Biophysical Chemistry 117 (2005) 263 – 273

Biophysical Chemistry

http://www.elsevier.com/locate/biophyschem

Adsorption of single chain Zwitterionic phosphocholine surfactants: Effects of length of alkyl chain and head group linker

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Received 29 March 2005; received in revised form 3 June 2005; accepted 3 June 2005

Available online 29 June 2005

Abstract

The adsorption of a range of single chain zwitterionic phosphocholine surfactants (C_nP_mC) at the air/liquid interface has been studied by a combination of surface tension and neutron reflectivity. The critical micellar concentration (CMC) for C_nPC (or C_nP_2C), where n varied from 12, 14 to 16, was found to be 0.91, 0.14, and 1.2×10^{-2} mM respectively, and followed the same trend as observed for other zwitterionic and non-ionic surfactants. The area per molecule at the CMC, A_{cmc}, for C_nPC was found to remain constant between 50 and 53 Å^2, indicating that the increase in the alkyl chain length had little effect on A_{cmc} at the interface. The neutron reflection measurement also showed an almost constant layer thickness (τ) of 20 ± 2 Å from all the alkyl chain deuterated PC surfactants (dC_nhPC) in null reflecting water (NRW), suggesting that the alkyl chains of the surfactant responded to changes in either chain length or solution concentration by varying their angle of tilt. In contrast, increasing the length of head group linker between P and N atoms in $C_{12}P_mC$, where $m = 2$, 4, to 6, resulted in a much slower decrease of CMC from 0.91, 0.7, to 0.5 mM, consistent with a different contribution to the free energy of micellization. A_{cmc} for $C_{12}P_mC$ did not vary when m was increased from 2 to 4, and this observation together with the thickness of the head group region indicated an almost perpendicular projection of the head group in $C_{12}P_2C$ and $C_{12}P_4C$. A further increase in m to 6 resulted in an A_{cmc} of 70 Å^2. This increase in A_{cmc} however did not result in any change in either the total layer thickness or the fraction of the head group region submerged in the aqueous subphase, suggesting that the head group in $C_{12}P_6C$ was bent away from the surface normal direction. Both increase in temperature from 25 to 40 °C and the addition of 0.1 M NaCl had little effect on the area per molecule or the thickness of $C_{12}P_mC$ surfactant layer, showing that the $C_{12}P_mC$ series behaved like C_nP_2C series. The main conclusion from this study is that for all the C_nP_mC surfactants studied, change in m or n has little effect on the total thickness, the thickness of the alkyl chain or that of the head group region.

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Keywords: Zwitterionic surfactants; Surface adsorption; Biointerface; Phospholipid; Surface tension; Neutron reflection

1. Introduction

In many commercial formulations mixed surfactants are widely used because they offer favourable interfacial properties and act synergistically [1]. In contrast, zwitterionic surfactants, characterised by both a positive and a negative charge chemically bonded in the same head group, offer a number of interesting properties. They have a critical micellar concentration (CMC) intermediate between ionic and non-ionic surfactants. They display surface and interfacial adsorption that are virtually independent of solution conditions such as temperature, salt and pH [2,3]. Zwitterionic surfactants are electrically neutral but the charges they carry in the zwitterionic head group do influence their hydrophilicity, making them different from non-ionic surfactants.

In a systematic study of surface and interfacial behaviour of surfactants, we have previously used a combination of surface tension and neutron reflectivity to investigate the characteristics of surface monolayers adsorbed from anionic, cationic and non-ionic surfactants [4–6]. More

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doi:10.1016/j.bpc.2005.06.001

recently we have extended this work to study the main features of single chain phosphocholine surfactants, C_nPC, where $n = 12$ and 16 [7]. These PC surfactants show similar adsorption behaviour to zwitterionic sulfobetaine [8] and carboxybetaines [9]. However the structure of the surface layer showed a different dependence to temperature change and salt addition from conventional ionic (for example, C_nTAB) surfactants and non-ionics (for example, C_nEO_m). In this work, we report a recent study that examines how the increase in alkyl chain length, n, and in the number of methylene units in the head group, m, of the PC surfactant affects the structural features of the surface monolayers. The general formula of the surfactants is $C_nH_{2n+1}PO_4^-C_mH_{2m}N^+(CH_3)_3$, which will be referred to as C_nP_mC, where n will be varied from 10, 12, 14, 16 to 18 and m from 2, 4 to 6. To examine the effect of the alkyl chain length, m has been fixed at 2 and the series is referred to as C_nPC (or C_nP_2C). To assess the effect of the length of head group linker, n has been fixed at 12 and the series is referred to as $C_{12}P_mC$.

The effect of the length of straight alkyl chain on the critical micellar concentration (CMC) for both ionics and non-ionic alkyl ethoxylates (C_nEO_m) has been extensively studied. A linear relationship between log[CMC] and the number of carbon atoms (N_c) in the alkyl chain is empirically applicable in most cases [10]. If the area per molecule at the CMC, A_{cmc}, is entirely controlled by the bulky size of the head group associated with charge and hydration, increase in alkyl chain length would not be expected to alter A_{cmc}. However, some extent of variation is often observed due to the changing hydrophobic interaction between neighbouring alkyl chains. The effect of alkyl chain length has been extensively studied from the adsorption of cationic n-alkyl-trimethylammonium bromide (C_nTAB) at the air/water interface with n from 12 to 18 [6,11–15]. Neutron reflectivity measurements revealed that the thickness of the surfactant layers stayed almost constant at 18–20 Å for all the chain lengths, when modelled as a uniform layer, with $A_{cmc} = 44$ to 48 Å^2. The lack of layer thickness variation with alkyl chain length is in part due to the capillary wave contribution to the effective thickness of the adsorbed layer but this observation also suggests an increased tilting of the alkyl chains away from the surface normal direction, resulting in the increase in layer packing density. The increased fluidity was consistent with the slight lowering in A_{cmc}, indicating an increased hydrophobic interaction within the surface layer. For $C_{10}TAB$, the thickness at the CMC was still similar, but A_{cmc} increased to some 60 Å^2 suggesting that as alkyl chain became shorter, they were stiffer, the hydrophobic attraction became less significant and the chains were closer to the surface normal than for the other longer chain C_nTAB's.

The non-ionic surfactants, $C_{12}H_{25}(OC_2H_4)_mOH$, $C_{12}(EO)_m$, have been used to examine the effect of head group size [4,16–18] on adsorption . It was found that for $m = 2$ and 4 the effective layer thickness became smaller with increasing area per molecule. The extent of the ethoxylated head group layers also became smaller than their fully extended length, suggesting that ethoxylates were bent or coiled with increasing head group size. A_{cmc} increased from 33 Å^2 for $m = 2$ to 44 Å^2 at $m = 4$, showing the dominant contribution of the ethoxylate head group to A_{cmc} [4]. An interesting observation was the occurrence of a strong intermixing between alkyl chains and ethoxylates within the interfacial layer as the size of the head groups increased. Further increase in m for $C_{12}EO_m$ series resulted in a steady increase in A_{cmc}, indicating the different packing adopted by the EO head groups from the alkyl chain and different interactions involved. Chain branching may however result in considerably different surface packing compared to the straight chain [19].

Changes in the molecular architecture of surfactant molecules have a profound implication on surface monolayer structure and related adsorption properties. An example of this is the interesting features revealed for the di-chain Gemini $C_{12}TAB$ surfactants with different length of linking spacer between the two cationic heads [20]. Within the monolayers, the chain–chain hydrophobic interaction tends to lower the polar head surface area on the surface of water, but these interactions cannot be considered on their own. These forces compete with the hydrophilic forces between the head groups and between the head group and water. In addition, as the length of linker increases, structural flexibility may arise from the increased hydrophobic interaction between the head group and the alkyl chain, causing the head groups to adopt a different conformation. Although the C_nP_mC series to be studied in this work has very different molecular configuration, the balance of interactions between the hydrophobic tail and hydrophilic head should be considered to be similar.

Other workers have used the two-chained phospholipid monolayers formed from 1,2 - dihexadecyl-sn-glycero-3-phoshocholine (DHPC) to investigate the head and tail interactions by Langmuir troughs and X-ray reflection [21]. Ethylene oxide (EO) groups, of 1, 2, and 3 units were incorporated between the chain and the phosphate group. This type of structural manipulation did not change the phosphocholine zwitterionic character but effectively increased the hydrophilic character of the head. The results have showed that as the head group length increases the influence of the head group on the chain lattice is reduced but its hydration is promoted. Others [22] have compared $C_{10}PC$ with a C_{10} analogue in which the choline head was replaced at the P-O position by two fixed $N(CH_2CH_2)_2O$ groups. This approach increased the number of carbons in the head, and hence increased the hydrophobicity. Such structural changes resulted in the removal of the important zwitterionic character of the head group, but had little influence on the hydrophobicity, the CMC, or A_{cmc}. Holmberg et al. have replaced a methyl group on the *N*-choline of C_nP_mC by straight chain hydrocarbon. The substitution showed a drop in CMC by orders of magnitude

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