Surfactant Effects on Acid-Catalyzed Reactions at Aqueous Aerosol Surfaces

*Shinnosuke Ishizuka[1], Tetsuya Hama[2], Shinichi Enami[1]

1. National Institute for Environmental Studies, 2. Institute for Low Temperature Science, Hokkaido University

The outermost layer of atmospheric aqueous aerosol is covered with amphiphilic organic compounds. Volatile organic compounds (VOCs) in the gas phase should encounter them first at the air/aerosol interface, rather than solute molecules homgeneously distributed in the bulk. It may control the whole reactivity of the aqueous aerosol and play key roles in birth, growth and degradation processes of atmospheric aerosols. Here we studied activities of quaternary alkyl trimethyl ammonium cations $CH_3(CH_2)_{n-1}(CH_3)_3N^+$ (n = 1, 4, 8, 10, 12, 14) at the surfaces of water using surface-sensitive spraying ionization mass spectrometry. The longer-chain alkyl ammonium cations are detected more prominently at the water surface of the equimolar solution, expressed as an exponential function of the alkyl chain length. We suggest the occurrence of competitive adsorption among the quaternary ammonium cations at water surface. Then, the surfactant effects on the gaseous uptake and subsequent reactions of VOCs was investigated. When isoprene is exposed to acidified water surfaces, proton transfer reaction from H_3O^+ to isoprene occurs, which is followed by chain-propagation reactions. We found that the longer-chain ammonium cations suppressed isoprene oligomer signals but rarely hindered chain-propagation reactions even at larger concentrations, e.g., the higher surface coverage. It suggests that gaseous isoprene is directly added to the protonated species at water surface. We conclude that competitive adsorption between isoprene oligomers and the ammonium cations suppressed the acid-catalyzed reactions. Driving force leading to the adsorptive competition will be argued based on experiments performed by adding anionic and neutral surfactants.

Keywords: The Air/Water Interface, SOA

