

# **MODERN TRENDS OF COLLOID SCIENCE IN CHEMISTRY AND BIOLOGY**

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## BIRTH, LIFE AND DEATH OF COLLOIDS

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### Summary

Colloids are dispersions with particles corresponding to a molecular weight of at least 1000, but small enough to pass through filter paper and to show little sedimentation. There are two categories. Lyophilic colloids form spontaneously from the ingredients and they are thermodynamically stable. Lyophobic colloids have to be prepared in a roundabout way. They have to be protected against irreversible aggregation by a protective layer around each particle.

Lyophilic particles are formed by chemical reaction (e.g. by polymerization) or reversible association (as with soap micelles). Some are biocatalysts, some show rubber elasticity and many can serve as protective agents for lyophobic colloids. They can be destroyed by chemical degradation, but from a physical point of view they may live eternally. Lyophobic particles are formed by irreversible condensation, or by comminution. Monosized particles can be prepared. Most of their applications are based on the possibility to mix incompatibles, such as oil in water or insoluble substances in a solvent. They find many technical applications in paints, inks, magnetic tapes, photographic films and in the kitchen. They are destroyed by irreversible agglomeration if the pro-

protective layers are taken away, but in some cases restoration of the dispersed state is possible. The solubility of lyophilic and the stability of lyophobic dispersions are both sensitive to small changes in the composition of the dispersion medium.

### Introduction

A good way of introducing the subject of colloidal systems is the presentation of a few examples. Mayonnaise, latex, soap solutions, protein solutions, smoke, photographic emulsions are all colloidal dispersions. They have in common that the dispersed particles are larger than normal small molecules, but small enough for sedimentation to be absent or very slow, and to allow them to pass through filter paper. Colloid dispersions are often called sols (hydrosol, alcosol, aerosol, depending on the dispersion medium). Dispersions of liquid droplets in a liquid are called emulsions. Sols look similar to solutions, but there are several systematic, quantitative differences.

The relatively large size of colloid particles implies slow diffusion, a characteristic already stressed by GRAHAM in 1861 and easily understood since

$$\text{Diffusion coefficient} \sim \frac{1}{\text{particle radius}} \quad (1)$$

The osmotic pressure is low since

$$\text{Osmotic pressure} \sim \frac{\text{mass concentration}}{\text{particle mass}} \quad (2)$$

The turbidity is rather high, because

$$\text{Turbidity} \sim \text{mass concentration} \times \text{particle mass} \quad (3)$$

Sedimentation is slow, since

$$\text{Sedimentation rate} \sim \frac{\text{particle mass}}{\text{particle radius}} \sim (\text{radius})^2 \quad (4)$$

and the proportionality constant is such that at a radius of 1  $\mu\text{m}$  the sedimentation rate in water is only of the order of 1 cm/hour, but at 10  $\mu\text{m}$  radius it is about 1 cm/minute.

These and other properties have led to the definition of colloid systems by the particle size range from 1 nm, corresponding roughly to a molecular weight of 1000, to 1  $\mu\text{m}$ , above which sedimentation becomes too pronounced. It should be obvious that these limits are not sharp and especially in many technical applications particle sizes somewhat above 1  $\mu\text{m}$  do occur.

Most colloidal dispersions have a funny, all or none type solubility in the sense that small changes in the temperature or in the composition of the solvent may have a dramatic influence on the solubility. For example a protein is salted out at a rather sharp salt concentration. Soaps are hardly soluble below the Krafft temperature, but very soluble above it, as illustrated in Fig. 1.

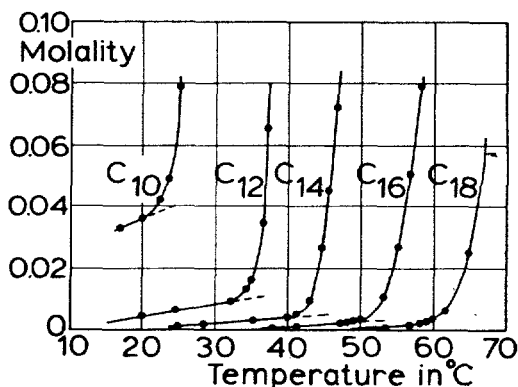


Fig. 1. Solubility in water of sodium alkylsulphonates of various chain lengths. Above the Krafft temperature solubility rises rapidly. TARTAR and WRIGHT, 1939.

A clean gold sol is indefinitely stable, but addition of 0.35 m mol/l  $\text{BaCl}_2$  causes rapid irreversible aggregation of all the gold in the sol.

### Two categories of colloids

When studying colloidal dispersions one soon discovers that they can be divided into two categories. In the first group the dispersions form spontaneously when the colloidal material and the solvent are brought into contact. Examples are: protein in water, soap in water and rubber in benzene. These dispersions are thermodynamically stable true solutions, differing only from solutions with low molecular weight solutes in the size of the dissolved particles. The colloidal material obviously has a certain affinity for the solvent. Such colloids are called lyophilic colloids (hydrophilic if the solvent is water), lyophilic meaning "solvent loving". Lyo- derives from the Greek,  $\lambda\upsilon\omega$  = Latin, solvo, both verbs meaning loosen, digest, dissolve. The particles in lyophilic colloids are either very large molecules (protein, rubber) or large reversible aggregates ("micelles" in soap solutions).

In the second group to which mayonnaise, latex, smoke, fog and the photographic emulsions belong, the particles have no affinity for the solvent. Dispersions of the usually polymolecular particles have to be prepared in a roundabout way, e.g. by supersaturation in the case of cloud formation or in the preparation of photographic silver bromide, or by vigorous stirring or shaking in the case of mayonnaise. These dispersions are not in thermodynamic equilibrium. Their particle size and other properties depend on details of the preparation. They are called lyophobic (hydrophobic), i.e. solvent fearing, colloids.

## Lyophilic colloids

Since dispersions of lyophilic colloids in a liquid medium are true solutions, there is no need to distinguish them with the special term sol. However, in the older literature the term sol is frequently used for protein solutions, soap solutions and the like.

Lyophilic colloids have to be distinguished into two subcategories, the macromolecular colloids and the association colloids.

a. In the case of the macromolecules the colloidal particles are born in a chemical reaction in which low molecular weight building blocks combine, usually one by one, to form straight or branched chains. The polymerization or polycondensation may occur randomly or (bio)organized. The macromolecules formed may be all identical (as with proteins) or they may have a more or less wide molecular weight distribution as with polystyrene or rubber. Once the macromolecules are there, they can be dissolved in suitable solvents, suitable implying that the standard free energy of solution is negative or at worst slightly positive, since the entropy of mixing is necessarily small. One good way to obtain a low standard free energy of solution in water is to introduce electric charges on the macromolecule. Most hydrophilic macromolecules are indeed polyelectrolytes.

b. In the other subcategory, the association colloids, the colloidal particles are formed in a reversible aggregation of many, more than 10, often 50 or more, low molecular weight amphipolar molecules. An amphipolar molecule contains a polar and a non polar part, but more specifically a fairly long hydrocarbon chain, say  $C_8-C_{18}$ , and a polar group which may be a small ion,  $-COO^-$ ,  $-SO_3^-$ ,  $-OSO_3^-$ ,  $-NH_3^+$  or a somewhat larger uncharged hydrophilic group, such as a sugar or a polyethyleneoxide. The solubility in water of single molecules or ions is small, since the hydrocarbon moiety is hydrophobic. By the formation of micelles (see Fig. 2) the hydrophobic chains are hidden from the water,

particles with a hydrophilic surface are obtained and the solubility shoots up.

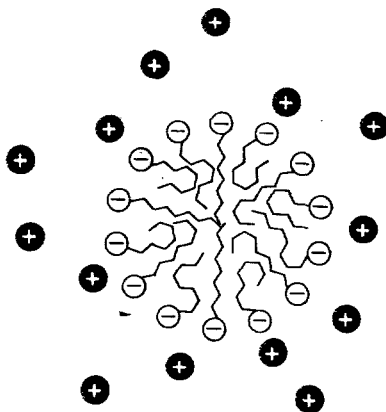


Fig. 2. Schematic picture of a micelle with counterions.

When amphipolar molecules are dissolved in nonpolar solvents "inverse micelles" may be formed, but already a small, hardly colloidal, aggregate may be big enough for hiding the polar groups from the solvent.

Micelles can solubilize molecules compatible with their interior nature. The solubilization of oil soluble dyes in aqueous soap micelles was one of the early and easy, although not very accurate, methods for determining the c.m.c. (critical micelle formation concentration) below which no micelles are found. A very interesting group of swollen micelles is formed by the micro-emulsions, one phase mixtures of water and oil, in which one or the other is solubilized in micelles. These micelles are often so large, that a description as small emulsion droplets gives a better picture than that of micelles swollen with solubilizate (PRINCE, 1977; ROBB, 1982).

After having described the formation, the birth of lyophilic colloids, let us now consider their properties and applications.

As with all colloid materials, diffusion is slow, although with association colloids rapid exchange between micelles and single dissolved molecules may speed up diffusion considerably (EVANS, MUKHERJEE, MITCHELL and NINHAM, 1983), solutions are somewhat turbid, solutions of polymer chains have a high viscosity. Macromolecules and soaps may both form gels (i.e. develop a yield stress) by forming cross linked networks. The sensitivity of the solubility to small changes in the environment is easily explained. The entropy of mixing is of the order of  $-k$  (minus Boltzmann constant) per particle. The energy of solution (more precisely: standard free energy) contains contributions of all the surface groups in a compact particle or of all the groups in a chaintype molecule, and a change by a small fraction of  $kT$  per group may switch the energy of solution from positive to negative and thus the solubility from very low to very high. An example of this sensitivity is seen in the salting out of proteins. The solubility of a specific protein changes from high to low within such a narrow range of salt concentrations that salting out with gradually increasing salt concentrations has been used widely for the separation of mixtures of proteins (see COHN and EDSALL, 1943).

Of the many applications of these colloids I will mention just a few. Biopolymers are biocatalysts (enzymes, nucleic acids), they are used for storage (glycogen, starch), used as building materials (cellulose, collagen, chitin). The whole rubber and plastic industry is based on polymers. Soaps could not play their role in cleaning, if micelle formation did not allow high concentrations to be combined with low activities. In enhanced oil recovery a combination of a surfactant solution and a polymer (usually polyelectrolyte) solution is used, the first one to develop the extremely low interfacial tension water-oil, that is also found in microemulsions, the second one because its high viscosity prevents channelling in the underground transport (BANSAL and SHAH, 1977).



Both soaps and other surfactants and polymers, especially polyelectrolytes, are important as protective agents for hydrophobic colloids.

Finally a few words about the destruction of the colloidal state, the death of lyophilic colloids. Chemical or biochemical degradation leads of course to the loss of high molecular weight or of the amphipolar properties. But since lyophilic colloidal solutions are in true equilibrium, physical changes, such as a change in solubility are reversible. In the physical sense these colloids are indestructable, they have eternal life. This may sound great, but it can be a terrible nuisance as we realize when we remember the complaints about persistent foams, about spoiling nature by leaving "all that plastic" on picnic areas and elsewhere, and thus came the search for making such products biodegradable.

#### Lyophobic colloids

As a start I mention a number of hydrophobic sols, just to illustrate the great variety of materials that can be brought into the lyophobic sol state. Some are very turbid (milk, latex, silver iodide), some are coloured (wine red gold, yellow arsenic trisulphide, brown ferric hydroxide), all have a low viscosity even at quite high concentrations, such as a 500 g/l AgI sol.

Perhaps the most striking aspect of these sols is that they can be maintained unchanged for long times. A gold sol prepared by MICHAEL FARADAY (1857) is still intact at the Royal Institution in London. Nevertheless lyophobic sols are far from equilibrium, since the large interfacial area carries a large amount of interfacial free energy. If the solubility of the dispersed material is not too low (solubilities vary greatly from substance to substance), Ostwald ripening occurs. This means that crystals become more perfect and larger particles, whether crystalline or liquid grow at the expense of smaller ones. At room temperature

this occurs with AgCl, but hardly with AgI in water. An emulsion of benzene in water (solubility 0.08%) coarsens notably, but an emulsion of hexadecane in water (estimated solubility  $10^{-6}\%$ ) does not change. Ostwald ripening is due to the increase in solubility of small particles caused by the Laplace capillary pressure. For a liquid drop, with radius,  $a$ , and interfacial tension,  $\gamma$ , the solubility,  $s$ , as compared to the solubility,  $s_0$  of a flat interface is given by

$$\ln \frac{s}{s_0} = \frac{2\gamma V}{aRT} \quad (5)$$

where  $V$  is the molar volume of the material in the drop. If  $\gamma = 100 \text{ mNm}^{-1}$ ,  $V = 100 \text{ cm}^3 \text{ mol}^{-1}$  and  $a = 10 \text{ nm}$ ,  $s/s_0 = 2.2$ , the solubility has more than doubled.

### Forces between particles

#### Attraction

The same intermolecular forces to which the surface and interfacial tension are due make their influence also felt at larger distances and are the cause of the Van der Waals attraction between colloidal particles. Any pair of molecules or atoms, 1 and 2, attract one another by Van der Waals forces. The energy of this attraction,  $V_{\text{vdW}}$ , is given by

$$V_{\text{vdW}} = - \frac{\lambda_{12}}{r^6} \quad (6)$$

where  $\lambda_{12}$  is a positive constant, the value of which depends on the nature of the molecules 1 and 2 and  $r$  is the distance between their centers. Eq. (6) is valid for intermediate distances from a few Å to about 15 nm. At distances above 15 nm retardation due to the finite velocity of electromagnetic signals sets in (CASIMI and POLDER 1946, 1948).

In a first approximation Van der Waals energies are additive.

Thus for two particles each consisting of many molecules the Van der Waals energy can be obtained by a simple summation or integration as given in eq. (7) and illustrated in Fig. 3.

$$V_{\text{vdW}} = - \sum_{\substack{\text{all pairs} \\ \text{of} \\ \text{molecules}}} \frac{\lambda_{12}}{r^6} = - \int_{V_1} \int_{V_2} \frac{\lambda_{12} q_1 q_2 dV_1 dV_2}{r^6} \quad (7)$$

where  $q_1$  and  $q_2$  represent the numbers of molecules 1 and 2 per unit volume.

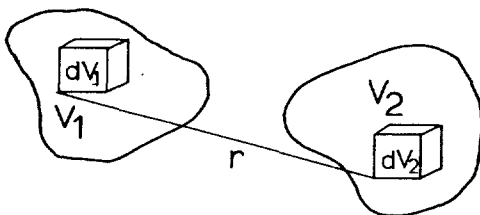


Fig. 3. Illustrating the Van der Waals attraction between particles 1 and 2.

We can see from eq. (7) that the Van der Waals energy is independent of the scale of Fig. 3, since  $dV_1 \cdot dV_2 = (\text{length})^6$  and thus Van der Waals energy has a long range comparable to the size of the particles, unless retardation sets in sooner.

HAMAKER (1936, 1937a) has calculated the integral (7) for several geometries, in particular for spherical particles and for flat parallel plates. For equal spheres, with radius  $a$ , distance between the centers  $r$ , distance between the surfaces  $H = r - 2a$ , the Van der Waals energy is approximately (OVERBEEK, 1977).

$$V_{\text{vdW}} \text{ (2 spheres)} \approx - \frac{A}{12} \left[ \frac{L}{H} + 2 \ln \frac{H}{L} \right] \approx - \frac{Aa}{12H} \quad (8)$$

where  $L = a + 3H/4$  and the Hamaker constant,  $A = \pi^2 q_1^2 q_2^2 \lambda$  with  $q_1 = q_2 = q$  and  $\lambda_{12} = \lambda$  and  $H \ll a$ .

HAMAKER (1937b) has also proven that even when the particles are submerged in a dense medium the Van der Waals interaction remains attractive, as long as the particles have the same composition. Two particles of different materials in a dense medium may show Van der Waals repulsion (VISSER, 1981; NEUMANN, OMENYI and VAN OSS, 1979). The inaccuracies involved in the replacement of the summation in eq. (7) by an integration and in the assumption of exact additivity of the forces between all pairs are avoided in a theory developed by LIFSHITZ (1954, 1956) and by DZYALOSHINSKII et al. (1961), which is based completely on macroscopic dielectric properties of the materials involved. Lifshitz's theory confirms the distance dependence as found by Hamaker, Casimir and Polder but gives somewhat more reliable values for A. The value of A depends strongly on the nature of particles and medium but is usually found between  $10^{-21}$  J and  $10^{-19}$  J. Values of A can be found in a paper by VISSER (1972) and in a book by MAHANTY and NINHAM (1976).

If the Van der Waals attraction would be the only interaction between particles, any lyophobic suspension or emulsion would agglomerate, flocculate, as rapidly as Brownian motion can bring the particles close together. Therefore lyophobic sols can only be stable if some kind of repulsion between the particles is stronger than the Van der Waals attraction at least for a range of distances.

### Repulsion

Two, possibly three, sources of repulsion have to be considered.

Electrostatic repulsion. In aqueous and other sufficiently polar media particles in general obtain an electric surface charge by dissociation of surface groups or by preferential adsorption of specific ions ( $Ag^+$  or  $I^-$  in the case of AgI). This charge mani-

manifests itself most clearly in electrophoresis, the motion of particles in an electric field. Because particles of the same material carry similar charges, they repel one another. Estimating this repulsion with Coulomb's law is too simplistic. The particle charge attracts counterions (= ions of opposite charge) and repels co-ions (= ions of similar charge). Entropy tends to randomize the ion distribution. As a result an electric double layer (see Fig. 4) develops in which space charge and potential decay exponentially with a decay length,  $1/\kappa$ , equal to the Debye length of the electrolyte solution.

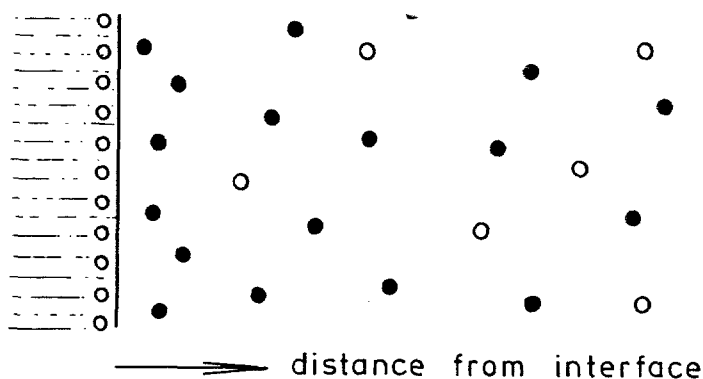


Fig. 4. Sketch of the distribution of ions in an electric double layer. o = surface ions and co-ions; • = counterions.

$$\kappa = \text{reciprocal Debye length} = \left( \frac{\sum c_i z_i^2 F^2}{\epsilon_r \epsilon_0 RT} \right)^{\frac{1}{2}} = \left( \frac{2cF^2}{\epsilon_r \epsilon_0 RT} \right)^{\frac{1}{2}} \quad (9)$$

the simplified expression being valid for a concentration,  $c$  of a uni-uni-valent electrolyte. Further  $c_i$  and  $z_i$  are the concentration and charge number respectively of the ion of type  $i$  in the solution,  $\epsilon_r$  is the relative dielectric permittivity and  $\epsilon_0$  the permittivity of the vacuum. The repulsion between two spherical particles decays with the same length,  $1/\kappa$  and is approximately given by (VERWEY and OVERBEEK, 1948a)

$$V_{\text{rep}} \approx 2\pi\epsilon_r\epsilon_0\left(\frac{RT}{zF}\right)^2 ae^{-\kappa H} \left[ 4 \tanh\left(\frac{\sinh^{-1}\left(\frac{zF\sigma}{2\epsilon_r\epsilon_0\kappa RT}\right)}{2}\right) \right]^2 \quad (10)$$

where  $a$  and  $H$  have the same meaning as in eq. (8),  $\sigma$  is the surface charge density and the electrolyte is assumed to be  $z$ - $z$  valent. The approximation in eq. (10) is best for not too small values of  $\kappa a$  (say  $\kappa a > 3$ ) and  $\kappa H > 1$ ).

Combination of Van der Waals attraction and electrostatic repulsion. With the attraction decaying as an inverse power of the distance between the surfaces of the particles (as  $1/H$  for spheres at small separations) and the repulsion decaying as an exponential function of that distance, and being also sensitive to the charge numbers and the concentrations of the electrolyte in the solution, an interesting situation has developed. The attraction is stronger than the repulsion both for small and for large distances, but the repulsion may be stronger at intermediate distances (of the order,  $1/\kappa$ ), in particular when the surface charge density is high and the charge number and the concentration of the counterions are low. This is illustrated in Fig. 5.

For a given combination of particles and solvent the attraction can hardly be changed, but the repulsion can be manipulated by changing type and concentration of electrolyte and by changing surface charge. Increases of  $z$  (especially of the counterions) and  $c$  "compress the double layer" and lower the maximum in  $V_{\text{tot}}$ . When the maximum is comparable to  $kT$  or even lower or absent the sol flocculates. If one chooses the situation in which the maximum is just at  $V_{\text{tot,max}} = 0$ , as the critical coagulation concentration (c.c.c.), it can be easily shown that  $H(\text{max}) = 1/\kappa$  and for high  $zF\sigma/2\epsilon_r\epsilon_0\kappa RT$

$$\text{c.c.c.} = \frac{73728 \pi^2 e^{-2} (\epsilon_r \epsilon_0)^3 (RT)^5}{z^6 A^2 F^6} \quad (11)$$

$$= (\text{for water at room temperature}) \frac{3.8 \times 10^{-36}}{z^6 A^2} J^2 \frac{\text{mmol}}{1}$$

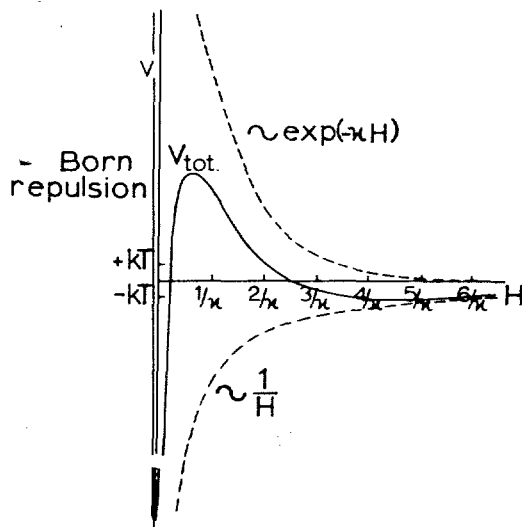


Fig. 5. The combination of an exponential repulsion and a  $1/H$  attraction with the Born repulsion due to the interaction of the outer electron clouds of the particles leads to free energy vs distance curve with two minima as drawn or monotonically decreasing from  $H = \infty$  to the deep minimum at  $H = 0$ .

The essentials of the above treatment have been given by DERJAGUIN and LANDAU (1941) and by VERWEY and OVERBEEK (1948). Several aspects of eq. (11) are in good agreement with the facts. There is little or no influence of particle size on the c.c.c. The factor  $\epsilon_r^3$  is in rough agreement with low c.c.c.'s in alcohols and acetone (DE ROOY, DE BRUYN and OVERBEEK, 1980), the factor  $A^{-2}$  is qualitatively confirmed by low c.c.c.'s for metal sols as compared to non-metals. The proportionality to  $z^{-6}$  was seen as a

considerable success of the theory, as it was in nearly quantitative agreement with the rule of SCHULZE (1882, 1883) and HARDY (1900) about the influence of the valence of the counterions on the c.c.c., as shown in table I.

However, the surface charge density,  $\sigma$ , as derived from electrophoresis is often not high at coagulation (OVERBEEK, 1982). In that case the theory predicts that the c.c.c. is proportional to  $z^{-2}$ , in gross contradiction with the facts. Furthermore eq. (11) leads only to correct values for the c.c.c. if  $A \approx 1 - 2 \times 10^{-19}$  J, which is too high by a factor of about 10. Therefore the surface charge density,  $\sigma$ , cannot be constant. It must be decreased by adsorption of counterions, the more so, the higher their charge number. Other refinements have also to be added in the theory (OVERBEEK, 1980). This makes the theory less elegant and at the moment there are insufficient data for a full check. Nevertheless, it appears that the essence of this theory of the stability of lyophobic colloids (Van der Waals attraction vs double layer repulsion) is correct.

Steric repulsion. Electrostatic repulsion is not the only mechanism available for keeping particles apart. Layers of molecules adsorbed or otherwise attached to the surfaces, but for the rest soluble in the solvent lead to a repulsion. Two aspects

Table I. Critical coagulation concentrations (c.c.c.) in millimol/l.  $c_z$  is the average c.c.c. for z-valent counterions.

| AgI (negat.) |       |           | As <sub>2</sub> S <sub>3</sub> (negat.)<br>(=Al <sub>2</sub> O <sub>3</sub> (posit.)) |       |           | Au (neg) |       |           | $z^{-6}$ |
|--------------|-------|-----------|---|-------|-----------|----------|-------|-----------|----------|
| z            | $c_z$ | $c_z/c_1$ | z   | $c_z$ | $c_z/c_1$ | z        | $c_z$ | $c_z/c_1$ |          |
| 1            | 142   | 1         | 1   | 55    | 1         | 1        | 24    | 1         | 1        |
| 2            | 2.43  | 0.017     | 2   | 0.68  | 0.012     | 2        | 0.38  | 0.016     | 0.0156   |
| 3            | 0.068 | 0.0005    | 3   | 0.09  | 0.0016    | 3        | 0.006 | 0.00025   | 0.0014   |



contribute to this repulsion, the first being the loss of entropy that the adsorbed molecules experience in the narrow gap between two particles. Moreover the increased concentration of the adsorbate in such a gap causes an increase in free energy and thus a repulsion. The phenomenon itself has been long known as protective action. It protects hydrophobic colloids against flocculation by electrolytes. The "protective colloids" of yesteryear were proteins, polypeptides, gums, etc. An example is the protection of a gold sol by gelatin which converts the gold particles into hydrophilic gelatin particles with a golden heart.

Nowadays one usually speaks of steric repulsion. It is particularly important for stabilizing suspensions in non-polar media, where electrostatic repulsion is not practical. Many pigments could not be stably dispersed in oil without steric stabilizers. In terms of potential energy curves steric stabilization usually keeps particles so far apart that Van der Waals attraction is negligible.

Theories of steric stabilization have slowly grown in combination with theories of polymer adsorption. We mention SILBERBERG (1962, 1967, 1968), HOEVE (1965), MEIER (1967), HESSELINK (1969, 1971), NAPPER (1968, 1970) and the recent work of FLEER and SCHEUTJENS (1982).

In applications of steric protection it is usually not too difficult to find a suitable protective moiety. It should be soluble and not too small. But it is often more difficult to find the other moiety (the "anchor" group) that must be easily adsorbed without making the whole molecule too insoluble. In this respect the work of Fleer and Scheutjens is important. They showed that for high molecular weight homopolymers the adsorption energy per group may vary within wide limits (a small fraction of  $kT$  to many times  $kT$ ) without affecting the protective action very much. The natural tendency to form a wide open coil is enough to counteract the tendency to lay flat on the surface and reach a state of low

free energy of adsorption.

### Structural repulsion

In recent years a third mechanism for repulsion between surfaces has been found in the disturbance of the molecular arrangement in a liquid near a solid interface. In extreme cases a layerlike structure can be observed (e.g. in computer simulations, SNOOK et al., 1982; GRUEN et al., 1981) that stretches out to 5 or 10 layers into the liquid. If two such disturbed regions overlap, there is further disturbance of the structure and this may lead to alternating repulsion and attraction both in calculations and in actual experiments (ISRAELACHVILI, 1982). However, uptill now no clear cut examples exist in which this simple structural effect of the solvent is enough to stabilize a suspension.

### Birth of lyophobic colloids

For the formation of lyophobic colloids not only the particles have to be supplied but also the protective mechanism. The particles may be prepared by grinding, shearing or other means of subdivision, provided the protective mechanism can reach the newly created interface rapidly enough. Such dispersion methods are rough, lead to strongly polydispersed systems, but they are nevertheless often practical. Examples are the formation and size reduction of emulsion droplets by shaking, stirring and homogenizing, or the preparation of most disperse paints. Particle sizes come rarely below 0.2  $\mu\text{m}$ .

Condensation methods in which the particles are allowed to grow from a low molecular weight solution by nucleation and (crystal) growth (of course in the presence of a protective mechanism) are much more refined. They allow very small particles to be formed. Often a high degree of monodispersity can be obtained. There is an interesting parallel with the formation of lyophilic particles by chemical chain reaction, except that there the lyophilic is

present in the particles themselves, whereas it has to be provided as an extra for lyophobic particles.

I shall treat three cases in some detail. The silver iodide sol is very simple. Solutions of KI and  $\text{AgNO}_3$  are mixed with one of the two (say KI) in excess to provide  $\text{I}^-$  ions to be adsorbed at the surface and give the particles their charge. If the final concentration remains below the c.c.c. (0.05 M is fine) a stable AgI sol is generated momentarily. The size distribution is wide with most particles below 50 nm.

The gold sol is a classic on which ZSIGMONDY (1906, 1925) did his fundamental work. If a dilute gold III-chloride solution is reduced by any of a great variety of reducing agents, atomic gold is formed slowly, it nucleates to small particles which grow by taking up more freshly reduced gold. The protective mechanism is fairly complicated. The final negative charge is carried by  $\text{Cl}^-$  or other anions, adsorbed as such or as complexes with gold. Rather isodisperse systems are obtained if the nucleation period is short compared to the growth period. Several growth mechanisms, whether diffusion controlled or surface reaction controlled then tend to narrow the original size distribution (OVERBEEK, 1981-1982). In Zsigmondy's Nobel prize (1925) citation his nucleation and growth method (das Keimverfahren) is alluded to. Later LA MER (1946, 1948, 1949 with SINCLAIR, 1952) used nucleation and growth for obtaining monodisperse sulphursols and aerosols.

My third example is latex. Latices of various polymers are formed in aqueous soap solutions by initiating radicals slowly which react with a monomer molecule and start a chain reaction. Soon the growing chain is so long that it becomes highly insoluble in water. It balls up, is protected by adsorbed soap (sometimes also by the ionic nature of its own end group) and soon both growth of existing chains and initiation of new ones takes place only in the existing particles. In favorable cases highly isodisperse latices may be formed (BRADFORD and VANDERHOFF, 1955, 1956).

Life of lyophobic colloids

Lyophobic colloids and slightly coarser systems find many small scale and large scale applications, based on the possibility to combine incompatibles or, in other words, to bring insoluble substances in a solvent and obtain a mixture behaving in many respects as a concentrated solution of low viscosity.

O/W and W/O emulsions are lyophobic colloids. This might be the place to stress that in general there appears to be no continuous transition between ordinary lyophobic emulsions and thermodynamically stable microemulsions. Attempts to make microemulsions with large droplets by using little surfactant result in a phase separation into a fairly concentrated microemulsion and a separate non colloidal phase.

Of the many applications of lyophobic suspensions we cite disperse paints and inks, in which insoluble pigments are used in such a fine division that to the eye the mixture seems homogeneous. Latex is an essential component in the rubber and plastics industry. Literally millions of tons a year are produced. Magnetic tapes, T.V. screens, and fluorescent tubes form another field where stable lyophobic suspensions are an essential part of the production process. Photography could not exist without the finely divided AgBr protected and kept in place by gelatin. In the oil industry making and breaking emulsions are an indispensable part of the trade. The suspension called "drilling mud" cools the drilling bit, carries the chips to the surface, seals the wall of the drillhole, and prevents (at least in most cases) oil and gas to escape from the formation to the surface. Nature itself uses lyophobic colloids. Clays, negatively charged remain suspended and dispersed in rivers, but contact with the salt water of the sea flocculates the clays and helps in building up the delta at the river mouth. Opals are ordered dispersions of isodisperse silica in a matrix of a slightly different refractive index.

Isodisperse suspensions have been used by Perrin to study Brownian motion and recently by Vrij and others as models of hard or soft sphere fluids (see OVERBEEK 1981-1982) The Dow Company isodisperse latices (BRADFORD and VANDERHOFF, 1955, 1956) have been widely used for the calibration of electronmicroscopes and quite recently high technology ceramics have also entered the field of isodisperse suspensions (BARRINGER and BOWEN, 1982).

Even in the kitchen lyophobic colloids are found. Mayonnaise and Béarnaise sauce are emulsions of oil in water stabilized by the proteins and lipids of egg yolk and stiffened by partial flocculation of the proteins.

#### Death of lyophobic colloids

When the protection is taken away a lyophobic colloid flocculates irreversibly. This is obvious for electrostatically protected colloids. By decreasing the surface charge and/or increasing the electrolyte concentration the maximum in the energy vs separation curve is lost and the particles will slide into the deep so called primary minimum. When the original conditions are re-established, the particles do not separate, the sol does not "repeptize", since that would require an increase in energy as illustrated in Fig. 6.

For a sterically protected colloid the situation is ambiguous. If the stabilizer, although inactivated e.g. by salting out, remains adsorbed, coagulation may be reversible because the inactive stabilizer may still provide the separation,  $\delta$ . If the stabilizer is desorbed, however, flocculation is irreversible.

But even in the electrostatic case flocculation is not always irreversible. For some colloids (HgS,  $V_2O_5$ , Carey Lea's Ag,  $Fe(OH)_3$ , others) repeptization after flocculation is even the standard method of preparation, and on closer inspection it turns

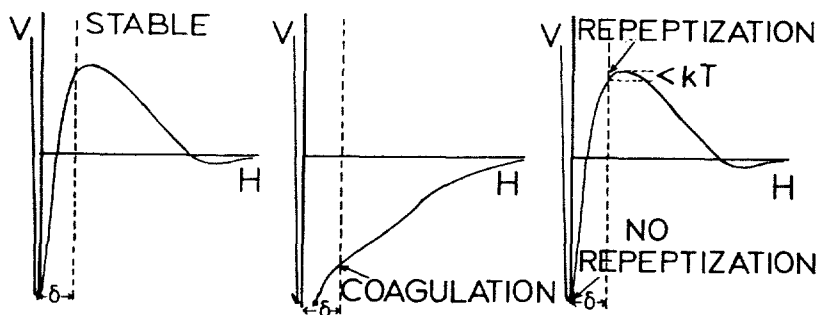


Fig. 6. Illustrates coagulation and reptization.  
 Left: Energy vs distance curve for stable sol.  
 Middle: All repulsion has disappeared.  
 Right: No reptization if coagulation took place in the deep primary minimum, but reptization may occur if the particles have kept a distance,  $\delta$ .

out that most flocculations can be undone provided that the flocculated state is only allowed to exist for a short time, and that only monovalent counterions were involved. Apparently the surfaces do not immediately come into close contact and it may well be that here structural repulsion plays a role. Fig. 6 shows that a separation  $\delta$  is enough to obtain both a driving force and a small activation energy for reptization after washing out the flocculating electrolyte. Calculations show that  $\delta$  need not be more than 4 or 5 Å to allow reptization (FRENS and OVERBEEK, 1972).

Flocculation is a rate process. The rate of rapid flocculation, which occurs when no energy barrier is left, is easily measurable. The rate constant is the same as that for a diffusion controlled chemical reaction and thus in principle independent of the particle size. Very good agreement between theory and experiments has been obtained by LICHTENBELT et al. (1974) with polystyrene latices of different sizes. The rate of slow flocculation in the presence of a small energy barrier still shows discrepancies

between theory and experiments (OVERBEEK, 1982).

Summarizing we may conclude that the lyophobic colloid state can be destroyed by physical changes. This destruction is often irreversible but in several cases reanimation is possible.

### General conclusion

Colloid behavior is reasonably well understood but it still offers many interesting scientific problems. Lyophobic colloid particles behave as gigantic molecules with sizes and interactions that can be manipulated by the experimenter. Many old and new applications may profit from a better understanding of the fundamentals. May the present meeting serve that purpose.

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