

MOLECULAR-SCALE THREE-DIMENSIONAL VISUALIZATION OF ELECTRIC DOUBLE LAYERS ON ANIONIC AND CATIONIC SURFACTANT MICELLE STRUCTURES

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Although the colloid probe AFM is a powerful technique for the microscopic studies of electric double layers (EDLs) formed on flat solid surfaces in electrolyte solution, it is difficult to obtain molecular scale information because of the large probe size and the detection sensitivity. Recently we successfully obtained local EDL forces between an AFM tip and a surface micelle structure made of surfactant using three-dimensional (3D) force mapping method based on frequency modulation AFM [1]. In this study, molecular scale EDLs formed on anionic and cationic surfactant micelle surfaces have been comparatively investigated by 3D force mapping method. We used sodium dodecyl sulfate (SDS) as anionic surfactant and cetyltrimethylammonium bromide (CTAB) as cationic surfactant. Each molecule has a hydrophilic head and a hydrophobic tail. Ionic surfactant molecules in aqueous solution form into micelles when the surfactant concentration is higher than critical micelle concentration (CMC). The micelle surface consists of the hydrophilic head groups having negative charge (SDS) or positive charge (CTAB). Thus EDL appears on each surface. A Si tip having a naturally oxidized surface is negatively charged in aqueous solution.

Figure 1(a) shows a 3D frequency shift map obtained at an SDS solution-graphite interface. It clearly indicates that hemicylindrical surface micelle structures are formed at the interface. Similar hemicylindrical structures also appeared in CTAB solution. The EDL forces were directly obtained from the frequency shift curves measured on the micelle structures and the local charge density was calculated by fitting the force data to the DLVO theory (Fig. 1(b)). Both force-distance curves on SDS and CTAB micelle show repulsive behavior (Fig. 2). In fact the EDL force acting between the two EDLs is composed of the electrostatic interaction between the two layers, which can be attractive or repulsive depending on the signs of the charges on the two surfaces, and the osmotic pressure, which is always repulsive. The results indicate that the osmotic pressure is dominant in both cases.

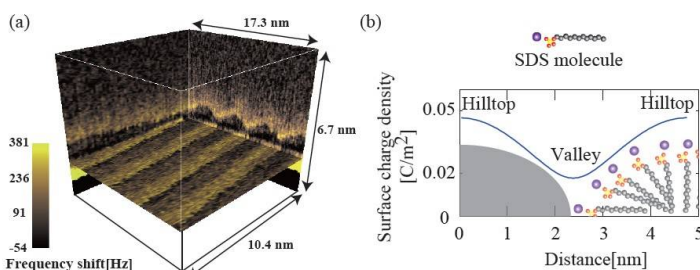


Figure 1: (a) 3D frequency shift map at SDS aqueous solution-graphite interface. (b) Surface charge density distribution of SDS micelle structure formed on graphite.

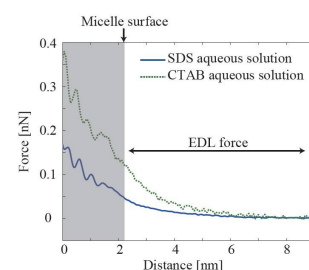


Figure 2: Force curves obtained on negatively (SDS) and positively (CTAB) charged micelle surfaces. The tip is negatively charged.