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

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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

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