Tulips R
University of Tsukuba Repository

Initial stage dynamics of bridging flocculation of polystyrene latex particles with low charge density polycation in a mixing flow near the isoelectric point

著者別名	小林 幹佳, 足立 泰久
journal or publication title	Colloid and polymer science
volume	293
number	12
page range	3585-3593
year	2015-12
権利	(C) Springer-Verlag Berlin Heidelberg 2015 The final publication is available at Springer via http://dx.doi.org/10.1007/s00396-015-3729-y
URL	http://hdl.handle.net/2241/00131156

doi: 10.1007/s00396-015-3729-y

Initial stage dynamics of bridging flocculation of polystyrene latex particles with low charge density polycation in a mixing flow near the isoelectric point

Lili FENG[1,2], Motoyoshi KOBAYASHI[1], Yasuhisa ADACHI[1]

1. Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8572, Japan

2. North China University of Water Resources and Electric Power, No.36, Beihuan Road, Zhengzhou, Henan, China

Corresponding author: Yasuhisa Adachi

Email: adachi.yasuhisa.gu@u.tsukuba.ac.jp

Abstract:

Dynamics of ortho-kintetic flocculation of PSL particles with long chain polycation of low charge density was studied together with the adsorption process of polyelectrolyte near isoelectric point as a function of ionic strength. Within the range of investigation, the initial rate of flocculation was found to take the maximum value immediately after the onset of mixing, but the flocculation gradually slows down with the progress of adsorption. The initial rate of flocculation goes through the minimum as ionic strength increases. Without salt-addition, the rate of flocculation is about three times faster than that of salt induced rapid coagulation. With slightly increasing ionic strength the rate of flocculation slows down because of the reductions of the stiffness and the size of polymer coil in solution and also of the smooth rearrangement of adsorbed chains. The adsorption process monitored by the electrophoresis demonstrates that the zero mobility appears much earlier than the time predicted by collision process in the presence of salt (KCl 100mM). This trend can be explained by the concept of electrokinetically stagnant layer and by smooth spreading of polyelectrolyte on the colloidal surface. The kinetics of adsorption is in good accordance with the change in the flocculation rate.

Keywords: low charge density polyelectrolyte, ionic strength, bridging flocculation, steric effect, adsorption dynamics of polyelectrolyte, reconformation of polymer at interface,

1. INTRODUCTION

Polyelectrolytes dissolved in water usually interact with immersed substrates and thus modify the surface properties and particle-particle interactions. For this reason, they are conventionally used to promote flocculation in various application fields such as water/wastewater treatment [1, 2], mineral separation [3] and paper industry [4]. Recently, usage of more than two species of polyelectrolyte has attracted extensive interest to induce more effective flocculation [5]. The dynamics of polymers at interface significantly affects flocculation performance. Thus the dynamics of single polyelectrolyte at interface should be understood much more clearly. The charge neutralization of colloidal particles [6] and the formation of bridges between more than two colloidal particles [7] are recognized as the main mechanism to induce flocculation. In either case, the dynamics of polyelectrolyte adsorption is critically important. So far, numerous researchers have addressed the topic and substantial efforts have been devoted to analyze the adsorption of polymer at interface in equilibrium state [8, 9]. It should be noted, however, that most processes involving the flocculation occur essentially at non-equilibrium state [10]. For instance, just after the start of mixing operation of colloidal dispersion with polymer flocculants, the elementary events like dilution of polyelectrolyte flocculants, transport of polyelectrolyte onto the surface, particle-particle collisions,

re-conformation of polyelectrolytes at the interface, etc., take place simultaneously at non-equilibrium state [11].

However, it is not easy to obtain snapshots in this stage, and also, under such chaotic condition, extraction of any elementary event is notoriously difficult. Our approach to cope with the difficulty is to analyze the flocculation in the standard mixing flow normalized in terms of the collision frequency [12]. The comparison of the rate of flocculation with/without polymer flocculants will reveal the effects of polymer flocculants on the flocculation process. This method has been applied to investigate the flocculation process of colloidal particles with neutral polymer/ high charge density polyelectrolytes [13, 14]. It was found that the rate of flocculation in the mixing flow greatly relates to the polymer conformation in solution [15-19].

Since Gregory [6] reported that the flocculation of polystyrene latex particles with oppositely charged polyelectrolytes proceeds faster than that of salt-induced rapid coagulation under low ionic strength, a great interest has been aroused and a series of studies have revisited the similar system [20-26]. It was clarified that the heterogeneous electrostatic attraction accelerates the rate of flocculation at medium polymer dosage and that the fastest flocculation generally occurs at the isoelectric point. This effect has been extensively reported in various oppositely charged

systems such as amidine latex particle with poly(styrene sulfonate) (PSS), sulfate latex particle with linear poly(ethylene imine) (LPEI), sulfate latex particle with PAMAM dendrimers. The existence of the additional attraction was further demonstrated by colloid-probe AFM measurements. The importance of heterogeneous attractive interaction was also confirmed flocculation in the flow field [27-29].

It is recognized that polyelectrolytes with low charge density will act as bridging agent [30-32]. In our previous study, Brownian flocculation of negatively charged particles with low charge density polycation (charge density of 4%) demonstrates that the maximum rate of flocculation observed near the isoelectric point is smaller than that of salt-induced rapid coagulation [33]. The detected layer thickness of adsorbed polymers demonstrates that enhanced flocculation by “bridging” is canceled by steric hindrance effects, even at the optimum dosage of flocculation. That is, the bridging flocculation should be dynamically reconsidered by taking the re-conformation process of adsorbing polymer into account [34,35].

It can be easily imagined that the mixing operation greatly influences the competition of “bridging” and steric effect, because the hydrodynamic mixing will

enhance the collision rates not only between colloidal particles but between colloidal particles and polymer chains. However, there is no data which stand for the qualitative analysis of the rate of collisions under optimal dosage of polymer flocculants. In the present study, we design the measurement of the kinetics of bridging flocculation induced with low charge density polymer in the mixing flow to clarify the effect of ionic strength which will dramatically induce the change of conformation in solution as well as interface and presumably re-conformation process at interface. The concept of idea is schematically illustrated in Fig.1. The rate of flocculation was measured at the isoelectric point as a function of ionic strength and analyzed together with kinetics of adsorption of polyelectrolyte.

2. RATE OF COLLISION IN A TURBULENT MIXING

A theory of collision process of droplet in a turbulent flow is applied to the analysis of the rate of flocculation and the estimation of the rate of polymer adsorption in the present study. It was worked out by Saffman and Turner [36] based on the concept of local isotropy of turbulent flow. Higashitani et al. [37] pointed out the significant role of hydrodynamic interaction. On the basis of these considerations, the rate of rapid coagulation of particles in turbulent flow can be expressed as [14],

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

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; *v*, the kinematic viscosity; and α_T, the capture efficiency taking into account the Van der Waals attractive force and the hydrodynamic interactions. The value of α_T without any electrostatic repulsions can be approximately expressed as,

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

where *A* denotes the Hamaker constant and *μ* is the viscosity of the fluid [38]. At the early stage of coagulation, Eq.(1) can be approximately integrated by assuming

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

The coagulation progress in the early 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 the measurements of the rate of salt induced rapid coagulation as a function of a_0 [12, 14, 16, 17].

When polymer molecules are added, the rate of flocculation might be enhanced by the increase of collision radius. Immediately after the attachment of polymer to the colloidal particle, the effective thickness of polymer layer, δ, can be obtained from

the ratio of the rate of flocculation with and without polymer molecules as，

$$\beta = \frac{(a_0 + \delta)^3}{\alpha_T a_0^{\ 3}} \quad . \tag{5}$$

In this derivation, the hydrodynamic interaction between particles with adsorbing polymers can be assumed to be negligibly small because of highly permeable structure of polymer layer.

If one assumes the adsorption process is limited by the transport of polymer molecules to the surface, the rate of adsorption can be obtained from the collision rate of colloidal particles and polymer molecules. Usually the size of polymer molecule is not sufficiently small to neglect the contribution of Brownian motion. Therefore, the flux of polymer molecules to one colloidal particle, J_p , can be expressed by the sum of diffusion flux by Brownian motion and the collision induced by turbulent flow. That is,

$$J_p = 4\pi D_{op} R_{op} N_p + \sqrt{\frac{8\pi\varepsilon}{15\nu}} \left(a_0 + a_p\right)^3 N_p \quad . \tag{6}$$

The first term represents the contribution of Brownian motion, D_{op} , the relative diffusion constant between colloidal particles and polymer molecules, is defined as,

$$D_{op} = \frac{kT}{6\pi\eta}\left(\frac{1}{a_0} + \frac{1}{a_p}\right) \quad . \tag{7}$$

R_{op} ,is the collision radius defined as,

$$R_{op} = a_0 + a_p \quad . \tag{8}$$

Where a_p , kT , η , N_p are the radius of polymer molecules, Boltzmann constant, the viscosity of water, the number concentration of polymer molecules, respectively. The applicability of Eq.(6) has been confirmed by our previous investigation [17].

3.EXPERIMENT

3.1 Materials

Latex: The employed polystyrene latex (PSL) was prepared by the standard emulsion polymerization of styrene in the absence of surfactant [39]. The diameter of particle, determined by electron microscopy, was found to be 1.36±0.01 μm. The surface charge density was calculated from the measured electrophoretic mobility as a function of ionic strength on the basis of Ohshima's theory and Gouy-Chapman theory [40,41] and found to be about - 50 mC/m^2. The PSL suspension was sonicated for 20 minutes to eliminate the aggregates before each experiment. In all flocculation and adsorption experiments, the initial number concentration of primary particles was adjusted to be 5×10^7 [1/cm^3].

Polymer: A linear copolymer, acrylamide-2-(dimethylamino) ethyl -methacrylates methyl chloride (kindly supplied by Kaya Floc Co. Ltd.) was employed as the flocculant. The structure formula of the copolymer is shown in Fig.2. The molecular weight and the ratio of charged segment in the chain are 5.2 Mg/mol and 0.04, respectively. Hereinafter this polycation will be referred as ADEM004. The effective size in the dissolved state was determined by viscometry on the basis of Einstein's

equation, as shown in Table 1. Stock solution of ADEM004 (100 mg/L) was prepared in pure water or in potassium chloride solution and used up within one week. All solutions were filtered through 0.2 μm millipore filters prior to use.

3.2 Electrophoretic mobility

Electrophoretic mobility was measured by laser Doppler velocimetry setup (Zetasizer Nano-ZS, Malvern, UK). After mixing colloidal dispersion with polymer solution for 5 min, the electrophoretic mobility of particles was measured. The measured electrophoretic mobility at different ionic strengths is plotted against polymer dosage in Fig.3 (some data is from Ref. [33]). Experiments of flocculation and adsorption are designed based on the data of electrophoretic mobility. It should be noted that the isoelectric point decreases with increasing ionic strength. The possible cause is that the slipping plane of electrophoresis shifts from the surface of colloidal particle due to the formation of adsorbed polymer layer. Some part of counter ions will be included in the proximate stagnant region. This effect will be enhanced by increasing ionic strength which induces the compression of electric double layer. This effect was discussed qualitatively Ref.[33] and will be revisited later (section 4.1).

3.3 Mixing and Flocculation Procedure

Flocculation experiment was performed in a mixing flow generated by a homemade end-over-end rotation apparatus. The detail information was described elsewhere [14]. In the beginning, 5 mL aqueous PSL suspension is put into one side of forked flask, and 5 mL polyelectrolyte solution or KCl solution is put into the other side. Then, colloidal suspension and polyelectrolyte solution or KCl solution were mixed end-over-end with the frequency of 1 Hz until the predetermined mixing time was reached. Then, the coagulation or flocculation was monitored by counting the total number concentration of clusters, *N(t)*, by means of Coulter Counter (Multisizer 3, Coulter Co. Inc.). By assuming $A = 6 \times 10^{-21} J$, one can estimate the value of ε and α_T: $\varepsilon = 7.06 \times 10^2 cm^2/s^3$ and α_T = 0.32 [14, 17]. Then, one can calculate the flux of polymer, J_p, by putting these values and the size of polymer indicated in Table 1 into Eq. (6).

In order to clarify the adsorption of ADRM004 on the colloidal particle, the electrophoretic mobility of PSL particles adsorbing polycation was also monitored as a function of mixing time without salt addition and at 100 mM KCl. Colloidal suspension and polyelectrolyte solution were mixed using the standard mixing apparatus until the predetermined mixing time was reached. Then the sample was quickly injected into the cell and the electrophoretic mobility was measured. It takes

additionally less than 2 min.by the end of this measurement after sampling.

4. RESULTS AND DISCUSSIONS

4.1 Kinetics of Adsorption of Polyelectrolytes

Electrophoretic mobility of PSL particles adsorbing polyelectrolytes (near the isoelectric point) at two different ionic strengths (no-salt addition and 100 mM KCl) is plotted as a function of mixing time in Fig.4. Upon mixing polyelectrolyte solution and colloidal dispersions, polyelectrolytes start to adsorb onto the surface of colloidal particles. But kinetics of adsorption is rather different at two ionic strengths.

At 100 mM KCl, the absolute value of electrophoretic mobility decreases instantly and reaches the plateau in five seconds. Probably, the presence of small amounts of salt induces ion condensation of polyelectrolyte chain and weakens the rigidity of polyelectrolyte chain [42]. As a consequence, polymers take shrunk conformation and only weak interaction acts between polymer chains and the surface [43]. Both effects will bring about the smooth rearrangement of attached polymer chains on the surface [44].

Adsorption of polyelectrolyte can be regarded as transport-limited process. However, the plateau of electrophoresis does not always correspond to the saturation of adsorption. On the basis of Eq. (6), one can roughly estimate there are

fifty polyelectrolyte chains reaching the particle surface in five seconds. The total positive charges of these polyelectrolyte chains are not enough to neutralize all negative charges of particles. From the mobility data, the total amount of charge on one latex particle is roughly estimated as 2.9×10^{-13} [c]. The amount of charge in one polymer chain is estimated to be 4.5×10^{-16} [c]. With these values, approximately 650 chains are necessary to neutralize the charge of one latex particle. Therefore, we can estimate that the amount of positive charge in the adsorbed chains is ten times less than that of surface charge of particle. Probably, the shift of slipping plane toward the bulk solution [45] induces the charge screening by the contribution of counter ions, as depicted in Fig. 5. All charged segments of adsorbed polyelectrolyte chains are located in the stagnant zone between the slipping plane and the particle surface. Negative charged of colloidal particle are compensated by positive charges of adsorbed polyelectrolytes and by counter ions provided from bulk solution. This picture can qualitatively explain zero mobility of colloidal particle covered with low charge density polyelectrolytes [33].

The conjecture discussed above can also be supported by the number of adsorbed polymers, namely fifty. If one believes that the adsorption had mostly completed in the first five seconds, only one percent of added polyelectrolyte chains

are adsorbed even though there are potentially available sites for polyelectrolytes in terms of electrostatic stoichiometry. This is not realistic. On the one hand, if one uses the number of fifty to calculate the surface area occupied by one chain, it is estimated to be a circle with a radius of 108 nm. This value is close to the hydrodynamic radius of the polymer (94.8 nm). One can generally regard that the particle surface is softly covered with polyelectrolyte chains. Since the Debye length of particle is about 1 nm at 100 mM KCl, it is reasonable to assume that stagnant layer is essentially extended by the presence of adsorbed polyelectrolytes. Therefore, we can conclude that the data of electrophoresis does not always provide the quantitative information on polyelectrolyte adsorption.

Without salt addition, the conformation of the polyelectrolyte chain in solution is extremely swollen and bulky, as indicated in Table 1. J_p is estimated to be about five times larger than that at 100 mM KCl. Probably the jump of electrophoretic mobility in the beginning corresponds to this estimation. The adsorption proceeds instantly upon mixing and the process is overall transport limited. However, the larger flux of bulky swollen polymers approaching the surface is preferable to induce “kinetically controlled adsorption” [46]. Since the electrostatic repulsion acts strongly between segments of polyelectrolytes in the long range, the attachment of new

comers will be easily interfered by pre-adsorbed segments and the adsorbed chains are also restricted to rearrange freely [47]. These actions certainly retard the sequential adsorption. However, strong attraction also acts between polymer segments and oppositely charged surfaces, and it ensures that the adsorption can proceed relatively fast. The electrostatic attraction between newly approaching chains and the surfaces will gradually decrease with continuous adsorption of polymers. Meanwhile, steric effect of adsorbed polymer chains might set in and interfere the futher attachment of chains onto the surface. Therefore, the overall driving force for adsorption will gradually weaken and eventually vanish. In the present case, the duration of this period was found to be approximately 40 s as indicated Fig.4.

4.2 Flocculation Behavior

Flocculation behavior is important for its own purpose but also provides supplemental information on the conjecture discussed above. The flocculation behavior of PSL particles with polyelectrolyte was monitored at various ionic strengths. We will firstly introduce flocculation kinetics without salt addition and then discuss the effect of ionic strength on the bridging flocculation.

Temporal evolution of the total number concentration of PSL particles with

ADEM004 without salt addition is plotted against mixing time in Fig. 6. On the basis of conductivity measurement, the ionic strength is estimated to be an order of 0.001 mM and the Debye length is several hundred nanometers. Fig.6a shows the flocculation behavior near the isoelectric point (0.6 ppm) and Fig. 6b at excess dosage (1.5 ppm). General trends can be interpreted qualitatively in the same manner. The flocculation takes place immediately upon the onset of mixing and initially proceeds in a constant rate. The initial slope of the plot is steeper than that of salt-induced rapid coagulation; the rate of flocculation is faster than that of salt-induced rapid coagulation. The fact convinces that initially adsorbed polymer chains stretch out far enough over the effective range of electric double layer. It possibly takes place in the transient stage of polymer adsorption. This transient condition continues for a while so that the rate of flocculation can be accelerated by “bridging”. The picture is close to non-equilibrium flocculation proposed by Pelssers et al. [48]. However, in our case, the charge of segments is opposite to the surface, as depicted in Fig. 7, even though the amount of charge is small, these charges will reduce the effective region of electrical double layer and give rise to more effective bridging flocculation.

However the lnN(t) vs. time curve becomes upward bending in the subsequent

stage. It means the flocculation process is retarded. The retardation can be considered as a result of the formation of steric layer of adsorbed polyelectrolytes. If we compare the onset of retardation of flocculation with kinetics of adsorption indicated in Fig. 4, one can conclude that the adsorption of polyelectrolyte has been inhibited by pre-adsorbed chains before the steric effect sets in. It should be noted that the timescale of arrangement is much shorter than complete equilibrium time (a few days or more) [49].

Ascribing the enhancement of the initial rate of flocculation to the increase of collision radius, one can deduce the effective collision radius by the comparison of the slopes of lnN(t) vs. time on the basis of Eq. (5). Since the value of β was found to be 3.2, the estimated value of δ by assuming $\alpha_T = 0.32$ is estimated as 5.4 nm. This value is not the same order of the polymer size in solution (665 nm). Probably, the attachment of particles is inhibited by thick electric double layer. That is, when we imagine the situation that only one polymer chain is attached on the surface of particles as depicted in Fig.8, the direction indicated in Fig.8a leads to the successful collision to form a bridge and other direction such as indicated in Fig.8b will be failed by the repulsive interaction of electric double layers. If we take into account this effect as a new factor of Eq.(5), we can obtain more realistic value that is close to the

size of polymer in solution. If we assume to use the value of 2.0 for this factor, the value of δ is estimated as 183 nm.

In Figs. 9a-d, temporal evolution of the total number concentration of PSL particles with ADRM004 at various ionic strengths is plotted against the mixing time. General trend is the same as that observed in Fig.5; the initial fast rate of flocculation and the subsequent retardation of flocculation. Two characteristic trends should be noted here. Firstly, the duration of the initial flocculation in the presence of salt is longer than that observed without salt addition. It means swollen chains are more effective to induce steric effects. If we regard the onset of the retardation corresponds to the end of adsorption, the interpretation of adsorption process can be rationalized in terms of collision flux. That is, the amount of adsorbed polymers can be crudely estimated by the product of the flux of collision and the duration of initial flocculation. The other noticeable trend is that the initial rate of flocculation goes through a minimum against ionic strength, as indicated in Fig. 10. Higher ionic strength would reduce the size of polymer coil in solution and induce the smooth rearrangement of polyelectrolyte chains on the particle surface, both of which would make polyelectrolyte less effective as bridging flocculant. However, increasing ionic strength will reduce the electric repulsion between particles so that even short

chains protruding on the surface can easily form bridges spanning particles, which will certainly enhance the bridging flocculation. The compromise of two competing effects results in a minimum rate of bridging flocculation at medium ionic strength.

5. CONCLUSIONS

Flocculation behavior of PSL particles with low charge density polyelectrolyte near the isoelectric point was studied together with polyelectrolyte adsorption process as a function of ionic strength. The accelerated rate of flocculation observed immediately after the start of mixing demonstrates the role of protruding conformation of polyelectrolyte chains in the formation of bridges. The initial rate of flocculation takes the maximum value without salt addition reflecting the non-flexible and bulky nature of polyelectrolyte chain. The increase of ionic strength induces smooth spreading of polymer chain on the surface. The initial rate of bridging flocculation goes through a minimum as the ionic strength increases. This is probably because the conformation of polyelectrolyte on the surface and the electrostatic interaction between particles are influenced by the presence of these small ions.

Acknowledgements

This work is funded by a Grant-in-Aid for Scientific Research (A22248025 and

15H04563) from JSPS. We acknowledge Prof. M.A.Cohen Stuart for his helpful discussion on the electrophoresis data and Miss Y. Wu for her additional measurements of electrophoresis. L. F. expresses her thanks to the China scholarship Council.

REFERENCES

[1] J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, 2nd Ed. IWA publishing Inc. 2006.

[2] B. Bolto, J. Gregory (2007) Organic polyelectrolytes in water treatment. Water Research 41: 2301-2324.

[3] Agne Swerin, Lars Ödberg, Lars Wågberg (1996) An extended model for the estimation of flocculation efficiency factors in multicomponent flocculant systems. Colloids Surf. A 113: 25-38.

[4] J. B. Farrow, J. D. Swift (1996) A new procedure for assessing the performance of flocculants. Int. J. Miner. Process 46: 263-275.

[5] G. Petzold, S. Schwarz (2014) Polyelectrolyte Complexes in Flocculation Applications. Adv. Polym. Sci. 256: 25-65.

[6] J. Gregory (1973) Rates of flocculation of latex particles by cationic polymers. J. Colloid Interface Sci. 42: 448-456.

[7] R. A. Ruehrwein, D. W. Ward (1952) Mechanism of Clay Aggregation by Polyelectrolytes, Soil Sci. 73: 485-492.

[8] G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Cosgrove, B. Vincent, Polymers at Interfaces. Chapman & Hall, 1993.

[9] R. R. Netz, D. Andelman (2003) Neutral and charged polymers at interfaces. Physics Reports 308: 1-95.

[10] J. Gregory (1988) Polymer adsorption and flocculation in sheared suspensions. Colloids Surfaces 31: 231-253.

[11] Y. Adachi (1995) Dynamic aspects of coagulation and flocculation. Adv. Colloid Interface Sci. 56:1-31.

[12] Y. Adachi, M. A. Cohen Stuart, R. Fokkink (1994) Kinetics of Turbulent Coagulation Studied by Means of End-over-End Rotation. J. Colloid Interface Sci. 165:310-317.

[13] Y. Adachi, M. A. Cohen Stuart, R. Fokkink (1994) Dynamic Aspects of Bridging Flocculation Studied Using Standardized Mixing. J. Colloid Interface Sci. 167: 346-351.

[14] Y. Adachi, T. Matsumoto (1996) Dynamics of initial stage flocculation of polystyrene latex spheres with polyelectrolytes. Colloids Surf. A 113 : 229-236.

[15] L. Besra, D.K. Sengupta, S. K. Roy, P. Ay, I (2004) Influence of polymer adsorption and conformation on flocculation and dewatering of kaolin suspension. Separation Purification Tech. 37:231-246.

[16] Y. Adachi, J. Xiao (2013) Initial stage of bridging flocculation of PSL particles

induced by an addition of polyelectrolyte under high ionic strength. Colloids Surf. A 435:127-131.

[17] K. Aoki, Y. Adachi (2006) Kinetics of polyelectrolyte adsorption onto polystyrene latex particle studied using electrophoresis: Effects of molecular weight and ionic strength. J. Colloid Interface Sci. 300:69-77.

[18] P. Somasundaran, X. Yu, S. Krishnakumar (1998) Role of conformation and orientation of surfactants and polymers in controlling flocculation and dispersion of aqueous and non-aqueous suspensions. Colloids Surf. A 133:125-133.

[19] J. Gregory, S. Barany (2011) Adsorption and flocculation by polymers and polymer mixtures. Adv. Colloid Interface Sci. 169: 1-12.

[20] L. Feng, Y. Adachi, A. Kobayashi (2014) Kinetics of Brownian flocculation of polystyrene latex by cationic polyelectrolyte as a function of ionic strength. Colloids Surf. A 440:155-160.

[21] I. Popa, G. Papastavrou, M. Borkovec (2010) Charge regulation effects on electrostatic patch-charge attraction induced by adsorbed dendrimers. Physical Chemistry Chemical Physics 12:4863-4871.

[22] I. Szilagyi, G. Trefait, A.Tiraferri, P. Maroni, M. Borkovec (2014) Polyelectrolyte adsorption, interparticle forces, and colloidal aggregation. Soft Matter 10: 2479-2502

[23] M. Borkovec, I. Szilagyi, I. Popa, M. Finessi, P. Sinha, P. Manoni, G. Papastavrou (2012) Investigating forces between charged particles in the presence of oppositely charged polyelectrolytes with the multi-particle colloidal probe technique. Adv. Colloid Interface Sci. 179-182, 85-97.

[24] I. Popa, G. Gillies, G. Papastavrou, M. Borkovec (2010) Attractive and repulsive electrostatic forces between positively charged latex particles in the presence of anionic linear polyelectrolytes, J. Phys. Chem. B 114: 3170-3177.

[25] M. Borkovec, G. Papastavrou (2008) Interactions between solid surfaces with adsorbed polyelectrolytes of opposite charge. Current Opinion Colloid Interface Sci. 13: 429-437.

[26] W.Lin, M. Kobayash, M.Skarba,C.Mu, P.Galletto, M.Borkovec (2006) Heteroaggregation in binary mixtures of oppositely charged particles. Langmuir 22:1038-1047.

[27] M. Kobayashi, H. Nanaumi, Y. Muto (2009) Initial deposition rate of latex particles in the packed bed of zirconia beads. Colloids and Surf. A.347: 2-7.

[28] Y. Adachi, L. Feng, M. Kobayashi (2015) Kinetics of flocculation of polystyrene

latex particles in the mixing flow induced with high charge density polycation near the isoelectric point. Colloids Surf. A 471: 38-44.

[29] Takuya Sugimoto; Yuji Watanabe; Kobayashi Motoyoshi (2015) Kinetics of turbulent hetero-coagulation of oppositely charged colloidal particles.Theoretical Applied Mechanics Japan 63:133-145.

[30] Y. Zhou, G. V. Franks (2006) Flocculation mechanism induced by cationic polymers investigated by Light Scattering. Langmuir 22: 6775-6786.

[31] Y. Zhou, G J. Jameson, G. V. Franks (2008) Influence of polymer charge on the compressive yield stress of silica aggregated with adsorbed cationic polymers. Colloids Surf. A 331:183-194.

[32] D. Bauer, H. Buchhammer, A. Fuchs, W. Jaeger, E. Killmann, K. Lunkwitz, R. Rehmet, S. Schwarz (1999) Stability of colloidal silica, sikron and polystyrene latex influenced by the adsorption of polycations of different charge density. Colloids and Surfaces 156: 291-305.

[33] L. Feng, Y. Adachi (2014) Brownian flocculation of negatively charged latex particles with low charge density polycation at various ionic strengths. Colloids Surf. A 454: 128-134.

[34] A. Elaissari, E. Pefferkorn (1991) Aggregation modes of colloids in the presence

of block copolymer micelles. J. Colloid Interface Sci.143: 343-355.

[35] L. Ouali, J. François, E. Pefferkorn (1999) Adsorption of telechelic Poly(ethylene oxide) on colloids: Influence on colloid stability. J Colloid Interface Sci.215: 36-42.

[36] P. G. Saffman, J. S. Turner (1956) On the collision of drops in turbulent clouds. J. Fluid Mech. 1: 16-30.

[37] K. Higashitani, K. Yamauchi, Y. Matsuno, G. Hosokawa (1983) Turbulent coagulation of particles dispersed in a viscous fluid. J. Chem. Eng. Jpn. 16: 299.

[38] T. G. M. van de Ven, S. G. Mason (1977) The microrheology of colloidal dispersions VII. Orthokinetic doublet formation of spheres. Colloid Polymer Sci. 255:468-479.

[39] J. W. Goodwin, J. Hearn, C. C. Ho, R. H. Ottewill (1974) Studies on the preparation and characterisation of monodisperse polystyrene laticee. Colloid Polymer Sci. 252: 464-471.

[40] M. Kobayashi (2008) Electrophoretic mobility of latex spheres in the presence of divalent ions: experiments and modeling. Colloid Polymer Sci. 286: 935-940.

[41] H. Ohshima, Electrophoretic mobility of charged particles, in: H. Ohshima (Ed.), Electrical Phenomena at Interfaces and Biointerfaces: Fundamentals and Applications in Nano-, Bio-, and Environmental Sciences, John Wiley & Sons,

Hoboken, 2012.

[42] T. Odijk (1977) Polyelectrolytes near the rod limit. J. Polymer Sci.: Polymer Phy. Ed. 15: 477-483.

[43] A. L. Becker, K. Henzler, N. Welsch, M. Ballauff, O. Borisov (2012) Proteins and polyelectrolytes: A charged relationship. Curr. Opin. Colloid Interface Sci. 17: 90-96.

[44] K. N. Bakeev , V. A. Izumrudov , S. I. Kuchanov , A. B. Zezin , V. A. Kabanov (1992) Kinetics and mechanism of interpolyelectrolyte exchange and addition reactions. Macromolecules 25 : 4249–4254.

[45] S. Barany (2014) Polymer adsorption and electrokinetic potential of dispersed particles in weak and strong electric fields. Adv. Colloid Interface Sci. doi:10.1016/j.cis.2014.09.009

[46] J. A. De Witt, T. G. M. van de Ven (1992) Kinetics and reversibility of the adsorption of poly(vinyl alcohol) onto polystyrene latex particles. Langmuir 8: 788-793.

[47] M. Santore (2005) Dynamics in adsorbed homopolymer layers: Understanding complexity from simple starting points. Current Opinion Colloid Int. Sci. 10:176-183.

[48] E. G. M. Pelssers, M. A. Cohen Stuart, G. J. Fleer (1990) Kinetics of bridging flocculation. Role of relaxations in the polymer layer. J. Chem. Soc. Faraday Trans. 86: 1355-1361.

[49] M. A. Plunkett, P. M. Claesson, M. Ernstsson, M. W. Rutland (2003) Comparison of the Adsorption of Different Charge Density Polyelectrolytes: A Quartz Crystal Microbalance and X-ray Photoelectron Spectroscopy Study. Langmuir 19 : 4673-4681.

Fig.1 Schematic concept of bridging flocculation in the initial stage. Bridging flocculation in the initial stage can be regarded as sort of competing process of collision between particles and between particles and polymer chains, and their re-conformation. Collision process is largely influenced by the conformation of polymer chain in solution as well as its transient behavior during adsorption. In the case of polyelectrolytes, ionic strength dramatically influences the conformation in solution and re-conformation process on the surface. Hydrodynamic shear is an essential factor since the rate of collision is proportional to the third power of collision radius. Adsorbing behavior is evaluated by the rate of flocculation and electrophoresis.

Fig.2. Chemical structure of the linear copolymer of acrylamide -2-(dimethylamino)ethyl -methacrylates methyl chloride (ADEM004) used as flocculant.

Fig. 3 Electrophoretic mobility of PSL particles coated with ADEM004 as a function of polymer dosage at different ionic strengths.

Fig. 4 Temporal variation of electrophoretic mobility of PSL particle in the process of adsorption of ADEM004 near the isoelectric point. Without salt-addition (◇, C_p=*0.65 ppm*) and 100 mM KCl (○, C_p=*0.4 ppm*)

Fig. 5 Landscape of negatively charged colloidal surface covered with low charge density polycation. Diffusive counter ions are located in the stagnant zone between the shifted slipping plane and the surface of colloidal particle. Negative charges of PSL particle are compensated by charges of adsorbed polyelectrolyte chains and counter ions provided by bulk solution.

Fig. 6 ln $N(t)/N(0)$ vs t without salt addition. (a) The experiment carried out near the iep (C_p=0.65 ppm). (b) The experiment carried out at excess dosage (C_p=1.5 ppm). The result of salt-induced rapid coagulation is also plotted as the reference. The Cp refers to the concentration of polyelectrolyte.

Fig. 7 Concept of non-equilibrium flocculation modified by the counter charge located in the chain of active polymer.

Fig.8 Typical directions of two approaching particles. If one particle will approach to the other particle with an orientation of the adsorbed polymer, the bridge will be successfully formed (a). Vice versa, the two particles can not be bridged due to the repulsive interaction of electric double layers.

Fig. 9 ln $N(t)/N(0)$ vs t at different ionic strengths: (a) 1 mM KCl (C_p=0.6 ppm), (b) 10 mM KCl (C_p=0.45 ppm), (c) 100 mM KCl (C_p=0.4 ppm), (d) 500 mM KCl (C_p=0.8 ppm).

Fig.10 The initial rate of bridging flocculation as a function of ionic strength.

Table1 Viscosity and hydrodynamic radius of polyelectrolytes at different ionic strengths

KCl [mM]	0.05	0.1	10	100	500
Intrinsic viscosity [L/g]	358	69.2	13.7	10.3	6.4
a_p^e [nm]	665	179	104	94.8	64

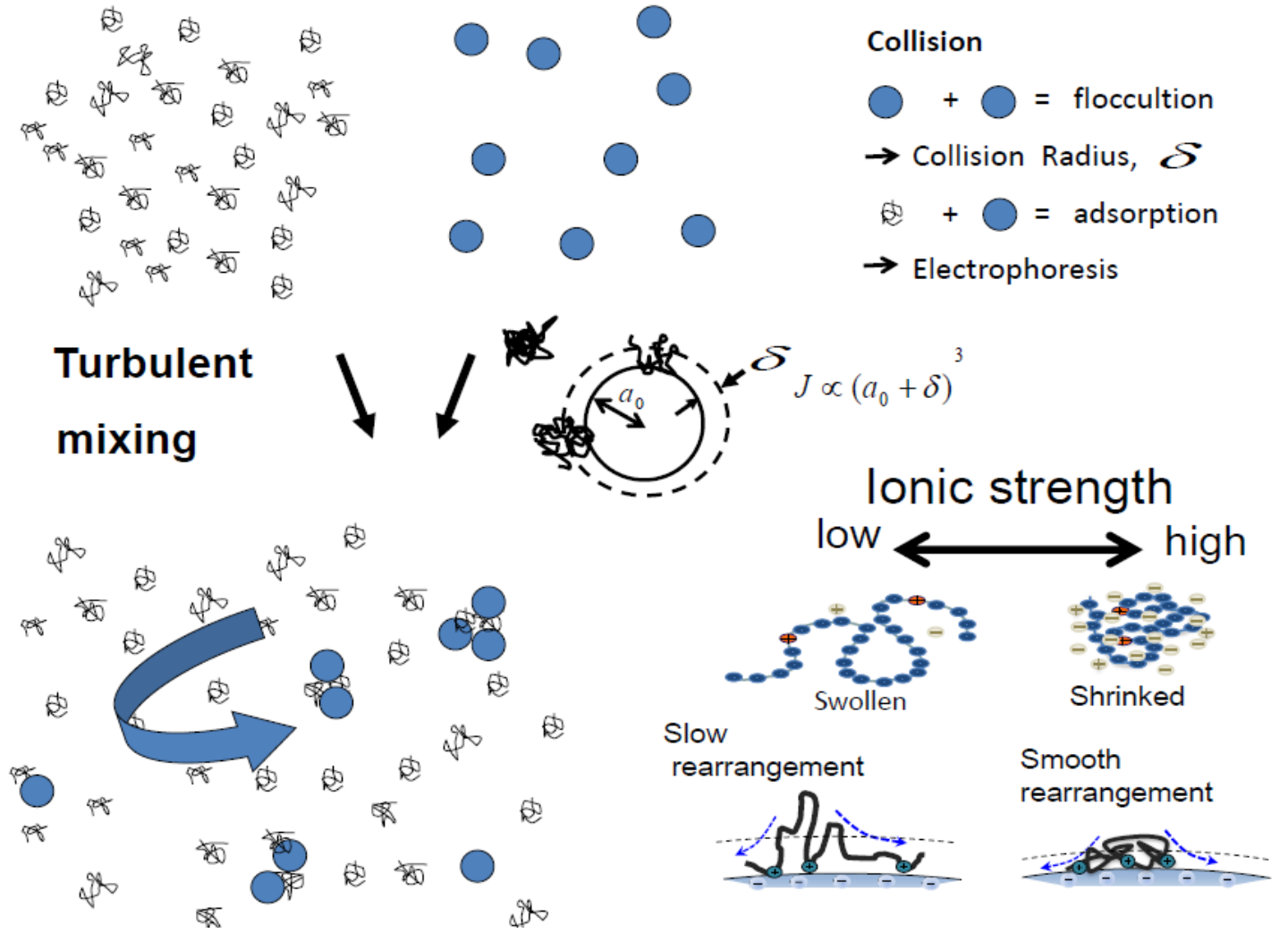

Collision
+ = flocculation
Collision Radius, δ
+ = adsorption
Electrophoresis
Turbulent mixing
δ
a_0
$J \propto (a_0 + \delta)^3$
Ionic strength
low
high
Swollen
Shrinked
Slow rearrangement
Smooth rearrangement

Fig.1

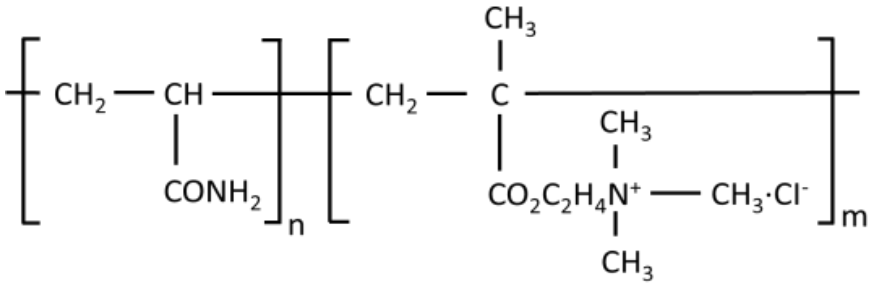


Fig.2

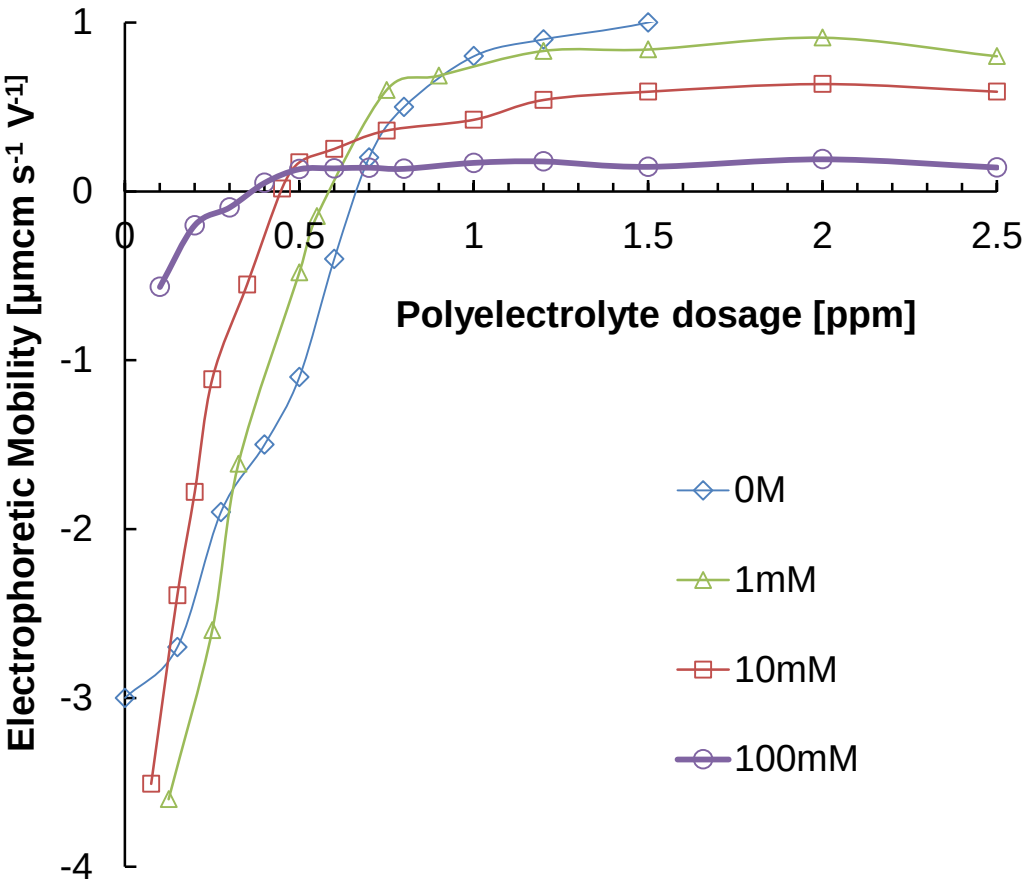

Electrophoretic Mobility [µmcm s-1 V-1]
1
0
-1
-2
-3
-4
0
0.5
1
1.5
2
2.5
Polyelectrolyte dosage [ppm]
0M
1mM
10mM
100mM

Fig.3

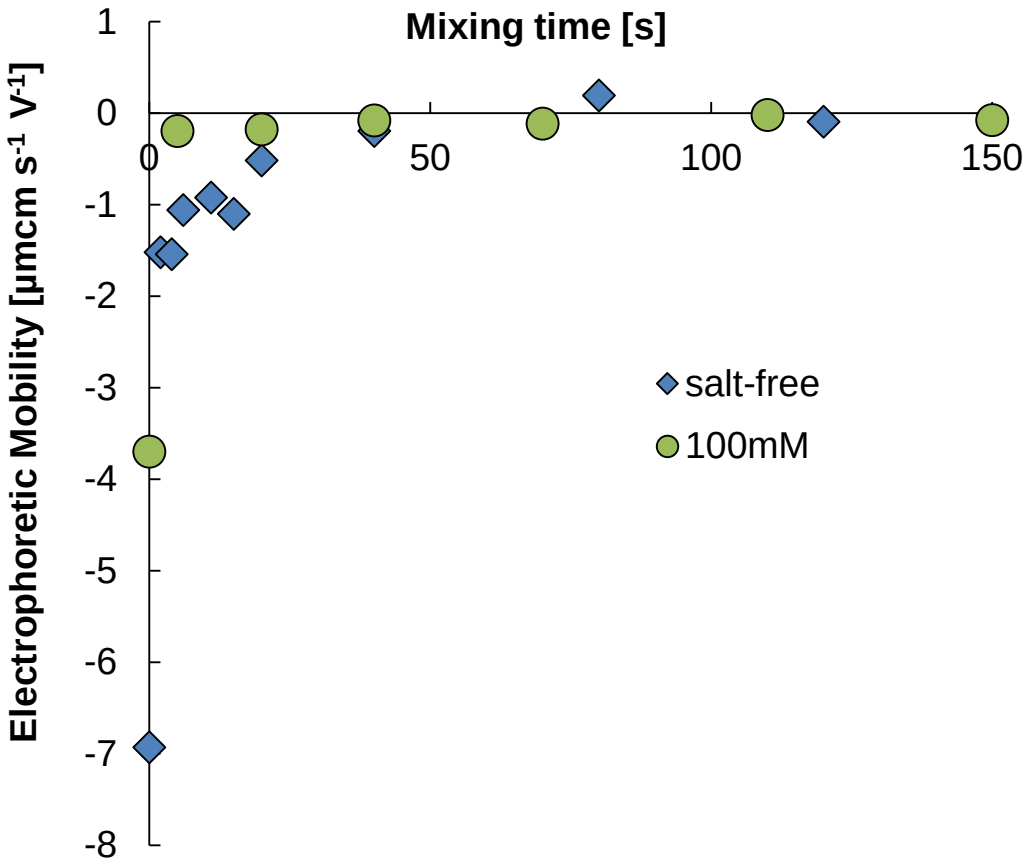

Mixing time [s]
Electrophoretic Mobility [μmcm s-1 V-1]
1
0
-1
-2
-3
-4
-5
-6
-7
-8
0
50
100
150
salt-free
100mM

Fig.4

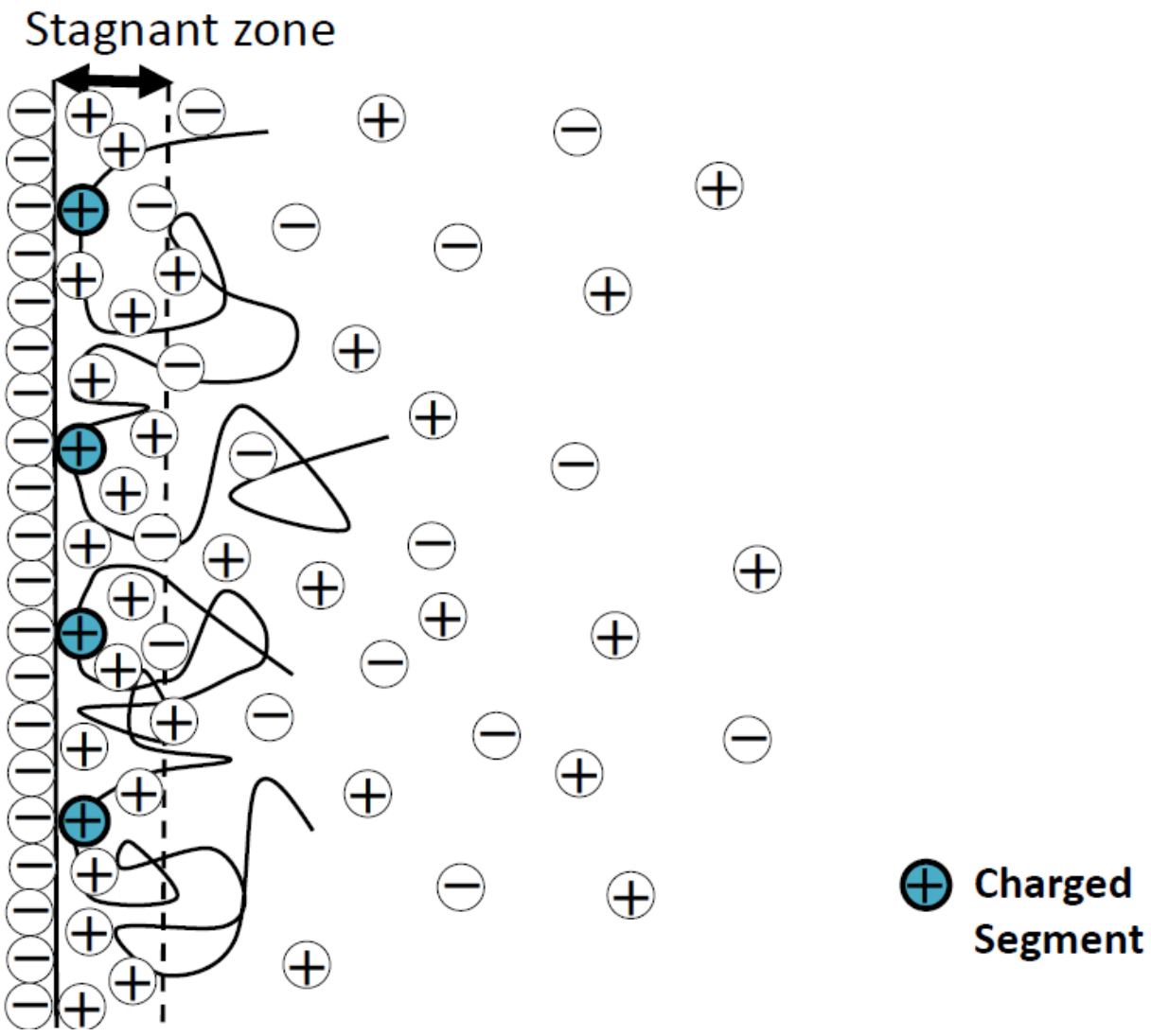
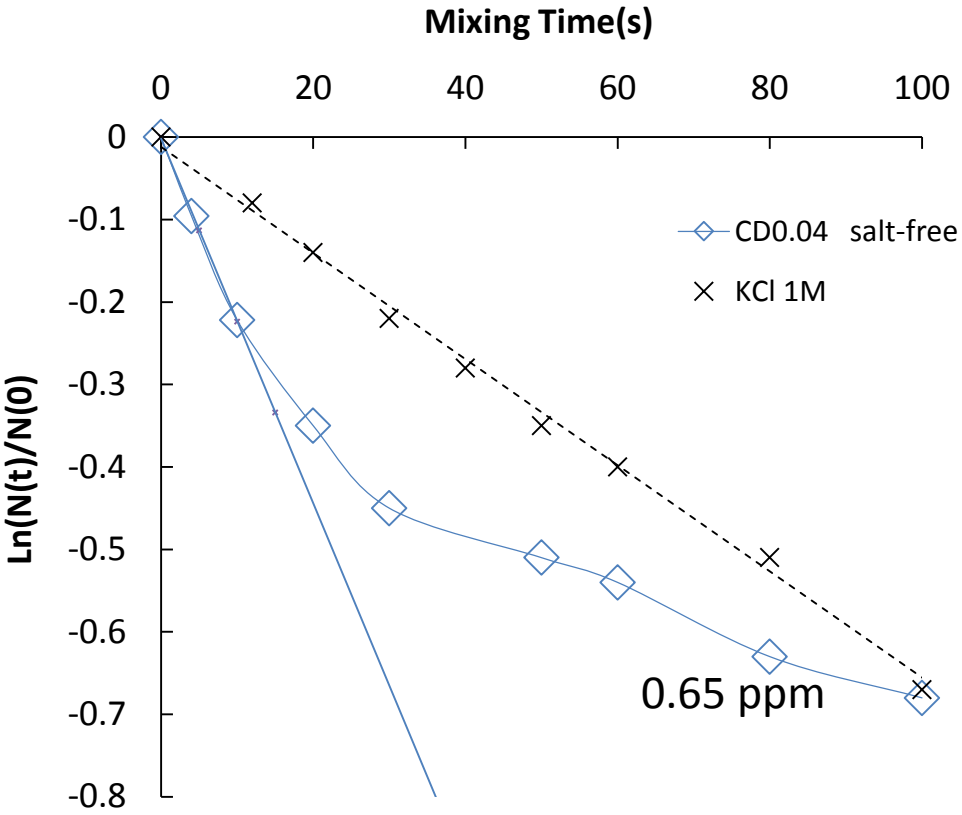


Fig.5

a)


Mixing Time(s)
0
20
40
60
80
100
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
Ln(N(t)/N(0)
CD0.04 salt-free
KCl 1M
0.65 ppm

b)

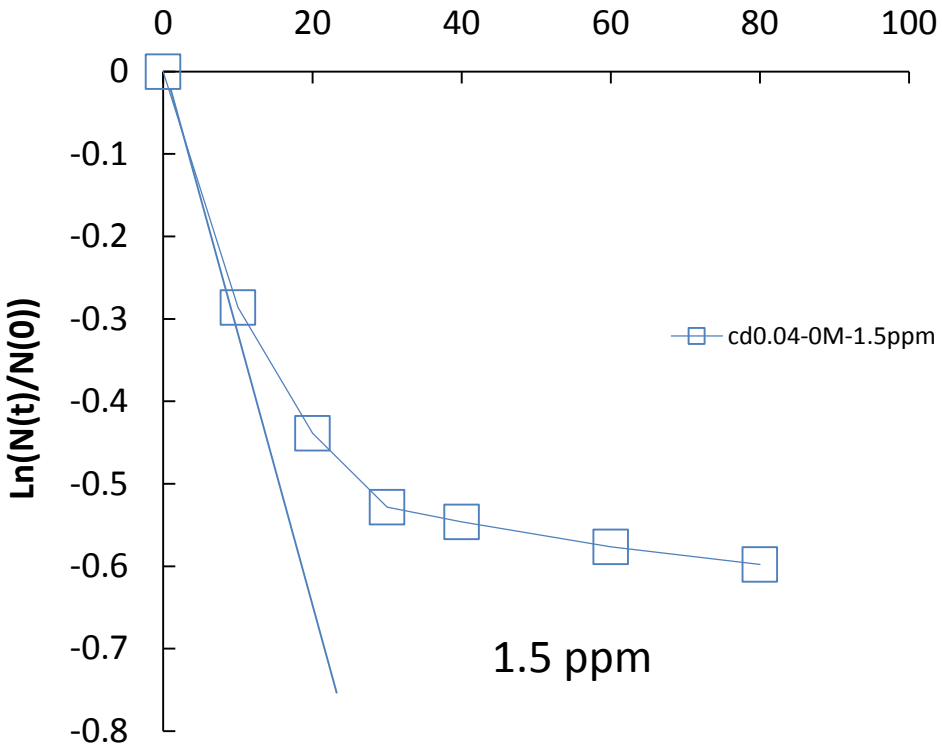

0
20
40
60
80
100
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
Ln(N(t)/N(0))
cd0.04-0M-1.5ppm
1.5 ppm

Fig.6

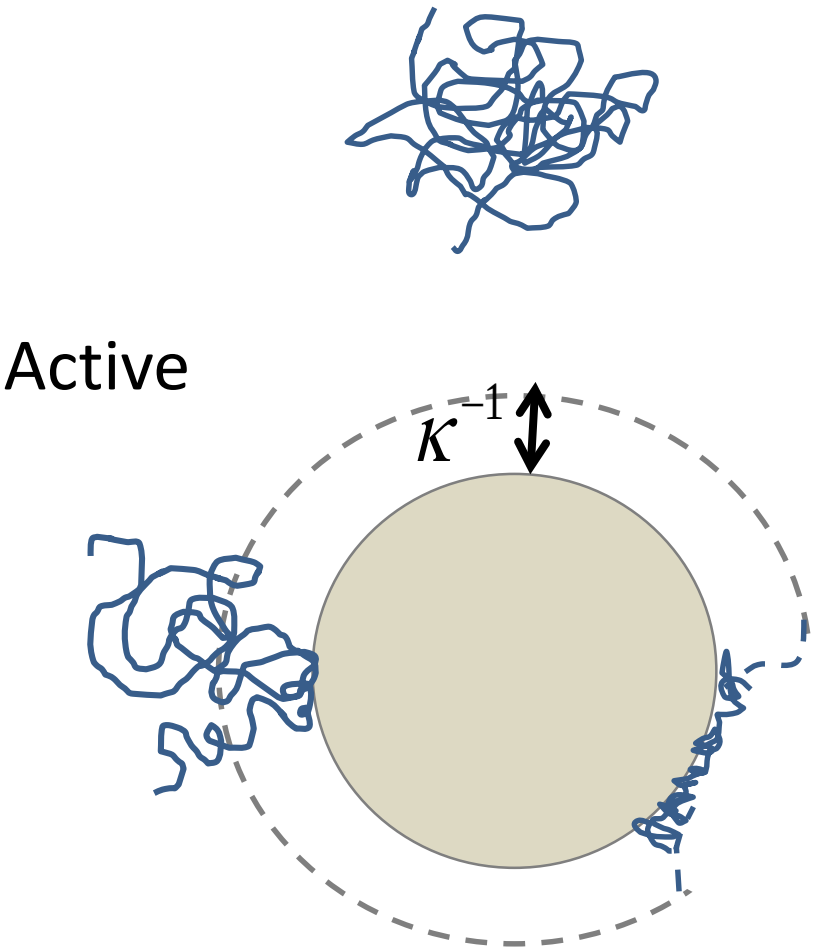
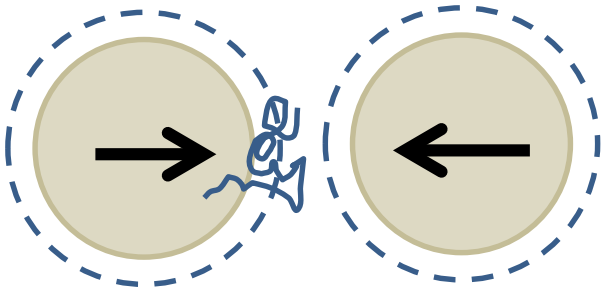
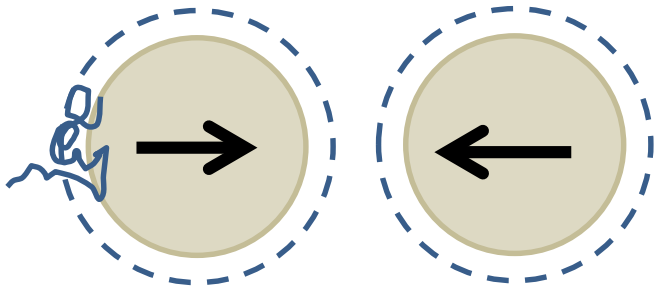


Fig.7

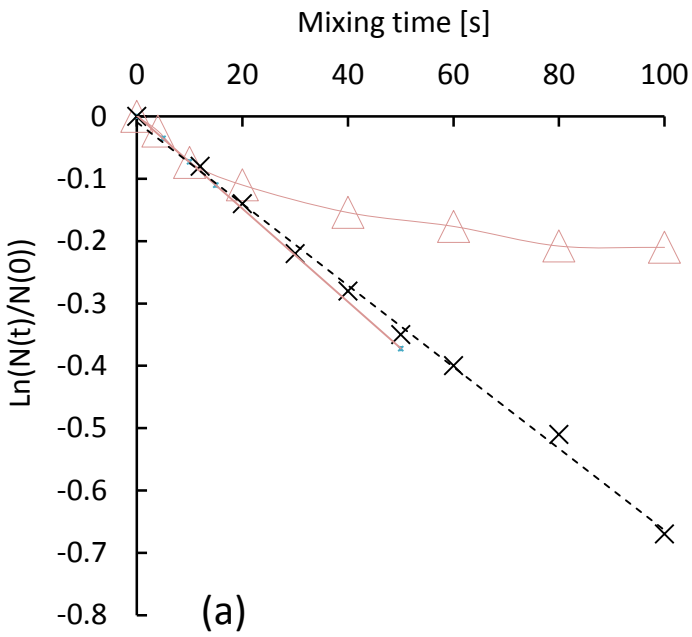


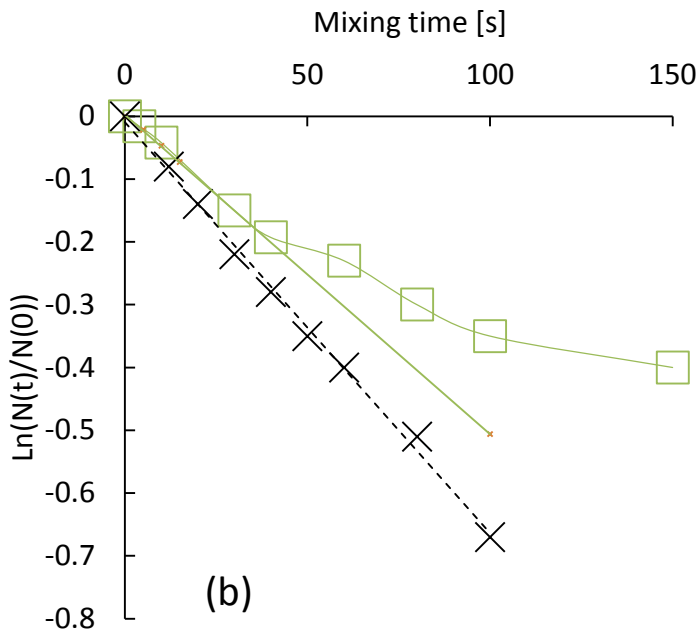
(a) Successful

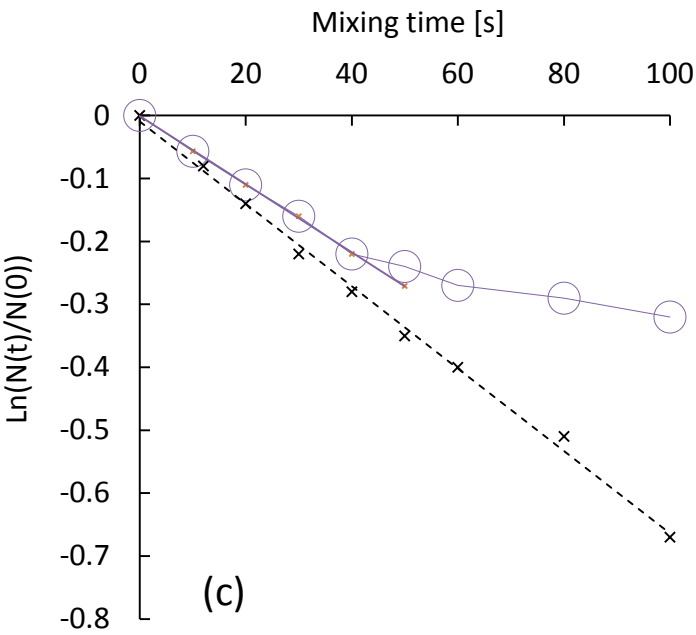


(b) Failed

Fig.8


Mixing time [s]
0
20
40
60
80
100
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
Ln(N(t)/N(0))
(a)


Mixing time [s]
0
50
100
150
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
Ln(N(t)/N(0))
(b)


Mixing time [s]
0
20
40
60
80
100
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
Ln(N(t)/N(0))
(c)

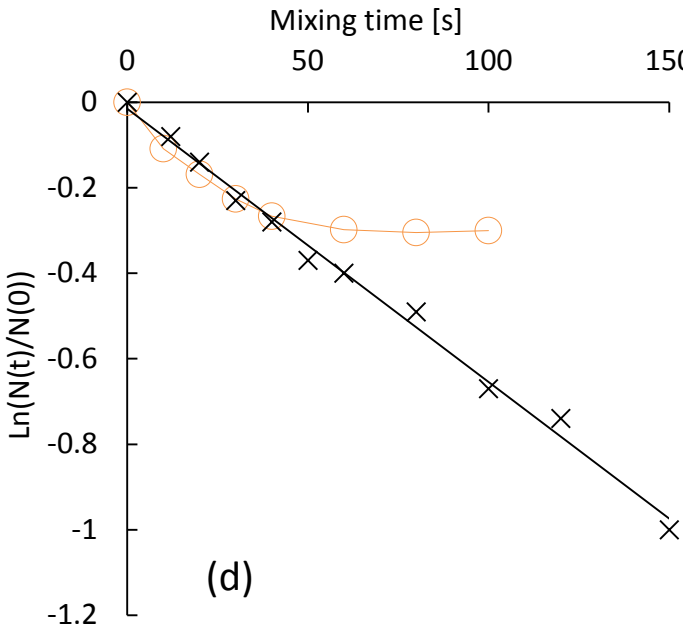

Mixing time [s]
0
50
100
150
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
Ln(N(t)/N(0))
(d)

Fig.9

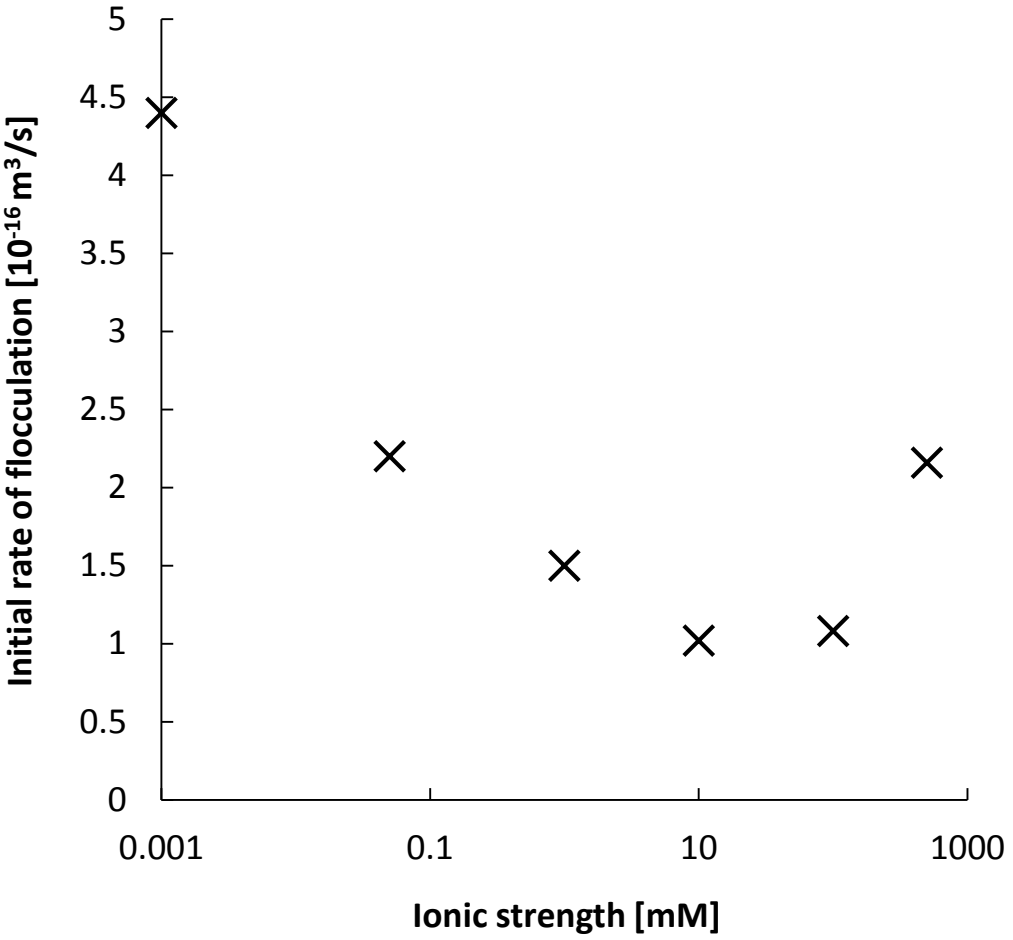

Initial rate of flocculation [10-16 m3/s]
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0.001
0.1
10
1000
Ionic strength [mM]

Fig.10