Colloids and Surfaces A: Physicochem. Eng. Aspects 343 (2009) 64–69

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Structural aspects in saccharide-derived micelles studied by a spin probe technique

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ARTICLE INFO

Article history:
Received 30 September 2008
Received in revised form 5 January 2009
Accepted 30 January 2009
Available online 5 April 2009

Keywords:
Sugar surfactants
Micelles
Electron paramagnetic resonance
Spin probe
Correlation time

ABSTRACT

Electron paramagnetic resonance spectroscopy (EPR) was used in this study to monitor micellization behavior of selected saccharide-derived surfactants in aqueous solutions by measuring the spin probe parameters of nitroxide labeled entities (5- and 16-doxylstearic acid methyl esters) as a function of temperature and surfactant concentration. A group of aldonamide-type surfactants of the following architecture was selected: a single-head single-tail structure (i.e., *N*-dodecyl-*N*-methylgluconamide—C_{12}MGA), a dicephalic representative (i.e., *N*-dodecyl-*N*,*N*-bis[3-D-gluconyl-amido)propyl]amine—C_{12}DGA and *N*-dodecyl-*N*,*N*-bis[3-D-lactobionylamido)propyl]amine—C_{12}DLA) and gemini one (i.e., *N*,*N*′-bisdodecyl-*N*,*N*′-bis[(3-D-gluconyl-amide)propyl]ethylenediamine—bis(C_{12}GA)). The anisotropy effect in the EPR spectra proved that molecules of the used spin probes penetrate effectively the studied micelles. Taking into account that the rotational correlation time magnitude correlated well with the probe mobility, the structure of formed aggregates and their microviscosity were achieved. It was found that the calculated values of rotational correlation times were relatively high and indicated large inhibition of rotations of the studied nitroxide probe molecules. The microviscosity of micelles increased slightly with the increase in surfactant concentration. Slope coefficients of the obtained temperature dependences under the studied concentration range were almost the same for both spin probes indicating the spherical shape of the aggregates. Our results show effectiveness of EPR technique for investigations of micelle formation and their molecular microenvironment.

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1. Introduction

Nonionic surfactants bearing a carbohydrate moiety as the hydrophilic part (so-called sugar surfactants) have recently achieved increasing interest because they have profound surface and performance properties, reduced environmental impact and can be synthesized from renewable sources [1–3]. Due to their outstanding properties, sugar based surfactants and colloidal systems derived from them find many practical applications, e.g., as environmentally and dermatologically acceptable surface active agents in cosmetic industry, or in medicine, as carriers for drugs [4,5]. These surfactants form micellar structures and mesophases that can be characterized by static light scattering (LS), small-angle X-ray (SAXS) and neutron scattering (SANS), polarization microscopy, rheological and conductivity measurements, and magnetic resonance spectroscopic techniques. Among many physicochemical methods, the electron paramagnetic resonance (EPR) of spin probes can be successfully applied for studying the aggregation behavior of different surfactants as well as the properties (microviscosities and local polarities) of the environment around the probe in the micelles [6]. This technique can be useful in the characterization of the surfactants chains ordering in various aggregates or the effect of different solubilizates on these properties and the dynamics of the micellization process [7]. The relative anisotropy observed in the EPR spectra is directly related to the rotational mobility of the probe, and can be correlated with the probe microenvironment. The change in probe mobility allows one to study the formation of aggregates in solution and often yields profitable data upon the aggregate structure [8]. The value of hyperfine splitting constant is dependent on the polarity of the probe environment and can be used to describe the local composition changes around the probe [9]. In particular, nitroxide labeled fatty acid ester probes (esters of n-doxyl stearic acids) has been used successfully to study the properties of a variety of surfactant micelles [10]. However, besides few reports [11–13] in the literature, the saccharide-derived surfactants have not been investigated yet by means of the spin probe techniques.

As a continuation of our previous studies [14–16,3] related to aldonamide-type surfactants and their unique aggregation properties we present here our recent findings on structural aspects

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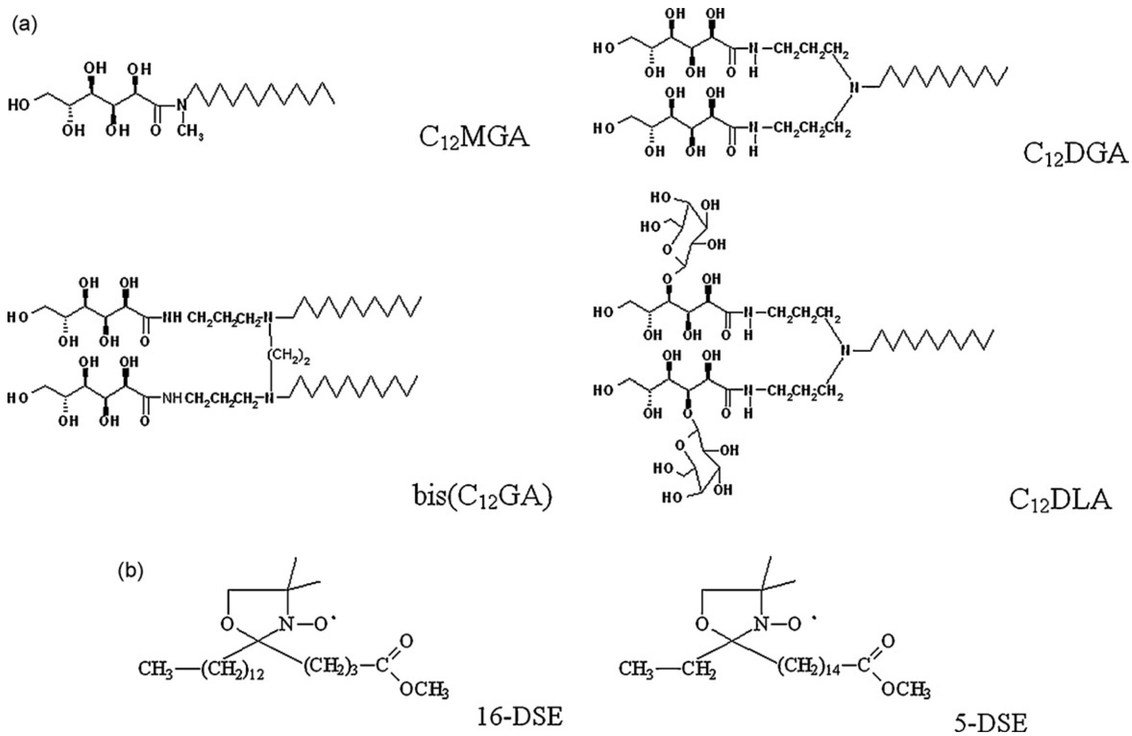
doi:10.1016/j.colsurfa.2009.01.030



Scheme 1. Structures of (a) examined surfactants and (b) spin probes used in EPR experiments.

in the micelles formed by *N*-dodecyl-*N*-methylgluconamide, *N*-dodecyl-*N*,*N*-bis[3-D-gluconyl-amido)propyl]-amine, *N*-dodecyl-*N*,*N*-bis[3-D-lactobionylamido)propyl]amine and *N*,*N*′-bisdodecyl-*N*,*N*′-bis[(3-D-gluconyl-amide)propyl]ethylenediamine, having the general formula (together with abbreviations) shown in Scheme 1(a). The main purpose of this work was to apply the electron paramagnetic resonance spectroscopy (EPR) and the 5- and 16-doxylstearic acid methyl esters (16-DSE and 5-DSE structures are placed in Scheme 1b) as spin probes in sensing modifications of the studied surfactants polar head geometry and area, local hydratation degrees of hydrophilic moieties, as well as temperature modifications of these parameters.

2. Materials and methods

2.1. Materials

Nonionic surfactants *N*-dodecyl-*N*-methylgluconamide (C_{12}MGA), *N*-dodecyl-*N*,*N*-bis[3-D-gluconylamido)propyl]amine (C_{12}DGA), *N*-dodecyl-*N*,*N*-bis[3-D-lactobionylamido)propyl]amine (C_{12}DLA) and *N*,*N*′-bisdodecyl-*N*,*N*′-bis[(3-D-gluconylamide) propyl]ethylenediamine (bis(C_{12}GA)) were synthesized according to methods given in [14–16]; 16-doxylstearic acid methyl ester (16-DSE) and 5-doxylstearic acid methyl ester (5-DSE) were purchased from Sigma–Aldrich. Water used for all experiments was doubly distilled and purified by means of a Millipore (Bedford, MA) Milli-Q purification system.

2.2. Methods

The EPR spectra were made with a Bruker ESP-300E spectrometer. The microwave power was 1.59 mW, sweep width 100 G, time constant 164 ms, and sweep time 168 s. The temperature was calibrated with the B-VT-2000 variable temperature device. The probe (16-DSE or 5-DSE)/surfactant molar ratio was about 1:400 [11]. All samples were shaken about 2 h after preparation. The rotational correlation time τ_R was calculated with the following formula [8]:

$$\tau_R = 6.51 \times 10^{-10}\left[\left(\frac{h_0}{h_{+1}}\right)^{1/2} + \left(\frac{h_0}{h_{-1}}\right)^{1/2} - 2\right]\Delta H_0 \quad [\mathrm{s}] \qquad (1)$$

where h_{+1}, h_0, and h_{-1} are the intensities of the low, central and high field peaks of the EPR spectrum, respectively, and ΔH_0 is the width of the central line (in Gauss). Eq. (1) is applicable in the fast motion region, i.e., rotational correlation times τ_R in the range of $10^{-11} < \tau_R < 3 \times 10^{-9}$ s [17]. The Debye–Stokes–Einstein equation (where R is the hydrodynamic radius of the tumbling entity) is believed to relate τ_R to the local viscosity, η:

$$\tau_R = \frac{4\pi\eta R^3}{3kT} \quad [\mathrm{s}] \qquad (2)$$

Furthermore, the nitrogen hyperfine splitting constant of the spin probe a_N can be calculated from the EPR spectra as a distance between the observed lines. This parameter reflects the polarity of the immediate environment of the spin probe.

3. Results and discussion

All the studied aldonamide-type surfactants, the single-head, single-tail C_{12}MGA, the dicephalic C_{12}DGA and C_{12}DLA, as well as the dimeric bis(C_{12}GA) constitute a group of nonionic environmentally friendly and biocompatible surfactants which can be easily synthesized from renewable and low-cost raw materials. They reveal very good surface, aggregation and performance properties [1,14–16,3,18]. In the present contribution we applied the EPR spectroscopy in order to acquire a better understanding of physicochemical properties of micelles formed by the selected structures.

According to literature [19], a variety of nitroxide labeled fatty acid probes can be successfully used to study the properties of surfactant systems. Taking into account that the aldonamide micelles have relatively long rotational correlation times the 16-doxylstearic acid methyl ester was chosen for our studies rather than the 5-doxylstearic acid methyl ester; the first mentioned

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