

## The effect of double layer repulsion on the rate of turbulent and Brownian aggregation: experimental consideration



T. Sugimoto<sup>a</sup>, M. Kobayashi<sup>b,\*</sup>, Y. Adachi<sup>b</sup>

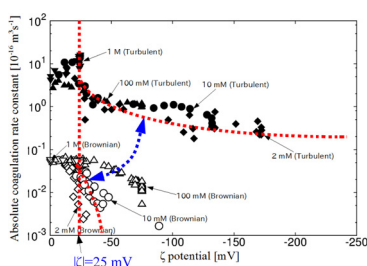
<sup>a</sup> Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8572, Japan

<sup>b</sup> Faculty of Life and Environmental Sciences, University of Tsukuba, Japan

### HIGHLIGHTS

- We measured Brownian and turbulent coagulation rate constants of carboxyl latex.
- The effect of charging behavior on the coagulation rate was studied.
- Reduction of coagulation rate with pH was more gradual in flow field.
- Zeta potential, not surface charge and potential, determines colloid stability.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 9 October 2013

Received in revised form

30 November 2013

Accepted 2 December 2013

Available online 9 December 2013

#### Keywords:

Coagulation kinetics

Absolute coagulation rate constant

Turbidity measurement with T-matrix method

Brownian coagulation

Turbulent coagulation

### ABSTRACT

Coagulation rates of well-characterized carboxyl latex particles with a diameter of 1.5  $\mu\text{m}$  were measured to study the effect of double layer repulsion on the kinetics of aggregation in the presence and the absence of turbulent flow. The absolute coagulation rate constants were determined by the turbidity measurement with T-matrix method, which is a computational method to calculate the extinction cross section of doublets. Measurements were conducted as a function of pH and KCl concentration. Turbulent flow was generated by an end-over-end rotation. Brownian coagulation was performed in quiescent condition. Both turbulent and Brownian aggregation rate constants decreased with increasing pH in 2, 10, and 100 mM KCl. In the case of 2 and 10 mM KCl, the decrease of turbulent rate constant with pH was more gradual than that of Brownian ones. Turbulent rate constants in 100 mM KCl showed lower critical pH, above which the rate decreases, compared to that of Brownian coagulation. These results are qualitatively consistent with theoretical calculation of coagulation constant. We consider that the effect of double layer repulsion on the reduction of the rate becomes small in a flow field because higher kinetic energy in a turbulent flow overcomes the energy barrier. Also, we demonstrated that fast coagulation regime is attained by reducing the magnitude of  $\zeta$  potential below 25 mV; a good indicator is  $\zeta$  potential, rather than surface potential and surface charge, when judging colloidal dispersion is stable or not.

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### 1. Introduction

The stability of colloidal dispersion and the kinetics of coagulation have been studied throughout the history of colloid science [1,2], because of scientific interest, the importance in

environmental technology (e.g. water purification, colloidal transport in natural system), and industrial applications such as food processing and cosmetics. The kinetics of coagulation is mainly determined by interparticle interaction and collision rate of colloidal particles in a suspension. The fundamental physicochemical interparticle interaction is given by the classical theory by Derjaguin, Landau, Verwey, Overbeek (DLVO) [3,4] that involves the van der Waals force and electrical double layer force. While the former force between similar particles is attractive, the latter force

\* Corresponding author. Tel.: +81 29 853 5721.

E-mail address: [kobayashi.moto.fp@u.tsukuba.ac.jp](mailto:kobayashi.moto.fp@u.tsukuba.ac.jp) (M. Kobayashi).

is usually repulsive originated by the overlap of electrical double layer. The collision rate is governed by Brownian motion and fluid motion such as laminar shear and turbulent flow [5].

The theory of coagulation kinetics due to Brownian motion and laminar shear flow was undertaken by Smoluchowski [6]. The coagulation in turbulent flow was formulated by Saffman and Turner [7] by using the Taylor theory of isotropic turbulence and Townsend's experimental result. Kolmogoroff's hypothesis of local isotropy of turbulence allows us to assume isotropic turbulence in microscale, where coagulation of colloidal particles occurs. Unfortunately, the original Smoluchowski and Saffman-Turner equations neglect any interparticle interaction although the colliding particles interact hydrodynamically and physicochemically each other in a realistic system. The improvement of Brownian coagulation kinetics (which is often called "perikinetics") was carried out by Fuchs [8] by considering an additional flux due to the potential gradient of physicochemical interaction. In addition, the Fuchs approach was modified by taking into account the hydrodynamic interaction in the diffusion coefficient depending on surface-surface distance [9,10]. The experimental verification of the kinetic theory with classical DLVO potential has been performed by many researchers [11–13]. Their results indicated that the classical DLVO theory qualitatively explains colloidal stability, but still remains far away from complete quantification even in the early stage of coagulation process where doublet (composed of two singlet particles) formation is dominant. To explain the discrepancies between experimental and theoretical values, many refinements have been suggested by taking account of additional parameters such as surface roughness and non-DLVO forces [14]. Recently, however, without introducing additional parameters, Behrens et al. [15] showed the quantitative validity of the classical DLVO theory for the prediction of stability ratio under the condition in which the surface of the particles is weakly charged.

The improvement of shear-induced coagulation kinetics (which is often called "orthokinetics") was performed by Van de Ven and Mason [16] by using the trajectory analysis in a laminar shear flow including the effect of the DLVO force and hydrodynamic retardation. Similar approach has been extended to the analysis of turbulent coagulation [17,18] in fast coagulation region where electrical double layer repulsion is negligible. These studies suggested that hydrodynamic retardation is significant and trajectory analysis is useful for the discussion in the turbulent coagulation because coagulation occurs in the microscale of turbulence, where the flow can be approximated as laminar shear flow. In slow coagulation region where electrical double layer repulsion reduces coagulation rate, the effect of ionic strength and shear rate on orthokinetic coagulation have been discussed experimentally by Sato and Kobayashi et al. [19,20]. Their results were qualitatively consistent with the prediction obtained from trajectory analysis; the larger critical coagulation concentration (CCC), which corresponds to the boundary of ionic strength between fast and slow region, and more gradual change of capture efficiency against ionic strength are expected for higher shear rates [16]. However, the effect of charge density or surface potential on orthokinetic coagulation has not been studied by systematic experiments in well-characterized system.

The pH-dependence of orthokinetic coagulation in terms of CCC was studied by Penners and Koopal by using hematite hydrosols [21]. Their results indicated that the CCC was increased as the pH departs from isoelectric point where the net charge on the particle surface becomes zero. The increase of CCC means that the electrical double layer repulsion increase as the surface charge density increases by the protonation/deprotonation of the hydroxide head-groups. However, in the Penners and Koopal study, the effect of charge density or surface potential on orthokinetic coagulation were not discussed in detail and the optical factor of doublet, which

is a prerequisite parameter to evaluate the coagulation rate constant, was not properly evaluated. In addition, rather surprisingly, the observed pH-dependence of the slope of temporal change of turbidity at CCC decreased as the pH approaches to isoelectric point although the slope at CCC should be independent of pH because the van der Waals force only should act as physicochemical force above CCC according to the DLVO theory. As mentioned above, although the shear-induced coagulations are important from an engineering point of view, systematic studies on the effect of charge density or surface potential on the shear-induced coagulation are scarce. The discussions of orthokinetic coagulation on the basis of the experimental data are not satisfactory compared with Brownian coagulation ones. Particularly, the effect of charge density or surface potential on the difference between perikinetic and orthokinetic coagulations has not been discussed by using the suspension of well-characterized charge-stabilized particles. Therefore, we still need more experimental data on orthokinetic coagulation as a function of repulsive force.

In this context, we have decided to systematically determine the absolute coagulation rate constant of well-characterized carboxyl latex from temporal change of turbidity (with absorbance) in Brownian and turbulent coagulations. In particular, to study the effect of electric double layer repulsion on the rate constants, measurements were performed as a function of pH at different ionic strengths. This choice of experimental parameter is due to the fact that the surface charge of carboxyl latex depends on pH. The charging behavior of the particle was characterized by the measurement of electrophoretic mobility and its theoretical analysis. Brownian coagulation measurements were carried out in quiescent condition, and turbulent ones were performed in a turbulent flow generated by an end-over-end rotation [18].

## 2. Theory

### 2.1. Electrophoresis and charging model

1pK-Gouy-Chapman (GC) model and Ohshima's equation were used to calculate theoretical electrophoretic mobility that is compared with experimental mobility data. In the 1pK-GC model, the surface charge is developed by the deprotonation of carboxyl head-groups written as



This dissociation equilibrium is characterized by the proton dissociation constant of the carboxyl head-group  $K$  defined as [22]

$$K = \frac{\Gamma_{-\text{COO}^-} a_{\text{H}^+}^s}{\Gamma_{-\text{COOH}}} \quad (2)$$

where  $\Gamma_{-\text{COO}^-}$ ,  $\Gamma_{-\text{COOH}}$  are the site density of respective surface head groups expressed by subscript,  $a_{\text{H}^+}^s$  is the surface activity of the protons. The dissociation constant is related to  $\text{p}K = -\log_{10} K$ . The surface charge density  $\sigma$  is determined by the site density of the deprotonated carboxyl head group as

$$\sigma = -e\Gamma_{-\text{COO}^-} \quad (3)$$

where  $e$  is the elementary charge. The surface activity of the protons is related to the surface potential  $\psi_0$  of the particle by the Boltzmann distribution as

$$a_{\text{H}^+}^s = a_{\text{H}^+}^b \exp(-\beta e\psi_0) \quad (4)$$

where  $a_{\text{H}^+}^b$  is the proton activity in the bulk with  $\text{pH} = -\log_{10} a_{\text{H}^+}^b$ ,  $\beta = 1/k_B T$  the inverse thermal energy,  $k_B$  is the Boltzmann constant,  $T$  is absolute temperature. To calculate the charge density of an

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