Initial stage of bridging flocculation of PSL particles induced by an addition of polyelectrolyte under high ionic strength

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ABSTRACT

Dynamics of colloidal flocculation of polystyrene latex (PSL) particles induced by cationic polyelectrolyte was studied in order to evaluate the effective layer thickness of adsorbing polyelectrolyte under sufficiently high ionic strength, where charges in polyelectrolyte chains are substantially shielded. The size of polyelectrolyte in the solution, a_p, was evaluated by the viscometry and by dynamic light scattering (DLS). Normalizing method of end-over-end rotation was adopted to analyze the initial-stage dynamics of flocculation. Rate of coagulation of monodispersed PSL particles induced by simple salt monitored by the Coulter Counter confirmed to be proportional to the initial number concentration, thus validating the method of analysis. Drimethylamino ethylmethacrylates with nominal molecular weights of 4.9 million and 2.0 million were tested as flocculants. In contrast to coagulation with a simple salt, the rate of flocculation just after the onset of mixing with polyelectrolyte was remarkably enhanced and then decreased or stopped abruptly after certain period. The protruding length of polyelectrolyte obtained from the enhancement of the rate of flocculation in the first stage, δ_{He}, was found to be several times larger than the size of polyelectrolyte in bulk solution determined by viscometry and DLS. Stretched conformation of polyelectrolyte chain in the mixing flow condition is the reason for the formation of apparently thick adsorbed polyelectrolyte layer.

1. Introduction

Water soluble polyelectrolytes are known to act as effective flocculants and have been used to enhance solid-liquid separation in the operation of water and wastewater treatment [1, 2]. The charge neutralization of colloidal particles or the formation of polymer bridges between more than two particles is recognized as main mechanisms to induce colloidal flocculation [3-9]. Both mechanisms are induced by the adsorption of polyelectrolyte to the colloidal surface, which is taking place in the mixing flow. The formation of effective flocs suitable for solid liquid separation is largely dependent on the adsorption process and adsorption conformation of polymer flocculants. Therefore, it is important to analyze the adsorption process of polyelectrolyte onto the surface of colloidal particles in relation to the dynamics of flocculation.

Most studies on the flocculation of colloidal particles with polyelectrolyte reported so far were performed mainly in terms of the flocculation efficiency, which is necessary for determining the optimum dosage [10-12]. Flocculation efficiencies are usually evaluated by the eventual result of flocculation monitored visually. However, critical events in the flocculation process take place just after mixing operation of the dispersion with the flocculants where the system is exposed to be far from equilibrium [13]. At this moment, the collision between colloidal particles, the adsorption of the polyelectrolyte onto the surface of these particles, and the break-up or rearrangement of flocs occurs simultaneously under the condition of turbulent flow. The adsorption of polyelectrolytes onto colloidal particles is followed by the reconformation of the adsorbed polyelectrolyte from the solution state into the adsorbed state, which is more or less a flattened conformation [14].

In our pervious studies, we have shown the way to characterize mixing flow in terms of collision process

between colloidal particles [15-17,27]. This method allows us to analyze the rate of flocculation as short as 1 s from the start of mixing. We found a remarkable enhancement of the rate of flocculation immediately after the addition of polymer flocculants. Ascribing this enhancement to an increase in the effective collision radius of colloidal particles due to the attached polymers, we confirmed that the effective thickness of the layer correlates with the size of polymer molecules existing in the bulk solution rather than the layer thickness estimated for equilibrium condition of adsorption. This conjecture has been confirmed by the data obtained for different Mw and ionic strength[18-19].

Our conclusion with regard to the kinetics of polyelectrolyte adsorption is summarized as follows. For the case of low ionic strength and high molecular weight, the rate of flocculation just after the onset of mixing of polyelectrolyte solution can be remarkably enhanced reflecting the size of polymer in solution. The largest length of protruding part of polymer attached on colliding particle is somewhat larger than the size of polymer present in static solution. However, under low ionic strength, the characterization of size of polyelectrolyte is disturbed by the effect of electrostatic repulsion between charged segments. In addition, the adsorption process and adsorbed amount of polyelectrolyte high molecular weight in the solution of low ionic strength is kinetically controlled. That is, more frequent collision between polymers and colloidal particles results in the higher amount adsorption. When we decrease the size of polymer or increase the ionic strength, the evidence of kinetically controlled adsorption detected by electrophoresis disappears. That is, the appearance of kinetically controlled polymer adsorption is related to the molecular weight of polyelectrolyte and the ionic strength of the solution. One can find the question on the role of hydrodynamic shear in the mixing flow which will enhance the collision frequency of objects with large

size, and will induce the stretching of polymer chains. These aspects are related to how the kinetically controlled polymer adsorption takes place.

So far, our studies have been carried out under relatively low ionic strength. However, the behavior of flocculation under extremely high ionic strength, such as that of sea water, has not been studied by this method. Under sufficiently high ionic strength, polyelectrolyte chains are expected to take shrunk conformation of random coils due to the shielding effect of electrostatic repulsion between neighboring charges contained in each segments. The persistent length is expected to be short to induce more flexible state of chain. Under this condition, cationic polyelectrolyte can be regarded effectively as neutral polymer. Data obtained by neutral polymer will be useful for theoretical analysis. In the present study, the size of polyelectrolyte in the solution is evaluated by the viscometry and by DLS. The flocculation experiment is performed in the standardized mixing flow generated by using an end-over-end rotation apparatus changing polyelectrolyte concentration. Coulter counter is used to measure the rate of coagulation and flocculation of PSL particles. From the comparison of the data of the size of polymer in solution, the estimated thickness of polyelectrolyte that is effective to the formation of bridge at the onset of mixing was a function of the rate of polymer supply and also found to be larger than size of polyelectrolyte in bulk solution.

2. Experimental
2.1. Materials

Monodispersed polystyrene latex (PSL) was prepared by the standard emulsion polymerization of styrene in the absence of surfactant [20,27]. The diameter of particles was determined by electron microscopy as 1356 nm with relative standard deviation of 0.04. Polyelectrolyte based on

the salt of dimethylamino ethylmethacrylate, as indicted in Fig. 1, with a nominal molecular weight of 4.9×10^6 g mol^{-1} and 2.0×10^6 g mol^{-1} kindly supplied by Kaya Floc Co. Ltd. and Mizusawa Kagaku Co. Ltd., respectively, were used. In order to estimate the effective size of the dissolved polyelectrolytes and their viscosity averaged molecular weight, the viscosity of dilute solution was measured in 1.0 M KCl solution by Cannon Fenske capillary viscometer The result of viscosity measurement is indicated in Fig.2. The molecular weight of the flocculant was calculated from the Mark-Houwink equation, $[\eta] = 3.73 \times 10^{-4} \, M_w^{0.66}$, where $[\eta]$ denotes intrinsic viscosity in 1 M KCl solution. The estimated value of the molecular weight can only be considered as a crude indication because of the expected polydispersity. The result of viscosity measurement are also used to determine the radius of polyelectrolytes on the basis

of Einstein's equation of viscosity. The hydrodynamic radius of polyelectrolyte was also monitored by DLS (FDLS-3000, Otsuka electronics Co. Ltd.). Obtained properties of flocculants are summarized in Table 1. As indicated in the figure, sizes of polyelectrolyte obtained by DLS are somewhat larger than those obtained by viscosity measurement. The ratio of radius determined by DLS (diffusion constant) to that by viscometry (the volume) is about 1.3 irrespective of Mw. We regard this is within the acceptable difference and the obtained radius can be used as an index of size of polymer chain in the static solution.

2.2 Method
2.2.1. Temporal evolution of coagulation and flocculation of colloidal particles

In a system with sufficiently high Peclet number where the contribution of Brownian coagulation can be regarded as negligibly small, the following equation for the temporal evolution of the number of colloidal particles per unit

volume, N(t), can be derived [14]

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

where a_0, ε and ν denote the radius of particles, the rate of energy dissipation per unit mass and kinematic viscosity, respectively. α_T is the capture efficiency between colloidal particles which takes into account the effect of hydrodynamic interaction. In the case of initial stage coagulation where we can assume, $N(t)^2 = N(t)N(0)$, approximate solution of Eq.(1) can be integrated as follows,

$$\ln\frac{N(t)}{N(0)} = -\alpha_T \sqrt{\frac{72\varepsilon}{15\pi\nu}} \phi \cdot t \qquad (2)$$

where ϕ denotes the volume fraction of particle.

When colloidal particles move with attached polymers, their collision radii are increased by the amount of δ_{He}. The rate of collision between colloidal particles is enhanced if the surface of the particle is not fully covered with polymer molecules so that the stabilizing effect does not appear. If we can assume that the permeable structure of the polymer layer eliminates the reducing effect of hydrodynamic interaction on the capture efficiency, the enhancement factor, β, of the rate of flocculation in the turbulent flow can be written as,

$$\beta = \frac{\left(a_0 + \delta_{He}\right)^3}{\alpha_T a_0^3} \,, \qquad (3)$$

where δ_{He} denotes the protruding length of attached polymer on the colloidal particle. Hence, if we measure the rate of flocculation of a certain mixing with and without the addition of polymers, we can derive the value of δ_{He} from the ratio of β. It should be noted that δ_{He} is the mean value of protruding length of polymer chains attaching to the colloidal surface reflecting the expected transient state from

that dissolved in solution to that adsorbed at interface. The large enhancement can be expected to disappear when the colloidal surface is fully covered by polyelectrolytes so that the effect of steric stabilization may appear.

2.2.2. Mixing procedure

Flocculation was induced by the standard procedure of colloid mixing. The solution was mixed with the same amount of colloidal dispersion using a standard end-over-end rotation apparatus with a forked flask. Initially, one side was filled with 5.0 ml of colloidal dispersion and the other with an equal volume of electrolyte (2.24 M KCl solution) or polyelectrolyte solution. Mixing was started by pouring the dispersion into the electrolyte or polyelectrolyte solution. The mixed dispersion was then poured back into the emptied side. This operation was repeated periodically until the predetermined number of mixing steps (t) was reached. The duration of one step was fixed to 1 s throughout this investigation. In order to evaluate the degree of coagulation or flocculation which occurred during sampling, sampling and dilution of the sampled dispersion were carried out exactly 10 s after the last mixing step. The rate of flocculation was measured by counting the total number concentration of clusters, N(t), with a Coulter Counter as a function of the number of mixing steps. All experiments were conducted at constant temperature room of 20°C.

3. Results and discussion

In Fig.3, temporal variation of the number of colloidal particles per unit volume for salt-induced coagulation is plotted as a function of the number of mixing steps. Each line represents results obtained for the different number concentration. As can be seen, it is quite reasonable to represent the data by straight lines over the whole range of

measurements. Since the duration of one step was fixed to 1 s, the slope of each sample, divided by 1 s, represent the rate of coagulation for each sample. The linearity of lines and the proportionality of the slopes vs N(0) verifies the validity of the applied method. From these results, we have estimated α_T as 0.31. The results for the kinetics of salt-induced coagulation provide a mean value of the mixing velocity gradient with which the kinetics of flocculation by polyelectrolyte as well as the kinetics of polyelectrolyte adsorption onto the colloidal surface can be analyzed.

Results of polyelectrolyte-induced flocculation for differing molecular weight are shown in Figs. 4 and 5. As indicated in these figures, the large enhancement of the rate of initial stage and abrupt stop of the flocculation is the common characteristics for the system of excess dosage irrespective of M_w of polyelectrolyte. In the case of moderate dosage, the gradual slope and long duration of initial stage was confirmed. This tendency is also confirmed for the system of lower ionic strength [14, 18].

3.3. Effective thickness of polymer layer

The effective length of the protruding polymer on the colloidal particle, δ_{He}, can be calculated using the difference of the initial slopes of flocculation on the basis of Eq. (3). The obtained result is summarized in Table 2. In some cases, the value of δ_{He}, calculated for lower polymer concentrations was estimated to be negative. This unrealistic result is due to neglecting the correction of capture efficiency between two colliding particles with adsorbed polymer layer. That is, in the derivation of Eq.(3), the capture efficiency of two colliding particles with adsorbed polymer is always assumed to be unity irrespective of the thickness of adsorbed layer. This assumption is acceptable for the thick layer with sufficiently high permeability. However, it is not the reality

for thin adsorbed layer. Unfortunately, no exact answer is available for this correction. We simply skip these unrealistic cases, and only the results with positive values are indicated in Table 2. It should be noted that the indicated values are minimum value. That is, if we take into the consideration of the decrease of capture efficiency due to the hydrodynamic interaction between permeable objects, the estimation of δ_{He} will increase. Nevertheless, as described in the table, remarkably large value of δ_{He} for the case of the highest dosage of polyelectrolyte was confirmed. It should be noted the values are several times larger than the size of polyelectrolyte obtained by viscometry and DLS.

The two reasons that can be considered so far are the stretching of polyelectrolyte molecules by fluid shear [21] and the formation of polyelectrolyte aggregates [22-24]. For the former, it should be noted that the critical shear rate above which a polymer chain yields to the stretched form is much higher than the effective shear rate. Our recent study on the Brownian flocculation of PSL particles suggested the formation of so-called loop-tail-train conformation of adsorbed polyelectrolyte under sufficiently high ionic strength [25]. The suggested tickness is roughly less than 50 nm for the same polymer. So, the result of our data on the detection of extremely thick layer is very remarkable as a detection of non-equiliblium aspect of polyelectrolyte in the mixing flow. For the latter; thick layer id due the presence of polyelectrolyte aggregate, although we are not able to deny completely its possibility, as was pointed out by our previous work, the time scale involved in the present study is much shorter than the time scale of hysteresis due to the formation of polyelectrolyte aggregate observed in the surface force measurement. It should also be noted that Polverari and van de Ven [26] reported that hydrodynamic layer thickness decreased when the measurement was performed in the presence of polyelectrolyte aggregate in the solution. Therefore, it is difficult to determine the effect

of the formation of polyelectrolyte aggregate.

4. Conculsion

   A reproducible method of colloid mixing carried out in our end-over-end rotation apparatus was normalized in terms of collision processes between colloid particles. The established procedure was applied to investigate the initial stage kinetics of flocculation induced by excessive addition of polyelectrolyte to the condition of sufficiently high ionic strength. The obtained results shed light not only on the kinetics of flocculation. That is, the max size of polymer layer, δ_{He}, in the role of fluid shear is larger than size of polyelectrolyte in bulk solution.

(1) The kinetics was characterized by an extreme enhancement of the rate of flocculation which will be leveled off rather abruptly after a certain period of mixing. This process was interpreted as a competition between polymer adsorption and flocculation.

(2) The effective thickness of the adsorbed layer of polyelectrolyte on the PSL particle was expressed as a function of the rate of polymer supply to the colloidal surface. It was found to be several times longer than the size of polyelectrolyte in bulk solution. This result means that stretching of polyelectrolyte chain by the hydrodynamic force upon mixing is significant in the dynamics of flocculation.

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Fig.1 Chemical structure of the salt of dimethylamino ethylmethacrylate.

Fig. 2 The intrinsic viscosity of polyelectrolyte as function of the concentration of polyelectrolyte and molecular weight. The KCl concentration is 1.0[M]. The M_w of polyelectrolyte: (◆) 4.9×10^6g mol^{-1}; (▲) 2×10^6g mol^{-1}.

Fig.3 Temporal variation of total number of clusters per unit volume in the case of salt-induced coagulation as a function of the number of mixing steps (t). [KCl]=1.12 M.
The total number concentration of PSL particle: (◆) 4.83×10^8 1 cm^{-3}; (■) 2.52×10^8 1 cm^{-3}; (●) 1.07×10^8 1 cm^{-3}; (▲) 5.11×10^7 1 cm^{-3}

Fig.4 ln(N(t)/N(0)) vs t for flocculation induced with an application of polyelectrolyte. The background solution of KCl is 1.0 M. N(0)= 5.11×10^7 1 cm^{-3}. (a) The results for higher molecular weight of polyelectrolyte ($M_w = 4.9 \times 10^6$g mol^{-1}). (b) Figure scaled up to 60 seconds. The solid line represents the regression line of the result of salt-induced coagulation taken from Fig. 4. C_p =(＋) 0.2 ppm, (×) 0.5 ppm, (▲) 1 ppm, (■) 3 ppm.

Fig.5 ln(N(t)/N(0)) vs t for flocculation induced with an application of polyelectrolyte. The background solution of KCl is 1.0 M. N(0)= 5.11×10^7 1 cm^{-3}. (a) The results for higher molecular weight of polyelectrolyte ($M_w = 2.0 \times 10^6$g mol^{-1}). (b) Figure scaled up to 60 seconds. The solid line represents the regression line of the result of salt-induced coagulation taken from Fig. 4. C_p =(＋) 0.2 ppm, (×) 0.5 ppm, (▲) 1 ppm, (■) 3 ppm.
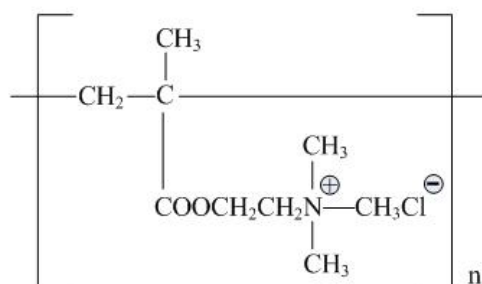
Fig. 1 - Chemical structure of the salt of dimethylamino ethylmethacrylate.
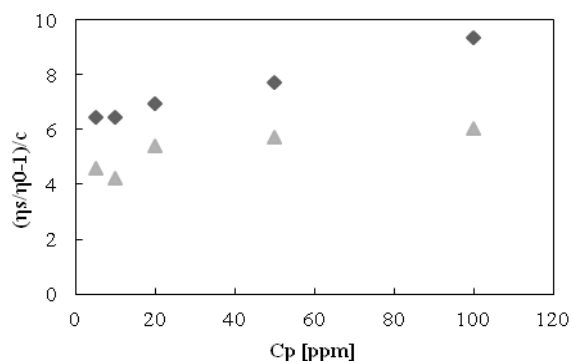
Fig. 2 - The intrinsic viscosity of polyelectrolyte as function of the concentration of polyelectrolyte and molecular weight. The KCl concentration is 1.0[M]. The M_w of polyelectrolyte: (◆) 4.9×10^6 g mol^{-1}; (▲) 2×10^6 g mol^{-1}.
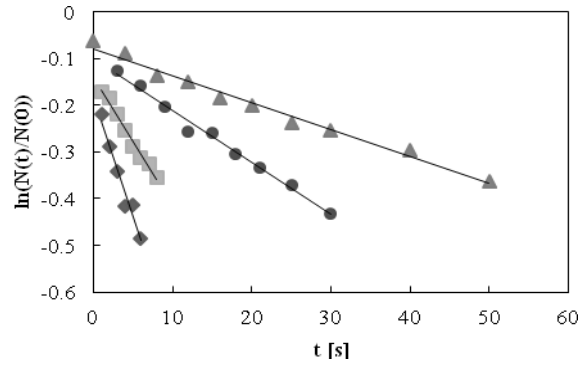
Fig.3 - Temporal variation of total number of clusters per unit volume in the case of salt-induced coagulation as a function of the number of mixing steps (t). [KCl]=1.12 M.

The total number concentration of PSL particle: (◆) 4.83×10^8 1 cm^{-3}; (■) 2.52×10^8 1 cm^{-3}; (●) 1.07×10^8 1 cm^{-3}; (▲) 5.11×10^7 1 cm^{-3}

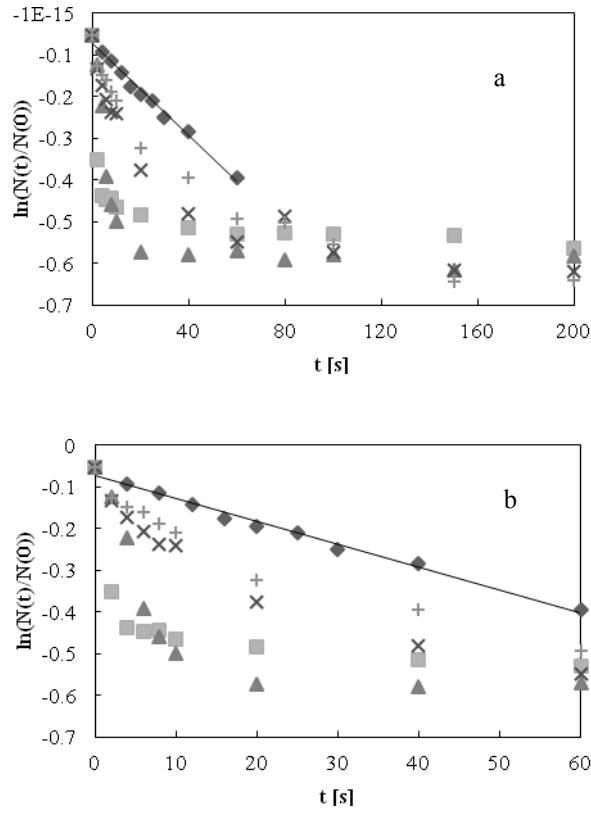**Fig. 4 - ln(N(t)/N(0)) vs t for flocculation induced with an application of polyelectrolyte. The background solution of KCl is 1.0 M. N(0)= 5.11×10^7 1 cm^{-3}. (a) The results for higher molecular weight of polyelectrolyte (M$_w$ = 4.9×10^{6}g mol^{-1}). (b) Figure scaled up to 60 seconds. The solid line represents the regression line of the result of salt-induced coagulation taken from Fig. 4. C$_p$ =(＋) 0.2 ppm, (✕) 0.5 ppm, (▲) 1 ppm, (■) 3 ppm.**
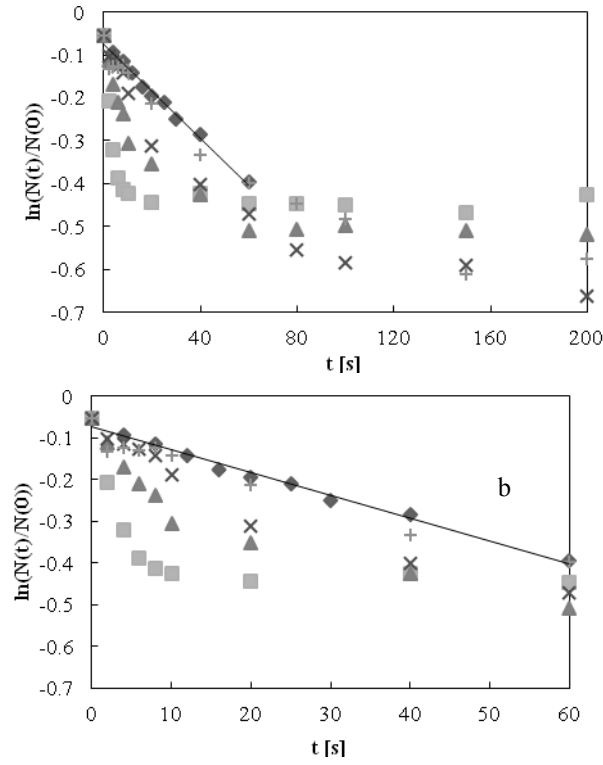
a

Fig. 5- ln(N(t)/N(0)) vs t for flocculation induced with an application of polyelectrolyte. The background solution of KCl is 1.0 M. N(0)= 5.11×10^7 1 cm^{-3}. (a) The results for higher molecular weight of polyelectrolyte ($M_w = 2.0 \times 10^6$ g mol^{-1}). (b) Figure scaled up to 60 seconds. The solid line represents the regression line of the result of salt-induced coagulation taken from Fig. 4. C_p =(+) 0.2 ppm, (×) 0.5 ppm, (▲) 1 ppm, (■) 3 ppm.

Table 1   Physical properties of flocculants

M_w (nominal, g mol^{-1}) [a]	M_η (viscosity, g mol^{-1}) [b]	a_{pv} (nm)[c]	$a_{p\,d}$(nm)[d]
4.9×10^6	2.6×10^6	64	83
2.0×10^6	1.4×10^6	45	61

[a] These values were given by the supplier.

[b] The concentration of flocculants was around 10 ppm when viscosity was measured.

[c] Estimated using Einstein's equation of viscosity on the basis of viscosity measurements.

d   Dynsmic ligth scattering

TABLE 2

Estimated Adsorbed Layer Thickness

Polyelectrolyte [ppm]	KCl 1.0M			
M_w[g/mol]	4,900,000		2,000,000	
	β	δ_{He}[nm]	β	δ_{He}[nm]
0.2	2.25	–	1.11	-
0.5	4.55	84.23	2.25	-
1	8.85	273.96	4.35	72.89
3	26.96	701.82	12.15	379.71