

Kinetics of Brownian flocculation of polystyrene latex by cationic polyelectrolyte as a function of ionic strength

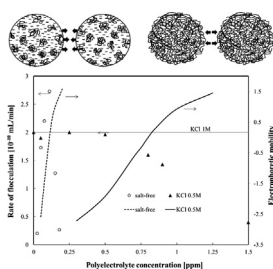
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HIGHLIGHTS

- ▶ Stability and electrokinetics were studied in PSL dispersion with polycation.
- ▶ The flattened conformation of adsorbed polycation was estimated at isoelectric point.
- ▶ Charge neutralization dominates in Brownian flocculation.

GRAPHICAL ABSTRACT



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ABSTRACT

Rate of Brownian flocculation of polystyrene latex particles with high molecular weight cationic polyelectrolyte is measured by coulter counter as a function of ionic strength. The rate of flocculation goes through a maximum against polyelectrolyte concentration. Under the condition of low ionic strength, it is confirmed that not only does the flocculation proceed faster than salt-induced rapid coagulation but also the breadth of flocculation region is relative narrow demonstrating a sharp peak. On the contrary, under the condition of high ionic strength, the flocculation proceeds like salt-induced rapid coagulation at low polyelectrolyte dosage, but the rate starts to slow down gradually with increasing polyelectrolyte dosage above a certain critical dosage. The flocculation region is confirmed to spread out in a relatively wide range. The isoelectric point, measured by electrophoretic mobility as a function of polyelectrolyte concentration, nearly keeps constant below a certain ionic strength then takes an obvious shift to the direction of a higher polyelectrolyte concentration with the increase of ionic strength. The isoelectric point corresponds to the peak point of flocculation rate for low ionic strength. The thickness of adsorbed polyelectrolyte layer was estimated on the basis of trajectory analysis of Brownian motion of a single particle. However, no remarkable thickness was observed at the isoelectric point.

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1. Introduction

Flocculation of colloidal particles is a fundamental issue for improving the performance of many solid–liquid separation processes. Polyelectrolytes are commonly used to increase the rate and efficiency of the flocculation and control the properties of separated sediment. However, detailed understanding of the mechanism of flocculation has not yet been completely achieved.

So far, mainly two concepts are widely used to explain the mechanism of flocculation. One is the concept of the “bridges” between colloidal particles [1–6]. That is, the flocculation is induced by the adsorption of polymer chain which attaches onto more than two colloidal particles simultaneously. Ruehrwein and Ward [7] proposed that the long polymer molecules are capable to attach upon more than two particles and then hold them together. On the basis of the appearance of optimum dosage of flocculants, Healy and La Mer [8] proposed that the flocculation is induced by the approach of polymer covered surface and uncovered surface, then the rate is proportional to the product, $\theta(1-\theta)$, where θ denotes the ratio of the coverage. Fler and Lyklema [9] reported the role of bare

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surface in the formation of bridge on the basis of the result that higher degree of flocculation was observed when bare particles are added on purpose. Ash and Clayfield [10] clearly demonstrated that polymer of high molecular weight will act more effectively in the flocculation as well as colloidal stabilization. In series of our previous studies [11–13], we verified the concept of bridge by the measurement of the rate of flocculation just after the onset of flocculation. It was found that the rate of flocculation has been obviously increased by the protruding part of adsorbed polymer which is detected as an increase in effective collision radius. Since the estimated length of the increased collision radius correlated the size of polymer in solution, we have concluded that the bridges are formed by the polymer chain. It should be noted that the hydrodynamic mixing operation is involved in the most study of bridging flocculation.

Flocculation is also induced by charge neutralization [14–17]. That is, when the original charge of colloidal particles is annihilated by the adsorption of oppositely charged polymer chain. This annihilation will eliminate the repulsive force between colloidal particles. Then flocculation is induced upon the collision between neutralized colloidal particles. Gregory confirmed this concept by the Brownian flocculation of polystyrene latex particles induced by an addition of cationic polyelectrolyte [18]. The rate of flocculation is a function of polymer concentration and takes its maximum at so-called optimum dosage. The maximum value of flocculation rate observed at low ionic strength was about twice that observed with high salt concentration. He also pointed out that the maximum rate will decrease with an increase of ionic strength. From the molecular weight dependency of the enhancement of the flocculation rate, he proposed the concept of “patch” of adsorbed polyelectrolytes. He concluded that the heterogeneous state of patched surface enabled the explanation of the enhancement of the rate of flocculation. This enhancement, the rate of polymer flocculation faster than salt-induced rapid coagulation, has aroused great interests. On the basis of a series of measurements of surface force between particles together with stability analysis, Borkovec et al. [19–23] have proved the concept of patch to be the origin of additional attractive force other than van der Waal's force, and concluded that this attractive force is an origin of the cause of the enhancement of the rate of flocculation. This conclusion is consistent with the theoretical prediction on the double layer forces between heterogeneous charged surfaces presented by Miklavic et al. [24].

On the other hand, as we have confirmed the bridging flocculation of latex particles with polyelectrolytes by means of standard mixing operation in series of our previous works. The chemical characteristics of polymer and colloidal particles applied in our previous investigations were mostly the same as that used by Gregory. In the present study, we will revisit the system studied by Gregory. That is, the Brownian flocculation of polystyrene latex particle induced by addition of cationic polyelectrolyte under different ionic strengths. The absolute rate of flocculation was measured by Coulter Counter as a function of polyelectrolyte dosage. In order to obtain information on the state of adsorbed polyelectrolyte, measurements of electrophoretic mobility and thickness of adsorbed polyelectrolyte layer were performed under different ionic strengths.

2. Rate of Brownian coagulation

The framework for the mathematical theory on the kinetics of flocculation was worked out by Smoluchowski [25]. The temporal variation of clusters size distribution can be written as

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} \beta(i, j) n_i n_j - n_k \sum_{j=1}^{\infty} \beta(k, j) n_j \quad (1)$$

where n_i represents the number concentration of i -fold clusters. $\beta(i, j)$ is the coagulation kernel which is determined by the mechanism of coagulation. When collisions are induced by Brownian motion, $\beta(i, j)$ is derived as,

$$\beta(i, j) = 4\pi D_{ij} R_{ij} = \frac{2k_B T}{3\mu} \left(\frac{1}{a_i} + \frac{1}{a_j} \right) (a_i + a_j). \quad (2)$$

For the initial stage of flocculation of monodispersion, we can assume $a_i \approx a_j$, then the value of $\beta(i, j)$ can be regarded as constant. This approximation allows us to write the temporal variation of the total number concentration of clusters as

$$\frac{dN(t)}{dt} = -\frac{4k_B T}{3\mu} N(t)^2, \quad N(t) = \sum_{j=1}^{\infty} n_j(t). \quad (3)$$

In practice, the correction factor of collision efficiency, α_B , is introduced to take into account the hydrodynamic interaction together with Van der Waal's attraction between colliding particles [26]. The total number concentration of cluster, $N(t)$, is analytically expressed as

$$\frac{1}{N(t)} - \frac{1}{N(0)} = \alpha_B \frac{4k_B T}{3\mu} t. \quad (4)$$

It should be noted that the correction factor, α_B , is less than unity. The value of 0.3–0.7 was reported for PSL particles coagulation in the salt solution [27]. When the flocculation takes place between particles with protruding structure due to adsorbing polymer, certain modification of hydrodynamic radius and collision radius in Eq. (2) and correction factor of α_B in Eq. (4) can be expected. The information on these factors can be obtained from the plots of $1/N$ against t and diffusion constant of a single particle.

3. Experimental

3.1. Materials

Monodispersed polystyrene latex (PSL) was prepared by the standard emulsion polymerization of styrene in the absence of surfactant [28]. The diameter of particles was determined by electron microscopy as 1.356 μm . The critical coagulation concentration of 1:1 electrolyte for this latex is about 0.3 M. Before each experiment, the aqueous PSL suspension was sonicated for 25 min to eliminate aggregates. The positively charged polyelectrolyte of dimethylamino ethylmethacrylates with molecular weight of 4.9×10^6 g/mol was employed as flocculants (kindly supplied by Kaya Flocc Co. Ltd.) [28]. The size of polyelectrolyte in the solution of 0.5 M KCl is evaluated by viscometry as 79.39 nm, which is close to 82.75 nm obtained by DLS (FDLS-3000, Otsuka Electronics Co. Ltd.) [29]. The charge density, i.e. the ratio of the number of charged monomer to the total number of monomers, is 100%. The repeating unit is shown in Fig. 1. Stock solution of polyelectrolyte (100 mg/L) was prepared by stirring the appropriate amount of polyelectrolyte with potassium chloride solutions for 72 h and used up within a week. The ionic strength was controlled with potassium chloride. All potassium chloride solutions and distilled water were filtered through 0.22 μm millipore filters.

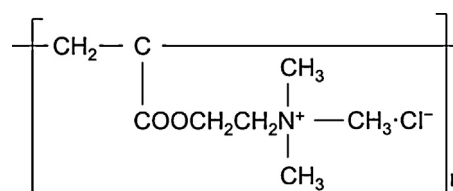


Fig. 1. The chemical structure of the positive charged polyelectrolyte.

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