Colloidal Gold. Part II

COLOUR, COAGULATION, ADHESION, ALLOYING AND CATALYTIC PROPERTIES

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In the first part of this review, published in the July, 1985 issue of this journal, historical, preparative and structural characteristics of gold colloids were discussed. In this final part their properties will be dealt with.

Colour

The beautiful ruby red colour has been for a long time the aesthetic characteristic of colloidal gold solutions containing uncoagulated particles of diameter less than 40 nm. The colour is due to a rather narrow absorption band at 520 nm. There is negligible scattering of light by particles whose diameter is less than 40 nm. With increase in particle size the absorption band shifts to longer wavelengths and light scattering becomes marked. When the gold sol is partially coagulated the colour becomes blue and absorption is accompanied by light scattering. In 1902 Gustav Mie (5) using classical electromagnetic theory calculated from bulk optical properties of metallic gold, the absorbance of colloidal gold particles as a function of the particle size. In 1952 Turkevich and Garton (31) using a graded set of monodisperse gold sols of varying particle size, confirmed experimentally the calculations of Mie (Figure 10). The optical spectra of the gold-platinum preparations (Figure 11) are not an additive superposition of the spectra of pure gold and platinum. The characteristic peak of gold at 550 nm is absent and is only apparent in the 75 weight per cent gold as a shoulder. The alloy spectra resemble that of platinum and are considered as evidence of alloy formation and the electronic effect of platinum on gold.

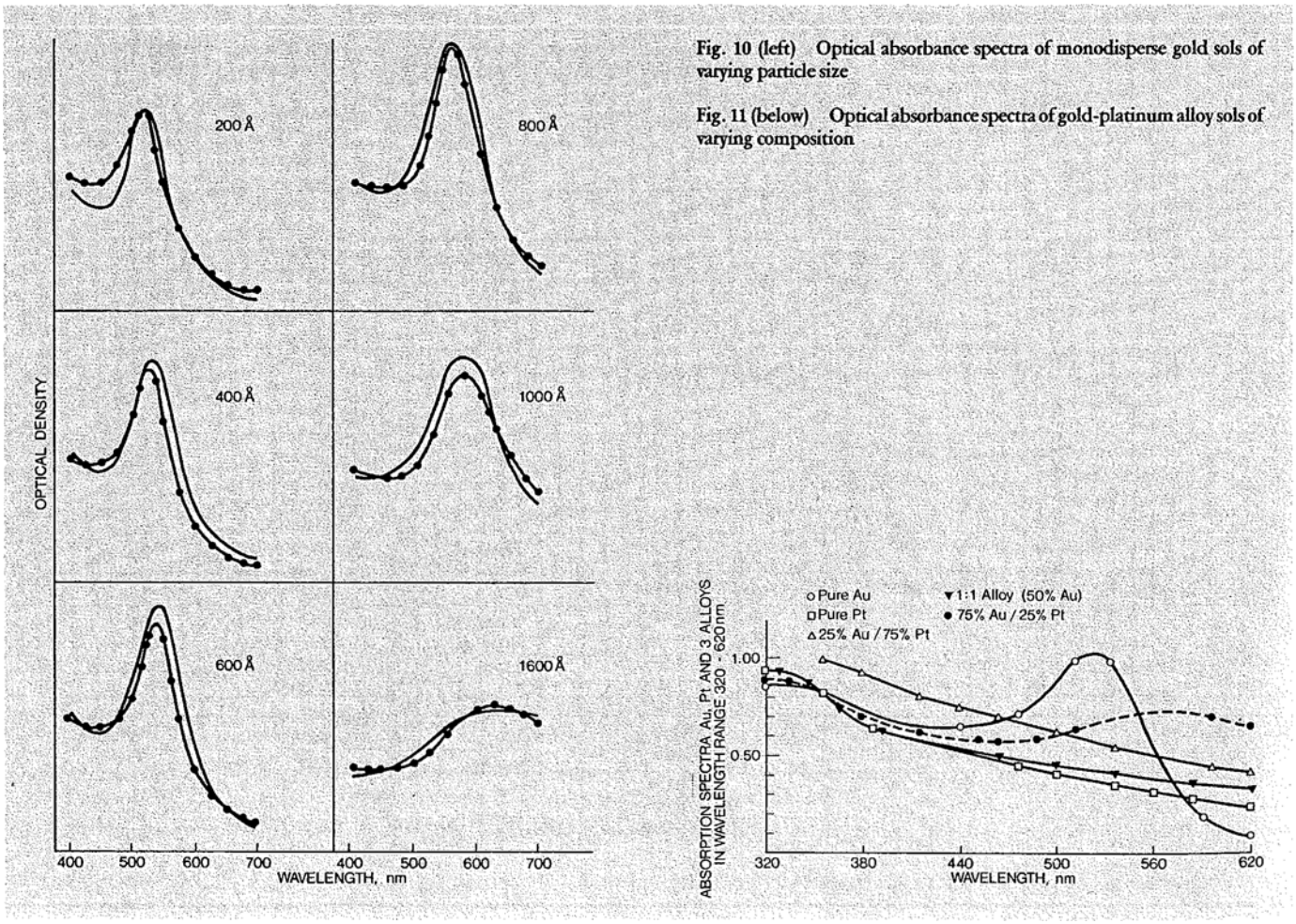

Fig. 10 (left) Optical absorbance spectra of monodisperse gold sols of varying particle size

Fig. 11 (below) Optical absorbance spectra of gold-platinum alloy sols of varying composition

Another approach, particularly useful in explaining the colour of partially coagulated gold colloid solutions, is to consider the conduction electrons in the particle as undergoing dipole plasma oscillations (32).

These oscillations are characterized by a polarizability given by the Lorenz formula

$$\alpha = a^3 \left(\frac{\varepsilon - n_0^2}{\varepsilon + 2n_0^2} \right)$$

where ε, the dielectric constant of the metal, is a function of the wavelength λ and is equal to $\varepsilon_1 + i\varepsilon_2$, a is the radius of the particle and n_0 is the index of refraction of the medium, water. Absorption is identified with that value of λ at which ε_1, makes α a maximum and this, in our case, is when $\varepsilon_1 = -2n_0 = -3.58$. ε_2 determines the half width of the absorption band.

On coagulation of the new gold sol a new band appears at 680 nm (Figure 12). The colloid assumes a blue colour and shows marked scattering of light. The appearance of this second band can be given the following explanation in terms of dipole plasma oscillations (32). When two metallic particles of the colloid come within two or three diameters of each other, their plasma dipoles interact. The three-fold degeneracy of the polarizability of the spherical particle breaks up into two components, a longitudinal and a transverse, given by

$$\alpha_\ell = \frac{8a^3}{3} \left(\frac{\varepsilon - 1}{\varepsilon + 3} \right) \qquad \alpha_t = \frac{16a^3}{3} \left(\frac{\varepsilon - 1}{\varepsilon + 5} \right)$$

This will give rise to two resonances and consequently two absorption bands at λ's corresponding to $\varepsilon_\ell = -3$ and $\varepsilon_t = -5$. This type of treatment can be extended to long linear chains of particles to give an explanation for the blue colour of a partially coagulated gold sol.

Recently there has been considerable interest in the anomalously intense Raman spectra of molecules adsorbed on metallic surfaces. The degree of this enhancement depends on the roughness of the metal surface and is particularly large for molecules adsorbed on metallic colloids e.g. pyridine on colloidal gold (32-35). The wavelength of the exciting radiation was found to lie within the envelope of the particle plasma resonance absorption band. The effect also depends on the state of aggregation of the colloid particles: linear chains showing the effect with individual particles and clusters playing a minor role. Furthermore this enhancement is particularly strong when excitation takes place in the longitudinal component of the plasma resonance band. Absorption in this band increases the electromagnetic field at the location of adsorbed molecules and thus amplifies the intensity of the Raman scattering.

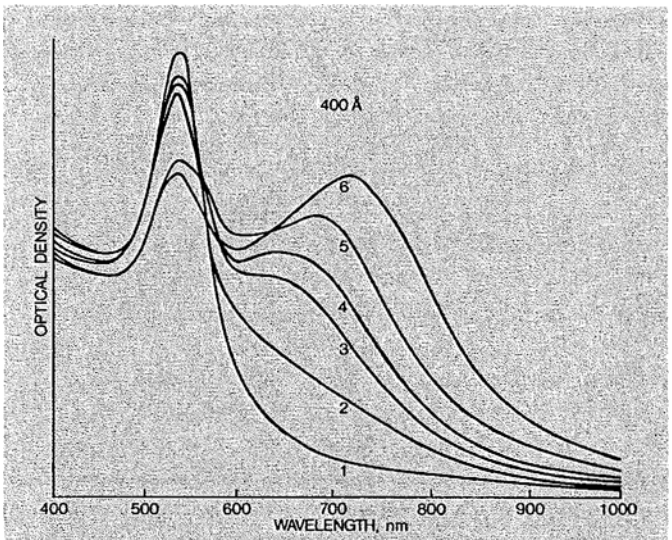

Fig. 12 Optical absorbance spectra of standard citrate sols containing 400 nm colloidal gold in varying states of coagulation by addition of aluminium nitrate solution viz:
1. Zero Al^{3+}
2. 0.001% Al^{3+}
3. 0.0017% Al^{3+}
4. 0.0025% Al^{3+}
5. 0.0033% Al^{3+}
6. 0.005% Al^{3+}

The gold concentration in each case was 42 mg/l

Coagulation

In the standard citrate sol, the gold particles have a negative charge as shown by their migration in the electric field toward the positive electrode. This negative charge, due to strongly adsorbed citrate ions, is balanced by loosely bound sodium cations making the overall solution neutral. The charge on the gold particles can also be made positive by the following procedure: most of the citrate is removed from the solution and the particles themselves by passing the colloid through an ion exchange column; the solution is then treated with low molecular weight N-hexyl pyridimium polyethylene bromide (36). The positively charged polymer is strongly adsorbed on the gold giving it a positive charge. This is neutralized by loosely bound negative bromide counter ion. The strongly adsorbed molecules with either negative or positive charge, form a sharp Stern layer on the particle which is then surrounded by a diffuse Debye atmosphere of positive (Na^+) or negative (Br^-) counter ions. The thickness of this diffuse Debye atmosphere depends on the strength χ of counter ions in solution and thus is given by

$$\chi = 3 \times 10^7 \sum_{i=1}^{n} z_i c_i^{1/2}$$

where z_i and c_i are the charge and concentration of all ions of opposite charge to that on the particle. The thickness of the Debye atmosphere is an important factor in determining the stability of the gold colloid.

The number of collisions that gold particles undergo with each

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other is very high being many thousands per second at ordinary dilutions of the standard citrate sol. In spite of this the particles under proper conditions of preparation do not coalesce. This stability is due to the repulse potential of the diffuse Debye counter ion atmosphere which comes into play as the two colloidal particles approach close to each other on collision. This is greater than the attractive van der Waals potential of the gold particles which would lead to the coalescence of the colliding particles. Verwy and Overbeek (37) gave the following expression for the resultant potential energy E between two particles as a function of their separation

$$E = \frac{64kT\gamma e^{-\chi d}}{\eta} - \frac{1}{4\pi d^2}$$

where d is the distance between the two particles, k is the Boltzmann constant, T is the absolute temperature, γ is a constant close to 1, A is the van der Waals constant. χ is the ionic strength and e is base of the natural logarithms. This relationship was checked by the Turkevich group (38) by determining the critical concentration of added counter ion which will just produce coagulation. According to the Verwey-Overbeek theory, rapid coagulation occurs not only when the resultant potential E is zero but when also its slope is zero, giving for the critical concentration the value

$$C = \frac{8 \times 10^{-22}}{A^2 z^6}$$

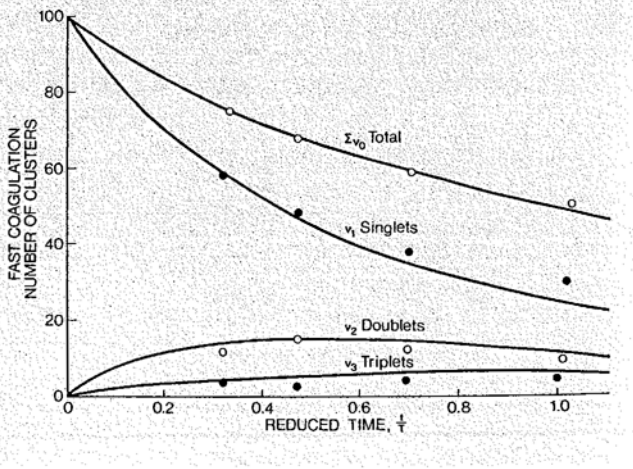
where z is the charge on the ion causing coagulation. One should note the strong dependence on the inverse sixth power of the charge on the counter ion. A strong dependence on the charge has been previously noted in 1882 by Schultze (6) and Hardy (7). The dependence was established quantitatively by Turkevich and Baker (38, 39) who studied the concentration necessary for coagulation by the perchlorates of Na^+, Mg^{2+}, Al^{3+} and Th^{4+} ions and found an inverse 5.6 power relationship. Turkevich and Naker, and later Enusten, Demirci and Turkevich (40, 3) were able to calculate the van der Waals, or more precisely the Hamaker, constant A as 0.87×10^{-13} erg. This compares favourably with the quantum mechanical value of 10^{-12} to 10^{-13}. The experimental determination is easier than the macroscopic measurements of Overbeek (41) who measured the force between two highly polished flat plates, of Deryagin (42) who measured the force between a plate and a hemispherical surface, and of Israelachvilii (43) who measured the force between two mica plates to obtain a value of 2.2×10^{-13} ergs.

Slow coaguation takes place when the concentration of the counter ions is lower than the critical concentration or when the electric charge on the colloidal gold particle is decreased by the desorption of the citrate ions from the Stern layer. In a detailed study of the slow coagulation Enustun and Turkevich (36) showed that the simple picture of fast coagulation caused by the compression of the diffuse Debye atmosphere is complicated in slow coagulation by exchange of ions of the coagulating salt with the citrate ions in the Stern layer and by redistribution of the citrate ions between different clusters of particles. Furthermore the potential around a doublet of particles is not spherically symmetric but is lower at the ends of the doublet. Under conditions of slow coagulation this favours the adhesion of a third particle at the end to give a linear triplet rather than a triangular cluster. Formation of linear aggregates is accentuated as the slow coagulation proceeds. The same linear morphology of the coagulum of gold particles is observed when the charge on the particle is decreased by exhaustive deionization of the colloidal solution or by mixing the negative sol with a positive sol.

Electron spin resonance of an organic nitroxide free radical was used by Turkevich and Soria (44) to study the adsorption of this uncharged molecule on standard citrate sol. The adsorbed free radical shows no signal so that as the adsorption takes place the signal decreases. Slow coagulation takes place and the signal reappears.

Let us now consider the kinetics of the coagulation process. In 1916 Smoluchowski (9) calculated the rate at which particles coagulate — how fast the singlets disappear, how fast the doublets, triplets, quadruplets, etc. increase and then decrease in number. Smoluchowski's theory of rapid coagulation was tested experimentally using the ultramicroscope, colorimeter and Tyndallometer measuring the change in the total number of particles with time. Baker and Turkevich (38, 39) used the electron microscope to verify in detail the number of clusters of a given size as a function of time. A dilute solution of 400 nm diameter gold particles was coagulated by the addition of sufficiently large concentration of salt to collapse the ionic atmosphere and to make every collision lead to aggregation. Advantage was taken of the finding that addition of a small amount of gelatin could stop the aggregation at any desired time. In this way samples could be obtained at different coagulation times and could be mounted for electron microscopic examination without changing the extent of

Fig. 13 Rate of fast coagulation of standard citrate sol



coagulation during the mounting process.

Figure 13 shows the variation of the number ν_k of clusters of a given state of aggregation k as a function of reduced time t/τ.

$$\tau = \frac{3\eta_\gamma}{4kT\nu_0}$$

where η_γ is the viscosity of water, and ν_0 is the concentration of singlets in the original colloid. Figure 14 shows the experimental verification of the Smoluchowski relationship between the number of clusters of k particles at two times during the aggregation process. As pointed out above, the kinetics of slow coagulation are more complex.

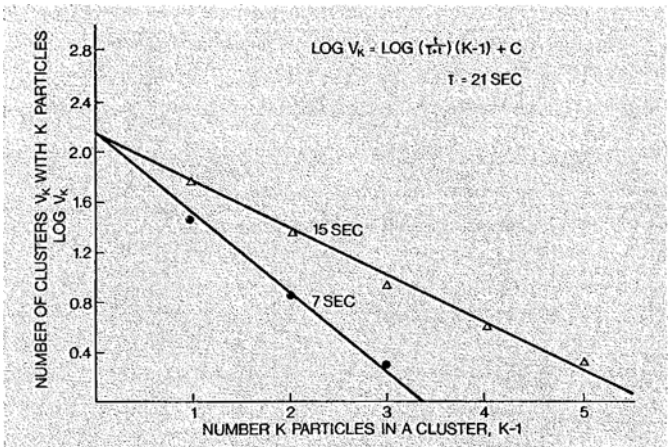


Fig. 14 Verification of Smoluchowski relation for fast coagulation

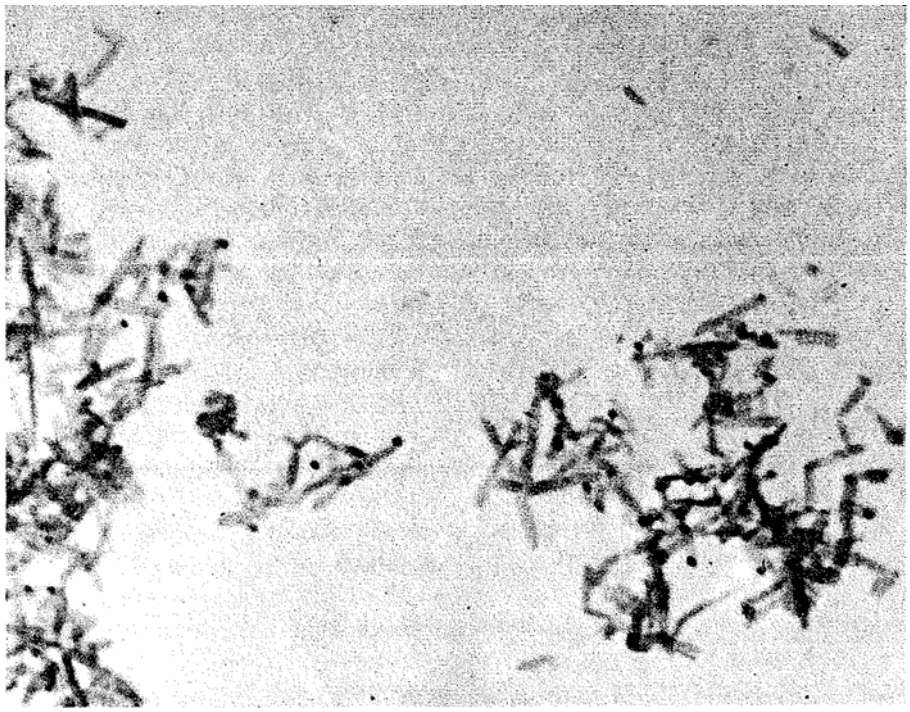
Adhesion

The charge on the colloidal particles can be used to adhere particles to surfaces. The surfaces so 'decorated' can be examined with the electron microscope to determine the locale of surface charges. Thiessen used for this purpose negatively and positively charged gold particles and showed that the charge on the edges of clay platelets was different from that on the surface of the plates. The Turkevich group prepared supported metallic catalysts by adsorbing colloidal particles of gold, palladium (51), platinum (52), and their alloys (27) on rods and plates of alumina (Figure 15).

It is well known from classical colloid chemistry that certain substances, particularly proteins, stabilize metallic colloids and prevent their coagulation. A subtle interaction between specific proteins and colloidal gold is the basis of the well established diagnostic spinal fluid test. As pointed out above, addition of gelatin, or low molecular weight polylysine during the coagulation process stopped the coagulation permitting an electron microscopic determination of the details of the coagulation process. Turkevich, Demerci and Skvir (45) used the electron microscope technique to study the adherence of gold particles on to membranes with and without a coating of protein. The membranes were evaporated carbon, cellulose nitrate or formvar films thin enough to be suitable for electron microscope examination.

These membranes were held vertically for definite periods of time in a series of solution of protein, water, colloid solutions, water, dried and examined with the electron microscope to determine the number of particles per unit area of 5×10^{-8} cm^2. After sixty minutes immersion in a standard citrate gold sol containing 5.0×10^{11} particles per ml the concentration was 38 particles. If the membrane was previously treated with 0.1 per cent gelatin solution, the surface concentration after 60 minutes immersion in the colloid was 1265 (Figure 16). During the first 40 minutes the concentration increases linearly with time and is proportional to concentration. The process follows the classical Sutherland-Einstein law for the diffusion according to which the number of particles colliding with a cross section A cm^2 of the

Fig. 15 Electron micrograph of 20% gold– 80% platinum catalyst adsorbed on alumina plates. x 300 000



membrane in time t seconds in a solution containing N_0 particles per ml is given by

$$N_t = DN_0At$$

where D is the diffusion coefficient

$$D = \frac{kT}{6\eta a}$$

with η the viscosity of water and a the radius of the gold particle. There is a surprisingly good agreement in the absolute number of particles that stick on collision.

For standard citrate sol 2 900 particles were observed after 35 minutes instead of the theoretical 19 208 giving an adhesion efficiency of 15 per cent. The theoretical value for a colloid solution of half the concentration after 40 minutes is 8 910 while the observed number was 1667, with 19 per cent efficiency of adhesion. In another experiment using gold particles of 20 nm radius and in a concentration of 7.5×10^{11} particles per ml the theoretical adhesion after 20 minutes was 345 particles while the number observed was 168 with an adhesion efficiency of 49 per cent. The membrane was then introduced into a standard 10 nm radius gold sol for 10 minutes. The concentration of the 10 nm particles on the membrane was 1 068 while the theory predicted 5490 with sticking efficiency of 19 per cent. There was an absence of adhesion of small particles around the larger ones and there seemed to be an area free of smaller particles around the larger ones. It was noted that in all the adhesion experiments the particles were scattered randomly as single units on the surface, but as the surface filled up, linear configurations of particles became apparent — the particles either touched one another or were separated by distances of multiples of the particle diameter. This phenomenon did not depend on the nature of the membrane or whether the protein was on the membrane or in solution.

Presence of the protein in solution in amounts sufficient just to coat the particles decreased the efficiency of adhesion by a factor of three while presence of gelatin on both membrane and particles produced weak adhesion and the particles could be easily washed off with distilled water.

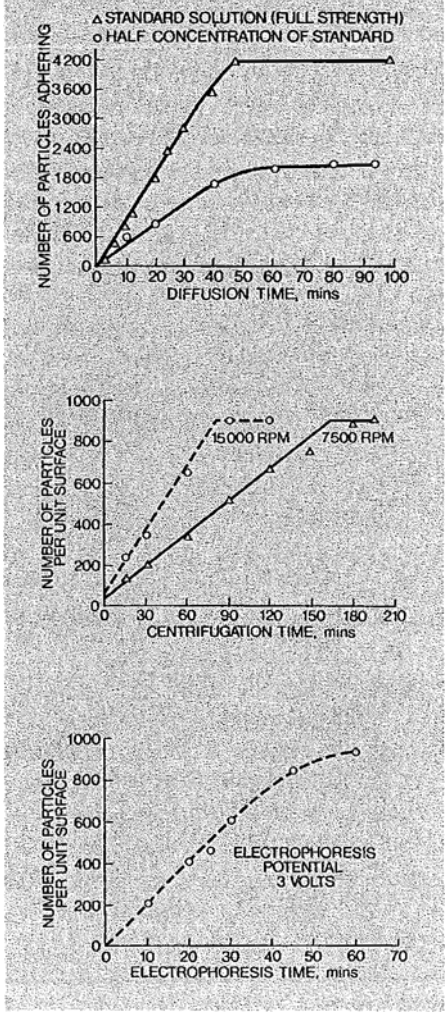
This technique, so successful in the study of the motion of colloidal particles in diffusion, was applied to centrifugation, electrophoresis and combination of the two. For centrifugation a gelatin-coated membrane was placed at the bottom of the centrifuge tube which was then filled with the colloid. Centrifugation was carried out in an International Centrifuge (Model H7) which has eight port holes for tubes located in the centrifuge head at 45° angle to the axis of rotation. Velocities up to 18 000 rpm were used. Centrifugation was first used to determine the optimum concentration of gelatin to obtain maximum adherence of particles. The optimum concentration of gelatin for pretreatment of membrane was 0.05 to 0.125 weight per cent while a much smaller concentration of gelatin, namely 2.5×10^{-4} to 10^{-2} weight per cent, was necessary for adhesion of particles coated with gelatin in solution. The course of accumulation of particles on the membrane is proportional to the time of centrifugation until all the gold in the sample is centrifuged on to the membrane. The time to do this is inversely proportional to the number of revolutions per minute (Figure 17). This time can be used to evaluate the particle diameter. The values found were 6 nm for the slower centrifugation rate and 4.4 nm for the faster rate. These are three and five times smaller than the diameter of 20 nm obtained from electronmicroscopy.

The same technique of using the electronmicroscope to characterize the motion of colloidal gold particles was applied to electrophoresis. The cell was 5 mm in diameter and 8 mm long with two female standard-taper joints at each end. Copper electrodes of size capable of holding standard electron microscope screens, were introduced at each end. A standard citrate gold solution was diluted up to 12-fold and a potential of 1.5 to 50 volts was applied. The particles adhered to the membrane on the positive electrode. Clusters of particles were present at all potentials in the concentrated solutions and at high potential in the dilute solutions. The 10-fold diluted standard solution at 3 volt potential difference gave the most evenly distributed particles whose concentration increased linearly with time of electrophoresis (Figure 18). The average electrophoretic velocity for 1 volt potential gradient was calculated to be 1.4×10^{-4} cm/sec. This compares favourably with the value

Fig. 16 (top) Adhesion of gold particles to membrane due to diffusion

Fig. 17 (middle) Adhesion of gold particles to membrane due to centrifugation

Fig. 18 (bottom) Adhesion of gold particles to membrane due to electrophoresis



of 2.16×10^{-4} reported by Burton (46).

The charge on a colloidal particle can be determined by a combination of centrifugation and electrophoresis. The motion of a charged colloidal particle in a centrifugal field can be retarded or even stopped by applying an electric field which moves the particle in the opposite direction. This is the colloid chemical analogue of the Millikan oil drop experiment.

Proper compensation of the two fields should produce no motion and avoid hydrodynamic distortion of the diffuse ionic atmosphere. The electrophoresis cell was placed in a centrifuge port hole in such a way that both electrodes could be attached to a small battery and potentiometer in an adjacent port hole. The experimental results (Figure 19) show that a positive potential of 2.7 volts just compensates the centrifugal force at the upper positive electrode while a negative potential of 3.3 volts just retards the action of the centrifugal force on particles near the lower electrode. The effective charge Z on a colloid particle can be determined by equating the electric force to the centrifugal force.

$$ZeE = 4/3\pi a^3 \Delta p \omega^2 X$$

where e is the value of the elementary charge, E is the electric field near the electrode, a is the radius of the particle, Δp is the difference in density of gold and water, ω is the frequency of rotation 523.6 per sec, X is the distance from the axis of rotation to the electrode, 5 cm for the top electrode and 7 cm for the lower one. The value of Z obtained for the top electrode was 239 while for the bottom it was 173 negative charges. Since the surface area of a 10 nm gold particle is 1.3×10^3 nm^2 there is a negative charge per square of surface whose side is 2.3 or 2.7 nm.

This method of determining charge avoids the difficulties of the previous methods which involve the motion of a massive charged particle surrounded by a diffuse charged atmosphere through a viscous medium defined by macroscopic viscosity.

Just as the charged gold particle can be used as a marker for locating the position of the opposite charge on a specimen, so colloidal gold preparations labelled with specific adsorbents are used extensively as markers for localization of specific chemical sites in biological and medical preparations (47, 48).

Alloys of Colloidal Gold

Alloys of precious metals have a long history of interest and application in catalysis. On the industrial side they have been used extensively because of their greater selectivity and stability. On the scientific side, alloying has been used to vary systematically the 'electronic' nature of the catalyst and to influence the number and distribution of active sites on the surface. Gold-platinum alloys are of particular interest. Gold has low catalytic activity (49,50) compared to platinum which is outstanding in its high catalytic activity for a large number of reactions. Although gold is adjacent to platinum in the periodic table and has a lattice constant 0.4070 nm, close in value to that of platinum (0.3912 nm), the alloy system is complex. When prepared in bulk or by vacuum evaporation this

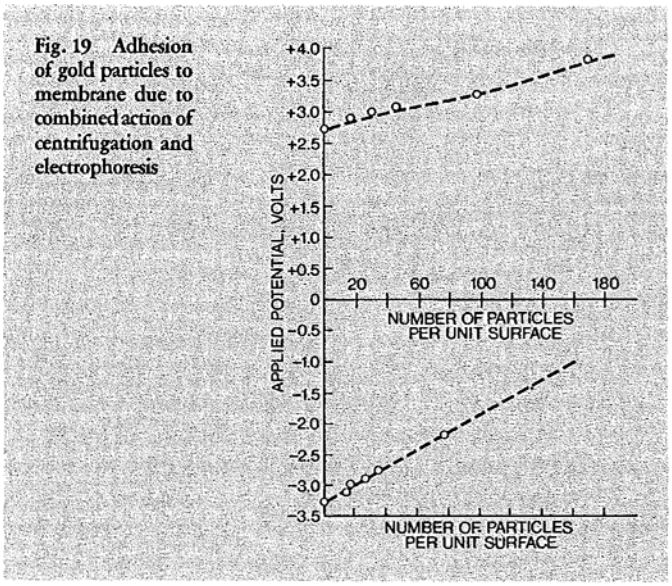


Fig. 19 Adhesion of gold particles to membrane due to combined action of centrifugation and electrophoresis

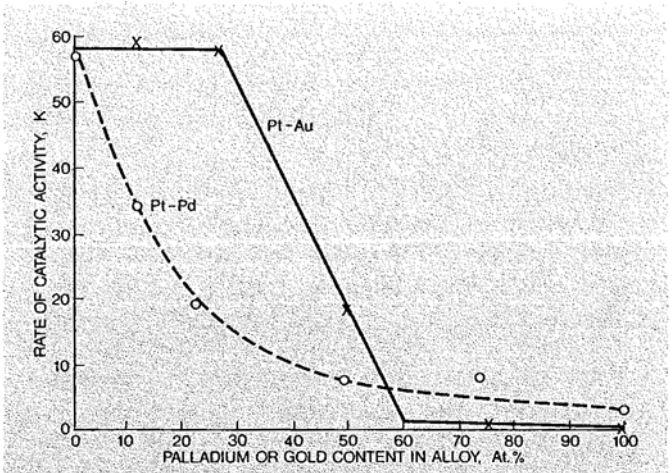
alloy system breaks up into three regions: a homogeneous solid solution from 0 to 2 weight per cent gold, another homogeneous solid solution of 85 to 100 weight per cent gold, and a heterogeneous region composed of varying amounts of the 2 per cent and 85 per cent alloys. The separation into two phases and the difficulties of determining the composition of finely divided alloy particles have handicapped the systematic investigation of the effect of gold on an active platinum catalyst. The preparation procedure for making monodisperse colloidal gold was extended to preparation of monodisperse palladium (51) and platinum (52) and also to monodisperse gold-platinum alloys (27).

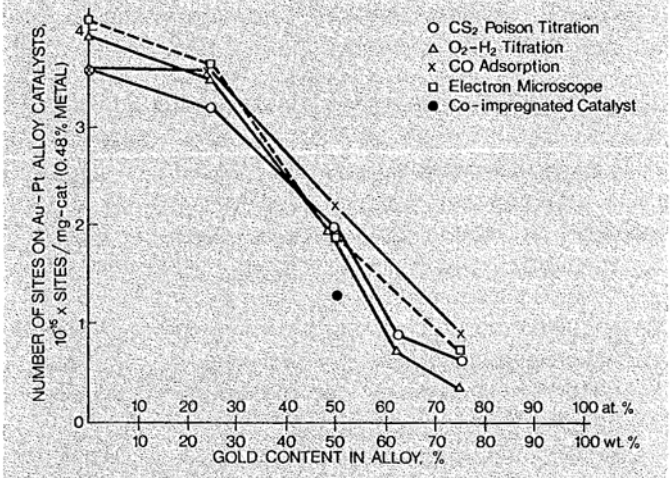
Using this colloidal approach homogeneous alloy particles were obtained and their homogeneity confirmed by physical techniques.

Catalytic Properties

The purpose of the colloid studies by the author's group at Princeton University was the application of colloid chemistry based on electron microscope techniques to prepare in solution monodisperse metal particles of varying size and to study their catalytic activity both in solution and in the gas phase. The primary objective was to determine the effect of size on catalytic properties. The material of choice for colloid studies with the electron microscope was colloidal gold. However, it is a poor catalyst for the two standard reactions: decomposition of hydrogen peroxide in solution and the hydrogenation of ethylene in the gas phase. Platinum is, on the other hand, an outstanding catalyst in both of these reactions. The use of platinum-gold alloys has been suggested for studying the electronic influence in catalytic effects but this has been handicapped by the complex nature of massive platinum-gold alloys. As shown above this has been circumvented by use of alloy particles made in solution.

In hydrogen peroxide decomposition gold has negligible activity





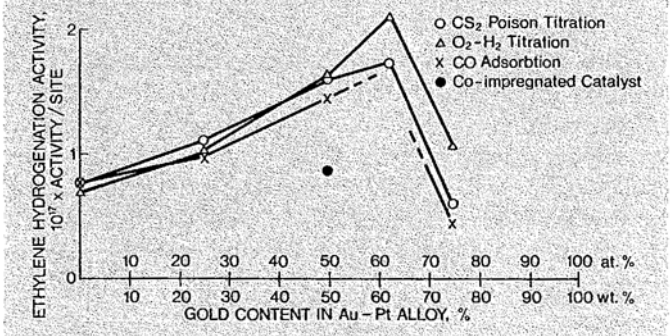


Fig. 20 (top) Rate of catalytic activity of platinum-gold alloys in hydrogen peroxide decomposition

Fig. 21 (middle) Number of sites on gold-platinum alloy catalysts

Fig. 22 (bottom) Activity per catalytic site for ethylene hydrogenation for different gold-platinum alloys

while platinum has the highest activity of any metal (Figure 20). Addition of up to 25 weight per cent gold to platinum does not affect the activity of the catalyst indicating that platinum endows the gold with activity.

There is a linear drop in activity of the catalyst between 25 to 65 weight per cent gold and no activity at higher gold concentration. This follows the number of active sites as determined by other methods (Figure 21).

In ethylene hydrogenation the number of active sites was determined by chemisorption of carbon monoxide, hydrogen-oxygen titration and poison titration (53). In the gold-platinum alloys the number of centres is constant until 25 per cent gold is reached then it decreases linearly to a small value reminiscent of the behaviour of these alloys in hydrogen peroxide decomposition. The number so obtained agrees with the number of surface atoms calculated from electron microscopic investigations, indicating no special concentration of one or the other metal on the particle surface. Activity per catalytic site for ethylene hydrogenation (Figure 22) shows a maximum at 62 per cent gold and then drops to a low value at 75 per cent gold. The maximum may be associated with a cluster of one platinum and two gold atoms. There is no simple correlation between the composition of maximum activity and the number of conductivity electrons as determined from the optical spectra. Catalytic activity must be associated with electrons bound to individual atoms of platinum and clusters of these atoms with those of gold.

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