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学 位 論 文 題 名

Adsorption of Sodium Dodecyl Sulfate and Dodecyl Pyridinium Chloride on Silica

(ドデシル硫酸ナトリウムとドデシルピリジニウムクロリドのシリカへの吸着)

1. Introduction

Surfactants that are amphipathic compounds composed of hydrophilic head and hydrophobic chain, tend to gather at interfaces and decrease the surface tension of water. Surfactants own many useful functions and huge applications in many fields related to our life and environment. Adsorption of surfactant on surfaces can change the surface properties, therefore surfactant is used for foaming, antifoaming, emulsification, demulsification, dispersion, flocculation, wetting, spreading, infiltration, lubrication, antistatic treatment, sterilization etc.

Surfactants sometimes become contaminants. However, their behavior in soils are not well known. As they are the simplest organic matters, the knowledge of their behavior in soils is worth for understanding the behavior of organic matters in soils. Silica is a ubiquitous material in soils. Therefore, adsorption of anionic (sodium dodecylsulfate, SDS) and cationic (dodecylpyridinium chloride, DPC) surfactants on a silica was investigated in this research. In order to make clear the mechanism of adsorption, the Langmuir equation was fitted to the isotherms and the influence of surface electrostatic properties were elucidated.

2. Materials and Methods

Silica was purchased from Sigma-Aldrich Co. LLC. USA with a purity of 99.5%. The specific surface area was 414 m²/g, the mean particle diameter 1.2 μm and the average pore diameter 7 nm. The surface charge density of silica was measured by acid base titration at 25 ± 1°C. A batch method was used to obtain the adsorbed amount of the surfactants, SDS and DPC. The SDS concentration was measured with an anionic surfactant selective membrane electrode and that of DPC was measured by UV-absorbance at 255 nm. Silica stability at different DPC adsorption was also tested by measuring the UV-absorbance at 540nm. Zeta potential of the silica particles were obtained by measuring the electrophoretic mobility and calculated with the Smoluchowski equation. The Langmuir equation included adsorption site potential was fitted to the measured adsorption isotherm. 1-pK basic Stern model was adopted in order to confirm the electrostatic properties of the silica surface.

3. Results and Discussion

SDS. At 0.1 mmol/L NaCl solution no SDS adsorption was observed, because the electrostatic repulsion between the surfactant and the silica was too strong. However, at NaCl concentration ≥ 1

mmol/L the repulsion was sufficiently reduced and SDS adsorbed through hydrophobic attraction.

Measured isotherms of SDS adsorption on silica at pH 4.5 and different electrolyte concentrations (NaCl) were compared. The adsorption decreased with decreasing electrolyte concentration and increasing pH. SDS adsorbed with hydrophobic interaction because the silica had hydrophobic surface on siloxane groups, $\equiv\text{Si-O-Si}\equiv$. When the pH increased, protons in silanol groups, $\equiv\text{Si-OH}$, are released from the surface and the negative charge increased. The influence of negative potential on the adsorption site was confirmed with the modified Langmuir equation. The slope of the SDS isotherm at lower SDS concentration showed larger than unit. This indicates the cooperative adsorption which is generated by the lateral attraction among the hydrophobic tails of SDS.

For the silica the decrease of the repulsive electrostatic potential with increasing NaCl concentration and decreasing pH were confirmed by the measured zeta potential, the surface charge density, and the electrostatic properties obtained from the 1-pK basic Stern model.

DPC. DPC adsorbed strongly on silica at pH 5, 7 and 100 mmol/L NaCl due to the combination of electrostatic and hydrophobic attraction. Adsorption isotherms showed four-region property. The adsorption became larger at high pH and low electrolyte concentration due to the increase of potential effect. The silica dispersed well at low and high surfactant concentration because the isoelectric point was at the middle surfactant concentration. Zeta potentials showed a reversal of the charge sign, which indicated the occurrence of bilayer type adsorption. The adsorbed amount of DPC was comparatively larger than that of SDS at the same equilibrium concentration, pH and electrolyte concentration.

4. Conclusion

In spite of electrostatic repulsion between negatively charged SDS and silica surface, adsorption happens. Silica adsorbs SDS because it has hydrophobic surface on siloxane. Because DPC adsorbs on silica by both electrostatic and hydrophobic attraction, the adsorption amount of DPC is comparatively larger than that of SDS at the same condition. When pH increases and/or electrolyte concentration decreases, the SDS adsorption decreases and the DPC adsorption increases due to the influence of electrostatic potential.

Silica is ubiquitous in soils and it adsorbs surfactants. It must be taken into account when we consider the fate of surfactants in soils. The result is also useful when considering the fate of agricultural chemicals and organic matters which contain electric charge and hydrophobic sites.