ELSEVIER

Physica A 214 (1995) 153–161

PHYSICA A

Formation of fractal structures by aggregation of anisometric iron(III)hydroxide particles

R. Brunner[a], S. Gall[a], W. Wilke[a], M. Zrinyi[b]

[a] *Abteilung Experimentelle Physik, Universität Ulm, 86069 Ulm, Germany*

[b] *Department of Physical Chemistry, Technical University of Budapest, H-1111 Budapest, Egry J. u. 20-22, Hungary*

Received 1 October 1994

Abstract

Coagulation of anisometric iron(III)hydroxide sols has been studied by dynamic light scattering, TEM and ultra-small-angle X-ray scattering. The anisometry of rod-like individual colloidal particles can be characterised with a mean aspect ratio of 10. It was established for the first time, that the aggregates formed by coagulation of anisometric particles show definite fractal structure with a mass fractal dimension of 1.95 ± 0.05.

1. Introduction

One of the characteristics of colloidal particles is their Brownian motion. When coagulation occurs aggregates form due to the attractive interactions between particles. During the process the particles meet on Brownian trajectories, and the Brownian motion can be supposed to make its influence felt on the structure of aggregates. The first numerical approach to the problem of random aggregation was proposed by Vold in 1963 [1]. She developed a method in which a computer was used to simulate the formation of aggregates. Since this pioneering work there has been considerable progress in computational techniques and scientific approaches. As a result of these, a wide variety of models are now available. Among these the most important for aggregation phenomena is the family of clustering of cluster models [2]. These models involve the effects of finite particle concentration, collision efficiency, restructuring as well as the multiple stationary growth. There is ground to suppose that in case of dilute sols the initial flocculation process can be described by the Brownian cluster–cluster aggregation model. There exist two limiting situations: a rapid, diffusion-limited, and a slow, reaction-limited aggregation [3]. Two colliding clusters stick together immediately in the diffusion-limited case

SSDI 0378-4371(94)00255-X

(rapid coagulation), whereas in the reaction-limited coagulation, the sticking probability is vanishingly small (slow coagulation). The common feature of mentioned clustering of cluster models is that they all show similar and characteristic properties: very tenuous structure, exhibiting in general more holes than matter. An important geometrical property is the self-similarity, which can be described by a fractal dimension d_f. Aggregates which grow under the condition of diffusion-limited aggregation have $d_f = 1.78$, whereas the chemically controlled structure formation can be characterized by $d_f = 1.94$. Also experimental measurements showing that the aggregation of particles, such as silica-, gold-, and polystyrene spheres results in fractal clusters, are well established [3–5].

It is important to emphasize that both computer simulations and experimental studies consider only spherical particles. The effects of anisometry of the single particles has not been taken into consideration as yet. It is well known that if the particles of a dispersion are anisometric, they are quite likely to form aggregates that have very loose structures [6]. However much less investigated and understood is the fractal dimension of aggregates formed by coagulation (flocculation) of anisometric particles. Therefore the main purpose of the present work is to study the coagulation of rod-like colloidal particles in order to establish the influence of particle anisometry on the fractal dimension of the aggregates. Previous experimental results support the assumption that aggregates of anisometric, rod-like particles are also fractal objects [7,8].

In this work an attempt is made in order to determine the fractal dimension by ultra-small-angle X-ray scattering.

2. Experimental

2.1. Materials

For the experiments iron(III)hydroxide sol was used which was prepared by Grahams' method [9]. The particles are positively charged in aqueous dispersion. The surface charge density was found to be $\sigma_0 = 86\ \mu C/cm^{-2}$. For the surface potential, $\psi_0 = 259$ mV was obtained by measuring the electrophoretic mobility. The iron(III)hydroxide particles are not spherical. Transmission electron microscopy with the aid of a Zeiss EM 902, has shown rod-like particles with a long axis of 20–30 nm and with a diameter of 2–3 nm, as can be seen in Fig. 1. Thus a mean aspect ratio of 10 can be used to characterize the anisometry.

The aggregation is initiated by addition of an electrolyte, for example KNO_3 or K_2SO_4. The growth rate is controlled by the concentration of the electrolyte and can be varied over orders of magnitude. The aggregation process can be stopped by addition of polyvinylalcohol (PVA) into the solution. The PVA provides a steric stabilization due to adsorbtion on the surface of the particles. Thus it is possible to achieve systems in which the clusters were formed at certain growth rates over certain time periods. After stopping the growth process it is possible to preserve the aggregates by embedding them into a gel. This preparation even prevents sedimentation of the aggregates of larger sizes.

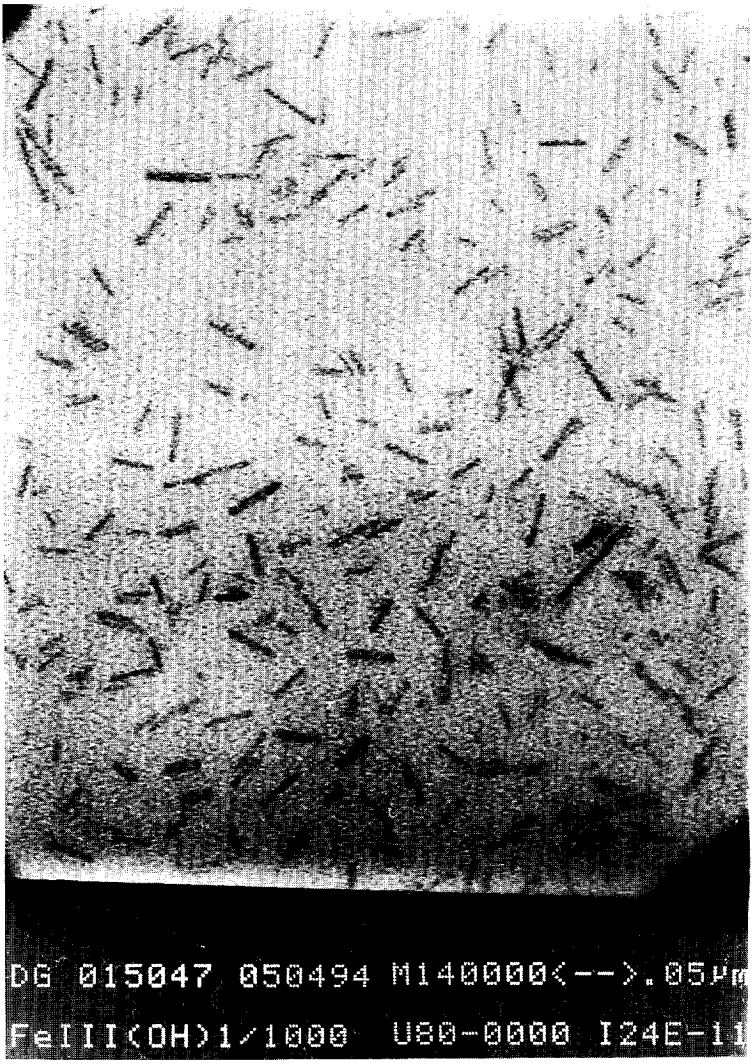

Fig. 1. Rod-like IS single particles.

A more detailed description can be found in [7].

2.2. Methods

We have investigated the structure formation of anisometric iron(III)hydroxide particles (IS) using dynamic light scattering (DLS), transmission electron microscopy (TEM) and ultra-small-angle X-ray scattering (USAXS).

DLS data were obtained using the Malvern K7032-OS correlator system [12]. The excitation source is an argon/krypton laser from Spectra Physics with a wave length of

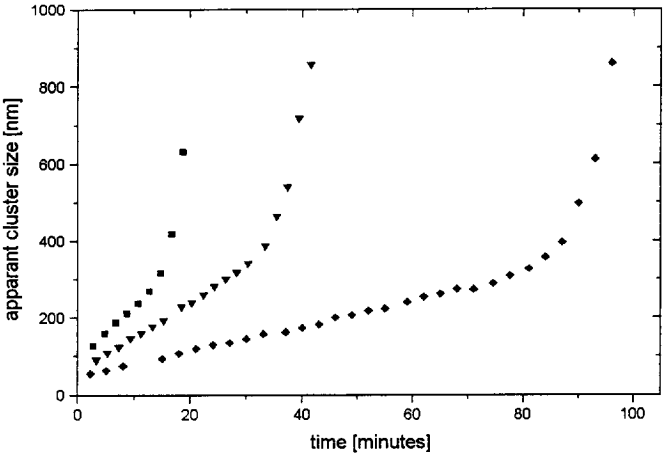

Fig. 2. The apparent cluster size vs. the period of time since initiation of aggregation for a system of iron(III)hydroxide particles using KNO_3 as electrolyte. The squares show data for a KNO_3 concentration of 1.82×10^{-3} mol, the triangles are for an electrolyte concentration of 1.52×10^{-3} mol and the diamonds for 1.36×10^{-3} mol.

488 nm. The measurements were performed at a scattering angle of 90°.

Transmission electron micrographs were obtained by elastic bright field imaging with the Zeiss EM 902 transmission electron microscope. In contrast with global bright field imaging the inelastically scattered electrons are faded out by an energy loss spectrometer, which is integrated into the optical axis of the microscope. The advantages of this operation mode are improved spatial resolution and higher contrast.

The scattering experiments were done at the HASYLAB/DESY on beamline BW4 (USAXS) with 0.154 nm X-rays. We were using a two-dimensional detector (Gabriel) with a diameter of 180 mm and 512 channels. The distance from the sample to the detector was 12.20 m. With this experimental setup the smallest accessible scattering vector $b = 2 \sin\theta/\lambda$ is about 2.7×10^{-3} nm^{-1}.

3. Results and discussion

With the dynamic light scattering experiments we measured the time evolution of the socalled apparent cluster size of the aggregates. The evaluation of this cluster size is based on the assumption of monodispers spherical particles with uniform density. There was no account taken on the fact that the growing clusters do not meet these requirements. Fig. 2 shows the size evolution at three electrolyte concentrations with the same particle concentrations. These concentrations are low enough to ensure, that no gelation process can occur. It is obvious from this plot that the growth rate of the aggregates increases with the electrolyte-concentration (here KNO_3), and therefore we now have the possibility to control growth process. It is remarkable that the growing process is slower at the beginning of the aggregation and it becomes significantly faster

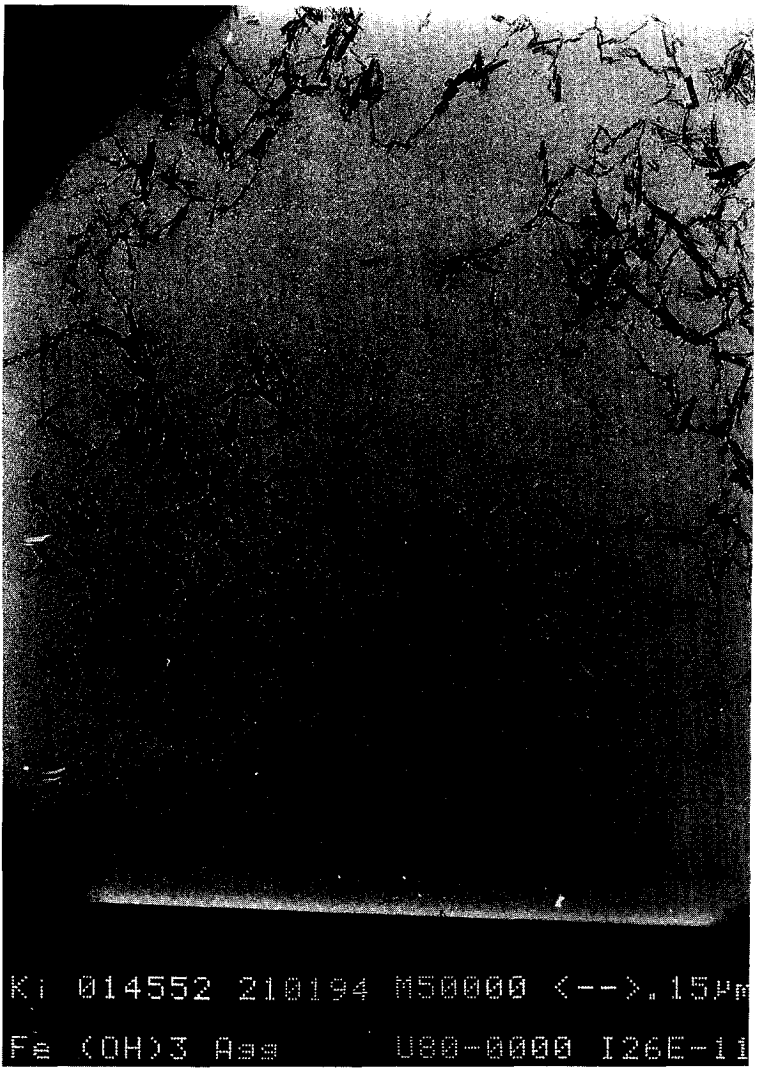

Fig. 3. Cluster of IS particles as result of fast aggregation. In the case of high growth rates very loose structures with only small regions of parallel arrangement of the monomers are formed.

after a certain time. It seems that this effect appears always by the same apparent cluster size, independent of the electrolyte-concentration.

Figs. 3 and 4 show electron micrographs from IS particle-aggregates formed with different growth rates. Fig. 3 is a result of fast aggregation, whereas the aggregate in Fig. 4 was grown over a period of 1 hour using a lower concentration of electrolyte. Of course, an exact interpretation of this effect requires both more experimental data (various particle and electrolyte concentrations, longer time scales) and a more detailed theoretical approach for evaluating the cluster size.

Obviously the structure of the clusters is strongly influenced by the reaction kinetics:

Fig. 4. Cluster of IS particles grown with a lower growth rate as the clusters of Fig. 3. The influence of the reaction kinetic can be seen: the regions of parallel arrangement of the rod-like single particles are larger, resulting in a more dense structure than in the case of fast aggregation.

in Fig. 4 much larger subunits, consisting of more or less parallel oriented particles were formed. In the case of fast aggregation the regions of this parallel arrangement of the rod-like monomers are smaller, resulting in a less dense structure of the aggregates.

The USAXS experiments were performed with gel-samples (polyvinylalcohol), filled with non-coagulated single particles and with clusters. Fig. 5 shows the scattering intensity as a function of the scattering vector obtained from a gel sample filled with single particles. It must be mentioned that the gel itself does not exhibit any scattering intensity in the observed range of the scattering vector. The anisometry of rod-like particles was

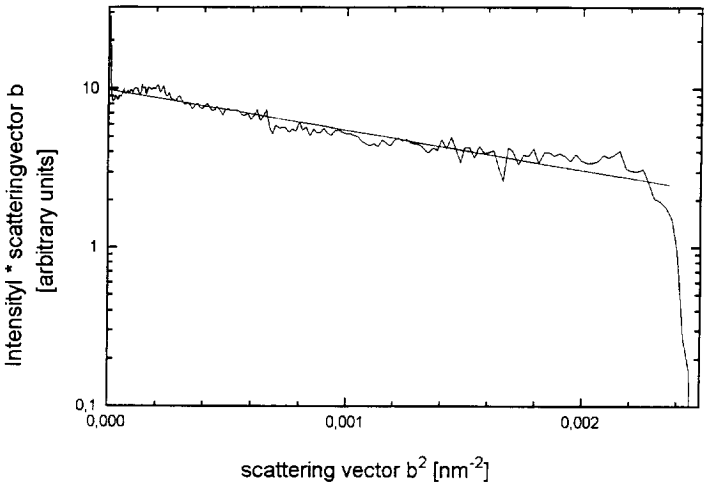

Fig. 5. The logarithm of the product of the scattering intensity $I(b)$ and the scattering vector b vs. the square of b. The data were obtained from a gel sample filled with single particles. The slope of the indicated straight line yields a cross-sectional radius of gyration of 3.57 nm for the rod-like single particles.

taken into account by multiplying the intensity $I(b)$ with the scattering vector b, thus yielding the cross-section function I_c,

$$I_c(b) = b \cdot I(b) ,$$

with

$$I_c(b) \propto e^{-(4/2)\pi^2 b^2 R_c^2} ,$$

where $b = (2\sin\theta)/\lambda$. For $I_c(b)$ is related only to the cross-section of the particles, the radius of gyration R_c is also related to the cross-section [13].

The evaluated value of $R_c = 3.57$ nm is well in agreement with TEM-analysis. This presents a further confirmation of the occurence of small bundles of parallel oriented rods, as they can be seen in the micrograph (Fig. 1). This indicates that even in the stable sol a reversible aggregation due to the secondary minimum of the DLVO-potential occurs. This was already mentioned by Maeda et al. [9] and Haas et al. [7], who observed the same phenomenon for IS-particles, which were incorporated in a polymer matrix.

Fig. 6 represents a double logarithmic plot of the scattering intensity for a gel sample filled with aggregates. The intensity $I(b)$ can be written as

$$I(b) \propto P(b) \cdot \overline{S(b)} ,$$

where $P(b) = \overline{|F(b)|^2}$ with the form factor $F(b)$ of the particle. $\overline{S(b)}$ is the effective structure factor

$$\overline{S(b)} = 1 + \frac{\left|\overline{F(b)}\right|^2}{\overline{|F(b)|^2}} \cdot [S(b) - 1] ,$$

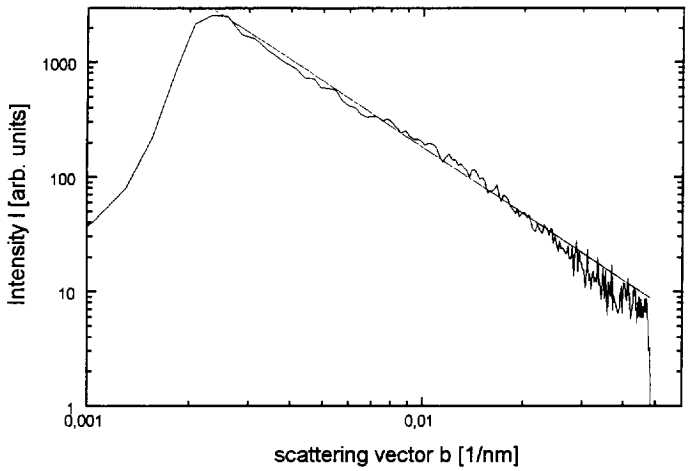

Fig. 6. Double logarithm representation of the scattering intensity $I(b)$ vs. scattering vector b for the data obtained from a gel sample filled with aggregates of anisometric particles. The intensity shows power-law decay with an exponent $d_f = 1.95$.

with the interparticle structure factor $S(b)$ [14]. The limiting behavior of $I(b)$ is given by

$$b \cdot r_0 \ll 1 \rightarrow P(b) \approx 1 : \qquad I(b) \propto \overline{S(b)} ,$$
$$b \cdot r_0 \gg 1 \rightarrow \overline{S(b)} \approx 1 : \qquad I(b) \propto P(b) .$$

r_0 is the characteristic length of the single particles. For a fractal object the self-similarity causes a power-law decay of the structure factor $S(b)$ – the Fourier transform of the density–density correlation function – in the regime $bR_g \gg 1 \gg br_0$:

$$S(b) \propto b^{-d_f} ,$$

with the fractal dimension d_f and the average radius of gyration R_g of the aggregates. The scattering data indicate, that the anisometric single particles form aggregates which are of a fractal nature with a dimension of $d_f = 1.95 \pm 0.05$.

Further X-ray experiments will reveal whether the fractal dimension of the aggregates is affected by the reaction kinetic: clusters formed with different growth rates will be built in gels. At the synchrotron facility (HASYLAB/BW4) we will make 'in situ' measurements from growing clusters, as well.

Acknowledgements

This report is based on a project which is supported by funds of the German Federal Ministry for Research and Technology (BMFT) under contract number 05 5VUAXI 1. The responsibility for the subject matter of this paper is taken by the authors. The support at Hungarian Academy of Sciences (OTKA No.: 2166) is highly acknowledged.

We thank the 'BW4-Team' (M. Bark, S. Cunis, R. Gehrke, D. Lewin) from HASYLAB for their technical assistance during the measurements.

References

[1] M.T. Vold, J. Colloid. Sci. 18 (1963) 684.
[2] T. Vicsek, Fractal Growth Phenomena (World Scientific, Singapore, 1989).
[3] M.Y. Lin, H.M. Lindsay, D.A. Weitz, R.C. Ball, R. Klein and M. Meakin, Phys. Rev. A 41 (1990) 2005.
[4] D.W. Schaefer and J.E. Martin, in: Kinetics of Aggregation and Gelation, F. Family and D.P. Landau, eds. (North-Holland, Amsterdam, 1984) p. 71.
[5] D.A. Weitz and J.S. Huang, in: Kinetics of Aggregation and Gelation, F. Family and D.P. Landau, eds. (North-Holland, Amsterdam, 1984) p. 19.
[6] H. Sonntag and K. Strenge, Coagulation Kinetics and Structure Formation (Plenum, New York, 1987).
[7] W. Haas, M. Zrinyi, H.-G. Kilian and B. Heise, Colloid Polym. Sci. 271 (1993) 1024–1034.
[8] M. Zrinyi, M. Kabai-Faix, Sz. Juhos and F. Horkay, Langmuir 9 (1993) 71–76.
[9] Y. Maeda and S. Hachisu, Colloids and Surfaces 6 (1983) 1.
[10] P. Meakin, Phys. Rev. Lett. 51 (1983) 1119.
[11] M. Kolb, R. Botet and R. Jullien, Phys. Rev. Lett. 51 (1983) 1123.
[12] Malvern Instruments, K7032-OS Correlator User Manual, Spring Lane, Malvern, Worcestershire.
[13] G. Porod, in: Small Angle X-ray Scattering, O. Glatter and O. Kratky, eds. (Academic, New York, 1982) p. 17.
[14] J. Teixeira, in: On Growth and Form, H.E. Stanley and N. Ostrowsky, eds. (Kluwer, Dordrecht, 1984) p. 145.