March, 1993] © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 709—713(1993)

On the Formation of Inorganic Colloid Particles

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(Received August 31, 1992)

A qualitative model for the formation of inorganic colloidal particles is presented. The model is based on the symmetry of the complexes in solution and on the symmetry of distribution, i.e., position and orientation of the binding sites of the complexes. These factors determine the final particle shape when particles grow by crystallization, while in the case of additional secondary aggregation, it is controlled also by the factors which determine crystal habit and stability of colloidal particles. In addition, kinetic factors have to be considered also because the systems are normally driven through various phases far from themodynamic equilibrium.

Colloidal particles with well defined characteristics, either in powdered form or in suspension (sol), are very important in many different areas of scientific endeavors. From the first studies, originating predominantly by scientific curiosity and even aesthetical desires of some scientists, they have become an important tool in theoretical colloid science and in their application in several industries such as ceramic (superconductors), protective coating, (micro) electronic, chemical (catalysis), etc. Their use is predominantly based on their special properties which are mainly due to the large surface to volume ratio. For most of the applications uniform, monodisperse, and spherical colloid particles are the preferred choice.

Due to all these facts the literature on the preparation of monodisperse colloidal particles, especially in sols, is numerous.1—3) However, most of the studies present only experimental conditions for the specific particle formation and not much is known or understood about the underlying mechanisms. For instance, same systems in very similar experimental conditions can give rise to very different colloidal particles.

Besides some inorganic polymerization reactions which produce, for example, silica sols4,5) and reactions with(in) aerosols,2,3) the majority of monodispersed inorganic colloids are prepared by precipitation from homogeneous solutions. The colloidal metal (hydrous) oxides or basic metal compounds which represent the vast majority of inorganic colloids, are usually prepared by forced hydrolysis. At elevated temperatures the water molecules coordinated to the metal ion deprotonate and the hydroxylated intermediates form colloidal particles upon polycondensation. These intermediates could also be obtained by the controlled release of hydroxide ions (or sulfide, etc.), upon thermal or chemical decomposition of organic molecules (urea, formamide), or by release of cations by thermal of chemical dechelation into basic solution. Typical examples for these three general preparation procedures are chromium(III) hydroxide, cerium(IV) oxide, aluminum hydrous oxide, hematite (forced hydrolysis), ruthenium oxide, zinc oxide and sulfide, lead(II) sulfide (release of anions) and oxides of copper, iron, cobalt, barium titanate, etc. (release of cations).2,3)

Many stable colloidal systems were also prepared from metal alkoxides.6—8) The mechanism of these reactions was studied7) and compared to classical La Mer model of the formation of monodisperse hydrosols.9,10) These approaches, however, addressed the issue of the homogeneity of the colloidal particles rather than their shape.

A typical example of the complexity of these processes is the formation of spherical and rodlike particles of cerium complexes. Uniform spherical or rodlike colloidal particles form upon aging of mixtures of cerium (IV) sulfate and sulfuric acid. The shape depends only on the ratio of the two reactants.11) The aim of this article is to present a qualitative model for the formation of various colloidal particles and particularly to explain the origin of different shapes of colloidal particles forced in similar experimental conditions.

Hypothesis and Model

Although the precipitation of colloid particles is either a process of crystallization or growth of amorphous solids with a possible secondary aggregation of the primary particles, the process itself could be hardly compared to classical crystallizations which normally occur close to thermodynamic equilibrium and in general produce much larger particles. Uniform colloidal particles are formed usually far from equilibrium conditions in solutions which relax its stress, i.e. higher energy metastable state, by sudden explosion of (crystal) nuclei. According to the La Mer model the thermodynamic driving force is supersaturation which balances the energy required for the creation of new surfaces. We propose that in such cases the whole metal complexes combine into crystallization nuclei and precipitate and the solid phase grows normally by polycondensation. That is in contrast to the classical crystallization where building blocks of crystals are atoms, ions or molecules. In this case the crystal system, and consequently the shape of microcrystallites, depends on the structure and symmetry of the complex(es) in the solution which is mainly a function of pH

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and relative and absolute concentrations of the reactants. The crystal habit and possible aggregation properties of nuclei themselves depend on the presence of various species, ionic strength, and kinetic phenomena. In the case of secondary aggregation the size and interactive properties, i.e. attractive and repulsive forces which determine the stability of colloidal particles, play an important role too.[7,12,13] The kinetics of aggregation can be described by a classical approach using Smoluchowski equation while some modern work uses the fractal concept.[12] Most of these studies, however, deal with the instability of preformed (stable) colloidal particles which aggregate into scale invariant aggregates in far from equilibrium conditions[14—16] and are therefore not relevant in the processes described here.

Results and Discussion

Two different systems will be analyzed. In the cerium(IV) system the shape of the complexes will be related to the final particle shape while in the example of iron(III) aqueous system the influence of kinetic effects, in addition to the symmetry of metal complexes in solution, on the morphology of the particles formed will also be discussed.

Cerium System. As described in the introduction and reported in details in Ref. 11, spherical or rodlike particles can be formed from cerium sulfate solutions. To explain this observation we propose that the building blocks of the colloid particles are the cerium(IV) complexes from the solution. They bind or condense into embryo which grows into spherical particles or grows and aggregates into a rodlike particle.

Spherical Particles: At lower Ce(IV) and SO_4^{2-} concentrations and at higher Ce/SO_4 ratios mononuclear $Ce(H_2O)_n(SO_4)^{2+}$ complex, with $n=5$ or 4 for uni- or bidentate binding of SO_4^{2-}, is stable in solution (Fig. 1a). At elevated temperatures some of the coordinated water molecules in the complex deprotonate and reactive $Ce(SO_4)(H_2O)_4OH^+$ (in the case of unidentate complexes) bind via elimination of water:

$$\begin{aligned}&(SO_4)(H_2O)_4Ce^+OH + HOCe^+(H_2O)_4(SO_4)\\ &\quad \rightarrow H_2O + (H_2O)_4(SO_4)^+Ce\text{–}O\text{–}Ce^+(SO_4)(H_2O)_4\end{aligned}$$

Because the octahedral complex is almost isotropic (spherically symmetric) and because the binding sites (hydroxyl) are spatially oriented in a cubic symmetry the Ce–O–Ce bonds can be made only in cubic lattice. If these small cubic nuclei aggregate they would probably form an amorphous particle. The cubic symmetry of the particles formed (CeO_2) indicate that they are probably grown by crystal growth, i.e., by binding new complexes on the cubic sites on the crystal embryo. For the operation of this mechanism a relatively fast exchange of ligands with the bulk is required.

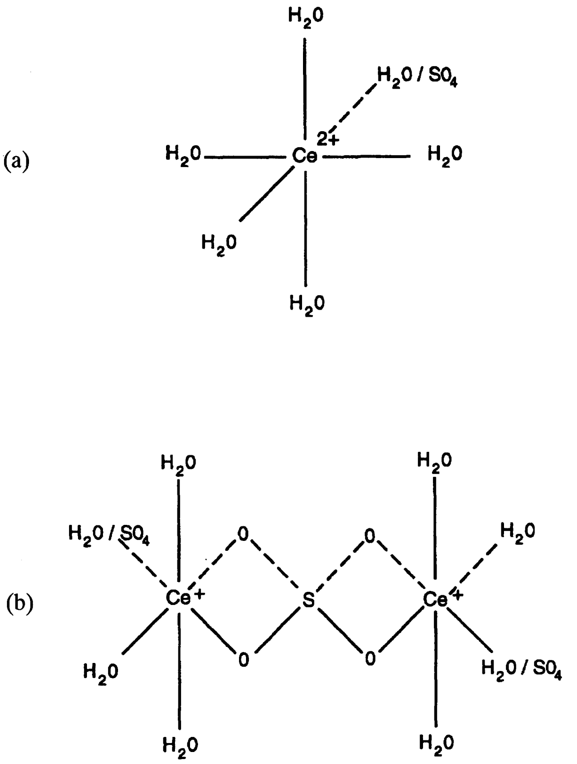

Fig. 1. Structural formula of mononuclear (a) and dinuclear (b) cerium complex in solution at different concentrations and ratios of Ce, SO_4, and H ions. The almost spherically symmetric mononuclear complex can bind into isotropic particles while the elongated di- (or poly-) nuclear complex can bind into anisotropic structure. From this model one would expect that spherical complexes would pack into cubic $(-Ce\text{–}O-)_n$ lattice forming cubic CeO_2. The dinuclear complex has orthorombic symmetry and one would expect that these complexes would aggregate, bind and crystallize via Ce–O–Ce bonds into orthorombic $CeOSO_4$. These two structures with corresponding crystal symmetries were indeed observed in colloidal dispersions as well as in the crystalline forms when the stress in corresponding solutions was relaxed in a kinetic or equilibrium procedure. The first one gives rise to metastable colloidal particles while the second one causes the formation of stable crystals/crystallites.

Rodlike Particles: At higher Ce^{4+} and SO_4^{2-} concentrations at higher SO_4/Ce ratios a dinuclear (possibly also polynuclear) complex is predicted. Such dinuclear complex bridged with sulfate anion is shown in Fig. 1b and has the chemical formula $Ce_2(SO_4)_m(H_2O)_n$ with m being ≥ 1 and $n=8-(m-1)$ for a bidentate sulfate bridge and $n=10-(m-1)$ for the unidentate bridge. Again, at elevated temperatures the coordinated water molecules become deprotonated and it is very likely that these elongated, linear complexes can bind and pack together only in an anisotropical way. The distruction of SO_4/H_2O ligands on equatorial and axial sites may determine the habit of the growing nucleus. The rodlike embryos can either grow or pack themselves into an acicular crystal habit yielding anisotropic (rodlike) particles. As observed in the electron microscope the second possibility is more likely. In the case of secondary aggregation the interparticle interactions and colloidal stability are very important.[7,12] Again, asymmetric particles may have asymmetric potential which results, as is the case of liquid crystals, in the growth of nonspherical aggregates.

Experimental

The model predicts that the spherical particles are cubic CeO_2 and rodlike are orthorombic $CeOSO_4$. The published crystal structures of both compounds[11,17] are in exact agreement with the structure predicted from this model. Orthorombic structure where SO_4 groups bridge Ce–O–Ce chains in a square lattice indicates that the active site of binding are axial sites on Ce(IV) ions, a fact one can expect from steric and electrostatic considerations. The model also predicts that the surface of CeO_2 particle is covered with sulfate groups. This agrees well with the experimental observation that remaining SO_4 groups can be washed by bases.

The proposed structure of the complexes in solution is also in agreement with the scarce literature data. Several studies have observed hydrated $CeSO_4^{2+}$ complex in the region of low concentration of sulfuric acid[18—23] while at higher concentrations dinuclear complex $[Ce_2^{IV}(SO_4)_3(H_2O)_6]^{2+}$ was observed.[24—26]

The experimental observation that the presence of NaCl, $NaClO_4$, and Na_2SO_4 does not influence the size of the particles, while $NaNO_3$ does, could also be undertstood by the solution behavior of Ce(IV) complexes. It is known the Ce(IV) does not form complexes with halide and perchlorate ions while it does with NO_3. Binding of NO_3 therefore interferes with H_2O binding and reduces the number of active sites and reduces the growth rate. Sulfate anions are already in a large excess and the complex does not change.

Iron System. Colloidal particles formed in aqueous solutions of iron(III) aqueous solutions may serve as another example. At low values of pH (<0) iron(III) ion exists as a hexaqua complex ($[Fe(H_2O)_6]^{3+}$), and at pH between 1 and 2 as a mononuclear pentaquahydroxo, tetraqua dihydroxo, or dinuclear $[Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{4+}$ complex.[27] At higher values of pH the hydrolysis is enhanced and polynuclear complexes condense and precipitate as a red brown gelatinous mass, $Fe_2O_3 \cdot nH_2O$. These systems are known to attain equilibria in a sluggish way.

Many experimental studies[28—32] have shown that iron(III) aqueous solutions in the presence of various anions result in the formation of uniform colloidal particles of either β-FeOOH or α-$Fe_2O_3 \cdot H_2O$ (hematite). The shape of these particles can range from rodlike, ellipsoidal, spindlelike, to prismatic, cubic, and spherical. In HCl solutions predominately rod-like FeOOH or spherical α-$Fe_2O_3 \cdot H_2O$ particles are formed. In HNO_3 solutions besides irregular particles mainly ellipsoidal particles are found while the variety of structures formed upon precipitation from $HClO_4$ solutions is richer.[28] In all cases, however, at lower values of pH (<1) no particle formation is observed and at pH>3 and $Fe^{3+}<0.01$ M spherical α-Fe_2O_3 particles are formed ($1\,M=1$ mol dm^{-3}). In between these two regions different particles can form, with respect to the anion and experimental conditions. Another interesting observation was, that in the presence of alcohols the processes were similar.[29] However, the kinetics was faster and in the first step predominantly rodlike FeOOH particles were formed which after recrystallization transformed into cubic α-Fe_2O_3 particles.

All these data can be, again, qualitatively explained by the geometry of the complexes formed and present in the aqueous solution prior to forced precipitation. At lower values of pH the iron ions are very soluble and do not precipitate. As the literature reports, in the presence of Cl^- ion, $FeCl_4^-$ complexes are very stable because the active sites for binding, i.e., "symmetry breakdown points" such as partially hydrolyzed $FeCl_3(H_2O)$, are practically non existent. At higher values of pH hydrolysis occurs and complexes can bind together and eventually form nuclei for growth of solid material. At the same values of pH the tendency to form di- and poly- nuclear complexes increases with iron ion concentration. And again, we find spherical particles at lower values of $[Fe^{3+}]$ where spherically symmetric and isotropic mononuclear complexes bind into a nucleation embryo. At higher iron concentrations elongated, rodlike and asymmetric, i.e., anisotropic, complexes form crystallization/precipitation nuclei and deviations from spherical shape are observed. The presence of other shapes, such as ellipsoids or spindles, can be explained by the balance of these two limiting growth mechanisms, while the appearance of cubes in this system probably indicates quenched crystallization far from equilibrium conditions.

The shape of the particles formed depends on the geometry of the crystallization/solidification embryos which in turn depends on the molecular symmetry (i.e., spatial distribution of the binding sites Fe–OH) of the complex in solution. The origin of the complex stereochemistry, i.e., the complex geometry as a function of concentration, pH, and anion, is beyond the scope of this article: Certainly it has to do with spatial distribution of electronic orbitals, i.e., geometrical distribution of electronic binding sites., as well as thermodynamic (solubility, bond strength, entropy character, i.e., structure breaking/making effect, etc.) properties of anions. Also, possible presence of inert substances, such as templates or adsorbed species[33] which can act as precipitation embrios with special geometries, or sterically shield particular sites on the growing nucleus, may have an effect. Furthermore, the situation may be further complicated by the coexistance of various complexes and equilibria among them in solution.

An interesting observation was that in some cases secondary changes of particle shape occur. In order to explain this we should invoke the definition of a kinetically controlled process as opposed to a thermodynamically controlled one.

The author believes that most of the processes which lead to the formation of uniform colloidal particles are kinetically controlled, i.e., driven far from the thermodynamic equilibrium. At conditions close to thermodynamic equilibrium these systems crystallize out (or precipitate as amorphous phase) in large (mono) crystals. However, in the cases above the systems are forced to change and this quick perturbation may result in the formation of numerous precipitation nuclei instead of only a few, what happens in the case of equilibrium processes. The states reached when the systems are driven far from equilibrium are normally metastable. The systems, so to say, just try to accommodate to the sudden stress by sliding into the nearest potential well because they simply do not have time to find the one with the lowest free energy. In the case of the iron(III) system the polynuclear complexes pack into elongated, anisotropic particles of metastable FeOOH and upon additional aging recrystallize into more stable α-$Fe_2O_3 \cdot H_2O$ which was kinetically not accessible. If the systems are driven closer to the thermodynamic equilibrium, (i.e., same aging times, but lower concentrations, less supersaturation, $\cdots$) the system may go into a more stable state directly and, as observed in experiments, spherical hematite particles are formed.

With other words, morphology of the particles formed can depend on the kinetics of their formation, i.e., it may be quite different if the particles were formed at equilibrium conditions, in a steady state, or far from equilibrium process. Similar observations were observed also in aluminium oxide and hydroxide colloidal particles$^{34)}$ as well as in organic colloidal particles, such as liposomes$^{35,36)}$ or stable coin-like micelles$^{37)}$ where the kinetic effect may play even more important role due to very low water solubilities of the aggregating molecules.

The above arguments indicate that the formation of uniform colloidal particles is a kinetic process in which the proper conditions have to be found to produce a sudden burst of numerous crystallization nuclei. Although some of the particles may be stable in solution for prolonged times they are not necessarily thermodynamically stable, and in many cases, they precipitate and grow into larger solid particles (although the time scales may be measured in decades). Their stability, of course, depends on many physical and chemical parameters, such as size, homogeneity, surface charge, pH, and ionic strength which dictates various enthalpy and entropy contributions to the free energy of the system.

The influence of lower alcohols on the particle formation is in agreement with the above conclusions. Lower alcohols are known to enhance hydrolysis and this probably forces the system even more into the kinetically controlled region.

In these complex systems, in which the final particle size and shape depends on many thermodynamic and kinetic factors which include structure, symmetry, stability, interactive potentials of complexes in solutions as well as of crystal embrios, it is much easier to explain, rather than predict, a set of phenomena. A very important factor is also the solubility. Nevertheless, according to this model the knowledge of the solution behavior of various metal complexes may be a good starting point to predict particle morphology. Working far from equilibrium conditions may produce more irregular and anisotropic particles, while spherical and regular particles may be produced in processes closer to a steady state and thermodynamic equilibrium. The addition of (block co) polymers as (steric) stabilizers of particles, in the beginning, or at a particular time point during the process, may be and additional means to control the size and shape of the produces particles. Also, in the kinetically controlled regime higher concentrations should produce larger particles due to shorter mean free paths, a dependence which has not been thouroughly studied yet.

This model can qualitatively explain shapes and possibly sizes of colloidal particles while the homogeneity of particles produced presents even more difficult challenge. In the case of liposomes, an organic colloid system which often gives rise to very broad size distributions, it was observed that in the cases when they are formed far from equilibrium conditions often a rather monodisperse population, close to the minimal possible size, is obtained. Of course, liposomes normally cannot grow after they are formed. Nevertheless this may imply that to start the process a quick relaxation of the system is required which can be continued by a steady state growth and that heterogeneity may appear only after a process, such as Ostwald ripening becomes faster than particle size growth.

To conclude, a qualitative model for the formation of uniform inorganic colloidal particles is presented. It states that the shape of the particles formed depends on the symmetry and symmetry of distribution of active binding sites on the complex in solution prior to forced precipitation. Several other factors which may influence these two parameters are also mentioned. The author hopes that the model presented will inspire some new physicochemical and/or computer experiments which would shed more light on the mechanism of various particle formation and on the whole field, where on one side so much is known and on the other, so little is understood.

The author would like to thank Dr. Egon Matijevic for helpful discussions.

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