CHAPTER 5

AGGREGATION OF SMALL PARTICLES

5.1 Introduction

5.1.1 Van der Waals attraction
5.1.2 Electrostatic repulsion
5.1.3 Diffusion limited aggregation
5.1.4 Reaction limited aggregation
5.1.5 Characterisation of the aggregates
5.1.6 Work included in this chapter

5.2 Aggregation of microclusters of sulphur

5.2.1 Introduction
5.2.2 Experiment and Observation
5.2.3 Discussion

5.3 Aggregation of microclusters of silver

5.3.1 Introduction
5.3.2 Experiment and Observation
5.3.3 Discussion

5.4 Aggregation of microclusters of silver iodide and mercuric iodide

5.4.1 Introduction
5.4.2 Experiment and Observation
5.4.3 Discussion

5.5 Conclusion

References
5.1 Introduction

Understanding kinetic aggregation of small particles to form clusters and the study of the structure of these clusters has been the prime goal in the field 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 recent developments including computer simulations (1,2) 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 (3). Since cluster aggregation is a kinetic non-equilibrium growth process, the structure of the aggregates is inherently related to dynamics of aggregation.

The particles dispersed in a liquid phase will be undergoing Brownian motion and will be continually colliding with one another. There should be a protective mechanism to prevent aggregation and to retain the individuality of the particles. The protection may be achieved through electrostatic stabilization or through steric stabilization. In the case of electrostatic stabilization the electrical
protection may be destroyed by an increase in the electrolyte content of the solution at a fairly sharp concentration. All electrolytes have this effect but counterions of high charge numbers are much more effective than those of low valence. This valance effect is known as the rule of Schulze (4) and Hardy (5). A sterically protected suspension may be caused to flocculate by the addition of a non-solvent for the protecting molecules. These protective mechanisms can only slow down the process of aggregation but cannot prevent it. The structure of the aggregates depends strongly on the mechanism of aggregation. If the repulsion between particles in a suspension is significant, the particles will coagulate only very slowly but when they do so they are observed to form very compact structures with little entrapped solvent. When the repulsion is not significant, the clusters stick to one another immediately and irreversibly upon collision and the aggregation rate is determined by the diffusion of the clusters. The key to the traditional understanding of both colloid stability and aggregation of small particles dispersed in a liquid medium is in the determination of the energy of interaction between two colloid particles as a function of their center-to-centre separation (6). The energy of interaction between particles may arise due to van der Waals attraction or by electrostatic repulsion.
5.1.1 Van der Waals attraction

The van der Waals forces between the atoms in two approaching particles are to some extent additive and the overall effect is an attractive force of quite long range. The idea has been worked out by De Boer (7) and especially by Hamaker (8). According to the widely used DLVO theory (9,10,11), the attractive van der Waals interaction between two spherical particles is

\[ V_a = A \left[ \frac{4a^2}{r^2-a^2} + \frac{4a^2}{r^2} + 2 \ln \left( \frac{r^2 - a^2}{r^2} \right) \right] \]

where A is the Hamaker constant, r is the separation of the centres and a is the sphere radius.

5.1.2 Electrostatic Repulsion

Suspensions of a solid phase in a liquid medium can be stable over a long period of time if the particles repel one another strongly enough to overcome the van der Waals attraction. Electrostatic repulsion if exists can be strong enough and can have a long enough range to do the job. In the case of electrostatic stabilization the repulsive screened coulomb forces is

\[ V_r = \frac{2^2 e^2}{\varepsilon r} e^{-kr} \]
\[ k^2 = \frac{4\pi n e^2}{k_B T} \]

where \( Z \) is the charge per sphere, \( \varepsilon \) the dielectric constant of the solvent \( K \) is the inverse screening length and \( n \) the total number of ions in solution.

The potential energy due to van der Waals' effect between two colloidal particles of the same material immersed in a fluid is negative. The repulsive force due to Coulombic interactions between particles lead to a positive potential energy. There is a primary and secondary minimum due to the attraction with a steep barrier between them. It is well established that the height of the barrier and the depth of the secondary minimum play a critical role in determining the extent of particle aggregation. Thus the energy barrier height \( E_b \) of width \( K^{-1} \) is the origin of the stability of a dispersion against aggregation. In a diffusion induced collision, two particles will approach to within \( K^{-1} \), and will overcome the energy barrier and stick together with a probability \( P = \exp(-E_b/k_B T) \) where \( k_B \) is the Boltzmann constant and \( T \) is the temperature. This type of an approach can be used to determine the initial rate of aggregation. The subsequent aggregation kinetics are more complicated as the clusters themselves also diffuse and grow. The mechanism
of aggregation observed in fresh and aged suspensions will therefore be different and fall into two universal regimes, namely diffusion limited aggregation (DLA) and reaction limited aggregation (RLA).

5.1.3 Diffusion Limited Aggregation

When $E_b \ll k_B T$ where $k_B$ is the Boltzmann constant, the aggregation rate is maximum and particles stick to one another quickly and irreversibly upon collisions. The aggregation is limited only by the diffusion of particles or small clusters of particles and this regime named diffusion limited aggregation (6,12) forms the first universal regime of kinetic aggregation. A general feature of this kind of aggregation appears to be the dilation symmetry exhibited by the resultant clusters, whether they are formed by accretion of single particles or by cluster-cluster aggregation. The tenuous, highly disordered structures of the clusters can be quantitatively characterized as fractals. The fractal dimension of the cluster aggregates is experimentally found (6) to be $d_f = 1.75 \pm 0.05$, which is in excellent agreement with the fractal dimension obtained from computer simulations of the cluster-cluster aggregation models (6). The fractal dimension remains the same when the diffusivity of the clusters is taken to be independent of the mass (13). The fractal dimension is also not sensitive to the form of
cluster mass distribution, remaining unchanged whether the aggregation occurs in a system of equal sized clusters (14) or in polydisperse distributions (15). Furthermore, small structural reorganisations to form a more stable configuration after the clusters stick do not appear to change the fractal dimension significantly (6).

5.1.4 Reaction Limited 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 (6). In the RLA regime, the structure of the clusters, as determined by their fractal dimension, the aggregation dynamics, and the cluster mass distributions all change dramatically from the DLA behaviour. The large clusters formed by RLA have a much more dense and compact appearance than that of the clusters formed by DLA. This may be due to the reason that the clusters will be able to interpenetrate one another to a greater degree than for DLA, leading to an increased fractal dimension \( d_f = 2.05 \pm 0.1 \) for the clusters (6). The bonds once they are formed, are very strong and rigid. This rigidity along with the complex geometry of the clusters, will ensure that the aggregates are still quite tenuous and that their structure is still fractal.
Thus the two universal regimes—DLA and RLA—appear to be sufficient to describe the mechanisms of homogenous aggregation of a large number of colloidal systems.

5.1.5 Characterisation of the Aggregates

The best way to study the structure of the highly dispersed colloidal aggregates would be to observe them in three dimensions. The very small size of the particles makes it necessary to use transmission electron microscope (TEM) to attain sufficient resolution to measure the structure down to length scales of the order of the individual particles (6). Analyses of aggregates using TEM has the disadvantage that the TEM image is a two dimensional projection of the three dimensional cluster and that the cluster have to be removed from the liquid phase and dried, a process that may distort the structure. Still TEM imaging is the most direct and convenient method to actually see and analyse the structure of aggregates and it has been shown that fractal dimension obtained by TEM analysis corresponds to that of the cluster in solution (6).

5.1.6 Work Included in this Chapter

In this chapter, the study of aggregation of microclusters of certain materials using TEM and electron
diffraction are discussed. Section 1 deals with the study of aggregation of microclusters of sulphur dispersed in water methanol mixture, Section 2 consists of the investigation of the mechanism of aggregation observed in Ag colloids in the presence of a stabiliser and in Section 3, the aggregation found in fresh and aged samples of microclusters of AgI and HgI₂ are discussed.

SECTION 1

5.2 Aggregation of Microclusters of Sulphur

5.2.1 Introduction

The process of aggregation of small particles to form larger clusters and the structure that result are important technologically and scientifically. All of our knowledge of the growth of these clusters has come from computer simulations (1,2,14,15) which have suggested that the resultant structures exhibit scale invariance and can be termed as fractals. Despite the accumulation of the wealth of theoretical results on the kinetics of aggregation, experimental work that can test the validity of modern theories have been rather sparse. Forrest and Witten (16) have analysed aggregation of metallic smoke particles and Weitz and Oliveria (17) investigated aggregates of uniform aqueous colloids of gold by TEM. Schafer et al (18) have
reported TEM analyses of silica particles. The structures formed in these cases were highly ramified exhibiting a scale invariance and are described as fractals.

This section consists of a study of aggregation of colloidal suspension 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 (21,22). The electron diffraction photographs have been used to study the mechanism of aggregation.

5.2.2 Experiment and Observation

Suspensions of small particles of sulphur used in this work were prepared by quickly adding measured quantity of a saturated solution of flours of sulphur in methanol at constant temperature in to doubly distilled water (23). Suspensions of two different concentrations (ratio of distilled water to sulphur solution) were used for the present study. The suspension of 2:1 concentration contained 0.113 gm of sulphur per litre and the 4:1 concentration contained 0.056 gm of sulphur per litre of the suspension. A drop of the freshly prepared suspension of sulphur was placed on the TEM grid and the liquid phase was allowed to
evaporate. The structure of the sulphur clusters were examined using a PHILIPS EM 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 (Figs. 5.1 and 5.3) and aged (Figs. 5.2 and 5.4) samples are reproduced to show the structure of the aggregates. Figures 5.5, 5.7 and 5.6, 5.8 are the electron diffraction photographs of aggregates in fresh and aged samples respectively.

5.2.3 Discussion

The random, tenuous clusters that are produced when colloids aggregate can be quantitatively characterised 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 (6). The random aggregates of sulphur particles produced in fresh as well as aged samples in the present study must also be self similar.
Figure Captions

Fig.5.1 - 5.4  Electron micrography of suspensions of small particles of sulphur.

Fig.5.1  Fresh sample (Con. 2:1)
Fig.5.2  Aged sample (Con. 2:1)
Fig.5.3  Fresh sample (Con. 4:1)
Fig.5.4  Aged sample (Con. 4:1)
Figure Captions

Fig.5.5 - 5.8  Electron diffraction photographs of suspensions of small particles of sulphur.

Fig.5.5  Fresh sample (Con. 2:1)

Fig.5.6  Aged sample (Con. 2:1)

Fig.5.7  Fresh sample (Con. 4:1)

Fig.5.8  Aged sample (Con. 4:1)
and could be termed fractals since aggregation has been amply well shown to be describable by DLA and RLA regimes (6).

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 (6) are 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 (20). The TEM micrographs (Figs. 5.1 to 5.4) show irregularly shaped, ramified structures for fresh and aged samples of suspensions of sulphur particles. 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 (Fig.5.7) limited number of spots indicating only thin packing of crystalline particles, thereby indicating a role of DLA. Electron diffraction photographs for aged samples (Fig.5.8) 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 (2:1) open structures are formed initially by DLA (Fig.5.5) and structures formed after 24 hours indicate an extreme case of close packing of particles, resulting in the formation of a poly crystalline mass with a limited number of crystallites (21,22). This is evident from the very limited number of diffraction spots (Fig.5.6).

SECTION 2

5.3 Aggregation of Small Particles of Silver

5.3.1 Introduction

Metal colloids have been known for a long time and are of great interest due to their technological, industrial and medicinal applications. Colloidal gold is the most traditional and widely studied colloid and was known at least as far back as the twelth century. Faraday's
scientific studies of colloidal gold was instrumental in the establishment of the discipline of colloid science. Many of the concepts of colloid science, especially the stability of colloids, were tested using colloidal gold. Colloidal silver also have been known long ago and prepared by various methods (24-26), of which the preparation of Carey Lea silver colloid dates back to 1889. Colloidal silver have been studied mainly for their optical properties (27-30). These colloids are also of interest in the areas of catalysis, especially when free organic radicles in solution are involved. More recently they gained interest with the surface enhanced Raman scattering technique (SERS) for the study of molecules adsorbed at the surface of colloidal particles. These studies emphasized that the various properties of small particles of silver are influenced by the size and shape of particles and more specially by their aggregation state. In this work an attempt has been made to characterise through electron microscopy the cluster aggregation observed in silver colloids produced by Bredigs method.

5.3.2 Experiment and Observation

Silver suspension used for the present study were prepared by Brediç's method (23,31) as described in section 2 of chapter 4. The resulting suspension was filtered to
remove coarser particles and kept undisturbed for two days for the particles to aggregate. The particles in the suspension were then subjected to TEM and electron diffraction studies to determine the effect of aging on the extent of aggregation. The TEM micrographs of the aggregates (see Fig. 4.2 of chapter 4) exhibits the tenuous ramified appearance characteristically observed for fractal aggregates. The electron diffraction photographs (see Fig 4.3 of chapter 4) show characteristic diffraction rings observed for crystalline material.

5.3.3 Discussion

The electron micrographs of aggregates of silver show the random tenuous nature exhibited by fractal aggregates. The aggregates formed when silver particles flocculate, can be due to DLA or RLA just as in the case of sulphur clusters discussed in section 1 of this chapter. Since no electrolyte is added to initiate aggregation in the silver suspension, the necessary condition for DLA, i.e. $E_b \ll k_B T$ may not be satisfied and the aggregation mechanism may not in general be DLA. Even though the probability of formation of clusters through DLA are small the chance for the presence of aggregates formed through DLA cannot be discarded, since at the time of preparation of the colloid the formation of clusters through DLA are probable.
In the case of silver colloid, the surface adsorbed ions cause the silver particles to be highly charged and the ionic strength of the solution creates a Debye-Huckel screening length of few atomic distances. The resulting double layer interaction between the particles makes the suspension very stable against aggregation. Since the repulsive double layer interaction is very strong ($E_b > k_BT$), the clusters will not stick to one another immediately on collision, but they may do so through the formation of a bond. Thus the rate limiting step in the kinetics of aggregation is the actual formation of a bond and we label this regime of aggregation as reaction limited aggregation (6). The electron diffraction pattern of the aggregates of silver show the characteristic diffraction rings (see Fig 4.3 of chapter 4). This indicates that the particles forming the aggregates are crystalline and they are packed closely and are much dense. It is established through experimental observations that the large clusters formed by RLA have a much more dense compact appearance (6). This result together with the results of the present study show that the aggregation produced in aged silver suspension may fall under the RLA regime.
SECTION 3

5.4 Aggregation of Microclusters of AgI and HgI₂

5.4.1 Introduction

Though the aggregation of metal clusters have been studied widely (16-18), the investigation of aggregation of clusters of inorganic compounds are rather few (32). Study of the dynamics of aggregation in inorganic colloids will provide a better understanding of the physical properties of the aggregates. The importance of silver iodide (32) in photographic processes has led to extensive investigation of their properties and intense interest in the mechanism of aggregation. Colloidal HgI₂ is also a material of wide industrial applications. In this section, the aggregation dynamics observed in fresh and aged samples of colloidal AgI and HgI₂ are discussed.

5.4.2 Experiment and Observation

Aqueous suspensions of AgI and HgI₂ used in the present work were prepared as discussed in section 2 of chapter 4. Fresh and aged samples of the suspensions of AgI and HgI₂ were subjected to TEM and electron diffraction studies. A well defined continuous ring structure was observed in the electron diffraction pattern of aged samples.
of HgI₂ (see Fig. 4.8) while fresh samples indicate a spotty pattern (see Fig. 4.7). Electron diffraction pattern of fresh suspensions of AgI indicates a spotty (see Fig. 4.9) behaviour while aged samples show rings with a limited number of bright spots (see Fig. 4.10).

5.4.3 Discussion

The TEM micrographs of clusters of AgI and HgI₂ (see Figs. 4.5 and 4.6) indicate the state of aggregation in these clusters. The stability of AgI and HgI₂ suspensions are found to be different. AgI suspension is found to be moderately stable while the suspension of HgI₂ flocculates within a very short time after preparation. The aggregation dynamics observed in fresh samples of the above suspensions falls in the DLA regime, since the probability of formation of clusters through DLA is large at the time of preparation of the suspension. It is established by experimental observations that the aggregates formed through DLA are less densely packed (6). The electron diffraction pattern of fresh samples of AgI (see Fig. 4.9) indicate thin packing of crystalline material and suggests that the aggregation dynamics observed falls in the DLA regime.

In the case of aged samples of AgI, the energy barrier between particles is significant and particles stick to each other only by the formation of a bond. The electron
diffraction pattern of aged samples of AgI (see Fig.4.10) shows almost continuous diffraction rings indicating a close packing of crystalline particles in the aggregates and thereby indicating that the mechanism of aggregation falls in the RLA regime.

The HgI₂ suspension which is very unstable aggregates within a short time after the preparation. No electrolyte is required to initiate aggregation. In this case $E_b < k_B T$ and the aggregation is limited only by the diffusion of particles. Thus in HgI₂, the aggregation observed in fresh and aged samples are the same and falls in the DLA regime (see Figs.4.7 and 4.8).

5.5 Conclusion

The process of aggregation of microclusters has been analysed by TEM and electron diffraction. The aggregates formed exhibit a fractal behaviour. The mechanism of aggregation observed in fresh and aged suspensions may fall under the regimes of diffusion limited aggregation or reaction limited aggregation according as the energy of interaction between the clusters.
References


   ibid (2) 27(1883) 320.


