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Biogenic amine – Surfactant interactions at the air–water interface

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ABSTRACT

The strong interaction between polyamines and anionic surfactants results in pronounced adsorption at the air–water interface and can lead to the formation of layered surface structures. The transition from monolayer adsorption to more complex surface structures depends upon solution pH, and the structure and molecular weight of the polyamine.

The effects of manipulating the polyamine molecular weight and structure on the adsorption of the anionic surfactant sodium dodecyl sulphate at the air–water interface are investigated using neutron reflectivity and surface tension, for the biogenic amines putrescine, spermidine and spermine.

The results show how changing the number of amine groups and the spacing between the amine groups impacts upon the surface adsorption. At lower pH, 3–7, and for the higher molecular weight polyamines, spermidine and spermine, ordered multilayer structures are observed. For putrescine at all pH and for spermidine and spermine at high pH, monolayer adsorption with enhanced surfactant adsorption compared to the pure surfactant is observed. The data for the biogenic amines, when compared with similar data for the polyamines ethylenediamine, diethylenetriamine and triethylenetetramine, indicate that the spacing between amines groups is more optimal for the formation of ordered surface multilayer structures.

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1. Introduction

Biogenic amines or polyamines, such as putrescine, spermidine and spermine, are important in a range of biochemical functions [1–3]. Polyamines are small flexible polycations, and are involved in a variety of physiological roles associated with cell growth and proliferation. Their interaction with different charged species in bio-macromolecules such as DNA and in the cell membrane is of central importance. As such they are associated with DNA compaction and precipitation [4–6], protein folding and unfolding [7] and have been exploited in the formation of polyplexes for potential gene delivery vehicles associated with gene therapy [8–10].

The focus of this paper is on the surface interaction between the biogenic amines and the anionic surfactant sodium dodecyl sulphate, SDS. Although this focus is rather specific, how the surface interaction is affected by the structure and molecular weight, MW, of the polyamine has much broader biological and technological significance and implications. In this broader context the poly(ethyleneimine), PEI, based polymers and the polyamines are important polyelectrolytes because of their widespread applications, and so have been extensively studied [11]. Hence the surface adsorption behaviour of polyelectrolyte/surfactant mixtures has also been extensively studied [12,13]. Depending upon the nature of the polyelectrolyte–surfactant interaction enhanced absorption in the form of a monolayer occurs down to relatively low surfactant concentrations due to polyelectrolyte–surfactant surface complexation. In many cases, close to charge neutralisation where the solutions are cloudy and precipitation/coacervation occurs, the surface structure is more complex and ordered layered structures from a trilayer to multiple bilayer structures are formed or adsorb at the interface. Recent studies attributed the surface multilayer formation to a wetting of the surface by a more surface active concentrated precipitated/coacervated phase which is highly surface active and has a lower surface tension than the coexisting dilute phase [14]. This surface ordering phenomenon and the systems where only monolayer adsorption accompanied by the partial desorption that occurs in the region of charge neutralisation are now described by a full thermodynamic treatment [15].

PEI is a particularly important polyelectrolyte, in which the nature of its interaction with surfactant varies with pH, MW, and polymer architecture (branched or linear) [16–18]. In combination with SDS PEI exhibits the full range of surface properties summarised in the previous paragraph. However, a notable feature is that the PEI–

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SDS interaction is strong at low pH when the polyelectrolyte is highly charged, and is equally strong at high pH when the polyelectrolyte is essentially neutral [16]. From surface adsorption studies on SDS with a range of oligoamines (from ethylenediamine to pentaethylenehexamine) Penfold et al. [19] attributed the nature of the interaction at high pH to a combination of an ion–dipole interaction between the sulphate headgroup of the SDS and the amine nitrogen group and the inter-alkyl chain interaction between neighbouring SDS molecules. Similar observations were made by Winnik et al. [20,21], and Sherstenin et al. [22], who reported evidence for electrostatic and non-electrostatic contributions to the binding of SDS to PEI. This is further supported by Jon and Chang [23] who described an additional interaction between SDS and amine modified polymers in the form of a ion–dipole interaction, and Ogawa et al. [24] who discussed the role of cation–dipole interactions in the layer-by-layer assembly of poly(lactic) acid and polylysine films.

Of direct relevance to the study reported here, the recent measurements [25–27] on a range of small linear and branched oligoamines with SDS have illustrated the importance of the oligoamine architecture, MW and charge density on the oligoamine/SDS adsorption. In particular the results demonstrate the extent to which these parameters affect the occurance of monolayer and multilayer adsorption at the interface. The lower charge density and greater rigidity of the branched oligoamines results in multilayer formation at the interface with SDS at low pH; whereas for the linear oligoamines multilayer formation occurs at higher pH [25]. For the linear oligoamines with SDS multilayer formation is strongly dependent upon the oligoamine MW. If the MW is too low multilayer formation is not optimal due to a lack of cooperativity, and does not occur at much higher MW's because of the greater entropic penalty arising from the flexibility of the polymer chain [26]. At the lower MW's, ethylenediamine to pentaethylenetetramine, there is a distinct switch in the pH dependence of the surface multilayer formation with MW [27]. For ethylenediamine, ditheylenetriamine, and triethylenetetramine, multilayer formation occurs at pH 3, and not at pH 7 and 10. For the slightly higher MW oligoamines, tetraethylenepentamine and penatethylenehexamine, multilayer formation is predominantly observed at pH 7 and 10, and at pH 3 only monolayer adsorption occurs. This illustrates the importance of the balance between the electrostatic attraction between the SDS headgroup and the amine nitrogen groups, the repulsion between neighbouring SDS headgroups and the cooperative interaction between the neighbouring alkyl chains of the bound SDS molecules. It is this aspect which is explored in more detail here in this paper, by varying the distance between the amine groups in equivalent oligoamines and biogenic amines. By comparing previous results for ethylenediamine, ditheylenetriamine, and triethylenetetramine [25–27] with those for putrescine, spermidine and spermine reported here, the importance of the competition between the major factors controlling the structure of the adsorbed layer is probed in more detail.

The formation of surface multilayer structures in surfactant, polymer and polymer–surfactant systems is increasingly encountered in a range of biological and technological circumstances. They are implicated in a range of diverse applications and potential applications, in lung surfactants [28,29], tissue lubrication [30,31], in fabric and hair conditioning [32], and in the potential for increasingly efficient detergency, soft lubrication, efficient delivery of active agents such as perfumes and anti-microbial/anti-bacterial agents and in encapsulation. Recent studies on the formation of surface multilayer structures in ionic surfactants induced by multivalent counterions [33–36] closely relate to the studies on the effects on surfactant adsorption of the polyamines and the biogenic amines which can be considered as flexible multivalent cations. Hence the results reported here are aimed at extending our understanding of the polyamine–surfactant interaction and the impact upon surface adsorption, and relate to both the biological function of biogenic amines and the diverse potential technological applications.

In this paper the determination of the surface adsorption behaviour of biogenic amine (putrescine, spermidine, and spermine)/SDS mixtures at the air–water interface, measured over a wide range of surfactant and biogenic amine concentrations and pH by NR and ST, are reported.

2. Materials and methods

2.1. Materials and measurements made

The biogenic amines putrescine, spermidine and spermine (1,4-diaminobutane, 1,5,10-triazadecane, and 1,12-dodecanedamine) were obtained from Sigma–Aldrich (>97% purity) and used as received. The structure of the biogenic amines is shown in Fig. 1a, and the corresponding equivalent polyamines ethylenediamine (diamine), diethylenetriamine (triamine) and triethylenetetramine (tetramine) are shown in Fig. 1b.

The alkyl chain deuterium labelled SDS (d-SDS) was obtained from the Oxford Isotope Facility [37] and purified before use by repeated recrystallization from ethanol [38]. The chemical purity of the surfactant was verified by surface tension, ST, where no minimum was observed about the critical micellar concentration, cmc, and from the adsorbed amount above the cmc measured by neutron reflectivity, NR. Deuterium oxide, D_2O, was obtained from Sigma–Aldrich and high purity water (Elga Ultrapure) was used throughout. The solution pH was adjusted by the addition of aqueous hydrochloric acid (5.0 M) or aqueous sodium hydroxide solution (5.0 M). The glassware and Teflon troughs used in the NR and ST measurements and sample preparation were cleaned in alkali detergent (Decon 90) and rinsed thoroughly in high purity water before use. Stock solutions of the biogenic amines and the d-SDS were prepared and the biogenic amine/SDS solutions mixed from the stock solutions. All solutions were left for at least 12 h to equilibriate before any measurements were made. The measurements were all made at 25 °C.

The neutron reflection, NR, measurements were all made for the polyamine/d-SDS solutions in null reflecting water, nrw (92 mol% H_2O/D_2O mixture) at pH 3, 7, and 10 for a biogenic amine concentration of 5 mM and SDS concentrations from 10^{-4} to 10^{-2} M for the biogenic amines putrescine, spermidine, and spermine. For spermine at pH 7 and spermidine at pH 3 and 7 measurements were also made at a fixed SDS concentration of 5 mM and biogenic amine concentrations from 0.5 to 10 mM. The ST measurements were made for 5 mM spermidine/SDS mixtures at pH 7 and 10,

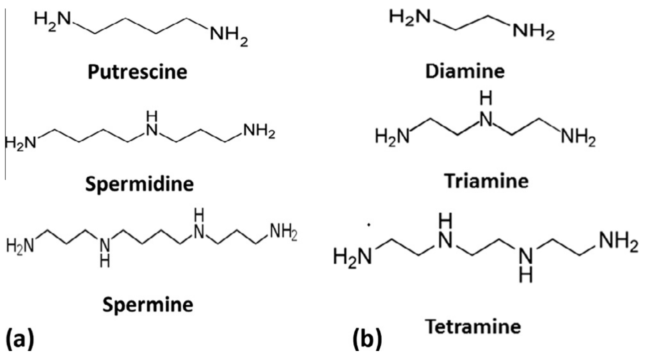

Fig. 1. Structure of (a) biogenic amines putrescine, spemidine and spermine, and (b) diamine, triamine and tetramine.

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