Flocculation Behavior of Negatively Charged Colloidal Particles with Polycations

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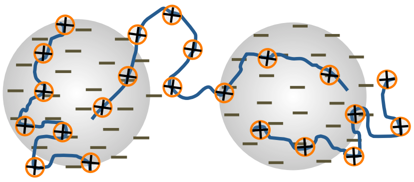
1 Introduction

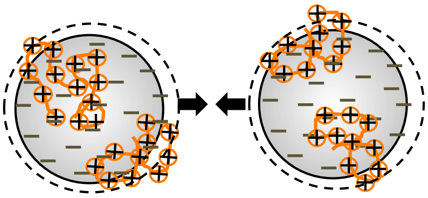
1.1 Background

Aggregation and dispersion of colloidal suspensions are important in many industrial processes, such as water/wastewater treatment, paper making, minerals recovery et al, as colloidal particle ranging from several micrometers down to several nanometers tend to keep disperse. Aggregation of particles increases the hydrodynamic size of transport unit and thus enhances the sedimentation rate of particles. Polymers/polyelectrolytes with a strong tendency to adsorb on the surface of colloidal particles are commonly used to flocculate the dispersion [1] and eventually achieve the process of solid-liquid separation. Cationic polyelectrolytes are particularly important, as negatively charged surfaces are abundant in nature.

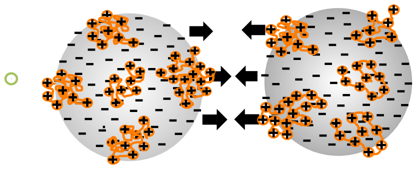
The aggregation of dispersion is mainly enhanced by two major mechanisms: bridging [2-7], charge neutralization [8-16]. Bridging flocculation is due to the adsorption of one polymer chain onto different particles. Polymers adsorbed on one particle will extend their long chains to other particles, and thus particles are linked together though the formation of bridges. Charge neutralization is due to the reduction in the electrostatic repulsion originating from the adsorption of oppositely charged polymers. The adsorption of oppositely charged polymers will reduce or completely neutralize the original charge of particles, and thus electrostatic repulsions between particles is reduced or eliminated. Particles can approach each other close enough to aggregate. The mechanism of charge neutralization is enforced by the concept of “patch” which suggests an additional electrostatic attraction between the bare areas of one particle and oppositely charged polyelectrolytes patches of neighboring particles.



Bridging



Charge neutralization



Patch attraction

Fig.1.1 Main flocculation mechanisms of colloidal particles with polyelectrolytes.

In most practical cases we are also concerned with a slow coagulation or even stabilization through interparticle repulsive forces. The stabilization of colloidal suspensions [17-21] mainly originates from electrostatic effect, steric effect or combined electro-steric effect (Fig.1.2). The electrostatic effect interacts between charged surfaces due to excess adsorption of oppositely charged chains, while the steric effect is mainly originated from the interferences between adsorbed layers of polymers. The former can be expected to be long-distance interaction and the latter, only operative in a range of adsorbed layer thickness, is more effective when the electrostatic interaction is largely screened. The mechanism of stabilization becomes more complex in the system of oppositely charged colloidal particles and polyelectrolytes where the influence of polyelectrolyte is traceable to both electrostatic and steric effects. Sometimes both steric effects and electrostatic repulsions play roles in the stabilization of colloidal suspension, which is called as is electro-steric stabilization. However, it is rather difficult to determine which effect is actually working.

A fundamental knowledge about the mechanism of flocculation and stabilization could contribute to optimize these processes, to stimulate the design of effective polymers, and to help to develop new methods for flocculation or stabilization of dispersions [22]. Because of their importance flocculation and dispersion have been studied and analyzed extensively, both experimentally and theoretically. However, in the practical applications, often a complex mixture of salt and different types of polymer is used. Analysis of the dominancy of these effects; electrostatic, bridging or steric effects, has not been clearly conducted so far, especially for oppositely charged particles and long chain polyelectrolytes. The aggregation behavior depends on the characteristics of materials (charge density, molecular weight of polymer, salt type, particles) and operating conditions (concentration, hydrodynamic condition, ionic strength et al). Some effects have been investigated in the chemically similar system, however, in general, an integrated investigation, including effects of polymer dosage, polymer charge density, ionic strength, particle size and flow condition, is limited.

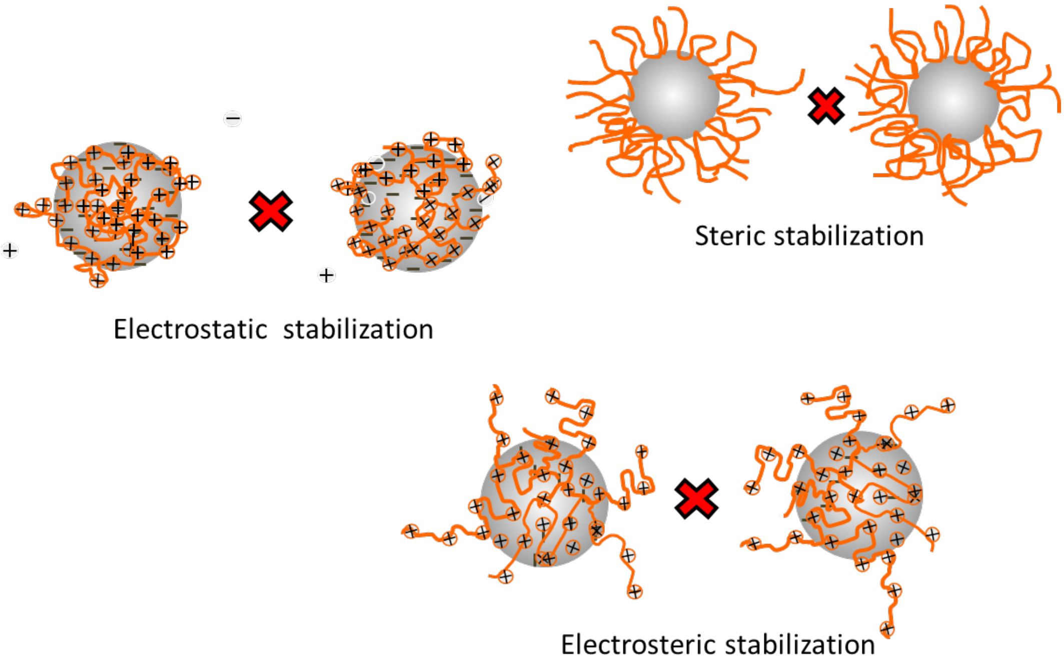


Fig.1.2 Main stabilization mechanisms of colloidal particles with polyelectrolytes.

1.2 Polymers and Polyelectrolytes at Interface

A flexible polymer molecule in solution is usually described as a random coil, and the size of the coil is dependent upon the solvent quality. However, upon adsorption of polymer molecules onto the interface the conformation of the polymer may change from that in the solution state. A general feature of adsorption of polymers is the fact that much more polymers can be adsorbed than the amount necessary to form a monolayer on the surface, so the formation of discrete monolayers may be precluded. The train-loop-tail model [38], as pictured in Fig.1.3, has been proposed to describe the conformation of polymers / polyelectrolytes at the solid-liquid interface [36]. A sequence of segments attached to the surface is called a train and a sequence of segments between trains, being solution without attaching surface, constitutes a loop. Relatively long tails are the free ends of each chain, extending further into the solution. In some cases, such as at very low polymer concentrations, the chains in contact with the surface tend to spread out, having a relatively large fraction of trains. This conformation is termed a pancake, as shown Fig. 1.4a. In other cases, for example, at rather high polymer doses, the chains compete for space at the surface. A frequent result might be the small fraction of trains, and a large amount of loops and long tails stick out into the solution, as shown in Fig. 1.4b.

Adsorption of the polymer on the surface is the results of the interactions between segments and the surface. The mechanism of adsorption can be very different in accordance with chemical conditions. The interaction parameters governing the adsorption of uncharged polymers are the adsorption energy parameter χ_s and the solvency parameter χ . For polyelectrolytes the electrostatic interaction is the additional contributor. Surface charge density, charge density of polymer and ionic strength are three main parameters. After all, in the system of the surface and oppositely charged polyelectrolyte, an electrostatic contribution to the segment-surface interaction will promote the adsorption, which is a strong attraction and operates in a long range.

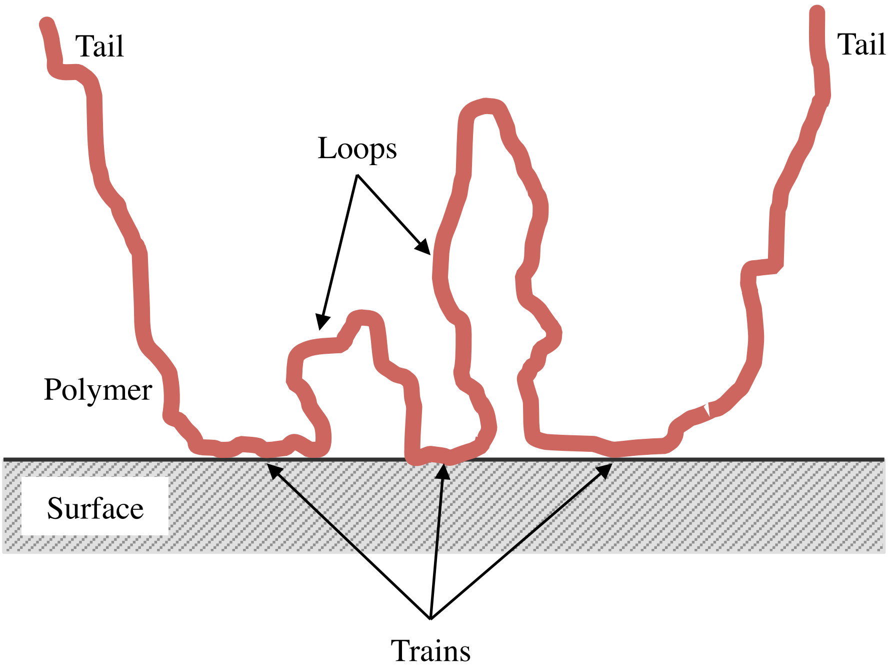


Fig.1.3 Train-loop-tail conformation of an adsorbed polymer chain on the surface [31].

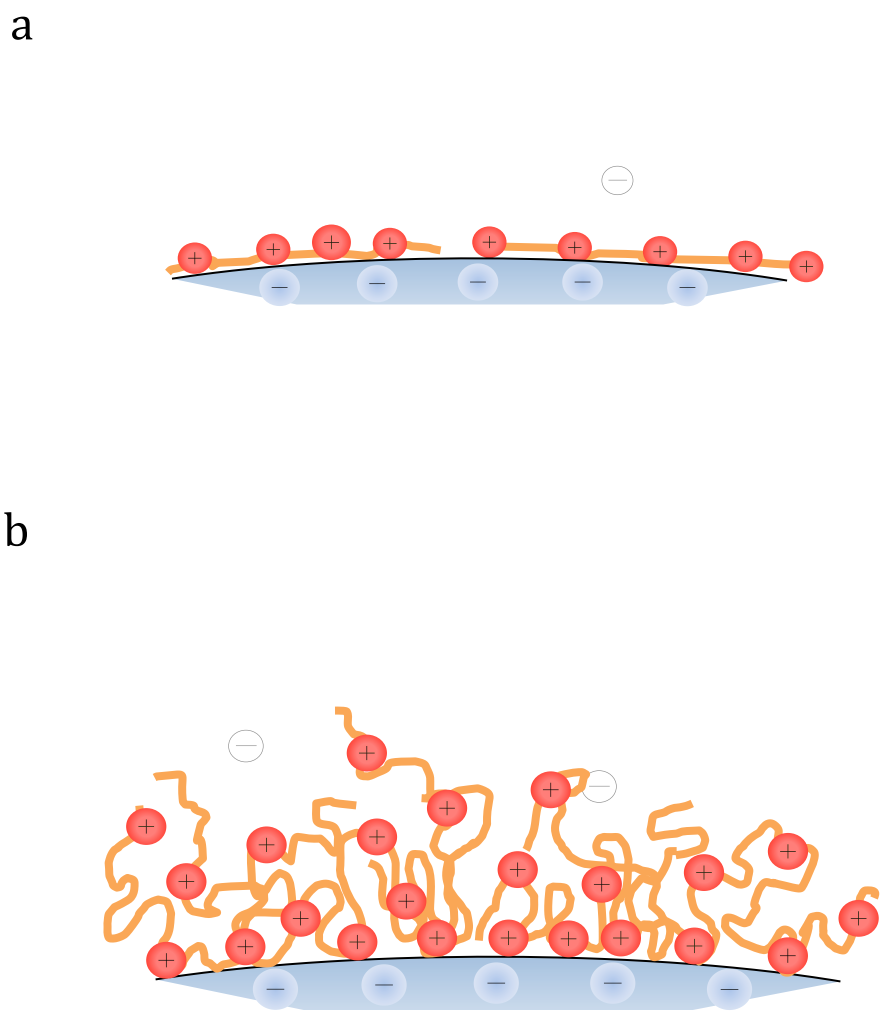


Fig.1.4 The conformation of polymers on the interface at different dosages of polymer; a) a pancake conformation of polymers, b) a brush conformation of polymers.

However, it cannot be the complete story, because the charge reversal of particle [39] upon addition of certain dosages of polyelectrolytes is well observed, and certain amounts of adsorption of polyelectrolytes [40] have also been reported at sufficient high ionic strength (for example, 1M) where electrostatic interaction has been largely screened. One or more non-electrostatic interactions [41, 42] must exist and contribute to the adsorption process. Several possibilities come to our minds immediately, such as van der Waals interaction, chemical bonding, hydrogen binding and hydrophobic bonding.

Kinetics of polyelectrolyte adsorption is a very important issue, which is also closely related to the flocculation process, but there are very few systematic studies. Some literatures investigated the change of the structure of adsorbed layer, and it was reported that the initially adsorbed layer of polymers is metastable, which tends to transform into a much flatter conformation. Akesberg et al [43] found a relatively extended conformation of polymers in the first hour and a flatter conformation for longer time in the adsorbed layer of polyacrylamide with 6.5% cationic groups on negatively charged cellulosic fibers. Results indicate sufficiently long time scales are needed to reach equilibrium due to the rather slow relaxation of adsorbed polyelectrolytes. Pefferkorn et al [44] investigated the adsorption amount of PVP on latex particles as a function of time. The structure relaxation of adsorbed layer is closely related to the rate of polymer supply in an adsorption experiment. Under conditions of slow transfer of solution polymers toward the surface, they first observe an important structure change of adsorbed layer and then a state of thermodynamic equilibrium due to excess adsorption of polymer. Under conditions of fast transfer, the surface was rapidly covered with polymers having a solution-like conformation, and later the structure of adsorbed layer reached a thermodynamic equilibrium via a desorption of initially adsorbed polymers.

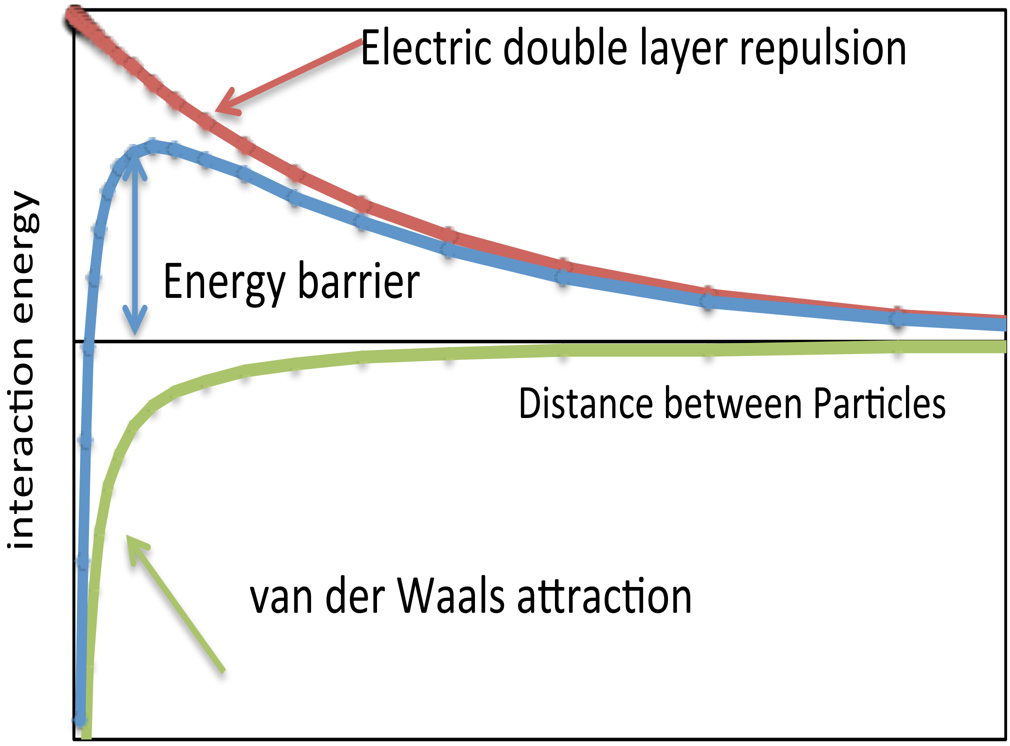


Fig.1.5 Schematic energy versus distance profiles of the DLVO interaction [45].

1.3 Aggregation of Colloidal Particles

The classical DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) assumes that the interaction potential of two colloidal particles is dominated by van der Waals attraction and double layer repulsion, and the energy profile (Fig.1.5) is used to predict the stability of colloidal particles. Addition of simple electrolytes such as potassium chloride, iron chloride or aluminium sulphate, to colloidal dispersion will reduce the electrostatic interactions between particles, and thus results in the aggregation of colloidal particles. There is a critical coagulation centration of salt which separates the aggregation process into a slow aggregation regime and a fast aggregation regime. The DLVO theory could qualitatively explain the coagulation of colloidal particles with salt, for example, the existence of the slow and fast aggregation regimes. However, the classical DLVO theory fails to predict quantitatively the discrepancy between theory and experimental data in describing the slope of stability curve. Behrens [37] found that the traditional discrepancy is related to the large surface charge of particles. For highly charged particles, the theory is applicable only semi-quantitatively [23, 24, 25]. Additional non-DLVO forces and additional mechanisms, for example, surface heterogeneity and roughness, have been considered, however, decisive explanations have not yet been given.

In the flocculation of particles with oppositely charged polyelectrolyte, the fast flocculation can be observed at a medium dose of polymer and slow flocculation is found at low and high polymer doses. The fast flocculation usually corresponds to the position of the IEP where the original charge of particles is overall neutralized [32]. The fast flocculation is mainly induced by attractive van der Waals forces. The slow flocculation at low and high polymer doses is due to electrostatic repulsions originating from original charge of particles or excess adsorption of polyelectrolytes. This characteristic behavior can also be rationalized within the classical DLVO theory.

However, Ruehrwein and Ward [4] observed that negatively charged particles can be flocculated by negative polyelectrolytes and that some nonionic polymers are powerful flocculants, even if the suspended particles possess a considerable charge. Which cannot be well explained by the DLVO theory. So they introduced the bridging concept: long segments of polymers extruding from one particle can adsorb onto other particles, thus particles are held together by polymer bridges. This bridging concept was supported by other investigations and accepted by most researchers. Healy and La Mer [5] also proposed that the flocculation is induced by the approach of polymer covered surfaces and uncovered surfaces, and that the rate is proportional to the product, $\theta(1\text{-}\theta)$, where θ denotes the ratio of the coverage. Fleer and Lyklema [6] observed effective flocculation by two-portion mixing method and clarified the importance of bare surface for the formation of bridge. Ash and Clayfield [7] clearly demonstrated that polymer of high molecular weight will act more effectively in the flocculation as well as colloidal stabilization. Adachi et al [26-31] reported the enhanced rate of flocculation due to an increase in effective collision radius. The importance of shear flow for bridges has also been proved. The bridging flocculation has been distinguished into two limiting cases: equilibrium flocculation due to relaxed polymers and non-equilibrium flocculation due to unrelaxed polymers. Pelssers [22] reported that both equilibrium and non-equilibrium flocculation are possible in the shear flow, whereas, in the case of Brownian motion, non-equilibrium flocculation does not occur because the attachments and collision processes are too slow to compete with the relaxation process.

Certain phenomena in oppositely charged particles-polyelectrolyte systems cannot be explained within the DLVO theory. Gregory observed the maximum rate of flocculation of polystyrene particles with polycations (high charge density but moderate molecular weight) is faster than that of salt-induced rapid coagulation. The flocculation of colloidal particles with dendrimers also exhibits an accelerated rate [11,12]. The fast aggregation regime has also been observed to widen with an increase of the molecular mass of polyelectrolyte, and the acceleration of rate decreases with increasing ionic strength. The heterogeneous distribution of adsorbed polyelectrolytes on the surface [8] has been proposed to explain this effect. Mosaic distribution of charges on the surface creates additional attractive force between suitably aligned patches. The characteristic feature has aroused great interests in researchers. A series of investigations of particulate surface force and stability behavior have also supported this concept. Borkovec et al [9, 10] have proved the presence of additional attractive non-DLVO forces, and concluded that the accelerated rate of flocculation is ascribed to this attractive force. This conclusion is consistent with the theoretical prediction on the double layer forces between heterogeneous charged surfaces presented by Miklavic et al [15]. However, patch-wise interaction has not yet been clearly demonstrated in the flocculation induced by long chain polyelectrolytes.

Low charge density polymers tend to adopt loops/tails conformation on the surface [34-35] and the flocculation induced by low charge density polyelectrolyte is often labeled as bridging flocculation. Audebert [33] studied the flocculation of a silica suspension by some cationic polyelectrolytes in the shear flow, and the results suggests that a long range interparticle bridging only can be found in the flocculation by low charge density polyelectrolytes (< 0.05) and that electrostatic interactions play a major role for polyelectrolytes with charge density larger than 0.15.

1.4 Objective

The central purpose of this study is to improve our fundamental understanding of the aggregation behavior of colloidal particles with oppositely charged long chain polyelectrolytes, so monodisperse spherical particles, negatively charged polystyrene latex particle, have been employed as well as the long chain polycations (similar in molecular weight but rather different in charge density) in this study. The monodispersed model spheres give constant collision efficiency in the early stage of aggregation and thus we can calculate the rate of aggregation on the basis of the Smoluchowski theory. And, also, due to the spherical shape of PSL particles the layer thickness of adsorbed polymer is measured on the basis of Brownian trajectory of particles.

The rate of flocculation, as well as mobility of particles and layer thickness of adsorbed polyelectrolytes, has been investigated in the presence of salts and polycations to achieve the following objectives.

► Clarifying charging properties of colloidal particle covered with polyelectrolytes at various ionic strengths.

►Figuring out flocculation behaviors of particles by polyelectrolytes subjected to Brownian motion and in a turbulent flow.

► Examining effects of charge density of polyelectrolyte, ionic strength and polyelectrolyte dosage on the flocculation of particles.

► Understanding flocculation mechanism of colloidal particles with oppositely charged long chain polyelectrolytes.

1.5 Outline of This Study

The dissertation is organized as follows:

In chapter 2, we reviewed the aggregation kinetics of colloidal particles subjected to Brownian motion and in a turbulent flow. The aggregation of colloidal particles subjected to Brownian motion was investigated in the presence of slat. The validity of the Smoluchowski solution was clarified by the linear relation between the reciprocal of the total number concentration of particles and time. The critical concentration of coagulation is detected to be about 0.3M of KCl. The kinetics of aggregation of colloidal particles with 1M KCl was also investigated in a turbulent flow. The linear relation of $Ln(N(t)/N(0))$ and mixing time has been verified as well, and the rate of aggregation can be estimated by the calculation of the slope of the plots.

In chapter 3, charging properties of colloidal particles with absorbing polyelectrolytes were studied by Zetasizer, and the thickness of adsorbed layer on the surface was estimated on the basis of the trajectory of Brownian motion of particles. Results show that high charge density polymers adopt a flat conformation on the surface and thus give less effect on the structure of double layer. Low charge density polymers were adsorbed on the surface with loops/tails extending into the solution. The presence of polymer layer on the surface modifies the structure of double layer, and thus weakens the mobility of particles.

In Chapter 4, Brownian flocculation of polystyrene latex by polyelectrolytes (different in charge density) was investigated as a function of polyelectrolyte dosage. The total number concentration was measured as a function of time, and, from this, the rates of aggregation were determined. For both polyelectrolytes, the rate of flocculation goes through a maximum against polymer dosage. However, in the case of high charge density polyelectrolyte, we observed an accelerated rate of flocculation at low ionic strength (≤ 1mM KCl). The accelerated flocculation is ascribed to the patch wise interaction between particles. In the case of low charge density polyelectrolyte, the rate of flocculation was always observed to be slower than that of salt-induced rapid coagulation at low ionic strength (≤ 10mM KCl). The characteristic feature is well explained by the picture of bridging flocculation competing with steric effects. At sufficiently high ionic strength, the flocculation of particles is controlled by charge neutralization until the onset of steric effects of adsorbed polymers in both cases, but steric effects of low charge density polymers set in from a very low dosage of polymer.

In chapter 5, our attention was focused on the orthokinetic flocculation of colloidal particles with polyelectrolytes. In order to estimate the role of electrostatic interaction, the flocculation of particles with polyelectrolyte (different in charge density) was investigated at the IEP where electric disturbance is negligible. In the case of high charge density polyelectrolyte, the aggregation process obeys the theory of aggregation kinetics. We observed an accelerated rate of flocculation at lower ionic strength and salt-induced rapid coagulation at higher ionic strength (> 10mM). The accelerated flocculation is ascribed to the patch wise interaction between particles. However, in the case of low charge density polyelectrolyte, the aggregation process is complicated. It only obeys the theory of aggregation kinetics in the early stage of less than 2 minutes and an upward bending curve is given in the latter stage. By taking dynamics aspects of polymer adsorption and relaxation into account, we are able to rationalize the data consistently. The initial stage flocculation obeying to the theory of aggregation is due to the formation of bridges between particles and the slowed rate of flocculation or even the stabilization in the latter stage is due to the onset of steric effects originated from the excess adsorption/relaxation of adsorbed polymer chains onto the surface.

All results and discussions are summarized in chapter 6, together with some suggestions for the future study.

References

[1] D. H. Napper, Polymeric Stabilization of Colloidal Dispersions. London: Academic Press; 1983.

[2] Y. Adachi, T. Matsumoto, Dynamics of Initial Stage Flocculation of Polystyrene Latex Spheres with Polyelectrolytes, Colloids Surfaces A, 113 (1996) 229.

[3] T. Matsumoto, Y. Adachi, Effect of Ionic Strength on the Initial Dynamics of Flocculation of Polystyrene Latex with Polyelectrolyte, J. Colloid Interface Sci., 204 (1998) 328.

[4] R. A. Ruehrwein, D. W. Ward, Mechanism of Clay Aggregation by Polyelectrolytes, Soil Sci., 73 (1952) 485.

[5] T. W. Healy, V.K. La Mer, The Energetics of Flocculation and Redispersion by Polymers, J. Colloid Sci., 19 (1964) 323.

[6] G. J. Fleer, J. Lyklema, Polymer Adsorption and Its Effect on the Stability of Hydrophobic Colloids. III. Kinetics of the Flocculation of Silver Iodide Sols, J. Colloid Interface Sci., 52 (1974) 228.

[7] S. G. Ash, E. J. Clayfield, Effect of Polymers on the Stability of Colloids Flocculation of Polystyrene Latex by Polyethers, J. Colloid Interface Sci., 55 (1976) 645.

[8] J. Gregory, Rates of Flocculation of Latex Particles by Cationic Polymers, J. Colloid Interface Sci., 42 (1973) 448.

[9] M. Borkovec, G. Papastavrou, Interactions between Solid Surfaces with Adsorbed Polyelectrolytes of Opposite Charge, Curr. Opin. Colloid Interface Sci., 13 (2008) 429.

[10] I. Popa, G. Gillies, G.Papastavrou, M.Borkovec, Attractive and Repulsive Electrostatic Forces between Charged Latex Particles in the Presence of Anionic Linear Polyelectrolytes, J. Phys. Chem. B, 114 (2010) 3170.

[11] I. Popa, G. Papastavrouz, Michal Borkovec, Charge Regulation Effects on Electrostatic Patch-Charge Attraction Induced by Adsorbed Dendrimers, Phys. Chem. Chem. Phys., 12 (2012) 4863.

[12] W. Lin, P. Galletto, M. Borkovec, Charging and Aggregation of Latex Particles by Oppositely Charged Dendrimers, Langmuir, 20 (2004) 7465.

[13] J. Kleimann, C. Gehin-Delval, H. Auweter, M. Borkovec, Super-Stoichiometric Charge Neutralization in Particle−Polyelectrolyte Systems, Langmuir, 21 (2005) 3688.

[14] W. L. Yu, F. Bouyer, M. Borkovec, Polystyrene Sulfate Latex Particles in the Presence of Poly (vinylamine): Absolute Aggregation Rate Constants and Charging Behavior, J. Colloid Interface Sci., 241 (2001) 392.

[15] S. J. Miklavic, D. Y. C. Chan, L. R. White, T. W. Healy, Double Layer Forces between Heterogeneous Charged Surfaces, J. Phys. Chem., 98 (1994) 9022.

[16] I. Popa, M. Trulsson, G. Papastavrou, M. Borkovec and B. Jönsson, Long-Ranged Attractive Forces Induced by Adsorbed Dendrimers: Direct Force Measurements and Computer Simulations, Langmuir, 25 (2009) 12435.

[17] J. Hierrezuelo, A. Sadeghpour, I. Szilagyi, A. Vaccaro, M. Borkovec, Electrostatic Stabilization of Charged Colloidal Particles with Adsorbed Polyelectrolytes of

Opposite Charge, Langmuir, 16 (2010) 15109.

[18] E. B. Zhulina, O. V. Borisov, V. A. Priamitsyn, Theory of Steric Stabilization of Colloid Dispersions by Grafted Polymers, J. Colloid Interface Sci., 137 (1990) 495.

[19] D. H. Napper, Steric Stabilization, J. Colloid Interface Sci., 58 (1977) 390.

[20] M. S. Romero-Cano, A. Martın-RodrıBguez, G. Chauveteau, and F. J. de las Nieves, Colloidal Stabilization of Polystyrene Particles by Adsorption of Nonionic Surfactant: II. Electrosteric Stability Studies, J. Colloid Interface Sci., 198 (1998) 273.

[21] A. Sadeghpour, E. Seyrek, I. Szilágyi, J. Hierrezuelo, and M. Borkovec, Influence of the Degree of Ionization and Molecular Mass of Weak Polyelectrolytes on Charging and Stability Behavior of Oppositely Charged Colloidal Particles, Langmuir, 27 (2011) 9270.

[22] E. G. M. Pelssers, Single Particle Optical Sizing: Aggregation of Polystyrene Latices by Salt and Polymer, Landbouwuniversiteit te Wageningen, Thesis (doctoral), 1988.

[23] N. H. G. Penners, L. K. Koopal, The Effect of Particle Size on the Stability of Haematite (α-Fe_2O_3) Hydrosols, Colloids Surfaces, 28 (1987) 67.

[24] R. H. Ottewil, J. N. Shaw, Stability of Monodisperse Polystyrene Latex Dispersions of Various Sizes, Discuss. Faraday Soc., 42 (1966) 154.

[25] J. Th. G. Overbeek, Recent Developments in the Understanding of Colloid Stability, J. Colloid Interface Sci., 58 (1977) 408.

[26] Y. Adachi, M. A. Cohen Stuart, R. Fokkink, Dynamic Aspects of Bridging Flocculation Studied Using Standardized Mixing, J. Colloid Interface Sci., 167 (1994) 346.

[27] Y. Adachi, M. A. Cohen Stuart, R. Fokkink, Kinetics of Turbulent Coagulation Studied by Means of End-over-End Rotation, J. Colloid Interface Sci., 165 (1994) 310.

[28] Y. Adachi, M. A. Cohen Stuart, R. Fokkink, Initial Rates of Flocculation of Polystyrene Latex with Polyelectrolyte: Effect of Ionic Strength, J. Colloid Interface Sci., 171 (1995) 520.

[29] Y. Adachi, K. Aoki, Early-stage flocculation Kinetics of Polystyrene Latex Particles with Polyelectrolytes Studied in the Standardized Mixing; Contrast of Excess and Moderate Polyelectrolyte Dosage, Colloids Surfaces A, 230 (2004) 37.

[30] Y. Adachi, J. Xiao, Initial Stage of Bridging Flocculation of PSL Particles Induced by an Addition of Polyelectrolyte under High Ionic Strength, Colloids Surfaces A, 435 (2013) 127.

[31] Y. Adachi, T. Matsumoto, M. A. Cohen Stuart, Effects of Hydrodynamic Mixing Intensity Coupled with Ionic Strength on the Initial Stage Dynamics of Bridging Flocculation of Polystyrene Latex Particles with Polyelectrolyte, Colloids Surfaces: A, 207 (2002) 253.

[32] J. Gregory, Flocculation of Polystyrene Particles with Cationic Polyelectrolytes, Trans. Faraday Soc. 65 (1969) 2260.

[33] T. K. Wang, R. Audebert, Flocculation Mechanisms of a Silica Suspension by Some Weakly Cationic Polyelectrolytes, J. Colloid Interface Sci., 119 (1987) 439.

[34] B. Vincent, the Effect of Adsorbed Polymers on Dispersion Stability, Adv. Colloid Interface Sci., 4 (1974) 193.

[35] J. Gregory, S. Barany, Adsorption and Flocculation by Polymers and Polymer Mixtures, Adv. Colloid Interface Sci., 169 (2011) 1.

[36] G. J. Fleer, M. A. Cohen-Stuart, J. Scheutjens, T. Cosgove, B. Vincent, Polymers at Interfaces, London: Chapman & Hall, 1993.

[37] M. Schudel, S. H. Behrens, H. Holthoff, R. Kretzschmar, M. Borkovec, Absolute Aggregation Rate Constants of Hematite Particles in Aqueous Suspensions: A Comparison of Two Different Surface Morphologies, J. Colloid Interface Sci., 196 (1997) 241.

[38] E. Jenkel, B. Rumbach, Z. Elektrochem, 55 (1951) 612.

[39] O. J. Rojas, M. Ernstsson, R. D. Neuman, P. M. Claesson, Effect of Polyelectrolyte

Charge Density on the Adsorption and Desorption Behavior on Mica, Langmuir, 18 (2002) 1604.

[40] N. G. Hoogeveen, M. A. Cohen Stuart, G. J. Fleer, Can Charged (Block Co)polymers Act as Stabilisers and Flocculants of Oxides? Colloids Surfaces: A, 117 (1996) 77.

[41] J. Lyklema, L. Deschenes, the First Step in Layer-by-Layer Deposition: Electrostatics and/or Non-Electrostatics? Adv. Colloid Interface Sci., 168 (2011) 135.

[42] J. Faraudo, A. Martin-Molina, Competing Forces in the Interaction of Polyelectrolytes with Charged Interfaces, Current Opin. Colloid Interface Sci., 18 (2013) 517.

[43] L. Wagberg, L. Odberg, T. Lindstrom, R. Aksberg, Kinetics of Adsorpton and Ion-Exchange Rections during Adsorption of Cationic Polyelectrolytes onto Cellulosic Fibers, J. Colloid Interface Sci., 123(1988) 287.

[44] E. Pefferkorn, A. Elaissari, Adsorption-Desorption Processes in Charged Polymer / Colloid Systems; Structural Relaxation of Adsorbed Macromolecules, J Colloid Interface Sci., 138 (1990) 522.

[45] J. N. Israelachvili, Intermolecular Surface Forces, Academic press, 2011.

2 Aggregation Kinetics of Colloidal Particles by Simple Electrolytes

Aggregation can be visualized as a two-step process: particle collision and subsequent attachment upon collision [1]. The collisions of particle are mainly governed by suspension hydrodynamics and surface force. In the quiescent condition, particle collisions are controlled by [2] the random "Brownian" motion of particles. In the flow field imposed velocity gradients will induce particle collisions. But the attachment process is determined by microscopic interaction force acting between particles. If attraction forces prevail, particles coagulate irreversibly in the deep primary potential well, giving a fast flocculation rate. If the repulsion is included, for example, due to electrical charge on the surfaces or adsorbed polymers, then potential energy barrier appears, in this case not each collision of particles results in their aggregation, and thus a slow aggregation is induced.

2.1 Kinetics of Aggregation

2.1.1 Population Balance Equation

The first attempt to predict the rate of interparticle collisions is that of Von Smoluchowski (1917) derived an expression for collision rate between two spherical particles. The number of collisions, J_{ij}, occurring between i-fold particles and *j*-fold particles in unit time and unit volume is given by

$$J_{ij} = \beta(i,j) \quad n_i n_j \tag{2.1}$$

The subscripts *i*, *j*, refer to the number of primary particles in aggregates, and thus the *i*-particle is an aggregate of *i* primary particles. n_i and n_i represent the number concentration of *i*-fold and *j*-fold aggregates. The aggregation coefficient, $\beta(i,j)$, depends on several factors such as particle size and transport mechanism. Thus, in effect, it is a measure of the transport efficiency leading to collisions.

If every collision results in a successful aggregation, then an expression for the rate of change of *k*-fold aggregates, originally proposed by Von Smoluchowski [3], can be written as follow,

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k}\beta(i,j)n_i n_j - n_k\sum_{j=1}^{\infty}\beta(k,j)n_j \tag{2.2}$$

The first term on the right hand side defines the rate of formation of *k*-fold particles by the aggregation of *i*-fold and *j*-fold particles where *i*+*j*=*k*. Each collision is counted twice and hence the factor 1/2 is included. The second term on the right hand side accounts for the loss of *k*-fold particles by aggregations with any other particles. The overall equation thus defines the temporal change in the number concentration of *k*-fold particles. It is important to note that the equation is for irreversible aggregation, since no allowance is made for break-up of aggregates. Also, it has been assumed that every collision is effective in forming an aggregate. A collision efficiency is needed when only a fraction of collisions are successful [4].

In the early stage of aggregation of monodisperse spheres, Equation (2.2) can be simplified as follows [3]

$$\frac{dn_1}{dt} = \beta_{11}\left(-\ n_1 \sum_{i=1}^{\infty} n_i\right)$$

$$\frac{dn_2}{dt} = \beta_{11}\left(\frac{1}{2} n_1 n_1 -\ n_2 \sum_{i=1}^{\infty} n_i\right) \tag{2.3}$$

$$\frac{dn_3}{dt} = \beta_{11}\left(\frac{1}{2}(n_2n_1 + n_1n_2) - n_3\sum_{i=1}^{\infty} n_i\right)$$

....

Taking the summation of equation 2.3, the temporal variation of the total number of particles, N(t), is given by

$$\frac{dN(t)}{dt} = -\frac{1}{2}\beta_{11}N(t)^2 = -kN(t)^2 \qquad (2.4)$$

The aggregation rate coefficient, k, is just half the collision rate coefficient for primary particles.

2.1.2 Aggregation Kinetics due to Brownian Motion

In the quiescence condition where the collisions between particles are induced by Brownian motion. The aggregation rate constant between particles is obtained by calculating the total flux [7]. By simplifying the collision process of Brownian particles the rate coefficient for unequal spheres is written as

$$\beta(i,j) = 4\pi D_{ij}R_{ij} = \frac{2k_BT}{3\mu}\left(\frac{1}{a_i} + \frac{1}{a_j}\right)(a_i + a_j) \qquad (2.5)$$

where k_B is the Bolztmann's constant, T the absolute temperature, μ the fluid viscosity, D_{ij} the diffusion constant and a_i, a_i are the radii of the colliding particles. In the initial stage of the aggregation of monodisperse sphere particles, we can assume $a_i \approx a_j = a$, then the size term in Equation (2.5) is approximately constant, with a value close to 4, so that the value of β_{ij} can be approximated as 8kT/3μ. By assuming a constant coefficient of collision rate, Smoluchowski shows that the previous expression for the early stage of aggregation, Equation (2.4), would apply throughout the aggregation process. Thus:

$$\frac{dN(t)}{dt} = -\frac{4k_BT}{3\mu}N(t)^2 \qquad (2.6)$$

Solving Equation (2.6) with an initial condition N(t)=N(0) at t=0 leads to

$$\frac{1}{N(t)} - \frac{1}{N(0)} = \alpha_B \frac{4kT}{3\mu} t \qquad (2.7)$$

The linear relationship of 1/N(t) versus t has been verified by experimental results, indicating the usefulness of the Smoluchowski solution. However, the experimental rate of aggregation is always smaller than the value predicted by Smoluchowski. In order to obtain the quantitative agreement between the theory and experiments, the collision efficiency, α_B, taking values less than 1, is introduced to take into account colloidal interactions between particles and hydrodynamic effects [5]. The value of 0.3-0.7 was reported for the coagulation of polystyrene latex particles by salt [6]. When the aggregation takes place between particles adsorbing polymers, one can expect certain increases in the collision radius and thus modification of the collision efficiency α_B. The information can be obtained from the diffusion constant of particles and the plots of 1/N(t) vs. t.

2.1.3 Aggregation Kinetics in a Turbulent Flow

In most practical case, the coagulation is accelerated by a turbulent flow which can be regarded as a superposition of eddies with different sizes. Kolmogoroff [8] proposed a hypothesis of local isotropy of turbulence. Quantities related to turbulence in the local area are statistically isotropic. An important length scale, called the microscale of turbulence, was introduced to characterize the size of an energy dissipating eddy.

$$\lambda = \nu^{3/4}/\varepsilon^{1/4} \qquad (2.8)$$

where ν, ε are kinematic viscosity and the rate of energy dissipation per unit mass. The magnitude of λ is roughly 30-100μm which is sufficiently larger than the collision radius of colloidal particle. In the aggregation of colloidal particles the hydrodynamic viscous force becomes predominant.

Saffman and Turner [9] carried out the collision frequency in an isotropic turbulence. The average number of *i*-fold particles (with a radius of a_i) colliding to the reference *j*-fold particles (with a radius of a_j), J, can be expressed as follow

$$J = 2\pi \left|\overline{\frac{\partial u}{\partial x}}\right| (a_i + a_j)^3 n_i \tag{2.9}$$

On the basis of the results of the statistical analysis of isotropic turbulence by Taylor and the assumption of a normal distribution of the velocity gradient, $\overline{\frac{\partial u}{\partial x}}$, they determined the mean absolute value as

$$\left|\overline{\frac{\partial u}{\partial x}}\right| = \sqrt{\frac{2\varepsilon}{15\pi\nu}} \tag{2.10}$$

Then the aggregation coefficient is written as

$$\beta(i,j) = \sqrt{\frac{8\pi\varepsilon}{15\nu}} (a_i + a_j)^3 \tag{2.11}$$

One of the simplest methods of generating turbulent flow is the mixing of colloidal particles by means of end-over-end rotation [10]. If we restrict our discussion to the initial stage where most collisions are between monomers we can postulate the following equation for the temporal evolution of the total number concentration of particles,

$$\frac{dN(t)}{dt} = -\alpha_T a_0^3 \sqrt{\frac{128\pi\varepsilon}{15\nu}} N(t)^2 \tag{2.12}$$

in which the contribution of Brownian motion of particle are not taken into account. The capture efficiency, α_T, is introduced to take the hydrodynamic and physicochemical interactions between colliding particles into account. It is difficult to rigorously evaluate the capture efficiency in a turbulent flow. Camp and Stein assumed that the collision mechanism of colloidal particles in a turbulent flow is analogous to that in laminar shear flow. As a first approximation, the capture efficiency obtained for the shear aggregation has been used for the turbulent aggregation where the shear rate was replaced with the mean absolute value of the relative velocity. Then the capture efficiency is expressed as

$$\alpha_T = \left(\frac{A}{36\pi\mu\sqrt{\frac{4\varepsilon}{15\pi\nu}}a_0^3} \right)^{0.18} \quad , \; G_T = \sqrt{\frac{4\varepsilon}{15\pi\nu}} \tag{2.13}$$

in which G_T is the mean absolute value of the relative velocity. Kobayashi et al measured the capture efficiency measured in the turbulent flow and found it similar to that predicted in the laminar shear flow. These findings also suggest the turbulent field in the Kolmogolov microscale can be treated as a sort of laminar shear flow.

The following approximate solution for the turbulent coagulation in the initial stage can be written as follow,

$$ln\left(\frac{N(t)}{N(0)}\right) = -\alpha_T\sqrt{\frac{24\varepsilon}{5\pi\nu}}\emptyset t \tag{2.14}$$

where $\emptyset$ is the volume fraction of particle in the suspension. Because of great importance of particle size, this expression only applies to the very early stage of aggregation. In spite that it is still difficult to rigorously evaluate the value of rate of energy dissipation, ε, in a turbulent flow. The calculation of rate of aggregation is possible by measuring the number concentration of aggregates as a function of time [10-12]. The practical usefulness of equation 2.14 was verified by the linear relation between Ln(N(t)/N(0) and time.

2.2 Experimental

2.2.1 Materials

The monodisperse polystyrene latex (PSL) particle was prepared by the standard emulsion polymerization of styrene in the absence of surfactant [13]. The diameter was determined by TEM to be 1356 nm, and the surface charge density was calculated from the measurement of electrophoretic mobility as a function of ionic strength on the basis of Ohshima's theory [14] and found to be respective 50 mC/m^2. The PSL suspension was sonicated for 20 min to eliminate the aggregates before each experiment.

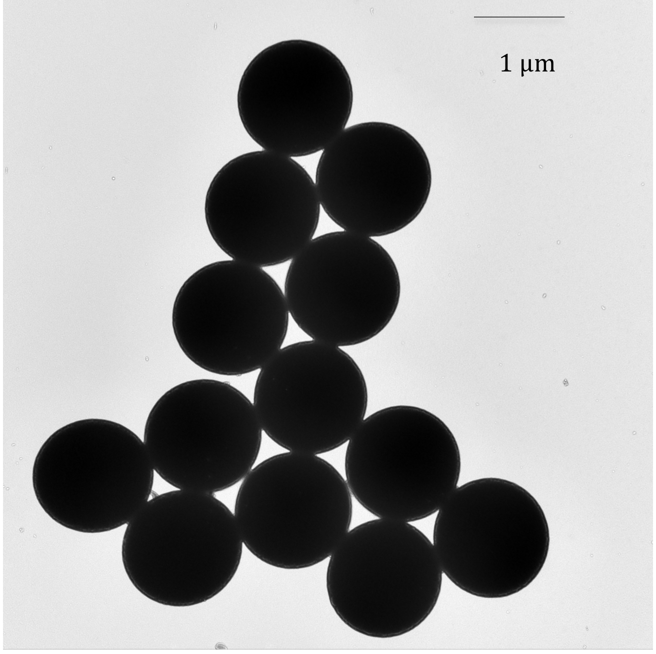


Fig.2.1 Picture of PSL particles with a diameter of 1.356 μm

2.2.2 Procedures

Brownian coagulation: As depicted in Fig.2.2, initially, one bottle was filled with 5 mL colloidal dispersion and the other one with an equal volume KCl solution. After initial pouring the colloidal dispersion into the electrolyte solution, the mixed dispersion was then poured back into the empty one. The pour-forth-back procedure was repeated for 5 s with a frequency of about 1 Hz. Then the mixed dispersion was left to stand for Brownian coagulation, the coagulation process was monitored every 10 min by Coulter Counter (Multisizer 3). The number concentration of aggregates, N(t), was obtained as a function of elapsed time.

Coagulation in the mixing flow: The coagulation of PSL particles by simple electrolytes (KCl 1 M) was also carried out in the mixing flow. The mixing flow generated by using homemade end-over-end rotation apparatus, and schematic diagram of this apparatus is shown in Fig.2.3. Two wheels with different diameters are connected to a crankshaft and a forked flask filled with solutions is mounted on the larger wheel. Turning the grip will produces the rotation of the wheels, and thus the liquid solution in one side of the flask can be poured forth and back into the other. In this experiment, 5mL aqueous suspension of PSL particles and the equal volume of KCl solution were filled in two sides of the flask separately. The mixing starts by turning over the grip pouring PSL particles into salt solution. Particles and salt were mixed in a reproducible manner with the frequency of 1Hz until the predetermined number of mixing steps was reached, the total number concentration of clusters, N(t), at different mixing steps was measured by Coulter Counter (Multisizer 3).

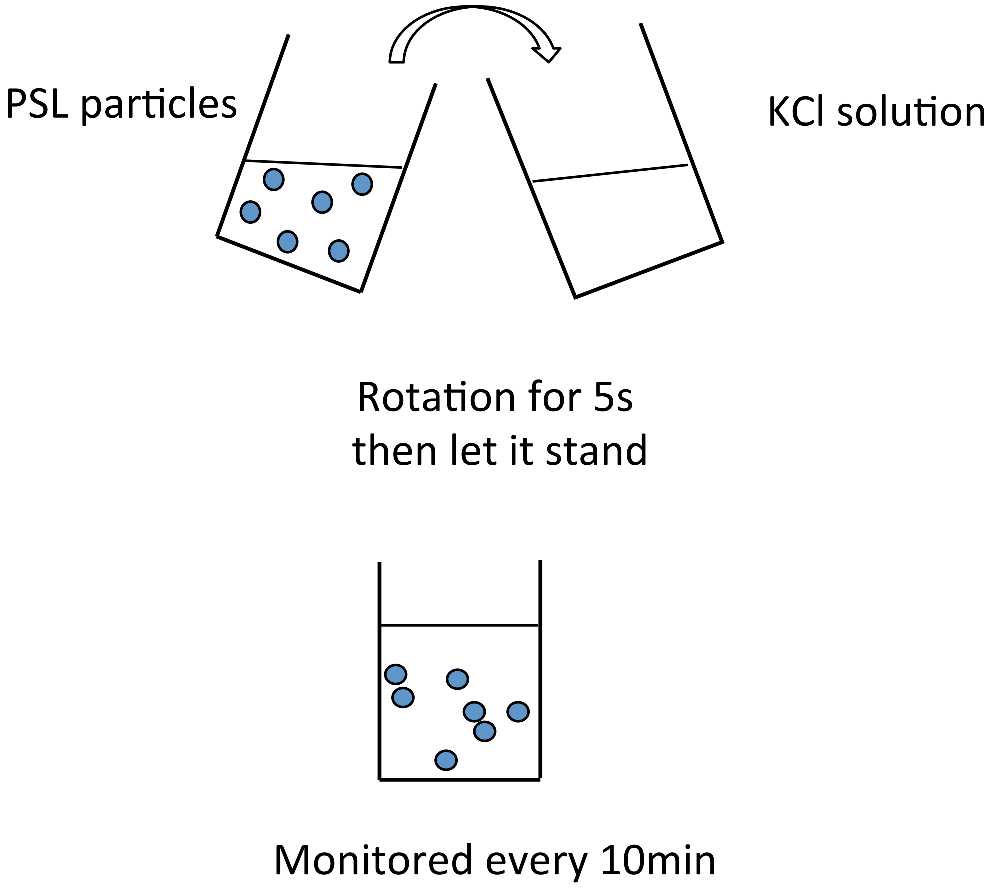


Fig.2.2 Procedures of the Brownian coagulation of PSL particles with KCl solution.

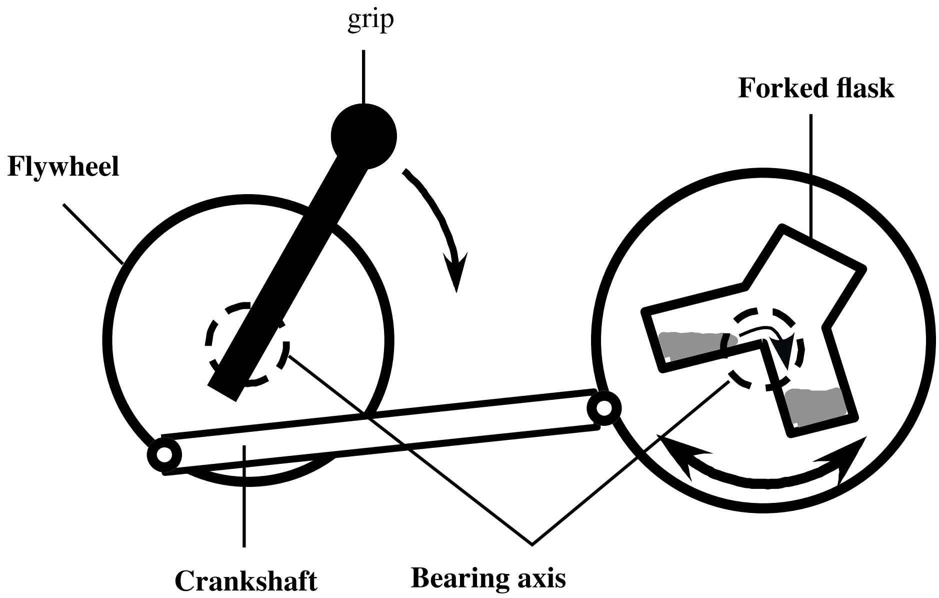


Fig. 2.3 Schematic diagram of the end-over-end rotation apparatus [11].

2.3 Results and Discussions

The temporal variations of the total number concentration of particles, *N(t)* , at different concentrations of KCl are shown as a function of time in Fig.2.4. The linear relationship between N(t) and t has verified the usefulness of the Smoluchowski solution as well. However, as we discussed in last section, the experimental rate of aggregation is smaller than the value predicted by Smoluchowski. The clear derivation can be observed in Fig.2.5. It means only a fraction of collisions are successful, even in a rapid aggregation regime where the repulsive electric force is negligible. The collision efficiency, α_B, is obtainted to be about 0.67 for the coagulation of the PSL particles with KCl.

The rate of coagulation can be obtained by calculating the slope of these plots, and the calculated values of the slopes of plots are summarized in Fig.2.6 where the rate constant of coagulation was shown as a function of salt concentration. As shown in the figure, the rate of coagulation increases with increasing salt concentration, and then keeps the constant value above the concentration of 0.3M KCl. This concentration is called as the critical coagulation concentration (C.C.C). Two aggregation regimes: slow coagulation regime and fast coagulation regime, are separated by the C.C.C. In the slow coagulation regime, the coagulation is reaction-limited process, as the rate of aggregation is controlled by collision frequency and van der Waals attractive potential. According to DLVO theory, the magnitude of electric double layer force decreases with increasing salt concentration, thus the rate increases with increasing salt concentration. Above the CCC, the aggregation is a diffusion-limited process and the rate of coagulation keep constant in this fast coagulation regime. This trend has been reported in many systems, and it confirms the qualitative validity of

DLVO theory. However, the discrepancy in the slow coagulation regime, as we previously mentioned in Chapter 1, has also been widely discussed [15,16].

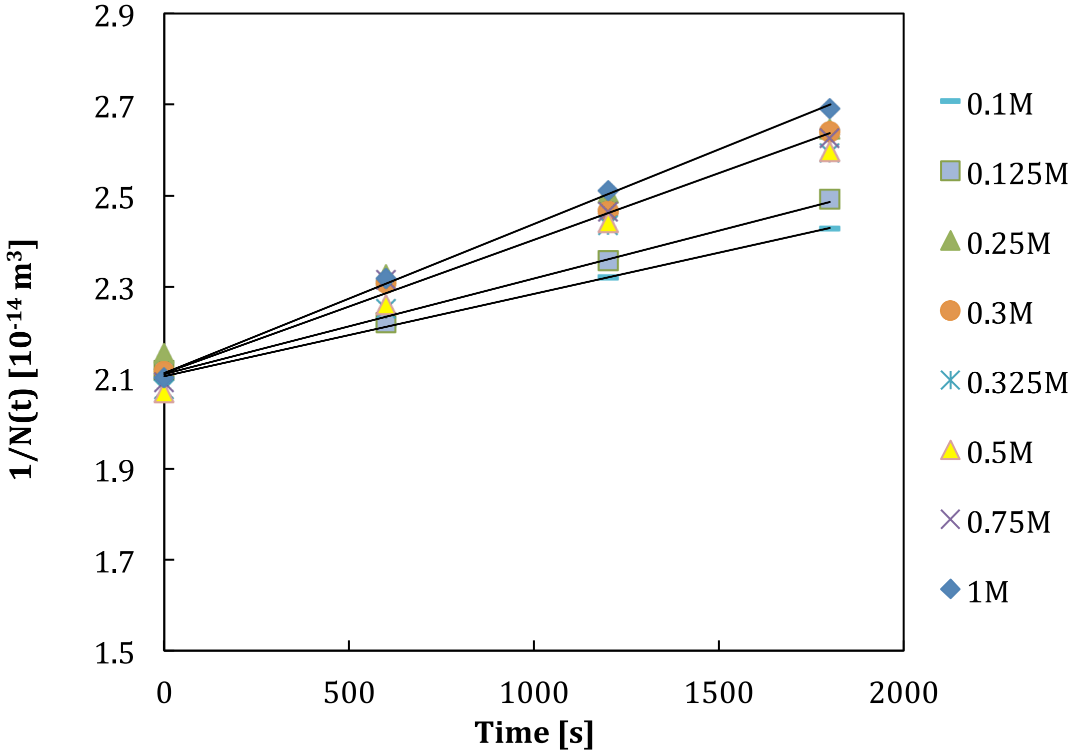


Fig.2.4 The temporal variations of the total number concentration of particles, *N(t)* , at different ionic strengths.

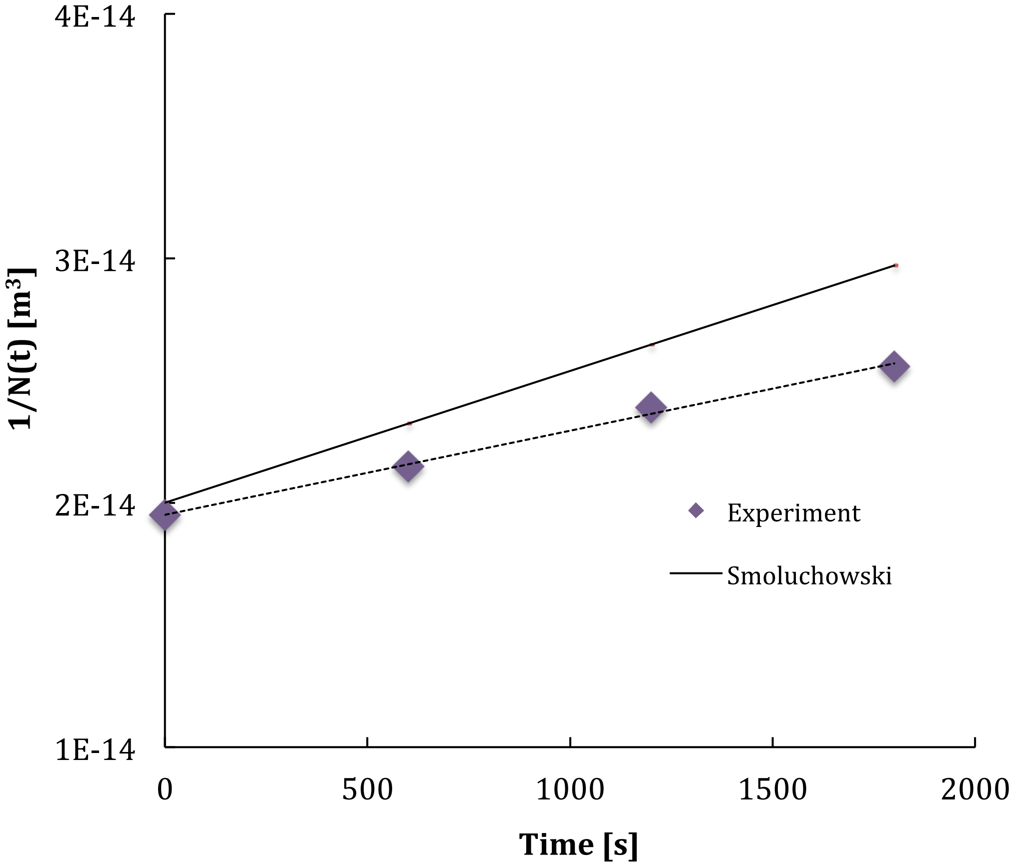


Fig.2.5 The temporal variation of the total number concentration of PSL particles with KCl 1M (salt-induced rapid aggregation). The Smoluchowski rate constant solution overestimates the fast aggregation rate.

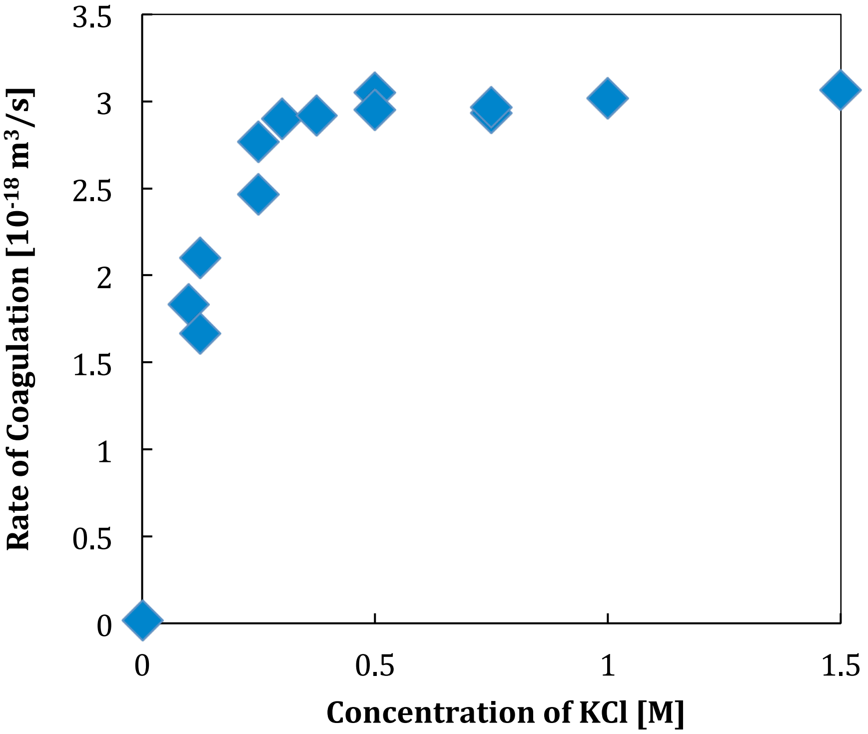


Fig.2.6 Aggregation rate constant as a function of KCl concentration.

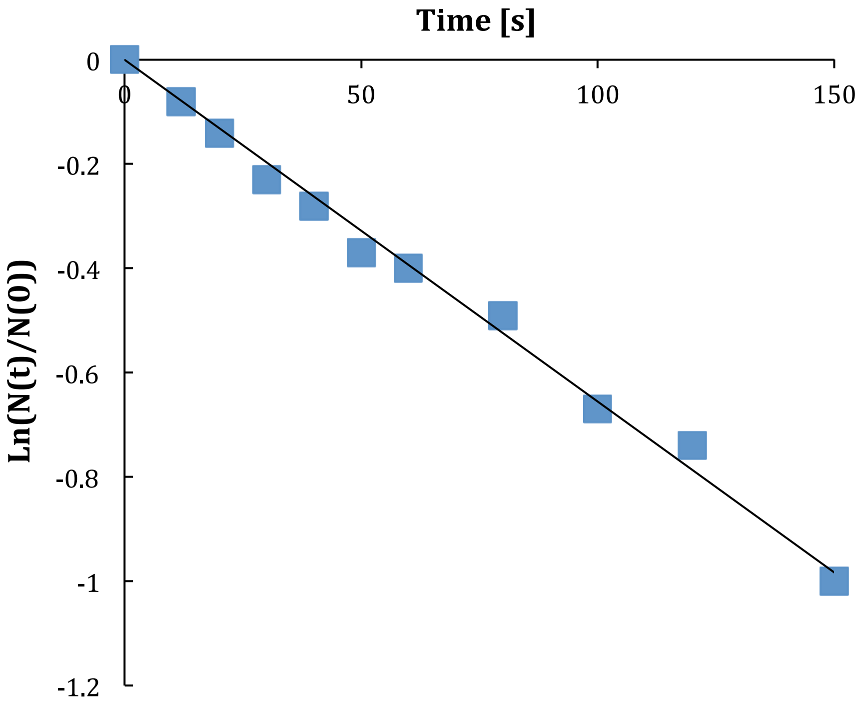


Fig.2.7 The temporal variation of the total number concentration of PSL particles with KCl 1M in the mixing flow, N(0)=5×10^7/mL.

The temporal variations of the total number concentration of particles, *N(t),* with 1M KCl in the mixing flow were shown as a function of mixing time in Fig.2.7. One can observe the linear relationship between ln(N(t)/N(0)) versus time. It suggests the validity of the equation in this mixing flow. Inserting $\mu = 0.01\ [g/cm \cdot s], \nu = 0.01\ [cm^s/s], a = 0.678\times10^{-4}\ [cm], N(0) = 5\times10^7\ [1/cm^3], A = 10^{-14}\ [erg]$ into Equation 2.13 and Equation 2.14, the rate of energy dissipation of the mixing flow, ε, can be calculated as well as the velocity gradient and collision efficiency, as shown in Table 2.1. The turbulent flow induced by the home-made apparatus is reproducible and the mixing intensity can be clearly described by these parameters. The standardized procedure of mixing will be applied in the following experiments.

Table 2.1 Turbulent flow induced by home made rotation apparatus.

Rate constant [10^{-16} m^3/s]	1.3
Collision efficiency α_T [-]	0.23
Velocity gradient $G = \sqrt{\frac{4\varepsilon}{15\pi\nu}}$ [1/s]	101
Microscale of turbulence $\lambda = \nu^{3/4}\varepsilon^{1/4}$ **[μm]**	53.8
Energy dissipation rate per volume ε **[m^2/s^3]**	0.1193

References

[1] V. Runkana, Mathematical modeling of flocculation and dispersion of colloidal suspensions, Columbia University, thesis, 2003.

[2] M. Kobayashi, Aggregation Kinetics of Colloidal Particles in Electric phenomena at interfaces and biointerfaces, Ohshima editor. Canada: Wiley, 2012.

[3] M. Von Smoluchowski, Versuch einer mathematischen thorie der koagulationkinetic kolloider leosungen. Z. Phy. Chem., 92 (1917) 129.

[4] D. N. Thomas, S. J. Judd, N. Fawcett, Flocculation Modelling: a Review, Water Res., 33 (1999) 1579.

[5] R. Hogg, T. W. Healy, D. W. Fuerstekau, Mutual Coagulation of Colloidal Dispersions, Trans. Faraday Soc., 62 (1966) 1638.

[6] Y. Adachi, Dynamic aspects of coagulation and flocculation, Adv. Colloid Interface Sci., 56 (1995) 1.

[7] K. Higashitani, Y. Masuno, Rapid coagulation of colloidal dispersion, J. Chem. Eng. Japan, 12 (1979) 460

[8] A. M. Kolmogoroff, Dokl. Akad. Nauk, SSSR, 30 (1941) 301

[9] P. G. Saffman, J. S. Turner, J. Fluid Mech., 1 (1956) 16

[10] Y. Adachi, M. A. Cohen Stuart, R. Fokkink, Initial Rates of Flocculation of Polystyrene Latex with Polyelectrolyte: Effect of Ionic Strength, J. Colloid Interface Sci., 171 (1995) 520.

[11] Y. Adachi, K. Aoki, Early-Stage Flocculation Kinetics of Polystyrene Latex Particles with Polyelectrolytes Studied in the Standardized Mixing; Contrast of Excess and Moderate Polyelectrolyte Dosage, Colloids Surfaces: A, 230 (2004) 37.

[12] Y. Adachi, J. Xiao, Initial Stage of Bridging Flocculation of PSL Particles Induced by an Addition of Polyelectrolyte under High Ionic Strength, Colloids Surfaces: A, 435

(2013) 127.

[13] J. W. Goodwin, J. Hearn, C. C. Ho, R. H. Ottewill, Studies on the Preparation and Characterisation of Monodisperse Polystyrene Latex, Colloid Polymer Sci., 252 (1974) 464.

[14] M. Kobayashi, Electrophoretic Mobility of Latex Spheres in the Presence of Divalent Ions: Experiments and Modeling, Colloid Polymer Sci., 286 (2008) 935.

[15] M. Borkovec, S. H. Behrens, Stability of Aqueous Colloidal Dispersions: Electrostatic and Steric Forces, in P. Somasundaran, A. Hubbard, Encyclopedia of Surface and Colloid Science, 2nd Ed. Marcel Dekker, New York, 2006.

[16] S. H. Behrens, M. Semmler, M. Borkovec, Aggregation in Sulfate Latex Suspensions: the Role of Charge for Stability Prediction, Progress Colloid Polymer Sci., 110 (1998) 66.