

NOTE

Initial Rates of Flocculation of Polystyrene Latex with Polyelectrolyte: Effect of Ionic Strength

The rate of flocculation of polymer latices immediately after the addition of polyelectrolyte was measured by applying the standardized procedure of colloid mixing. It was found that the rate of flocculation in the initial stage is remarkably enhanced by the addition of polyelectrolyte and that the extent of this enhancement decreases with an increase in the ionic strength. The conformation of polyelectrolyte in the solution is considered to have a direct influence on this result. © 1995 Academic Press, Inc.

The flocculation of colloidal dispersions is a common operation in many industrial processes and in water and waste water treatment. Usually, this process is initiated by the addition of a small amount of polymer into the colloidal dispersion mixed by turbulent agitation. However, the inevitably complex situation of the turbulent flow makes quantitative analysis of the mechanism of flocculation difficult. Recently, we showed a way to characterize the mixing flow condition in terms of collision processes between colloidal particles (1). This method allows us to analyze the temporal evolution of flocculation within times as short as 1 s from the start. By this method, we found a remarkable enhancement of the rate of flocculation of polystyrene latex upon the addition of poly(ethylene oxide), which was used as a bridging agent (2). The enhancement was ascribed to the increase in the effective collision radius due to the attachment of polymer molecules onto the surface of the colloidal particles. Since the values that we found for this increase in size correlated with the size of the polymer molecules in solution rather than with the equilibrium hydrodynamic thickness of the adsorbed layer (which can be measured separately by photon correlation spectroscopy), we concluded that the flocculation rate reflects the conformation of the dissolved polymer. Apparently, a nonequilibrium process is quite important during the formation of flocs, and probably a similar behavior will be observed in another important version of flocculation, i.e., the charge neutralization of a colloid by an oppositely charged polyelectrolyte.

Normally, a polyelectrolyte chain takes a swollen conformation in the solution due to electrostatic repulsions between segments of like charge. If we increase the ionic strength of the solution, the electrostatic interaction will be screened and, as a consequence, the swollen polyelectrolyte will shrink. When the charge is completely screened, the polyelectrolyte will behave like a homopolymer. It is generally accepted that highly charged polymers adsorb in a flat conformation onto an oppositely charged surface (3) and that they induce flocculation by way of charged neutralization (4-6). However, very little is known about the dynamics of the process. If the conformation of a free polymer chain has a direct influence on the kinetics of flocculation (as we observed for the bridging flocculation with homopolymer), a smaller rate of flocculation is expected to occur when a less swollen polymer is used, i.e., at higher ionic strength. In contrast the equilibrium thickness of adsorption is expected to increase upon increasing the ionic strength of the bulk solution because the adsorbing conformation will approach that of homopolymer, which typically consists of long loops and tails. In this case, the rate of flocculation is expected to increase with an increase in ionic strength.

In order to clarify which process takes place, we measured the rate of flocculation of negatively charged polystyrene latex with positively charged

polyelectrolyte while varying the ionic strength of the solution. Application of the standardized mixing procedure allows us to evaluate the flow conditions in terms of the collision process between the colloidal particles. In our experiment, a standard emulsifier-free polystyrene latex particle with a diameter of 555 nm was flocculated with a cationic polymer of trimethylaminoethyl methacrylate. According to the supplier, its molecular weight is approximately 5.6 million and the content of charged monomers is 100%. The study of the same system has been reported by several groups (4-6), revealing that this system constitutes a typical example of flocculation by charge neutralization. That is, the optimum dosage of flocculant corresponds to the condition when the charge of the colloidal is apparently eliminated by the adsorption of the oppositely charged polymer. The concentration of the polyelectrolyte in the final mixture was adjusted to 0.26 ppm. The relative viscosity of the polyelectrolyte solution at $KCl = 5 \times 10^{-4} M$ was measured and found to be less than 1.002. This result guarantees that the effect of viscosity change on the kinetics of flocculation is negligibly small.

The experimental results are shown in Fig. 1. We plot $\log(N(t)/N(0))$ as a function of the number of mixing steps, in accordance with the first-order kinetics expected for the initial flocculation rate. From the slope, we obtain the effective collision radius (1, 2). As a reference, the result of the rapid coagulation, i.e., coagulation induced only by salt in the absence of electrostatic repulsion taken from (1, 2), is indicated. As can be seen, the rate of flocculation by polyelectrolyte in the initial stage is remarkably enhanced. At $t = 10$, however, flocculation stops abruptly as the particles

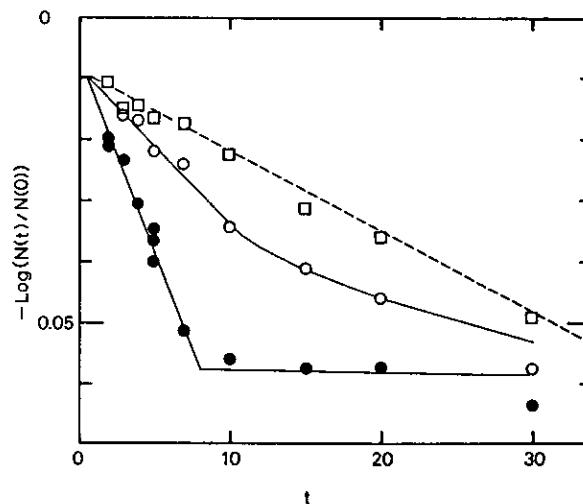


FIG. 1. Total number concentration of clusters $N(t)$ as a function of the number of mixing steps. One mixing was carried out in 1.36 s. The initial number concentration of polystyrene latex particle was 1.55×10^8 $1/cm^3$. The concentration of polyelectrolyte was 0.26 ppm. The concentrations of KCl were (●) 5.85×10^{-4} , (○) 5.85×10^{-3} , and (□) $5.85 \times 10^{-2} M$, respectively. The dashed line is the result of rapid coagulation, i.e., coagulation induced only by salt in the absence of electrostatic repulsive forces, and was taken from (2).

become protected by a fully developed polymer sheath. The largest rate of flocculation which was observed for $KCl = 5.85 \times 10^{-4} M$ is approximately six times larger than the rate of rapid coagulation by salt. If we ascribe this enhancement to the increase in collision radius due to the attached polymer layer as was done previously (2), the value of the layer thickness is estimated to be approximately 150 nm. Since the degree of enhancement clearly decreases by increasing the ionic strength of the solution, we are forced to conclude that it is the conformation of the polymer dissolved in the solution that determines this enhancement.

In most of the literature, the collision efficiency of bridging flocculation has been discussed simply in terms of the fraction of the surface covered with polymer (7, 8). Our result clearly reveals the importance of the transient conformation of the adsorbing polymer which should be taken in to account when analyzing the nonequilibrium flocculation. Attached polymer protruding far into the solution leads to a collision efficiency (with respect to bare particles) which is larger than unity. More systematic research for this regime should further elucidate the bridging mechanism.

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