CHAPTER 11

PATTERN FORMATION IN INTERACTING SUSPENSIONS

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References
11.1 Introduction

Theoretical analysis of periodic structures, Liesegang rings, have dealt with the question of supersaturation (1), colloid coagulation (2) and band spacing (3,4); and in all these treatments the existence of a spatial gradient of cations, and in opposite direction a gradient of anions, has been considered essential. Experiments have shown that the presence of macroscopic concentration gradient is unnecessary for the development of structures, and that spatially inhomogenous structures can be produced in initially homogenous reaction diffusion systems (5). Flicker and Ross have proposed a new mechanism for periodic precipitation phenomenon, one based on a type of chemical instability due to the coupling of the autocatalytic growth of particles combined with the transport process of diffusion. It was shown that the process of importance occurs in the post nucleation period, ie, in the period when Ostwald ripening takes place.

Even though Liesegang bands have been reported in a variety of cases of interacting electrolytes and in a much
fewer number of cases pattern formations have been studied in uniform dispersions (7,8). Such phenomena have not been reported in the case of interaction of nanoparticles of two different materials. The interaction between nanoparticles has invited the attention of researchers; and the fundamental importance of these reactions has been though in a limited way, brought to light. Studies have shown that such interactions are actually feasible in many cases, the cause of interaction being chemisorption (9,10). Freundlich and Moor (11) have reported the interaction of silver suspension with arsenious trisulphide suspension and have indicated the possibility of bulk reaction between the two sols leading to the formation of the compound silver thioarsenate. In this chapter the results of the study of interaction between suspensions of nanoparticles of silver and arsenious trisulphide allowed to meet at a diffusion controlled rate are discussed. Sodium metasilicate gel has been used in these experiments as the medium to control the diffusion of the suspensions. The two suspensions interact, and the product of interaction appears as a dispersion of fine particles. These particles are found to be arranging either in a system of periodic rings or as macroscopic deposits at a later stage due to a symmetry breaking instability of the system of particles. The results show that under conditions at or near equilibrium, macroscopic
length scale inhomogenities do not regress but are amplified, and the macroscopic symmetry breaking transition producing clumps and Liesegang bands arises as an amplification of the microscopic fluctuations.

11.2 Experiment and Observation

11.2.1 Preparation

Suspensions of nanoparticles of silver and arsenious trisulphide were prepared as given in section 1 and section 3 of chapter 4, respectively (12,13). The two sols were allowed to meet through a diffusion controlled process using a gel formed by acidifying a solution of sodium metasilicate of specific gravity 1.04 using tartaric acid to a pH from 5 to 7.

11.2.2 Electron Microscopy, Electron Diffraction Analyses

Silver and arsenious trisulphide particles were analysed under an electron microscope to study the size range of the particles. Silver particles were found to have a mean size of about 10 nm, and arsenious trisulphide particles have a mean size of about 8 nm. Electron diffraction photographs of both silver and arsenious trisulphide (see Figs.4.3 and 4.12 of chapter 4) were found to be spotty indicating that both types of particles have crystalline structure inspite of the size-limited state. An
estimation of the d-spacing shows that both silver and arsenious trisulphide have suffered a lattice contraction. This as expected, might be due to the large value of surface-to-volume ratio of the particles and the resultant excess Gibb's free energy.

11.2.3 Straight Tube Experiments

Equal volumes of suspensions of silver and acidified sodium metasilicate solution were mixed well, and the mixture was allowed to gel in a test tube. Arsenious trisulphide suspension was then placed on the perfectly set gel to a height of about 5cm. As the arsenious trisulphide suspension diffused in to the gel, it reacted with the silver suspension and the product of interaction appeared as a smooth distribution of particles. The extent of this distribution increased with time. A ring structure evolved from this uniform distribution of particles within 48 to 78 hours, and on an average, rings appeared at intervals of 24 hours (Fig 11.1) The space between the rings was turbid in the beginning, but became clearer in course of time. Experiments were repeated a number of times, and the pattern of rings had been found to be easily reproducible. Neither turbidity in the gel nor the ring pattern was observed when arsenious trisulphide was incorporated in the gel and silver taken on the gel surface. This might have been due to the
slackened diffusion of silver particles into the gel because of their larger size. The bands had an average thickness of 1 mm and the interband distance varied from 2 mm to 3.4 mm. Because of the large amount of time involved in the formation of rings, no accurate quantitative verification of the spacing law was feasible.

11.2.4 U-Tube Experiments

In these experiments gel was allowed to set near the bent part of u-tubes and the two suspensions were taken separately in the two limbs. A turbid distribution of particles of the product of interaction spread from the interface between the gel and the silver suspension. As time elapsed the rings developed from this distribution of particles within 4 to 5 days (Fig 11.2). The rings were well defined and were reproducible. After the formation of the rings was complete, macroscopic deposits which acquired a size up to 0.2 mm developed between the rings and also attached to the ring (Fig.11.3). These deposits were found to be aggregates of finer particles and not contiguous crystallites.

11.2.5 Effect of pH

The formation of Liesegang bands and macroscopic deposits were observed for pH values between 5 and 7 only.
Figure Captions

**Fig.11.1** Pattern formation observed when suspensions of small particles of silver and arsenious trisulphide interact in a gel medium in straight tubes.

**Fig.11.2** Pattern formation observed when suspensions of small particles of silver and arsenious trisulphide interact in a gel medium in U-tubes.

**Fig.11.3** Macroscopic deposits formed by the interaction of suspensions of small particles of silver and arsenious trisulphide in a gel medium in U-tubes.
It was seen that in straight tubes the rings were more spaced at a pH of about 5 than at a pH of 7. This change in the nature of spacing was not evident in U-tubes, probably due to the presence of excess amounts of both suspensions, and the pH being determined more decidedly by the suspensions rather than that of the gel. The formation of macroscopic deposits were not appreciably affected by the change in pH values.

11.2.6 Analysis of the Product of Interaction

The chemical analysis of materials forming the Liesegang bands and macroscopic deposits was difficult because of the difficulty in separating it from the gel. However, EDAX and electron diffraction analysis were carried out on the coagulated mass obtained by directly mixing the suspensions of silver and arsenious trisulphide. EDAX analysis results indicated the presence of silver, sulphur and arsenic in the mass, but the evidence of a direct stoichiometric interaction was difficult to draw, since the precipitate probably contained unreacted silver or arsenious trisulphide or both. But electron diffraction gave a clearer evidence of the interaction, since the pattern obtained was quite different from that of silver and arsenious trisulphide. The electron diffraction pattern of the product of interaction was found to consist of diffuse rings.
(containing reflections from unreacted silver), indicating that the material was amorphous.

11.2.7 Estimation of Diffusion Coefficient

The formation of periodic bands and macroscopic deposits may be considered as due to a symmetry breaking instability in the system. In our experiments it was observed that as the arsenious trisulphide suspension diffused into the gel charged with silver suspension, the gel column became turbid. The formation of rings started only sometime after the appearance of turbidity. As the rings became more and more distinct, the turbidity decreased, and when the rings attained maximum visibility, the turbidity attained a minimum. It may reasonably be assumed that the rings form due to the diffusion of the particles causing turbidity to the regions of the rings. This type of mechanism should give rise to a system of almost equally spaced rings. The rings observed in the present study are of this nature. The mean interspacing between the rings should be a measure of the diffusion length \((Dt)^{1/2}\) of the particles (where \(D\) is the diffusion coefficient of the product of interaction), from which diffusion coefficient may be estimated. In the present study the diffusion coefficient at a pH of 5 is found to be approximately \(5.213 \times 10^{-3}\) mm/hour.
11.3 Discussion

The observation of periodic bands and macroscopic deposits may be explained on the basis of a chemical instability of autocatalytic reaction mechanism of colloid growth and nucleation (8). In the present experiments, the product of interaction was uniformly precipitated in the form of colloidal particles as the outer nutrient diffused into the gel and met the other nutrient. Naturally, there will be a distribution of particle sizes (14). Since the reactants are suspensions of the components of the product material, the influence of by products (as in the case of electrolytes) is totally avoided. The theory of macroscopic structure formation in initially uniform colloids is based on the hypothesis of the occurrence of a chemical instability. Prior to the ring formation, a broad and spatially smooth distribution of colloidal particles exists in the system. The stability of a colloidal particle depends on its size due to the positive Gibbs free energy contribution (15). The dynamics of particle growth is on a short time scale, and hence each particle quickly comes to equilibrium with its environment. Because of surface tension the equilibrium concentration of particles depends on particle size (16). If, by a natural fluctuation or applied perturbation, some particles grow larger than their
neighbours, a spatial gradient of particles is established, and the larger particles will grow further at the expense of the smaller neighbours (Ostwald ripening). The competition in any volume element tends to make the distribution of particle size peak at some value of the typical particle radius. In the early stages of production of particles of the product of interaction, a large spectrum of sizes can survive. But as time \( t \) goes on, each sub volume will enter, depending on the diffusion length \( (D_t)^{1/2} \) into competition for particles. Eventually, even widely separated regions will communicate, and one will win over the other. It may be reasoned that the mechanism for the formation of periodic bands and macroscopic inhomogeneities, comes from the instability of the distribution function of particle sizes to patterned perturbations corresponding to small variations in the particle size distribution function from subvolume to subvolume. Thus the transition of a uniform distribution of particles to patterning is due to the interaction between diffusion and competitive growth leading to a symmetry breaking instability in the evolution of the particle size distribution function.

The ring structures evolve relatively quickly in a region of spatially smooth distribution of colloidal particles. The time required for the completion of a visible
ring is relatively short, compared to the time between formation of two rings. The rings are very sharp compared to the broadness of the colloid distribution from which it emerges. Once a ring is formed the regions on both sides of the ring show a reduction in turbidity. This is due to the fact that the particles in this region are removed by diffusion to be incorporated into the growing ring. If symmetry breaking instability coupled with diffusion is the cause of patterning, the patterns should be equidistant, since the factor controlling the separation of bands is diffusion (assuming that the particle size distribution function has the same value throughout the gel medium). The ring system in straight tubes as well as in u-tubes is fairly equidistant, which supports this point. The formation of macroscopic deposits along with rings in only u-tubes must be due to the presence of excess of both nutrients. This excess, influence the size distribution function and thereby the mechanism of the symmetry breaking transition.

11.4 Conclusion

Periodic precipitation by the interaction of suspensions of silver and arsenious trisulphide in a gel medium can be explained on the basis of a macroscopic symmetry breaking transition. Since the time associated with
the formation of a ring is large, no accurate verification of the spacing law is possible. Macroscopic deposits are only found in u-tubes, which may be because of the presence of excesses of both nutrients. This may influence the size distribution function, and hence the mechanism of chemical instability.
References

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