Colloids and Surfaces A: Physicochem. Eng. Aspects 413 (2012) 92–100

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Hydration of sugar based surfactants under osmotic stress: A SAXS study

Caroline Bauer, Pierre Bauduin*, Luc Girard, Olivier Diat, Thomas Zemb

Institut de Chimie Séparative de Marcoule, ICSM-UMR5257 (CEA/CNRS/UM2/ENSCM), 30206 Bagnols sur Céze, France

ARTICLE INFO

Article history:
Received 2 November 2011
Received in revised form 5 March 2012
Accepted 6 March 2012
Available online 15 March 2012

Keywords:
Octyl-beta-glucoside
Small angle X-ray scattering
Surfactant micelle
Salt effect
Hofmeister series
Hydration

ABSTRACT

The effect of adding salts to micelles made of a sugar based surfactant, n-octyl-beta-glucoside, has been investigated using small angle X-ray scattering (SAXS) and dynamic light scattering (DLS) techniques. It was shown that adding salts leads to change the outer shell hydration of the micelles i.e. where the glucose moieties are situated. No ion adsorption at the micelle surface was detected. Three regimes have been determined as a function of the ionic strength (IS): (i) at low IS (<1 M), no significant effect on the hydration of the surfactant sugar moieties was detected while at (ii) intermediate IS (1–1.8 M) a salting-in effect was observed, i.e. a strengthening of the hydration of the glucose polar heads at the micelle surface, and at (ii) higher IS a strong salting-out effect is detectable i.e. strong dehydration of the polar head inducing an increase in the micelle size. It is noteworthy to remark that such a transition from a salting-in to a salting-out effect is observed with classical polyethoxylated surfactants (CiEj) when measuring the cloud point as a function of a salting-in electrolyte concentration i.e. the cloud point shows an increase and then a decrease by addition of the electrolyte.

1. Introduction

Sugar based surfactants, mainly alkyl (poly)-glucosides (APGs), have been extensively studied the last two decades [1]. Their increasing importance in the detergent industry is due to their biodegradability and their production from natural and renewable resources. Moreover they are extensively used to extract membrane proteins from their native environment because they prevent the protein denaturation and they can be afterwards easily separated from the protein by dialysis owing to their high hydrophilicity [2,3]. A review on APGs aggregation and surface activity dealing with many physical properties can be found in reference [1].

The determination of the basic structural parameters of surfactant self aggregation is necessary for understanding the physical mechanisms that drive the formation of their molecular assemblies in solution e.g. when they are used to form microemulsions. In aqueous solution, micelles are formed; they consist of a limited number of surfactants, typically between 50 and 150, forming a non-rigid and closed dynamic structure with a liquid-like core in order to minimize the contact between the surfactant hydrophobic tail and water [4]. This effect is known as the "hydrophobic effect" [5]. The head group (or polar head) of the surfactant, which is for APGs composed of sugar moieties, forms an outer hydrophilic layer towards the water phase. The size, shape and polydispersity of the micelles are dependent on the surfactant structure (typically an alkyl chain with at least 7 carbon atoms is required to form micelles), concentration, temperature and composition of the surrounding aqueous phase, e.g. presence of salt, and can only be determined in time average [6]. In water the size/shape of a surfactant micelle results then from a compromise between the hydration of the head groups, which tends to promote spherical aggregates, and the minimization of the hydrophobic contact between the alkyl chain and water, which drives the system towards a bilayer structure i.e. where the area per surfactant in the aggregate is minimum. The geometrical concept of the packing parameter, P, introduced by Israelachvili [7], picks up very well the aggregation of surfactant in water. In this concept aggregation is considered from the molecular level of the surfactant defining P as $P = V/al_C$ with V the volume of the hydrophobic chain(s), l_c the chain length (which is usually 80% of the extended chain length) and a the area per head group. These parameters, especially a, do not only depend on the surfactant geometry, given by the van der Waals radii of the atoms, but are sensitive to the experimental conditions (salts controlling electrostatic interactions, nature of oil used when present, temperature, pH, etc.), the term "effective" packing parameter is then more suitable. Depending on the packing parameter value of a surfactant the following aggregate shape can be formed in solution: (i) $P < 1/3$ spherical direct micelles, (ii) $1/3 < P < 1/2$ elliptical, rod shaped or cylindrical micelles, $1/2 < P < 1$ bilayered structures (as lamellar phase, liposomes or vesicles), $P > 1$ reverse aggregates globular micelles, rods, etc.

Octyl-beta-glucoside (C8G1) is by far the most studied APG by diverse methods [8–10]. Because of its relatively high hydrophilicity resulting from the strong hydration of the glucose moiety and its

* Corresponding author. Tel.: +33 466339288.
E-mail address: Pierre.bauduin@cea.fr (P. Bauduin).

0927-7757/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2012.03.006

relative short alkyl chain, C8G1 shows a rather high critical micellar concentration (cmc) in water, between 19 and 25 mM depending on the references and on the technique used [8–10]. Many studies have shown by different techniques (SAXS, SANS, DLS, NMR, etc.) that C8G1 do not form spherical micelles [11] but more biaxial ellipsoid micelles that grow in size with increasing concentration [12]. For dodecyl maltoside (C12G2) the reason for the formation of ellipsoid micelles was proposed to be due to steric constraints in the bulky hydrated sugar head [13]. Small angle neutron scattering (SANS) and SAXS confirmed the concentration-dependant change in C8G1 micelle size, which is restricted to changes in the micelle length and not diameter. The SAXS data analysis gave also a proof of a short-ranged interaction between the C8G1 micelles. This short-ranged hydration force sets in at a distance of a few water molecules suggesting that C8G1 are strongly hydrated with six water molecules per head group [14].

Some papers focusing on the influence of salts on APG's micelle size can be found in the literature. For example Ericsson et al. have investigated the effects of cations and anions on the micelle size of C9G1 using dynamic light scattering [15]. The evolution of the micelle size as a function of salt concentration shows a pronounced difference for sodium salts when the nature of the anion is varied from kosmotropic (salting-out) to chaotropic (salting-in) following the Hofmeister series $SO_4^{2-} > Cl^- > NO_3^- > I^- > SCN^-$ [16,17]. For example I^- and SCN^- are salting-in anions, which give rise to a moderate decrease in the micelle size as compared to the system without salt whereas the salting-out anions SO_4^{2-} and Cl^- increases the micelle size [15]. These effects were interpreted in terms of hydration of the polar head with the salting-out salts reducing hydration and with the opposite effect for salting-in salts which promote hydration. For salting-out salts, it is suggested that a decrease in the polar head hydration leads to a decrease in the apparent polar head area, noted a in the spontaneous packing parameter expression ($P = v/al$). This means a reduction of the curvature, i.e. a tendency towards a more planar arrangement, and consequently a micellar growth.

A similar investigation was performed for alkali metal cations (Li^+, Na^+, K^+ and Cs^+), by varying the nature of the anions [15]. At constant salt concentration, the size of the micelles was found to be larger for chloride salts of heavier alkali metals, following then the Hofmeister series of cations ($Li^+ > Na^+ > K^+ > Cs^+$). This effect was linked to an increase in polarizability of the cation by increasing the ionic radius. Pastor et al. studied the effect of $CaCl_2$ content on the aggregation number of C8G1 micelles [18]. These authors suggested, from their speed of sound and fluorescence measurements, that the increase in the micelle size (salting-out effect) is due to a contraction of the surfactant hydration shell made of the glucose moieties. This interpretation of the salting-out effect is then in agreement with the dehydration of the glucose moieties of the surfactants as proposed by Ericsson et al. for C9G1.

Aveyard et al. investigated the effect of NaCl addition on the distribution, surface tension and aggregation of C10G1 in biphasic toluene/water systems. Interestingly they observed a salting-in effect that they interpreted in terms of ion adsorption on the sugar moieties [19]. They could even estimate a formation constant ($K_{comp} = 0.24\ M^{-1}$) for this complex. Hofmeister effects are discussed in many recent studies in terms of the ability of ions to adsorb at an interface (salting-in effect) or to deplete from an interface (salting-out effect) [20]. Noteworthy is that the difference in polarizability of hydrated ions versus pure solvent was proposed by Yaminsky and Ninham to be the key parameter of the fundamental explanation of Hofmeister effects, the more polarizable the ion the stronger its propensity to adsorb [21]. This is fully consistent with the interpretation of Aveyard et al. Moreover ion-sugar complexation is known for many systems and has attracted much attention in the literature [22,23]. Nevertheless glucose is known as a non-complexing agent. Consequently a controversy exists on the mechanism of salt effect on glucoside surfactants with two possible interpretations based on a change in glucoside hydration on one side and on an ion adsorption mechanism on the other side. The aim of this paper is to give insights on the precise mechanism of salt effect of C8G1, beyond the simple case of monovalent ions.

The choice was made to investigate C8G1 micelles in the presence of salts ($LiNO_3$, $Nd(NO_3)_3$ and $LiNO_3/Nd(NO_3)_3$) by small angle X-ray scattering (SAXS). Aside from the evolution of the shape and size of the micelles, SAXS gives information on the electron density in the micellar shell as this technique is sensitive to the local electron density difference at the micellar scale. The electron density in the micellar shell depends directly on the two effects of interests here: ion adsorption on glucose moieties and hydration of the micelle shell. Dynamic light scattering (DLS) experiments were also performed in order to confirm the evolution in the size of the micelles, observed by SAXS, due to salt addition. To the best of our knowledge this problem was not yet investigated in the literature.

2. Experimental

2.1. Samples

The samples were prepared simply by mixing the components with water. The effect of surfactant concentration and the type and concentration of salt added were studied. Stock solutions containing different salts ($LiNO_3$, $Nd(NO_3)_3$ and $LiNO_3/Nd(NO_3)_3$) at different concentrations ($LiNO_3$: 0.15; 1.3; 1 M, $Nd(NO_3)_3$: 10; 50; 150; 300 and 500 mM) were prepared first. C8G1 was then added to reach concentrations of 45 mM and 150 mM. The sample compositions are listed in Table 1. The stock solutions without surfactant, in the first part of the table, are useful to perform the background subtraction in the SAXS spectra of the samples containing the surfactant.

2.2. Methods

2.2.1. DLS measurement

DLS experiments were performed on the samples in order to determine the size of the C8G1 micelles. DLS determines the time correlation of the light scattered intensity fluctuations from the sample in order to determine the diffusion coefficient of the scattering objects, here the micelles. The size of the micelles can be calculated from the diffusion coefficient using a spherical shape approximation. The size obtained from DLS is expressed as hydrodynamic diameter (D_H) that includes the micelles and its solvent shell. Hence sizes obtained by DLS are usually larger than the sizes determined by other techniques such as SAXS or SANS. For C8G1 the situation is different as it forms elliptical micelles (see the SAXS results), consequently only a rough estimation of the micellar size is accessible from DLS. Nevertheless it gives useful information concerning the relative change in the micellar size that can be used to validate the size parameter, a, i.e. the long axis of the ellipsoid micelle, obtained from the fitting of the SAXS spectra.

2.2.2. Small angle scattering experiments (SAXS)

2.2.2.1. Methods and background subtraction procedure. SAXS spectra were collected at the European Synchrotron Research Facility (ESRF) in Grenoble (France) on the beamline ID02. The energy of the incident beam was selected at 12.4 keV and the distance sample-detector was kept constant at 1 m to access a q-range from 0.1 to 4.87 nm^{-1} that corresponds in real space ($2\pi/q$) to a range from 1.3 to 62.8 nm. Standard procedures were applied at the ESRF to calibrate the q-range and to obtain the scattered intensity in absolute scale, $I(q)$ expressed in mm^{-1}.