

# Induced Crystallization of Polyelectrolyte-Surfactant Complexes at the Gas-Water Interface

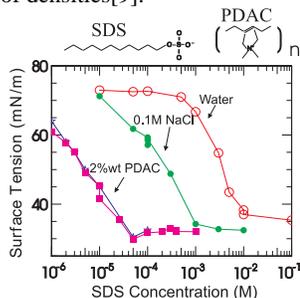
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## Introduction

There has been a growing interest in the phase-behavior, aggregation and precipitation of polymer-surfactant mixtures; in particular, ionic surfactants and oppositely charged flexible polyelectrolytes (PEs)[1-4], or semi-flexible PEs, such as DNA[5] or actin[6]. In addition to the fundamental interest in the principles governing phase-behavior, aggregation and precipitation of polymer-surfactant mixtures, understanding the behavior of these complex systems is crucial for technological applications concerning detergents, paints, cosmetics, DNA transfection[7], and others. Some important aspects regarding the formation of flexible PE-surfactant complexes present exciting challenges. The role played by the interface in the growth and nucleation of these complexes, for example, is to a large extent unknown, although neutron and X-ray reflectivity studies provided invaluable insight into the density profile across the interface of the PE/surfactant solutions[8]. The role salt concentration has on aggregation and precipitation of PE and PE-surfactant solutions is also an open problem. Recent studies suggest that at high salt concentrations, macromolecules may be over-screened by counterions, effectively reversing their charge, and same-charge macromolecules may attract each other at a range of densities[9].



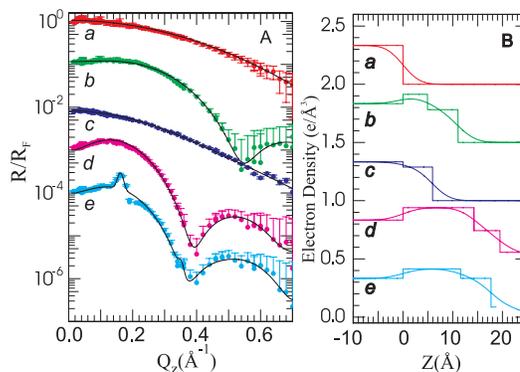
**Figure 1:** Chemical structure of sodium dodecyl sulfate (SDS) and poly-diallyldimethylammonium chloride (PDAC), used in this study. Surface tension as a function of SDS concentration in water, and 0.1M NaCl and 2% wt. PDAC both at 0 and 0.1M NaCl, practically indistinguishable.

Previous studies on surfactant-PE complexes have focused on bulk properties and self-assembly as driven by surfactant concentration. The present study focuses on interfacial behavior; in particular on the role played by the gas-water interface in the precipitation process, and how the self-assembly may be controlled by the weakening of the electrostatic interactions. Herein, we report surface sensitive synchrotron X-ray diffraction studies, both reflectivity and diffraction at grazing-angles of incidence (GIXD), on a model system consisting of sodium-dodecyl-sulfate (SDS) and Poly-diallyldimethylammonium chloride (PDAC) (shown in Fig. 1). A major portion of this research activity was published recently[10].

## Methods and Materials

SDS and PDAC were purchased from Sigma-Aldrich. PDAC at 2% wt. in pure water (Milli-Q Millipore Corp.) and in 0.1M

NaCl were used in all experiments, varying SDS concentration. Surface sensitive X-ray diffraction studies of the structure of free gas/solution interface were conducted on the Ames Laboratory Liquid Surface Diffractometer at the Advanced Photon Source (APS) beamline 6ID-B, described elsewhere[11].



**Figure 2:** A) Reflectivity normalized to the reflectivity of ideally flat water interface, for: a)  $10^{-4}$ M SDS in water, b)  $10^{-4}$ M SDS 0.1M NaCl, c) 2%wt PDAC in pure water d)  $10^{-4}$ M SDS in 2%wt PDAC solution, e)  $10^{-4}$ M SDS 2%wt PDAC after the addition of 0.1M NaCl. (reflectivities are shifted for clarity) B) Electron density profiles ( $Z = 0$  is the molecule-solution interface) used to generate the fitted reflectivity (solid lines in A), the step-like functions (box-model) are generated assuming no surface roughness.

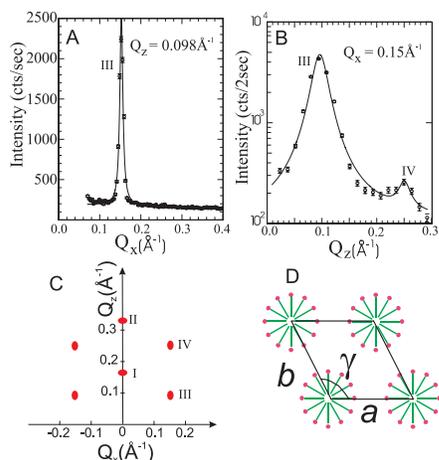
The highly monochromatic beam ( $\lambda = 1.5498$  and  $0.76533$ Å), selected by a downstream Si double crystal monochromator, is deflected onto the liquid surface to a desired angle of incidence with respect to the liquid surface by a second monochromator [Ge(111) and Ge(220) crystals]. Specular X-ray reflectivity experiments yield the electron density (ED) profile across the interface, and can be related to molecular arrangements in the film[11,12]. The GIXD measurements are performed at a fixed-angle incident-beam smaller than the critical-angle for total-reflection from the surface, yielding the in-plane ordering within the penetration depth of the X-ray beam[11,12].

## Results and Discussion

Surface tension versus SDS concentration in salt solution (0.1M NaCl) and in pure water for comparison are shown in Fig. 1, and similarly for 2% wt PDAC solutions in pure water and in 0.1M NaCl solution. The critical micelle concentration (CMC) of SDS in pure water is reduced with the addition of 0.1M NaCl, a result documented in the literature[13]. The onset for the reduction in surface tension at 0.1M NaCl occurs at SDS concentrations two orders of magnitude lower than those of SDS in pure water. Likewise, in the presence of PDAC, Fig. 2 shows that the lowering of surface tension occurs at even lower SDS concentrations, suggestive of the formation of highly hydrophobic surfactant-polyelectrolyte complexes.

X-ray reflectivity and GIXD studies of PDAC-solutions surfaces were conducted at various SDS concentrations (with and without 0.1 M NaCl). Figure 2 shows a sequence of normalized

reflectivities, ( $R_F$  is the calculated reflectivity of an ideally flat water interface) for a typical SDS concentration, in pure water and in PDAC solutions, and after adding 0.1M NaCl to the same solution.

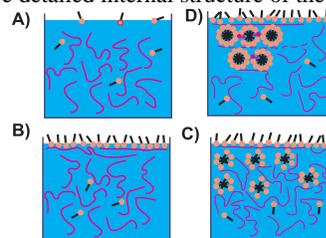


**Figure 3:** A) A scan along  $Q_x$  of (10) peak at fixed  $Q_z$ . B) A rod scan along the  $Q_z$  (logarithmic scale) also revealing the (11) peak. C) The observed peaks in the  $Q_x \times Q_z$  plane. D) A schematic illustration of the suggested model structure with the oblique unit cell. The long axes of cylindrical micelles are parallel to the liquid surface.

At SDS concentrations greater than  $10^{-4}M$  (in pure water), the reflectivity [Fig. 1(A)] is similar to that of a pure water surface, although with a surface roughness significantly larger than that measured for a water surface under similar conditions. The enhanced surface roughness is evidence for the presence of a dilute inhomogeneous SDS-film at the air/water interface. The addition of NaCl to the SDS solution modifies the reflectivity giving rise to a minimum due to the formation of a more homogeneous film. The detailed analysis yields the ED profile shown in Fig. 2 (B). Additional reflectivity studies as a function of SDS concentrations (with and without NaCl) show a systematic increase of total film-thickness. The reflectivity from 2% wt. PDAC solution (no SDS) shown in Fig. 1(A) demonstrates the effect of pure PE on the surface, even at this high concentration is negligible. The addition of SDS to 2% PDAC solution brings the minimum in  $R/R_F$  to  $Q_z \sim 0.38 \text{ \AA}^{-1}$ , showing the film is thicker ( $\sim 22.5 \text{ \AA}$ ) and more organized than that of SDS in water or salt solution. The head-group region is significantly thicker than that of SDS solutions ( $\sim 11 \text{ \AA}$ ), suggesting the interfacial film consists of a PDAC-SDS complex. The ED and thickness of the topmost slab indicate the hydrocarbon tails are loosely packed as in a 2D liquid state. The most dramatic effect in the reflectivity is observed with the addition of salt to the PDAC-SDS solution with Bragg reflections superimposed on the reflectivity at  $Q_z^1 = 0.165 \text{ \AA}^{-1}$  and at  $Q_z^2 = 0.345 \text{ \AA}^{-1}$ . These two peaks, as shown below are the first and second order Bragg reflections from hexagonal structures due to closely-packed cylindrical micelles with their long axis parallel to the liquid surface. At small angles, the GIXD reveals several discrete Bragg reflections of a diffraction pattern from crystals highly oriented with respect to the water surface. These reflections are related to those observed in the reflectivity. As shown in Fig. 3(A) and (B), these peaks are sharp, characteristic of 3D ordering, with no rod-like scattering typical of a quasi-2D system. The positions of the peaks observed and their layout as shown in Fig.3(C) are consistent with a slightly distorted hexagonal structure, as depicted in Fig. 3(D) with  $a = 40.3 \text{ \AA}$ ,  $b = 44.6 \text{ \AA}$ , and  $\gamma = 121^\circ$ . The peaks observed are similar, although not the same, as those observed

by Chu and co-workers[1,2], in small angle X-ray scattering experiments from related systems. Based on the anisotropy observed, we propose a simple structure of stacked cylindrical micelles with their long axis parallel to the water-surface, forming a 2D polycrystalline system with preferred orientation with respect to the surface. The distorted hexagonal diffraction pattern indicates the growth is anisotropic and implies the interface plays a role in initiating complexation (aggregation) processes. Another important result is the effect the addition of salt (NaCl) has on promoting PE/surfactant crystallization. Our heuristic interpretation of the aggregation and subsequent crystallization is depicted in Fig. 4.

In summary, we have shown the fundamental role played by the interface in nucleating PE surfactant complexes and how crystallization may be induced by salt concentration at minute surfactant concentrations. The location of the PE and the ions in this crystallization process is not known, but we hope that the application of anomalous X-ray reflectivity and GIXD techniques utilizing heavier ions[14] (CsCl, for instance) will provide a more detailed internal structure of the crystals.



**Figure 4:** Schematic pathways of complexation and subsequent crystallization. A) Negligible surfactant concentration - the PE is repelled from the interface. B) Below the CAC a PE surfactant is formed at the interface. C) CAC micellization occurs. D) The addition of salt transforms micelles to cylindrical shape and crystallizes them. The arrangement and location of the PE in the crystalline regions (shown with a dashed line) was not be determined in this study.

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