.73. ^{1}H NMR (DMSO-d_6): δ 0.84 (t, 3H, CH_3), 1.22 (broad, 18H, $9CH_2$), 1.93 (m, 2H, $CH_2CH_2N^+C_{10}H_7$), 3.00 (s, 3H, CH_3), 4.99 (t, 2H, $CH_2N^+C_{10}H_7$), 8.05 (t, 1H, Ar-H), 8.07 (d, 1H, Ar-H), 8.26 (dt, 1H, Ar-H), 8.54 (dd, 1H, Ar-H), 8.59 (d, 1H, Ar-H), 9.40 (d, 1H, Ar-H). MS-ESI (+): 312 $[M]^+$. Anal. Calcd. from $C_{22}H_{34}IN$: C, 60.13; H, 7.80; N, 3.19. Found: C, 60.16; H, 7.79; N, 3.20.

2.2.2. N-(n-Dodecyl)-4-methylquinolinium chloride (*3a*)

The strong basic ion exchanger was previously conditioned in sequence in a column with water, 10% aqueous NaOH, 10% NaCl and washed thoroughly with water to remove any inorganic salt excess. Finally, the ion exchanger was filtered on a Buchner funnel and conditioned with methanol. The resin was put in a chromatographic column and was conditioned with 2–3 column volumes of methanol. The iodide salt (**3c**) was dissolved in methanol and was eluted through an ion exchange column. The effluent was recovered and the solvent was evaporated under reduced pressure. The final product was crystallized at least thrice from acetone, obtaining white crystals. Yield: 99%. M.p. 105–108 °C. UV (ethanol) λ_{max} 243, 319 nm, log ε = 3.82, 3.70. ^{1}H NMR (DMSO-d_6): δ 0.84 (t, 3H, CH_3), 1.22 (broad, 18H, $9CH_2$), 1.93 (m, 2H, $CH_2CH_2N^+C_{10}H_7$), 3.00 (s, 3H, CH_3), 5.02 (t, 2H, $CH_2N^+C_{10}H_7$), 8.05 (t, 1H, Ar-H), 8.08 (d, 1H, Ar-H), 8.26 (dt, 1H, Ar-H), 8.54 (dd, 1H, Ar-H), 8.60 (d, 1H, Ar-H), 9.46 (d, 1H, Ar-H). MS-ESI (+): 312 $[M]^+$. Anal. Calcd. from $C_{22}H_{34}ClN$: C, 75.94; H, 9.85; N, 4.03. Found: C, 75.96; H, 9.82; N, 4.03.

2.3. Conductivity measurements

Conductivity measurements were performed on a conductivity meter equipped with a conductivity cell having a cell constant of 0.943 cm^{-1} as already reported [6]. The temperature was 25.0 ± 0.1 °C and the standard deviation for conductivity was estimated around 2% as a maximum over three runs. The addition of concentrated surfactant solution by a titrator and the collection of the conductivity data were performed by using a computer controlled automated system, working with a program written in Quick Basic, available from the authors. Water of MilliQ quality (conductivity: 0.05 mS; surface tension: 72.8 mN/m at 20 °C) was used for the measurements.

2.4. Surface tension measurements

The surface tension was measured by using a digital tensiometer. Measurements were made at 25 ± 0.1 °C using the Wilhelmy plate [13]. Sample temperature was controlled to 0.1 °C by using a circulating water thermostatic bath. The instrument was calibrated against MilliQ water, equilibrated against atmospheric CO_2, each time measurements were done. Since cationic surfactants adsorb onto negatively charged glass surfaces, all glassware was thoroughly soaked with the solution to be measured; soaking solutions were discarded. Sets of measurements were taken at 15 min intervals until no significant change occurred, provided that stability was attained in 1 h or less. Standard deviation of the surface tension measurements was less than 0.1 mN/m. The absence of a minimum in the surface tension vs. log concentration plot in the post-cmc region showed that there was very little or no surface active impurity present in the final products.

Before tension measurements, all the surfactants have been purified. Surfactant solution purification was carried out on RP-18 cartridges modifying a literature procedure [14,15]. Instead of using a syringe directly attached to the RP-18 cartridge, our method is similar to a flash chromatography, with a glass column directly connected at the bottom of the cartridge. RP-18 columns were wetted with 2 ml of methanol and then three washings with 5 ml of MilliQ water were performed. Then, an aqueous solution of the surfactant (about 50 ml), at a concentration five times the expected cmc, was passed through the column in order to absorb hydrophobic impurities. This step was repeated five times. The concentration of surfactants in the effluent from the column was determined by UV absorbance. From this stock solution, dilutions were prepared (25 ml). Every diluted surfactant solution was further purified in the same way, by flowing it through the same RP-18 column (10 times, nearly 10–15 min total time). In this way, preferential adsorption of more hydrophobic impurities occurs. After checking the correct surfactant concentration, the surface tension of solutions was measured. The method used by Lunkenheimer [16] has the advantage of being automatic, but it is time consuming and the preparation of the PC controlled machine is not trivial. Even if our procedure cannot guarantee for a certain result (sometimes even the Lunkenheimer method fails), a test can be done to check for the surface tension stability to be attained in one hour, for both the mother solution and at least one dilution.

3. Results and discussion

3.1. Synthesis

Surfactants **1b** and **2b** were prepared by refluxing pyridine or 4-methylpyridine, respectively, with dodecyl bromide in dry toluene following a modification of a standard procedure [6]. The use of toluene as solvent, instead of a big excess of alkyl halides [15], gave better yields, making the purification steps easier. Compounds **1a**–**2a** were thus obtained by ionic exchange as described in Scheme 1.

In a previous work we reported the synthesis of **3b** following the standard procedure using 4-methylquinoline and dodecyl bromide as the solvent [6] (Scheme 1, pathway 1). While this reaction is simple to manage and the product is easily obtained, its purification and the subsequent ionic exchange to obtain **3a** were difficult (coloured impurities were difficult to remove, even by several crystallizations), thus reducing considerably the final yield. To overcome these problems, highly pure compound **3c** was prepared by reacting the 4-methylquinoline with dodecyl iodide in dry toluene at reflux (Scheme 1, pathway 2). At the end of the reaction, a phase separation occurred on cooling to room temperature, giving a red oily phase as product. This oil, washed with ethyl ether to remove the residual reactants, gave a fine yellow powder after its treatment with water. This powder was finally crystallized three times from absolute ethanol. Compounds **3a–b** were thus prepared by ionic exchange from compound **3c**. The ionic exchange step was