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# A dynamic light scattering study on aggregation of rodlike colloidal particles

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## Abstract

The kinetics of aggregation of rodlike iron(III)hydroxide colloids in aqueous solution have been investigated by dynamic light scattering.  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$  electrolytes were used in different concentrations as controllers for the aggregation kinetics. The experimental results of the cluster growth were fitted in the fast regime to the diffusion limited aggregation (DLA) and are characterized by a power law with a fractal dimension  $d_f = 1.71$ . Clearly, the slow aggregation shows the exponential kinetics of the reaction limited aggregation (RLA). In the growing curves of the colloid clusters, a transition to a very fast aggregation kinetic was observed. The transition occurred at a typical aggregate size which was crucially dependent on the colloid concentration. This was taken as an evidence for a percolation process.

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## 1. Introduction

In recent years it has been shown that the concept of fractal geometry is of significant importance for the description of aggregates built by a wide variety of colloids [1, 2]. The investigation of the dynamics of the cluster growth process is appropriate to analyse the scale invariant properties of the aggregates. The method of dynamic light scattering (DLS) [3, 4], allows the growth process to be studied without perturbing the aggregates. In the DLS experiments the time autocorrelation function of the scattered light intensity was measured, and from this it was possible to get information over the time fluctuations of the scattering particles in solution, so that their diffusion coefficient  $D$  can be analysed. With the assumption of spherical

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scattering particles and the Einstein–Stokes relation, it is possible to determine the hydrodynamic radius  $R_H$ .

Numerous experiments with monodisperse and spherical colloidal systems such as silica [5], polystyrene [6] and gold-colloids [7], showed that two fundamental mechanisms of aggregation kinetics exist. These are the fast diffusion limited aggregation (DLA), where every contact of particles ends in a permanent binding, and the slow reaction limited aggregation (RLA) where an energy barrier influences the growing process. The DLA is characterized by a power-law evolution of  $R_H$ , where the fractal dimension  $d_f$  of the clusters defines the exponent:  $R_H \propto t^{1/d_f}$ . On the other hand, the RLA shows an exponential growth of the aggregate size.

In the present paper we report DLS investigations of rodlike iron(III)hydroxide colloids having an average diameter of 3 nm and a length of 30 nm. The aggregation of these colloids was initiated and controlled in an aqueous solution by the use of the electrolytes  $\text{KNO}_3$  or  $\text{K}_2\text{SO}_4$ . Also in the case of the rodlike iron(III)hydroxide colloids it was possible to distinguish the limiting regimes of DLA and RLA. Furthermore, we observed a transition to a fast growth process at an aggregate size which was essentially dependent on the colloid concentration. We discuss a percolation process as a possibility for this behaviour.

## 2. Materials and methods

The iron(III)hydroxide colloids were prepared by Graham's method from iron(III) chloride and ammonium carbonate [8]. In aqueous solution the particles are positively charged. The charge density was found to be  $\sigma_0 = 86 \mu\text{C cm}^{-2}$  and a value of 259 mV was obtained for the surface potential ( $\Psi_0$ ). The equilibrium dispersion medium was found to be chemically equivalent with a  $10^{-4}$  M HCl solution. Transmission electron micrographs of the iron(III)hydroxide colloids showed rodlike particles with a long axis of about 30 nm and with a diameter of 3 nm. Thus a mean aspect ratio of 10 can be used to characterize the anisotropy [9]. The original iron(III)hydroxide-sol was highly concentrated (11.86 g/100 ml). For the DLS experiments it was necessary to dilute the solution. Instead of distilled water an equilibrium medium ( $10^{-4}$  M HCl solution) was used as diluent, in order to leave the surface charge density unchanged. In all, we prepared five different colloid concentrations in sufficient quantity for all the following experiments.

The aggregation was initiated and controlled by the addition of different electrolytes with a variation of their quantities. To guarantee comparable conditions for each experiment, we used two stock solutions of the electrolytes. We dissolved  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$  in bidistilled water to produce concentrations of 7.58 mol/ml and  $1.69 \times 10^{-7}$  mol/ml respectively.

The DLS experiment was carried out with the aid of an argon-laser (Spectra Physics 164,  $\lambda = 488$  nm, 400–600 mW). The incident beam of the laser was focused in the centre of the cuvette (Helma 119.000 F) which was used as a scattering cell.

A photomultiplier (EMI 9863 B/100) detected the scattered light at an angle of  $90^\circ$  with respect to the transmitted beam. The signals were processed with a 64-channel correlator (Malvern K 7032 C). The measurements were carried out at a temperature of  $26^\circ\text{C}$ . All measurements with the DLS method were performed in the same way. At first the colloid solution was poured in a clean glass reaction vessel. Then the electrolyte solution was added to the sol by using of a pipette. The mixture was shaken for a few seconds. This moment was considered to be the beginning of the aggregation process. A short time after the initiating of the aggregation the scattering cuvette was filled with the liquid from the glass vessel and was placed in the sample holder in the DLS apparatus.

The Stokes–Einstein relation, which is used for the evaluation of the autocorrelation function, is exactly valid only for monodisperse spherical particles. Therefore, for the aggregation clusters, it is only possible to discuss an apparent hydrodynamical diameter  $\Delta_{\text{app}}$ .

### 3. Results and discussion

We first describe DLS measurements on aggregating iron(III)hydroxide colloids carried out with a relative low electrolyte concentration. Fig. 1 shows a logarithmic-linear plot of the typical cluster size  $\Delta_{\text{app}}$  versus the aggregating time for an aggregation process taking place over many hours. For this experiment a colloid concentration of  $5.93 \times 10^{-4}$  g/ml and a  $\text{KNO}_3$  solution of  $0.76 \times 10^{-4}$  mol/ml was used. The solid curve represents the fit of an exponential law to our data as expected for a characteristic RLA process. This phenomenon is identical to that observed in several other experiments with spherical colloids [6, 7].

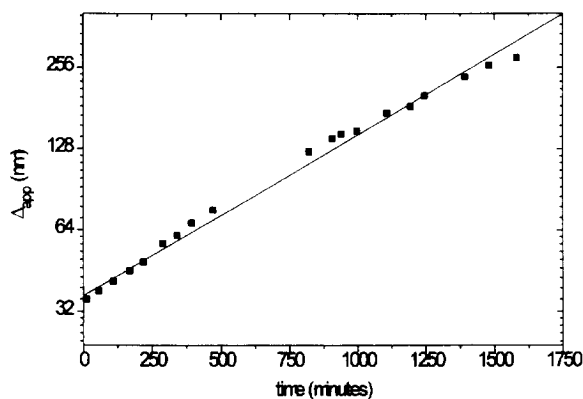


Fig. 1. The diameter of the apparent cluster size as a function of time in a log-lin form. The aggregation in a  $5.93 \times 10^{-4}$  g/ml iron(III)hydroxide concentration was initiated by a  $\text{KNO}_3$  solution of  $0.76 \times 10^{-4}$  mol/ml. The data (squares) are fitted by the exponential law of a RLA process.

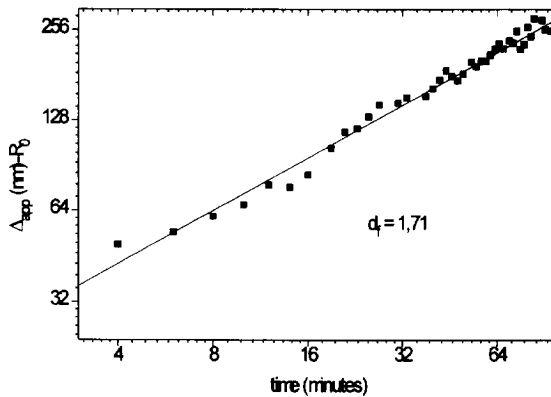


Fig. 2. Dependence of the cluster size on time for rapid aggregation in a double logarithmic form. The solid curve represents a diffusion limited aggregation with a fractal dimension of  $d_f = 1.71$ .

On the other hand we expected a power law for the cluster growth for the fast diffusion limited aggregation, where the reciprocal exponent determines their fractal dimension  $d_f$ . Fig. 2 shows a double logarithmic diagram of the aggregation of a  $2.97 \times 10^{-4}$  g/ml colloid concentration induced by a  $1.69 \times 10^{-7}$  mol/ml  $K_2SO_4$  concentration. The fitted power law yields a result for  $d_f = 1.71$  and this is also plotted as a solid curve in the figure. This result for the fractal dimension is in good agreement with values from measurements on other colloidal particle systems, for example: polystyrene  $d_f = 1.75$  [6] or synthetic melanin  $d_f = 1.80$  [10]. In a former work, we extensively studied the structure of the iron(III)hydroxid colloid clusters by the use of ultra small angle X-ray scattering and obtained a value  $d_f = 1.95$  [9]. The difference in the fractal dimension in the same colloidal systems can be attributed to the distinct reaction processes. In the X-ray investigations, the clusters' size increased over many hours, so that we had to deal with a reaction limited aggregation and not with a fast aggregation. Higher values of  $d_f$  in the RLA regime compared to the DLA are explained in the literature and were also observed in other colloidal systems [11].

Next we studied the velocity of the cluster growth as a function of the electrolyte- and colloid-concentration. For this purpose we prepared four different colloid solutions and induced the aggregation process in each solution with several different  $KNO_3$  concentrations. Two representative examples of the results are given in Figs. 3(a) and 3(b). In each case the apparent cluster size  $\Delta_{app}$  is plotted as a function of the aggregating time. In the diagrams we recognized a continuous growth process where the velocity of the aggregation rises with the increasing of the electrolyte concentration. In each growing curve we can distinguish two separate regions of very different aggregation kinetics. This special feature was observed in all experiments and also in the fast aggregation regime it becomes more obvious when the time axis is stretched. The threshold is characterized by a critical point, with nearly the same size for each colloid concentration. It seems that only a slight increase of the critical size is

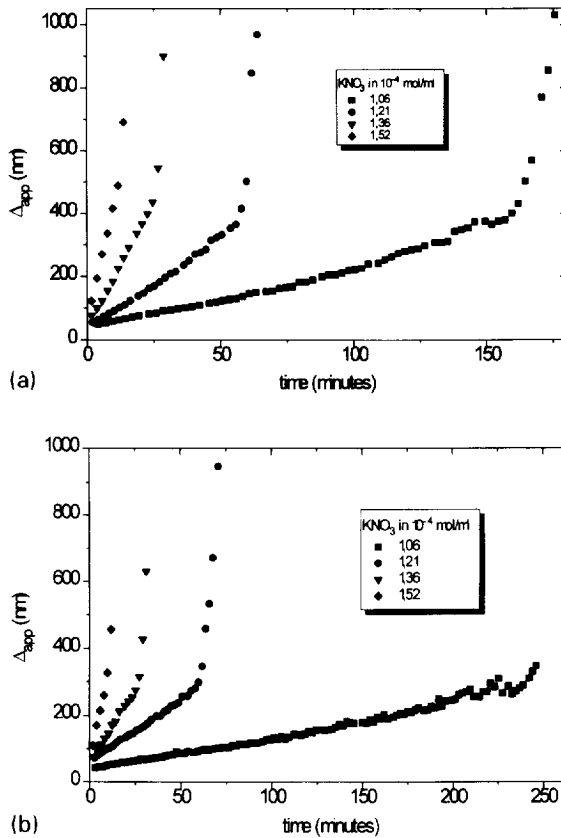


Fig. 3. Increase of characteristic cluster size by variation of the electrolyte concentration in two different colloid solutions ((a)  $5.93 \times 10^{-4}$  g/ml, (b)  $2.97 \times 10^{-4}$  g/ml). The kink in the growing curves depends on the colloid amount but not on aggregation speed.

produced by rising the electrolyte concentration. The two plots (Figs. 3(a) and (b)) show that the critical threshold size was increased by decreasing the colloid concentration. This result is verified by the data of the other used colloid concentrations.

When inspecting the diagrams in Figs. 3(a) and (b), it seems that the curves of the two colloid concentrations could be scaled to each other, with the electrolyte concentration (Fig. 3(a) respective Fig. 3(b)) defining the timescale. In order to get a quantitative interpretation of the dependence of the aggregation velocity and the special electrolyte concentration, it was necessary to analyse the different growing curves for each colloid solution.

For an individual colloid concentration we selected one cluster size and determined the time required for the aggregate size to reach this value for all growing curves and their electrolyte concentrations. Since the critical threshold size is nearly independent of the electrolyte concentration we could also refer to that value and read out  $t_k(c)$ , the threshold time for each electrolyte concentration  $c$ . After the determination of all the

Table 1

Colloid concentration in g/ml	$p$	$q$
5.93	$2.58 \pm 0.1$	$4.9 \pm 0.5$
2.97	$3.13 \pm 0.02$	$4.1 \pm 0.2$
1.48	$3.77 \pm 0.02$	$3.5 \pm 0.2$
0.95	$3.87 \pm 0.05$	$3.1 \pm 0.1$

threshold times  $t_k(c)$  for the different colloid concentrations we tried to fit the obtained values. For the fit-function we had to take into account, the existence of a limiting electrolyte concentration  $c_0$ , below which no aggregation occurs [6]. For this purpose we chose the power law:  $t_k(c)/t_0 = (p/(c/c_0 - 1))^q$ , where the normalization constant  $t_0$  is set to be one minute,  $p$  and  $q$  are fit parameters and in preliminary experiments  $c_0$  was found to be  $0.6 \times 10^{-6}$  g/ml. Table 1 shows the evaluated fit parameters for different colloid concentrations. It was found that the exponent  $q$  decreases and the value  $p$  increases with the rise of the electrolyte concentration.

Using this power law, we scaled the time axis of the growing curves of the different colloid concentrations. As examples, we present in Figs. 4(a) and (b), the scaled growing curves of the same colloid concentrations known from Figs. 3(a) and (b). It seems that scaling becomes better for higher  $\text{KNO}_3$  concentration. This is probably due to the stronger attractive interactions between particles, which results in fast coagulation. In case of smaller electrolyte concentrations a cross-over between fast and slow coagulation occurs.

The difference from an exact overlapping of the curves, can be attributed to the change of the kinetics from the diffusion limited regime to the slow reaction limited behaviour. In order to understand the appearance of the critical point in the aggregation curves, we suggest a percolation process [12] and discuss this in a simple model. The aggregation process starts in a solution of the total volume  $V_1$  containing  $N_0$  single particles. The colloids grow to clusters with the fractal dimension  $d_f$  that means, the number of particles  $N_k$  in a fractal aggregate is proportional to  $r_k^{d_f}$  with  $r_k$  is the radius of the object, or  $N_k = f^* r_k^{d_f}$  where  $f^*$  is the proportionality factor. Since the mass of an aggregate is proportional to  $N_k$  and the volume it occupies is proportional to  $r_k^3$ , the density of the aggregates decreases during the growth process. Therefore, the clusters fill more and more of the total volume of the solution. The critical cluster size is reached when the motion of a cluster is suddenly restricted by the expansion of all other aggregates. A dynamical percolation process occurs. A continuous percolation cluster appears to be unnecessary, the obstruction of the aggregates motion is sufficient. With the simplified assumption of monodisperse clusters with spherical occupied volumes and spherical covering surfaces at the critical point, we express the relationship between  $V_1$  and the volume of an aggregate with the critical size  $V_c$  in an equation:  $V_1 = N f_1^{-1} f_2^{-1} V_c$ . The factor  $f_1^{-1}$  takes into account the density of the packing and  $f_2^{-1}$  is the percolation factor.  $N$  is the number of the clusters at the

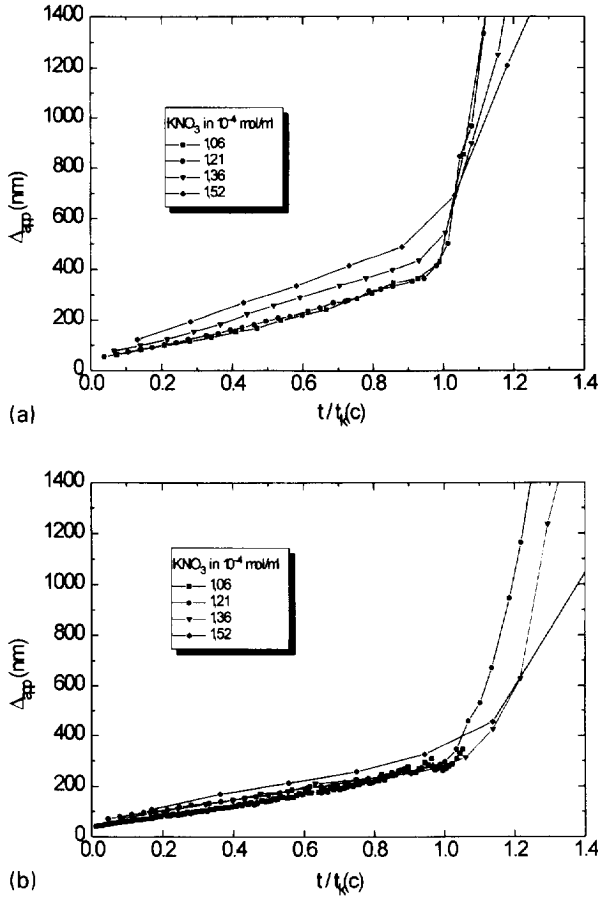


Fig. 4. Scaled growing curves for two different colloid solutions ((a)  $5.93 \times 10^{-4}$  g/ml, (b)  $2.97 \times 10^{-4}$  g/ml). The scaling law considers also the existence of a limit electrolyte concentration ( $t_k(c)/t_0 = (p/(c/c_0 - 1))^q$ ). The normalization constant  $t_0$  is one minute, the parameters  $p$  and  $q$  are shown in Table 1.

beginning of the percolation process. This can be calculated from the number of the single particles in the solution  $N_0$  and the number of the particles in a cluster with the critical size  $N_c$ :  $N_0 = NN_c$ .  $N_0$  is determined by the colloid concentration used. For  $N_c$  we arrive at the function:  $N_c = f^* r_c^{d_f}$ , where  $r_c$  is the radius of an aggregate with the critical cluster size. Now we are able to express  $r_c$  as a function that only depends on a constant factor, the colloid concentration and the fractal dimension of the aggregates:

$$r_c = \left( \frac{3}{4\pi} f_1 f_2 f^* \frac{V_1}{N_0} \right)^{1/(3-d_f)}$$

Fig. 5 shows the measured critical radius of our experiments versus the different colloid concentrations. This derivation is only valid under the assumption of

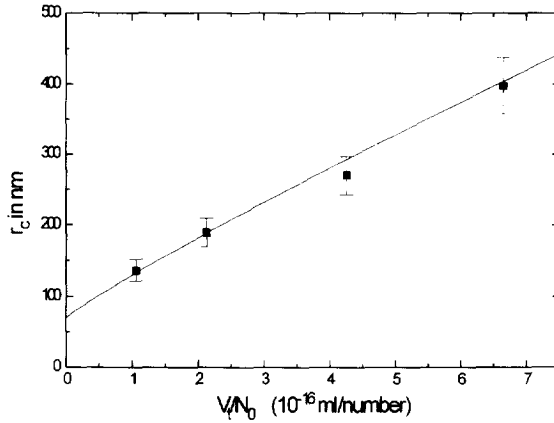


Fig. 5. Critical cluster radius as a function of  $V_t/N_0$ . The solid curve represents a theoretical attempt to describe the phenomenon with a percolation process.

non-penetrating fractal clusters. For high concentrations ( $V_t/N_0 \rightarrow 0$ ) this equation cannot be used, but in order of the existence of a finite limiting value, we introduce a constant size  $r_0$ ,

$$r_c = \left( \frac{3}{4 \cdot \pi} f_1 f_2 f^* \frac{V_t}{N_0} \right)^{1/(3-d_f)} + r_0.$$

The fit of this equation to our experimental values is also demonstrated in Fig. 5. A good description of our data was possible using only one free parameter.

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