

MODERN TRENDS
OF COLLOID SCIENCE
IN CHEMISTRY AND BIOLOGY

Edited by
Hans-Friedrich Eicke

MODERN TRENDS OF COLLOID SCIENCE IN CHEMISTRY AND BIOLOGY

International Symposium
on Colloid & Surface Science, 1984
held from October 17-18, 1984
at Interlaken, Switzerland

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Hans-Friedrich Eicke**

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Foreword

From 17-19 October 1984, the Swiss Association of Chemists held for the first time in Interlaken, one of its well-known conferences: an international symposium entitled "Modern Trends of Colloid Science in Chemistry and Biology". The goal of this conference was to demonstrate the present state-of-the-art and recent developments in colloid science as applied to the fields of Chemistry, Biology, and Biochemistry.

Within the time traditionally available for such symposia, sixteen lectures were selected covering various aspects of modern colloid and surface sciences. The topics included adsorption on solid/liquid interfaces; thermodynamically stable emulsions (microemulsions) and liquid crystals; property-structure relationships between surfactants and their aggregates; catalysis at colloidal metals and semiconductors; organized interfaces of amphiphiles (molecular engineering); and rheologic and sedimentary properties of strongly interacting particles (concentrated dispersions) and the importance of the ζ -potential. Particular emphasis was placed upon modern experimental techniques which played an important rôle in the renaissance of modern colloid science and which are indispensable for characterizing colloidal systems: NMR-spectroscopy and neutron-, x-ray and quasi-elastic light scattering techniques. The power of such modern technical facilities was demonstrated for solving highly sophisticated biochemical problems and those encountered in molecular biology.

It was an aim of this first Interlaken-symposium to reflect the full width and interdisciplinary nature of modern colloid science. As a result, detailed discussions pertinent to practical applications had to be limited: The Swiss Association of Chemists considered this to be in line with the general flavour of the conference. However, it has been agreed that,

for future meetings, fewer topics should be discussed and more emphasis should be placed on the application of theory to experiment.

Many people, including the organizing committee, participants and myself, are convinced that the Interlaken-symposium has helped to stimulate interest in this interdisciplinary and, for industry, highly relevant topic.

It is sincerely hoped that the pleasant scientific and personal atmosphere prevalent at this conference is reflected in these proceedings.

Finally, I would like to express my special thanks to Dr. P. Rhyner, president of the Swiss Association of Chemists, for his personal interest and endeavour in making this symposium possible; and to the members of the organizing committee for their efforts and untiring help in making it successful. In particular, I am grateful to Professor H. Hauser for his indispensable advice regarding the bio-sciences. Last not least I am obliged to Professor H.P. Pfander and, most particularly, to Mrs. B. Köchli for her efficient organising of the technical details and far-sighted planning. It is due to her efforts that the proceedings could be published so soon after the symposium.

H.-F. Eicke

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, alcocol, 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.

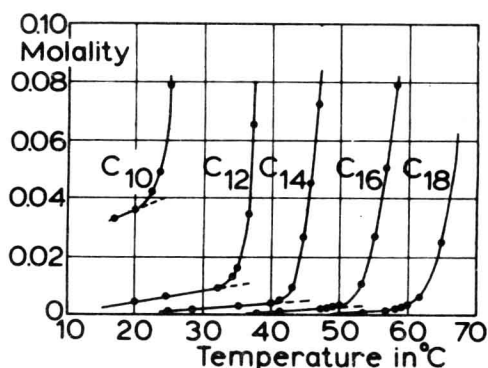


Fig. 1. Solubility in water of sodium alkylsulphonates of various chain lengths. Above the Krafft temperature solubility rises rapidly. TARTAR and WRIGHT, 1939.

A clean gold sol is indefinitely stable, but addition of 0.35 m mol/l 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.

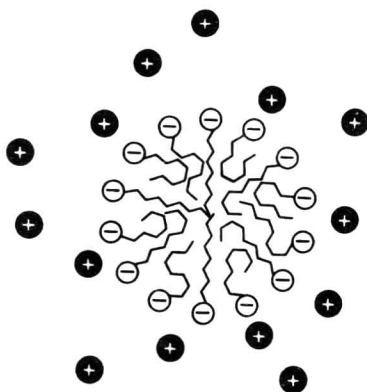


Fig. 2. Schematic picture of a micelle with counterions.

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 solubilize (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 chain type 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