Surface Structures of Cationic Surfactant Monolayer on Solid Substrate: A Sum Frequency Generation (SFG) Study

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Surfactants play important roles in a variety of technological processes such as detergency, emulsification, coating, lubrication, mineral flotation, and oil recovery.1,2 Dioctadecyldimethyl ammonium bromide (DODAB) is a synthetic cationic surfactant with a polar ammonium group and two long hydrophobic alkyl chains, which is widely used in detergent industry as a softening agent but is hard to be decomposed in nature environments. Many efforts have been made to develop new type of surfactants for this purpose.

In the present study, π-Å isotherm and SFG vibrational spectroscopy have been applied to study the surface structures for monolayers of a number of cationic surfactants. SFG is known as a surface specific technique with a unique sensitivity to alkyl chain conformation and ordering/disordering.3-5 Figure 1 shows a SFG spectrum of DODAB monolayer deposited on a fused quartz surface by LB method with a surface pressure of 20 mN/m. Two peaks at 2876 and 2941 cm⁻¹ can be attributed to symmetric and Fermi resonance of C-H stretching of terminal CH₃ group, respectively, while that at 2850 cm⁻¹ can be attributed to symmetric C-H stretching of CH₂ group. Since the SFG signals from the CH₂ groups in the alkyl chains are forbidden in an all-trans conformation, appearance of SFG peak from CH₂ group in the spectrum indicates that some gauche defects present in the monolayer, which is considered as a result of strong repulsive interaction between terminal ammonium groups between DODAB molecules in the monolayer. The ratio of SFG intensity of CH₂ group \([v_s(CH_2)]\) to the CH₃ group \([v_s(CH_3)]\), which can be regard as an indicator of disordering in the monolayer, decrease with exposure to air. This suggests improvement of chain ordering and a reconstruction process should occur in the process. Detailed results and discussions will be given in the poster presentation.

2) Sharma, R.; Ed. Surfactant Adsorption and Surface Solubilization; ACS symp. Ser. No. 615; American Chemical Society: Waxhington DC, 1995
3) Shen, Y. R., Ostroverkhov, V. Chem. Rev. 2006, 106, 1140
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