

Analysis of Adsorbing Behavior of Various Types of
Polyelectrolytes and Their Binary Mixture on the
Negatively Charged Polystyrene Sulphate Latex Particles
Studied by Means of Particle Tracking of Brownian
Motion and Electrokinetics

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In natural water system, organic contaminants popularly present as negatively charged colloidal particles. Polyelectrolytes have been widely used as flocculants due to effective its applications in wastewater treatment. For example, polycations which have strong affinities to oppositely charged surfaces due to electrostatic interactions have used increasingly to induce flocculation via adsorption onto colloidal particle in the solid-liquid separation process. Besides, the colloidal particles of negative charge currently present with negatively charged organic molecules such as humic substances which are usually found to be negative charge in natural condition. Adsorption of polycations onto the negative colloidal particles has been carried out both theoretically and experimentally. Whereas, adsorption of polyanions which have electrostatic repulsions and/or weak affinities to surfaces of same charge sign have been still unclear. Therefore, understanding the dynamic of adsorption of single polyelectrolytes and binary oppositely charged polyelectrolytes onto the negatively charged particle surfaces under different conditions is necessary to improve the efficiency of flocculation in practice. The main factors considered herein to be strongly effective on adsorption are types of polyelectrolytes such as polyanions, polycations with different charge densities; size of colloidal particles; ionic strength and presence of other polyelectrolytes of opposite charge sign. In this thesis, we have designed experimental concepts to clarify the adsorption behaviors of single polyelectrolytes as well as dual oppositely charged polyelectrolytes in various ionic strengths onto the colloidal particles of negative charge. Monodispersed negatively charged polystyrene sulfate latex particles (PSL, Thermo Fisher Scientific, Inc., Waltham, MA, USA) of different diameters of about 1.2 μm and 2.0 μm with standard deviation of 0.1 μm and 0.052 μm , respectively, were used as colloidal particles. Polyanion poly(acrylic acids) (PAA, Wako Pure Chemical Industries, Ltd., Osaka, Japan) with nominal weight of 5000 g/mol are employed as a model of humic substances. Two linear polycations of various charge densites are applied in adsorption experiments including a homo-polymer of poly-trimethylamino ethyl methacrylate (PTMA5M, Kaya Floc Co. Ltd., Tokyo, Japan) with the nominal molecular weight of 4.9×10^6 g/mol and a co-polymer of its and acrylamide (PTMC5M, Kaya Floc

Co. Ltd., Tokyo, Japan) with the nominal molecular weight of 5.2×10^6 g/mol. The charge density (σ) of PTMA5M and PTMC5M is 100% and 4%, respectively. The adsorption behaviors are evaluated by temporal changes of adsorbed layer thickness (δ_H), electrophoretic mobility (EPM), Fourier transform infrared (FT-IR) spectroscopy and conductivity measurements after incubation under different ionic strength conditions.

In the present thesis, the main research topics are introduced from the chapter 2 to the chapter 4, as following:

In chapter 2, the adsorption of Polyanions PAA onto the highly negatively charged PSL particles was confirmed through the changes of δ_H , charging surface, solution conductivity and functional groups by particle tracking of Brownian motion, the electrophoretic mobility measurement, the conductivity measurements and the Fourier transform infrared (FT-IR) spectroscopy, respectively, under different ionic strength conditions. PAA adsorbed on PSL due to non-electrostatic interactions such as hydrogen bonds, dipole-ions and dipole-dipole. The positive effects of presence of electrolyte ions were proved. The adsorbed layer thickness of PAA on PSL and the magnitude of electrophoretic mobility of PSL in the presence of PAA increased with increasing ionic strength. In case of adsorption of 5 ppm PAA, the adsorbed layer thickness increased slightly about 2 times corresponding with 41.28 to 80.37 nm while the electrophoretic mobility of PSL changed from -4.871 to -6.307 $\mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$ with increasing 100 times of the ionic strength from 0.1 to 10 mM KCl. The change of surface functional groups of PSL after PAA adsorption was thoroughly determined by the Fourier transform infrared (FT-IR) spectroscopy. The distinction between the electrostatic and the non-electrostatic interaction which contributed to the adsorption of PAA on the PSL particles and the adsorbed polymer conformations at different salt concentrations was clearly clarified. Interestingly, it was proposed the more vertically-swollen conformations of adsorbed PAA on PSL surface. Also, the multiple layers of PAA are formed on the PSL surfaces.

In chapter 3, the relaxation changes of δ_H and electrophoresis of PSL particles after overshooting of oppositely charged polyelectrolytes differing 25 times of the charge density were systematically measured. Decreasing PSL curvature, δ_H of PTMA5M is flatter while that of PTMC5M does not change so much. Some different tendencies were also found. In the case of PTMA5M, the temporal δ_H significantly decreases while EPM remains as a function of the elapsed time due to fixed-charge groups inside adsorbed layer. In the case of PTMC5M, the temporal δ_H remains while EPM decrease in one hour due to the decrement of total charge density. Following, two desorption concepts were suggested. That is, the removal of randomly sequential attachment to the oppositely charged surface of particle is expected for the chains of high charge density while chains of low charge density will desorb aligning to the direction of perpendicular to the particle surface.

In chapter 4, the effects of presence of polyanions PAA on adsorption of polycations PTMA5M ($\sigma= 100\%$) on the negatively charged PSL particles were investigated in different ionic strengths. PTMA5M-PAA complexations were formed at solid-liquid interface. At any polyelectrolyte concentration ratio between PAA and PTMA5M, the temporal δ_H significantly decreases due to desorption. Whereas, EPM remains as a function of elapsed time due to fixed-charge groups within adsorbed layer at the low polyelectrolyte concentration ratio while EPM increases at the high polyelectrolyte concentration ratio due to polyanion desorption and then re-conformation of polycations. Extremely thick adsorbed layer was confirmed for the case of excess dosage of polycation. The thickness of adsorbed layer decreased more significantly by the addition of PAA than by the increment of ionic strength. Interestingly, PTMA5M remarkably shrunk in the presence of oppositely charged polyelectrolytes even at lower ionic strength than only increasing ionic strength.

Summarily, the driving forces for the adsorption of polyelectrolytes on the colloidal particles are the electrostatic attractions and/or the specific interactions such as hydrogen bondings, dipole-dipole, dipole-ions not only between polyelectrolyte segments

and particle surfaces but also between polyelectrolyte segments. The PSL particle size, the substrate charge density and the charge density of polyelectrolytes influence on the swelling of adsorbed layer. Two approximated desorption concepts are suggested to depend on the charge density of polyelectrolytes under overshooting condition. The presence of other oppositely charged polyelectrolytes more strongly affects the hydrodynamic adsorbed layer thickness and the net particle charge than the increment of ionic strength. The more shrinkage of high-charge-density polycations on the PSL surface is found with the more addition of polyanions. The adsorption behaviors of individual polyelectrolytes as well as dual oppositely charged polyelectrolytes in various conditions are comprehensively studied in the present thesis. The desorption is considered as the reason of temporal decrement of δ_H while the changes of EPM can be explained by Ohshima's theory. The obtained data can be expected to improve the enhancement of flocculation in practice in the future.