Pramana – J. Phys., Vol. 37, No. 4, October 1991, pp. 321–326. © Printed in India.

Electron microscopy study of aggregation of microclusters of sulphur

M ABDULKHADAR and K C GEORGE

School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam 686631, Kerala, India

MS received 15 July 1991; revised 21 August 1991

Abstract. A study of aggregation of sulphur particles in colloidal suspension of sulphur in water-methanol mixture using TEM and electron diffraction is reported. From the micrographs the aggregates formed have been found to be random and tenuous indicating a fractal structure. The electron diffraction patterns of the aggregates are used to study the mechanism of diffusion and reaction limited aggregation.

Keywords. Electron microscopy; microclusters; fractals; DLA; RLA

PACS No. 61·16

1. Introduction

Understanding the kinetic aggregation of small particles to form clusters and the study of the structure of these clusters have been the primary goal of colloid physics for many years. The interest in this field was aroused not only due to the fact that colloid aggregation represents one of the major applications and experimental tests of modern statistical theories of kinetic growth, but also because recent developments including computer simulations (Witten and Sander 1981, 1983) have made it feasible to quantitatively characterize the aggregates, despite their very random and disordered appearance. The random, tenuous clusters that are produced when colloids aggregate exhibit dilation symmetry and can be termed as fractals (Mandelbrot 1982). Since colloid aggregation is a kinetic, nonequilibrium growth process, the structure of the aggregates is inherently related to dynamics of the aggregation. The key to the traditional understanding of both colloid stability and colloid aggregation is the determination of the energy of interaction between two colloid particles as a function of their centre-to-centre separation. According to the widely used DLVO (Verwey and Overbeek 1948) theory, the energy barrier height E_B of width K^{-1} (where K^{-1} is the Debye–Huckel screening length) is the origin of the stability of the colloid against aggregation. When $E_B \ll k_B T$, where k_B is the Boltzmann constant, the aggregation rate is a maximum and particles stick to one another quickly and irreversibly upon collision. The aggregation is limited only by the diffusion of particles and this regime named diffusion limited aggregation (DLA) (Weitz *et al* 1983, 1987) forms the first universal regime of kinetic aggregation. When $E_B > k_B T$ the rate of aggregation is many orders of magnitude less than that for DLA. In this case, the rate limiting step in the kinetics is the actual formation of a bond and we label this regime reaction limited aggregation (RLA) (Weitz *et al* 1987). In

the RLA regime, the structure of the clusters, as determined by their fractal dimensions, the aggregation dynamics and the cluster mass distribution all change dramatically from the DLA behaviour. Thus the two universal regimes appear to be sufficient to describe all the regimes of the homogeneous aggregation of a large number of colloidal systems. Despite the abundant theoretical results available on the kinetics of aggregation, experimental work that can test the validity of modern theories has been rather sparse. Forrest and Witten (1979) have analyzed aggregates of metallic smoke particles and Wietz and Oliveria (1984) investigated aggregates of uniform aqueous colloids of gold by TEM. Schaefer and Martin (1984) have reported TEM analysis of silica particles. The structures formed in these cases were highly ramified exhibiting a scale invariance and are well described as fractals (Forrest and Witten 1979; Weitz and Oliveria 1984; Schaefer and Martin 1984; Voss *et al* 1984; Hurd 1987). Analysis of aggregates using TEM has the disadvantage that the clusters have to be removed from the liquid phase and dried, a process that may distort the structure and that the TEM image is a two-dimensional projection of the three-dimensional cluster. Nevertheless TEM imaging is the most direct and convenient method to actually see and analyse the structure of aggregates and it has been shown (Weitz 1987) that the fractal dimension obtained by TEM analysis corresponds to that of the cluster in solution.

The authors report here a study of aggregation of aqueous colloidal suspensions of sulphur particles by TEM and electron diffraction. The aggregates formed have been found to be random, tenuous and could be termed as fractals. The electron diffraction patterns of the aggregates are found to be spotty, indicating that the aggregating particles are crystalline (Grundy and Jones 1976). The electron diffraction photographs have been used to study the mechanism of aggregation.

2. Experimental

Sulphur hydrosol used in this work was prepared by quickly adding measured quantity of a saturated solution of flours of sulphur in methanol at constant temperature into doubly distilled water (Weiser 1949). Hydrosols of two different concentrations (ratio of sulphur solution to distilled water 1:2 and 1:4) were used for the present study. A drop of freshly prepared sulphur sol was placed on the TEM grid and the liquid phase was allowed to evaporate. The structure of the sulphur clusters was examined using a PHILIPS 301 TEM. By examining the full area of the TEM grid, clusters of widely varying degree of aggregation could be found and photographed. The same microscope but now in the electron diffraction mode was used for the determination of crystallinity of the sulphur particles and selected area electron diffraction photographs were taken. The samples were allowed to age at constant temperature for 24 hours and these were also subjected to TEM and electron diffraction studies to determine the effect of aging on the extent of aggregation of the particles. Electron micrographs of fresh (figures 1 and 3) and aged (figures 3 and 4) samples are reported to show the structure of the aggregates. Figures 5, 7 and 6, 8 are the electron diffraction photographs of aggregates of fresh and aged samples respectively.

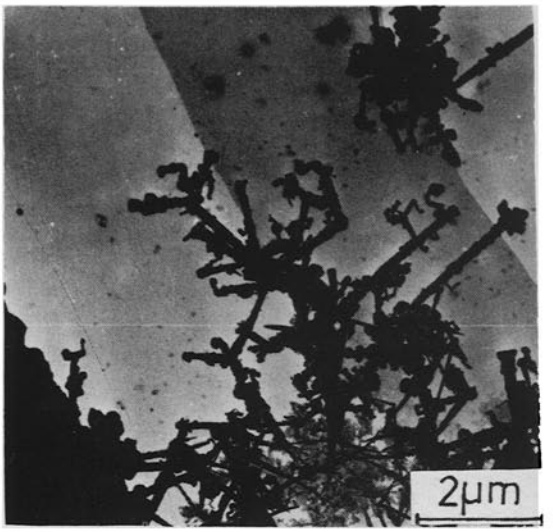

Figure 1.

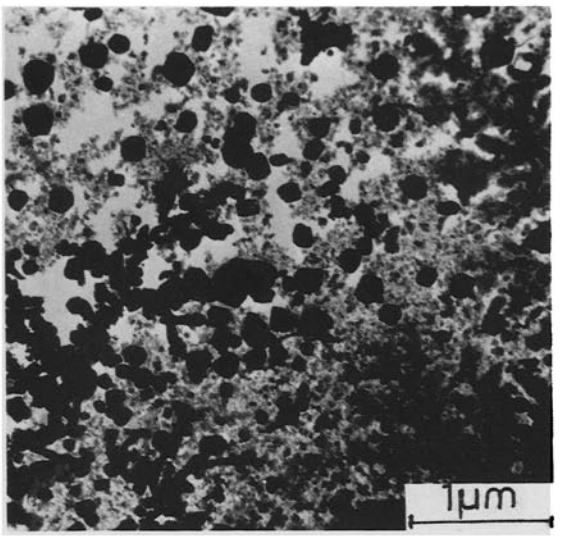

Figure 2.

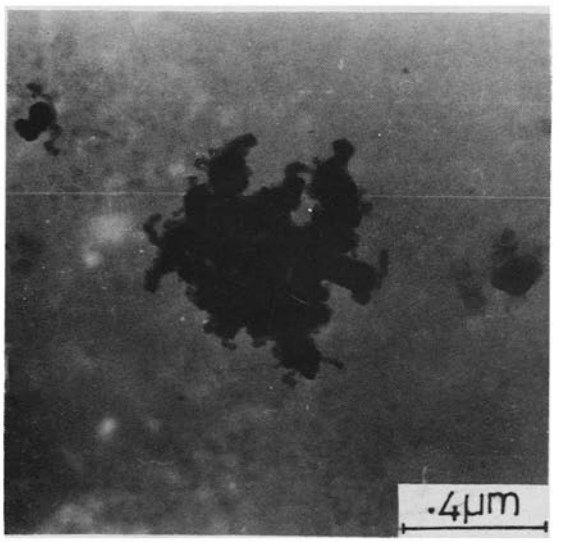

Figure 3.

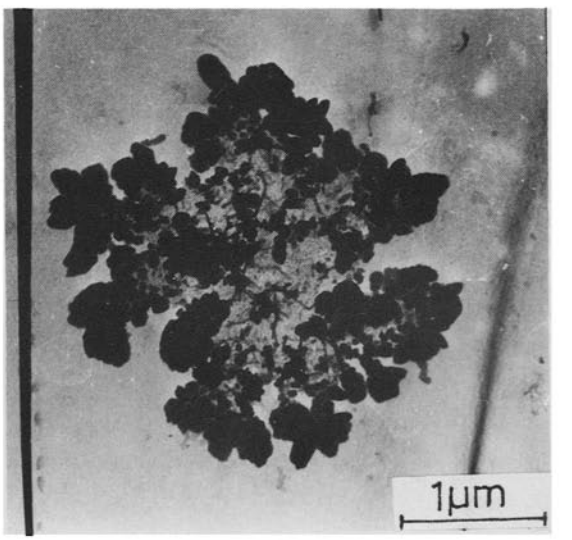

Figure 4.

Figure 1–4. Electron micrographs of aggregates of sulphur: **1.** Fresh sample (con. 1:4); **2.** fresh sample (con. 1:2); **3.** Aged sample (con. 1:4); **4.** Aged sample (con. 1:2).

Figure 5.

Figure 6.

Figures 5–8. Electron diffraction photographs of aggregates of sulphur: **5.** Fresh sample (con. 1:4); **6.** Aged sample (con. 1:4); **7.** Fresh sample (con. 1:2); **8.** Aged sample (con. 1:2).

3. Discussion

The random, tenous clusters that are produced when colloids aggregate can be quantitatively characterized as DLA or RLA despite their very disordered appearance. It has been shown that the aggregates produced through the reaction-limited and diffusion-limited process show dilation symmetry and can be termed as fractals (Weitz *et al* 1987). The random aggregates of sulphur particles produced in fresh as well as

aged samples in the present study must also be self-similar and could be termed fractals since aggregation has been amply shown to be describable by DLA and RLA regimes (Weitz *et al* 1987).

Theoretical and experimental studies reported in the literature indicate that the clusters themselves may diffuse via Brownian motion and growth occurs when two clusters aggregate. These cluster–cluster aggregation models (Weitz *et al* 1987) are the better representation of the actual experimental situation than the attachment of particles one by one on a growing aggregate. Also in the RLA regime in which the bond formation is the rate limiting step, this model may even lead to chemical reaction upon aggregation. Each tiny cluster getting added to a growing cluster, made up of crystalline particles and the crystalline nature of the particles forming a tiny cluster may not hamper the formation of aggregates exhibiting fractal structure. The TEM micrographs (figures 1, 2, 3 and 4) show irregularly shaped, ramified structures for fresh and aged samples of sulphur sol. The structure of aggregates of sulphur observed in fresh samples should be more open and must fall in the DLA regime while structure of aggregates of aged samples should be more dense and should fall in the RLA regime. The electron diffraction photographs of the structures formed in fresh samples of low concentrations show (figure 5) limited number of spots indicating only thin packing of crystalline particles, thereby indicating a role of DLA. Electron diffraction photographs for aged samples (figure 7) of low concentrations show much larger number of spots (almost rings) indicating close packing of crystalline particles. This indicates that aggregates formed in aged samples of low concentration must be more dense and must be formed through RLA mechanism. At high concentrations (1:2) open structures are formed initially by DLA (figure 6) and structures formed after 24 hours indicate an extreme case of close packing of particles, resulting in the formation of a polycrystalline mass with a limited number of crystallites. This is evident from the very limited number of diffraction spots (figure 8).

4. Conclusion

The process of aggregation of sulphur clusters was analyzed by electron diffraction for different concentrations. The aggregates formed exhibits a fractal behaviour. The aggregation produced in fresh samples were due to DLA while in aged samples it may be due to RLA.

Acknowledgement

We are thankful to Materials Research Centre, Indian Institute of Science, Bangalore for providing electron microscope facilities.

References

Forrest S R and Witten T A 1979 *J. Phys.* **A12** 109

Grundy P J and Jones G A 1976 *Electron microscopy in the study of materials* (eds) Bryan R Coles and Edward Arnold, (London: Edward Arnold)

Hurd A J 1987 *Physics of complex and supermolecular fluids* (eds) Samuel A Safran and Noel A Clark, (New York: John Wiley) p. 493
Mandelbrot B B 1982 *The fractal geometry of nature* (Sanfrancisco: Freeman)
Schaefer D W and Martin J E 1984 *Phys. Rev. Lett.* **52** 2371
Verwey E J W and Overbeek T J T 1948 *Theory of the stability of lyophobic colloids* (Amsterdam: Elsevier)
Voss R F, Laibowitz R B and Allessandrini E I 1984 *Phys. Rev. Lett.* **52** 2371
Weiser H B 1949 *A text book of colloid chemistry* (New York: John Wiley) p. 146
Weitz D A, Huang J S, Lin M Y and Sung J 1983 *Phys. Rev. Lett.* **53** 1657
Weitz D A, Lin M Y and Huang J S 1987 *Physics of complex and supermolecular fluids* (eds) Samuel A Safran and Noel A Clark (New York: John Wiley) p. 509
Weitz D A and Oliveria M 1984 *Phys. Rev. Lett.* **52** 1433
Witten T A and Sander L M 1981 *Phys. Rev. Lett.* **47** 1400
Witten T A and Sander L M 1983 *Phys. Rev.* **B27** 5686