Direct Observation of Cationic Surfactant Adsorption via in-situ Raman Spectroscopy

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Surface active agents (surfactants) have been used in a variety of fields for their unique characteristics consisting of two parts, a hydrophilic head and a hydrophobic (lipophilic) tail. The double affinity of surfactants allows the molecules to migrate to an interface and change interfacial properties. Many studies on surfactant behaviour utilise indirect experimental techniques and/or molecular dynamics (MD) simulations. To better understand the phenomenon, a direct observation of surfactant distribution in multiphase systems is required. This work presents the development of a research platform to study surfactant adsorption using in-situ Raman spectroscopy, combining surface enhanced Raman scattering (SERS) and Raman imaging (mapping) techniques. The SERS amplifies Raman signals, enabling an investigation at a wide range of the surfactant concentrations. Raman imaging was used to directly observe how a model cationic surfactant, cetylpyridinium chloride (CPC), adsorbed in solid-liquid systems. Four concentrations of the surfactant aqueous solution were studied: (i) 5 mM, (ii) 50 mM, (iii) 0.5 mM and (iv) 50 mM, where the first three are pre-CMC (critical micelle concentration), and the final is post-CMC. Two- and three-dimensional maps were generated to better understand a local concentration of the surfactant molecules in multiphase systems. A denser surfactant population at the surface was observed with increasing surfactant concentration, and the presence of micelles was identified at the post-CMC via the Raman imaging. Also, a line map of the molecules across an interface enabled a quantification of the surfactant distribution. The mapping result was compared with the Gibbs adsorption isotherm to quantify surfactant packing at the interface.