Kinetics of flocculation of polystyrene latex particles in the mixing flow induced with high charge density polycation near the isoelectric point

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HIGHLIGHTS

- Rate of flocculation in the mixing flow by charge neutralization was analyzed.
- Highest rate was observed at the lowest ionic strength.
- The scenario from non-equilibrium adsorption to patch wise attraction was confirmed.

GRAPHICAL ABSTRACT
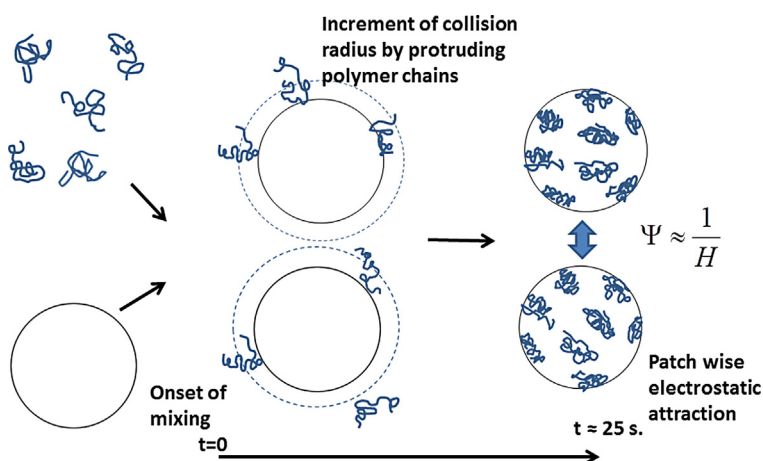
ARTICLE INFO

ABSTRACT

Rates of flocculation of PSL particles induced by the addition of cationic polyelectrolyte of high charge density in the mixing flow near isoelectric point were measured as a function of ionic strength. Homopolymer of dimethylamino ethylmethacrylate with charge density of 100% and nominal molecular weight of 4900k (hereafter called TMAEMA) was used as a flocculant. Except just after the very short incubation time for adsorption of polymer to PSL particles at the period of the start of mixing, the rate of flocculation keeps constant value. The incubation period increases with an increase of ionic strength. While the rate of flocculation increases with a decrease of ionic strength. The highest rate observed for the condition of no-salt addition was found to be 2.4 times larger than that of salt induced rapid coagulation. Substituting this value to the equation of capture efficiency, this factor was found to correspond to the presence of attractive force approximately twenty times larger than that of Van der Waals force.

1. Introduction

Polyelectrolytes interact strongly with oppositely charged colloidal particles to modify the surface properties and the interaction forces acting between colloidal particles, thus to induce

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aggregation or to enhance the stability of colloidal suspension. For this reason, they have been focused in agricultural, environmental, industrial, medical and biological applications, such as soil conditioner [1], water/wastewater treatment [2,3], mineral processing [4], paper making [5], solid–liquid separation in powder technology [28] and so on. Actually, many types of natural and synthesized polyelectrolytes have been used as flocculants for these applications. Cationic polyelectrolytes are increasingly being used due to abundant presence of negatively charged colloidal particles in nature. Due to stoichiometric advantage to neutralize the negative surfaces, high charge density polycations are selected as the most effective agent against negatively charged colloids.

One of the original clear results was reported by Gregory [6] using PSL suspension flocculated with highly charged polyelectrolyte. That is, flocculation is most effectively induced at so called optimum dosage. The remarkable point of his results is that the rate of flocculation at the optimum dosage increases with a decrease of ionic strength. On the basis of this result, the concept of heterogeneous patch formed of the adsorbed polyelectrolytes was proposed to induce attractive interaction. This picture has been confirmed more systematically by the grope of Borkovec applying the multi-particle colloidal probe technique on the AFM adsorbed with oppositely charged dendrimer and linear polyelectrolyte [7–9]. They have confirmed the presence of strong attractive forces between patch wise heterogeneously coated surfaces with oppositely charged dendrimer and subsequently linear polyelectrolytes. Their result confirmed that the lower the ionic strength, the higher force of attraction appears at the iep. One of their conclusion is the main mechanism of flocculation is charge neutralization enforced by heterogeneous patch interaction.

One should note, however, that flocculation in many practical application is performed under the condition of fluid mixing. Dynamic aspects of flocculation influenced by hydrodynamic motion should be counted. In the normal situation of application such as water treatment, flocculation is induced by an addition of polymer flocculants to the colloidal suspension under the condition of turbulent flow. It can easily be imagined that a condition of turbulent flow will be involved in many elementary processes such as, dilution of the flocculants into a homogeneous solution, elongation and extension of polymer chain by hydrodynamic mixing, collision between colloidal particles, transportation of polymer flocculants towards the surface of colloidal particles, unfolding and re-conformation of adsorbed polymer on the surface of colloidal particles, formation of a bond (or bridge) between colloidal particles, rearrangement and breakup of the whole structure of a floc, etc. [11,12]. These events take place simultaneously in chaotic situation of turbulent mixing. In such situation, analyses of kinetics, i.e., transport phenomena on the basis of rate equation, unravelling of equilibrium and non-equilibrium aspects, are critically important for the analysis of the process of flocculation.

In our series of investigations, we have proposed the normalizing method to characterize the condition of turbulent flow in term of collision frequency between colloidal particles which is equivalent to the rate of salt-induced rapid coagulation [13]. After getting information of turbulent mixing flow in terms of collision frequency, we have investigated the effect of the addition of polymer to the same mixing system [14,15]. This method has been applied to the analysis of the transient dynamics of polymer or polyelectrolyte adsorption as well as colloidal flocculation. The result of the analysis obtained for the overshooting condition has demonstrated the clear cut of the role of polymer conformation in the bulk solution and folding behavior of polymer in the collision process of colloidal particles [16–20]. Most of these results support the concept of bridging flocculation.

The present study is designed to analyze the flocculation behavior in the mixing flow with high charge density polycation which is confirmed to induce flocculation by the mechanism of charge neutralization and patch wise interaction under Brownian motion [10].

2. Kinetics of flocculation in a turbulent flow

The rate of coagulation in a turbulent mixing flow can be derived by considering the collision frequency between colloidal particles in a unit volume. Saffman and Turner [22] derived the collision frequency for rain drop formation in turbulent flow. This result can be applied to the rate of coagulation in the mixing in water. In a colloidal dispersion composed of mono dispersed spheres of radius a_0, the rate of coagulation can be expressed as [14,23],

$$\frac{dN(t)}{dt} = -\alpha_T \sqrt{\frac{128\pi\varepsilon}{15\nu}} a_0^3 N(t)^2 \tag{1}$$

where $N(t)$ denotes the total number of particles or flocs per unit volume, a_0 the radius of a primary particle, ε the rate of energy dissipation per unit mass, ν the kinematic viscosity and α_T is the capture efficiency taking into account the Van der Waals attractive force and the disturbance due to hydrodynamic interactions. In case of simple shear flow, the value of α_T can be calculated numerically. In our previous study, it was confirmed that the value of α_T for the case of turbulent flow, can be expressed by replacing the shear rate with its effective value. That is, following approximate expression

$$\alpha_T = \left(\frac{A}{36\mu\pi\sqrt{(4\varepsilon/15\pi\nu)}a_0^3} \right)^{0.18}, \tag{2}$$

can be used [25]; where A denotes the Hamaker constant and μ is the viscosity of the fluid. Note that the value of α_T is determined by the ratio of hydrodynamic force and attractive surface force. With this result, in the case of early stage of coagulation, Eq. (1) can be approximately integrated assuming,

$$N(t)a^3 = N(0)a_0^3 = \text{Const.} \tag{3}$$

That is, the progress of coagulation in the turbulent mixing flow in the initial stage can be written as follows,

$$\ln\frac{N(t)}{N(0)} = -\alpha_T \sqrt{\frac{128\pi\varepsilon}{15\nu}} N(0)a_0^3 t \tag{4}$$

The validity of this expression was confirmed by our previous measurements of the coagulation rate as a function of a_0 in a mixing devise of liquid to produce a turbulent flow by the end-over-end rotation of forked flask.

The concept of collision process can be also applied to the analysis of adsorption process of polymer to a colloidal particle when it is limited by the transportation of polymer molecules from bulk solution to the surface of a colloidal particle. Since usually the size of polymer molecules are not sufficiently small to neglect the contribution of Brownian motion, the rate of polymer supply to the reference colloidal particle, J_p, can be expressed by the sum of diffusion flux by Brownian motion and collision induced by turbulent mixing. That is,

$$J_p = 4\pi D_{op} R_{op} N_p + \sqrt{\frac{8\pi\varepsilon}{15\nu}} (a_0 + a_p)^3 N_p \tag{5}$$

where D_{op}, R_{op}, a_p, N_p denotes the relative diffusion constant between polymer molecules and colloidal particles, collision radius between polymer molecules and colloidal particles, the radius of polymer molecules, the number concentration of polymer molecules, respectively.