CHAPTER 2

PREPARATION AND STABILITY OF
SUSPENSIONS OF SMALL PARTICLES

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2.1 Introduction

In a true solution, the ultimate particles of the solute are of molecular size. The radius of the solute molecules in this case is seldom more than a nanometer and usually rather less. Solute and solvent molecules are of comparable sizes. In the case of systems consisting of particles dispersed in a liquid phase, the kinetic units are very much larger in size than the molecules of the liquid phase. The lower limit of size for the particles in dispersion of this kind is around 1nm and the upper limit is normally set at 1μm (1). The distinguishing feature of dispersed systems is that the area of contact between the dispersed particles and the dispersion medium is relatively large. The energy associated with creating and maintaining the interface is significant and the study of surface characteristics is an integral part of investigation of these dispersions.

The general methods of preparation of suspensions of small particles have been known for a long time (2-5). Recent studies by many workers have led to the production of dispersions in which the particles all have almost the same size and shape (monodispersed systems). The fine particles...
dispersed in a medium will be undergoing Brownian motion. They will be continually colliding with other particles and will remain as individual particles only if these collisions do not result in permanent associations. Such systems will remain stable only if some mechanism prevents aggregation during collisions. Stability can be attained by giving the particles a surface charge or by coating the particles with an adsorbed layer of some material, which prevents their closer approach. These procedures will slow down the process of aggregation, but cannot prevent it. The preparation of suspensions of fine particles, and the stability and aggregation of these suspensions are discussed in the following sections.

2.2 Methods of Preparation

The various methods of producing suspensions of small particles are classified into two groups: the dispersion methods and the condensation processes. There are different procedures in each of the above classes for producing dispersions of small particles in a liquid medium. A number of other variations like photo-decomposition, hydrolysis etc are also used for the production of dispersions of this kind. In this section methods of preparation used in the present study are discussed.
2.2.1 Dispersion Methods

1. Dispersion by Irradiation with Ultrasonic waves

An oscillating quartz disk is able to produce very high intensity ultrasonic vibrations which produce spectacular effects of dispersion. This phenomenon was first observed by Wood and Loomis (6) and further investigated by Freundlich (7,8), Sollner (9) and many others. This method of producing fine particles has the great advantage that the particles can be prepared without introducing foreign substances into the system. This type of dispersion is most effective when the material is in the form of a precipitate. The stability of the dispersion produced by this method is variable depending on the particle size. Coarse systems are usually relatively unstable.

2. Electrical Dispersion

Bredig (1898) was the first to prepare dispersions of small particles of metals using a direct current electric arc (10). Two wires of the desired metal are immersed in a suitable liquid containing a small quantity of stabilizer (electrolyte or steric stabilizer) and by completing an electrical circuit an arc is struck between the ends of the wires. The vapours of the metal, produced by the arc, condenses and is dispersed in the liquid medium as small
particles. The resulting suspension is found to be polydisperse. To remove the heat involved in the process the liquid must be kept cooled and stirred to prevent evaporation. Svedberg modified this method by introducing an alternating current arc (10). Use of an alternating current arc will produce particles of comparatively uniform size.

3. Dispersion by Chemical Means

Precipitated substances can be brought into a dispersion of small particles by chemical means also. In this method the precipitate is peptized (dispersed) by means of a suitable electrolyte. Precipitates, like small particles, carry a net charge. If the particles of a precipitate carry a negative charge, they are peptized by \( \text{OH}^- \) ions. If they are positively charged they may be dispersed by acids. Precipitates which contain large amounts of adsorbed or occluded electrolytes can sometimes be peptized by washing the precipitates with water. Many other agents like vanadium pentoxide, hydrogen sulphide etc, besides acids and bases may cause peptization. There is no peptization if the precipitate contains too much or too little electrolyte. Too high concentrations of electrolytes discharge the particles which then cling together because of the secondary valency forces and van der Waals attraction. Too low concentrations of the electrolytes have the same
effect: the particles do not adsorb the necessary net charge required for peptization and remain as a precipitate. Optimum peptization occurs at certain medium concentrations of the electrolyte.

2.2.2 Condensation Methods

Small particles of materials can be synthesised by joining molecules and ions into larger units. The simplest way to accomplish this is to pour a micromolecular solution into another liquid in which the solute is practically insoluble. Because of the decrease in solubility the solute is then precipitated as small particles. The stability of the resulting dispersion of small particles depends on the presence of electrolytes and small amounts of alkalies have a strong stabilizing effect. Decrease in solubility, however, is not the only way to make a dispersion of small particles by means of condensation. More important are the condensations performed by chemical means(2). The basic idea is to perform a chemical reaction in which an insoluble or difficultly soluble substance is formed so that the solid remains dispersed as small particles. The particles formed in many instances, have a crystalline structure. Thus condensation may be regarded as a process of crystallisation.
The size of the particles produced by condensation depends on two factors: the rate of formation of nuclei, \( W \) and the rate of growth of the crystals, \( Q \). The degree of dispersion is proportional to the ratio \( W/Q \) (2). Increase of temperature can either promote or retard the formation of small particles. Heat enhances the process of diffusion and Brownian motion, and the rate of reaction is increased. Thus the rate of formation of the nuclei \( W \) and the rate of crystallization \( Q \) are increased. But on the other hand the solubility of crystals also increases with increasing temperature. Experiments show that temperature affects differently the crystallization of moderately soluble and almost insoluble substances. The former precipitates in larger crystals from hot solutions than from cold. This is because the solubility increases quite considerably with temperature. Because of the larger surface the smaller crystals dissolve faster, and after cooling the material precipitates out on the larger crystals. For highly insoluble substances the influence of the temperature on the solubility of the particles is very small, but a temperature rise greatly increases the rate of formation of the nuclei. Consequently a very large number of minute particles are formed at high temperatures.

There are four main groups of chemical reactions in which small particles dispersed in a medium can be formed.
They are oxidation-reduction reactions, hydrolysis of salts, combination of ions and decomposition reactions.

2.3 Electrical Charge and Stability

The aggregation of small particles dispersed in a liquid medium is a usual process which leads to profound changes in the behaviour of the system. To have a stable suspension, there should be some method to prevent coalescence of the dispersed particles. Dispersed systems can remain stable for an appreciable time only if some mechanism prevents aggregation. There are two ways in which aggregation can be prevented. The particles can be given an electric charge and if all the particles carry the same charge they will repel one another more or less strongly as they approach each other. Also the particles can be coated with an adsorbed layer of some material which prevents their close approach. The former is known as electrostatic stabilization and the later steric stabilisation.

2.3.1 Electrostatic Stabilisation

The stability of a suspension of a solid phase in a liquid medium is determined by the charge carried by the particles. At the interface between any two phases, there is a tendency for charges (electrons and ions) to accumulate (1). In a dispersed system containing electrolytes the
attained by giving the particles a surface charge. This electrostatic stabilisation energy decays exponentially. The van der Waals energy between neighbouring particles decays in an inverse manner. At large distances the van der Waals attraction is always stronger than electrostatic repulsion. But at intermediate distances the electrostatic repulsion will be stronger, making the dispersion more stable.

2.3.2 Steric Repulsion

In many circumstances the electrostatic protection of suspensions is difficult or impossible. The electrolyte concentration required for stabilisation may be too high, or in non-polar media there may not be enough ions to give the surface a sufficient charge. In such cases large molecules which are adsorbed or chemically bound at the interface of the particles may form an efficient barrier against coagulation. If a long molecule adsorbed or free, is confined in a narrow space, it has fewer conformations available than in the bulk solution. This results in a lower entropy, a higher free energy and thus a repulsion. In addition, when two layers of long molecules come close together, the concentration is enhanced in the overlap region, which leads to an osmotic repulsion. A further effect of the layer of molecules is a modification of the van der Waals attraction especially if the polarizability of
the adsorbed layer differs from that of the dispersed medium. Thus addition of a long molecule will protect the particles from coming into contact and this type of protection is called steric stabilization.

2.4 Aggregation

A colloidal system is unstable if collisions result in the formation of aggregates. The aggregation observed in such a system is a process which leads to pronounced changes in the behaviour of the system. Aggregation will generally cause faster sedimentation of the dispersed particles. The sedimentation rate depends on the number of particles in the aggregates (11). The aggregation behaviour can be studied microscopically and macroscopically. For the microscopic study we would seek to follow the individual collisions between pairs of particles to determine the rate of formation of aggregates and must relate the diffusive motion of particles and the forces between them. Even when a highly dispersed system of small particles in a liquid medium appears macroscopically stable, aggregation and sedimentation may be going on but the rates of aggregation and sedimentation may be extremely slow. In this regime the presence of a stabiliser sets up a repulsion barrier between approaching particles. This decreases the efficiency of collisions so that 1 in say $10^5$ or $10^{10}$ or even more...
collisions actually result in a permanent particle-particle contact. If aggregation is allowed to continue for a long enough time, the particle aggregates become large enough to be macroscopically visible. These aggregates have a well defined symmetry, as their structure remains invariant under a change in length scale. This is called dialation symmetry and objects which possess it are called fractals (12). Knowledge of the structure of the aggregates makes it possible to determine the physical properties of the aggregates as they grow, as well as their mutual interactions which determine the growth process itself. Furthermore, the study of cluster aggregation represents one of the major applications and experimental tests of the modern statistical theories of kinetic growth.
References