



introduction

to

COLLOID & SURFACE CHEMISTRY

FOURTH EDITION

胶体和表面化学导论

第4版

DUNCAN J SHAW

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Introduction to Colloid and Surface Chemistry

Fourth edition

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Preface

This book has been written to fill a gap in the literature by offering a standard and overall coverage of colloid and surface chemistry intermediate between the brief accounts found in most textbooks of physical chemistry and the comprehensive accounts found in specialised treatises on colloid and/or surface chemistry.

In writing the book, I have kept a number of audiences in mind – particularly: university and polytechnic students studying for an honours degree or its equivalent, or commencing a programme of postgraduate research; scientists in industry who desire a broad background in a subject which may have been somewhat neglected during academic training; and those interested in branches of natural science, for whom an understanding of colloid and surface phenomena is essential.

The subject matter is, in general, approached from a fundamental angle, and the reader is assumed to possess a knowledge of the basic principles of physical chemistry. Opportunities have also been taken to describe many of the practical applications of this subject. In addition, some numerical problems (with answers) and a list of references for further reading (mainly books and review articles) are given at the end of the book.

The general character of this fourth edition is similar to that of the third edition. The text has been revised and updated throughout, the major change being the extension of Chapter 5 to include a section on the composition and structure of solid surfaces.

I wish to thank my colleagues, particularly Dr A.L. Smith, for their many helpful suggestions, and my wife, Ann, for her help in preparing the manuscript and checking the text.

D.J.S.
Southport, 1991

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1 *The colloidal state*

Introduction

Colloid science concerns systems in which one or more of the components has at least one dimension within the nanometre (10^{-9}m) to micrometre (10^{-6}m) range, i.e. it concerns, in the main, systems containing large molecules and/or small particles. The adjective 'microheterogeneous' provides an appropriate description of most colloidal systems. There is, however, no sharp distinction between colloidal and non-colloidal systems.

The range of colloidal systems of practical importance is vast, as is the range of processes where colloid/surface chemical phenomena are involved.

Examples of systems which are colloidal (at least in some respects) are:

Aerosols	Foodstuffs
Agrochemicals	Ink
Cement	Paint
Cosmetics	Paper
Dyestuffs	Pharmaceuticals
Emulsions	Plastics
Fabrics	Rubber
Foams	Soil

Examples of processes which rely heavily on the application of colloid/surface phenomena are:

Adhesion	Ore flotation
Chromatography	Precipitation
Detergency	Road surfacing

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Electrophoretic deposition	Sewage disposal
Emulsion polymerisation	Soil conditioning
Food processing	Sugar refining
Grinding	Water clarification
Heterogeneous catalysis	Water evaporation control
Ion exchange	Water repellency
Lubrication	Wetting
Oil-well drilling	

As can be seen from the second of these lists, the existence of matter in the colloidal state may be a desirable or an undesirable state of affairs, and so it is important to know both how to make and how to destroy colloidal systems.

Colloid science is very much an interdisciplinary subject, albeit with certain areas of physics and physical chemistry most prominent. Owing to the complexity of most colloidal systems, the subject often cannot be treated readily with the exactness that tends to be associated with much of these major subject areas. It is probably a combination of this lack of precision and its interdisciplinary nature, rather than lack of importance, that has been responsible in the past for an unjustifiable tendency to neglect colloid science during undergraduate academic training.

Until the last few decades colloid science stood more or less on its own as an almost entirely descriptive subject which did not appear to fit within the general framework of physics and chemistry. The use of materials of doubtful composition, which put considerable strain on the questions of reproducibility and interpretation, was partly responsible for this state of affairs. Nowadays, the tendency is to work whenever possible with well-defined systems (e.g. monodispersed dispersions, pure surface-active agents, well-defined polymeric material) which act as models, both in their own right and for real life systems under consideration. Despite the large number of variables which are often involved, research of this nature coupled with advances in the understanding of the fundamental principles of physics and chemistry has made it possible to formulate coherent, if not always comprehensive, theories relating to many of the aspects of colloidal behaviour. Since it is important that colloid science be understood at both descriptive and theoretical levels, the study of this subject can range widely from relatively simple descriptive material to extremely complex theory.

The natural laws of physics and chemistry which describe the behaviour of matter in the massive and molecular states also, of course, apply to the colloidal state. The characteristic feature of colloid science lies in the relative importance which is attached to the various physicochemical properties of the systems being studied. As we shall see, the factors which contribute most to the overall nature of a colloidal system are:

- Particle size
- Particle shape and flexibility
- Surface (including electrical) properties
- Particle-particle interactions
- Particle-solvent interactions

Classification of colloidal systems

Colloidal systems may be grouped into three general classifications:

1. *Colloidal dispersions* are thermodynamically unstable owing to their high surface free energy and are irreversible systems in the sense that they are not easily reconstituted after phase separation.
2. *True solutions of macromolecular material* (natural or synthetic) are thermodynamically stable and reversible in the sense that they are easily reconstituted after separation of solute from solvent.
3. *Association colloids* which are thermodynamically stable (see Chapter 4).

Dispersions

The particles in a colloidal dispersion are sufficiently large for definite surfaces of separation to exist between the particles and the medium in which they are dispersed. Simple colloidal dispersions are, therefore, two-phase systems. The phases are distinguished by the terms *dispersed phase* (for the phase forming the particles) and *dispersion medium* (for the medium in which the particles are distributed) – see Table 1.1. The physical nature of a dispersion depends, of course, on the respective roles of the constituent phases; for example, an oil-in-water (O/W) emulsion and a water-in-oil (W/O) emulsion could have almost the same overall composition, but their physical properties would be notably different (see Chapter 10).

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Table 1.1 Types of colloidal dispersion

<i>Dispersed phase</i>	<i>Dispersion medium</i>	<i>Name</i>	<i>Examples</i>
Liquid	Gas	Liquid aerosol	Fog, liquid sprays
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Liquid	Foam	Foam on soap solutions, fire-extinguisher foam
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Sol, colloidal suspension; paste (high solid concentration)	Au sol, AgI sol; toothpaste
Gas	Solid	Solid foam	Expanded polystyrene
Liquid	Solid	Solid emulsion	Opal, pearl
Solid	Solid	Solid suspension	Pigmented plastics

Sols and emulsions are by far the most important types of colloidal dispersion. The term *sol* is used to distinguish colloidal suspensions from macroscopic suspensions; there is, of course, no sharp line of demarcation. When the dispersion medium is aqueous, the term *hydrosol* is usually used. If the dispersed phase is polymeric in nature, the dispersion is called a *latex* (pl. *latices* or *latexes*).

Foams are somewhat different in that it is the dispersion medium which has colloidal dimensions.

The importance of the interface

A characteristic feature of colloidal dispersions is the large area-to-volume ratio for the particles involved. At the interfaces between the dispersed phase and the dispersion medium characteristic surface properties, such as adsorption and electric double layer effects, are evident and play a very important part in determining the physical properties of the system as a whole. It is the material within a molecular layer or so of the interface which exerts by far the greatest influence on particle-particle and particle-dispersion medium interactions.

Despite this large area-to-volume ratio, the amount of material required to give a significant molecular coverage and modification of the interfaces in a typical colloidal dispersion can be quite small, and substantial modification of the overall bulk properties of a colloidal

dispersion can often be effected by small quantities of suitable additives. For example, pronounced changes in the consistency of certain clay suspensions (such as those used in oil-well drilling) can be effected by the addition of small amounts of calcium ions (thickening) or phosphate ions (thinning)¹⁸.

Surface science is, therefore, closely linked with colloid science; indeed, colloid science is inevitably a part of surface science, although the reverse does not necessarily hold.

The surface or interfacial phenomena associated with colloidal systems such as emulsions and foams are often studied by means of experiments on artificially prepared flat surfaces rather than on the colloidal systems themselves. Such methods provide a most useful indirect approach to the various problems involved.

Lyophilic and lyophobic systems

The terms *lyophilic* (liquid-loving) and *lyophobic* (liquid-hating) are frequently used to describe the tendency of a surface or functional group to become wetted or solvated. If the liquid medium is aqueous, the terms *hydrophilic* and *hydrophobic* are used.

Lyophilic surfaces can be made lyophobic, and vice versa. For example, clean glass surfaces, which are hydrophilic, can be made hydrophobic by a coating of wax; conversely, the droplets in a hydrocarbon oil-in-water emulsion, which are hydrophobic, can be made hydrophilic by the addition of protein to the emulsion, the protein molecules adsorbing on to the droplet surfaces.

This terminology is particularly useful when one considers the phenomenon of surface activity. The molecules of surface-active materials have a strong affinity for interfaces, because they contain both hydrophilic and lipophilic (oil-loving) regions.

The general usage of the terms 'lyophilic' and 'lyophobic' in describing colloidal systems is somewhat illogical. 'Lyophobic' traditionally describes liquid dispersions of solid or liquid particles produced by mechanical or chemical action; however, in these so-called 'lyophobic sols' (e.g. dispersions of powdered alumina or silica in water) there is often a high affinity between the particles and the dispersion medium – i.e. the particles are really lyophilic. Indeed, if the term 'lyophobic' is taken to imply no affinity between particles and dispersion medium (an unreal situation), then the particles would not be wetted and no dispersion could, in fact, be formed. 'Lyophilic'

traditionally describes soluble macromolecular material; however, lyophobic regions are often present. For example, proteins are partly hydrophobic (hydrocarbon regions) and partly hydrophilic (peptide linkages, and amino and carboxyl groups).

Structural characteristics

Experimental methods

The experimental procedures for determining particle size and shape can roughly be categorised, as follows:

1. Observation of the movement of particles in response to an applied force (see Chapter 2).
2. Direct observation of particle images (microscopy and electron microscopy) (see Chapter 3).
3. Observation of the response of particles to electromagnetic radiation (see Chapter 3).
4. Measurements which relate to the total surface area of the particles (gas adsorption and adsorption from solution) (see Chapters 5 and 6).

Particle shape

Particle asymmetry is a factor of considerable importance in determining the overall properties (especially those of a mechanical nature) of colloidal systems. Roughly speaking, colloidal particles can be classified according to shape as *corpuscular*, *laminar* or *linear* (see, for example, the electron micrographs in Figure 3.2). The exact shape may be complex but, to a first approximation, the particles can often be treated theoretically in terms of models which have relatively simple shapes (Figure 1.1).

The easiest model to treat theoretically is the sphere, and many colloidal systems do, in fact, contain spherical or nearly spherical particles. Emulsions, latexes, liquid aerosols, etc., contain spherical particles. Certain protein molecules are approximately spherical. The crystallite particles in dispersions such as gold and silver iodide sols are sufficiently symmetrical to behave like spheres.

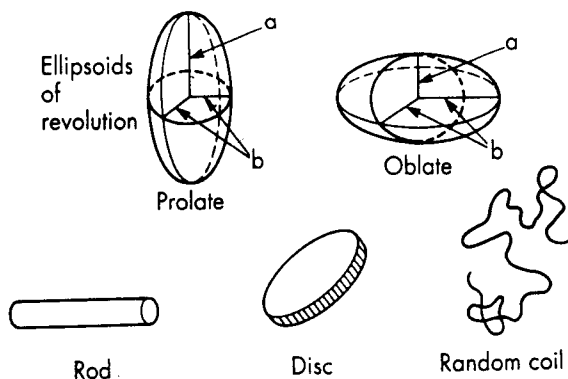


Figure 1.1 Some model representations for non-spherical particles

Corpuscular particles which deviate from spherical shape can often be treated theoretically as ellipsoids of revolution. Many proteins approximate this shape. An ellipsoid of revolution is characterised by its axial ratio, which is the ratio of the single half-axis a to the radius of revolution b . The axial ratio is greater than unity for a prolate (rugby-football-shaped) ellipsoid, and less than unity for an oblate (discus-shaped) ellipsoid.

Iron(III) oxide and clay suspensions are examples of systems containing plate-like particles.

High-polymeric material usually exists in the form of long thread-like straight or branched-chain molecules. As a result of inter-chain attraction or cross-linking (arising from covalent bonding, hydrogen bonding or van der Waals forces) and entanglement of the polymer chains, these materials often exhibit considerable mechanical strength and durability. This is not possible when the particles are corpuscular or laminar.

In nature, thread-like polymeric material fulfils an essential structural role. Plant life is built mainly from cellulose fibres. Animal life is built from linear protein material such as collagen in skin, sinew and bone, myosin in muscle and keratin in nails and hair. The coiled polypeptide chains of the so-called globular proteins which circulate in the body fluids are folded up to give corpuscular particles.

When particles aggregate together, many different shapes can be formed. These do not necessarily correspond to the shape of the primary particles.

Flexibility

Thread-like high-polymer molecules show considerable flexibility due to rotation about carbon-carbon and other bonds. In solution, the shape of these molecules alters continuously under the influence of thermal motion and a rigid rod model is therefore unsuitable. A better theoretical treatment is to consider the polymer molecules as random coils, but even this model is not completely accurate. Rotation about bonds does not permit complete flexibility, and steric and excluded volume effects also oppose the formation of a truly random configuration, so that, in these respects, dissolved linear polymer molecules will tend to be more extended than random coils. The relative magnitudes of polymer-polymer and polymer-solvent forces must also be taken into account. If the segments of the polymer chain tend to stick to one another, then a tighter than random coil, and possibly precipitation, will result; whereas a looser coil results when the polymer segments tend to avoid one another because of strong solvation and/or electrical repulsion.

Solvation

Colloidal particles are usually solvated, often to the extent of about one molecular layer, and this tightly bound solvent must be treated as a part of the particle.

Sometimes much greater amounts of solvent can be immobilised by mechanical entrapment within particle aggregates. This occurs when voluminous flocculent hydroxide precipitates are formed. In solutions of long thread-like molecules the polymer chains may cross-link, chemically or physically, and/or become mechanically entangled to such an extent that a continuous three-dimensional network is formed. If all of the solvent becomes mechanically trapped and immobilised within this network, the system as a whole takes on a solid appearance and is called a *gel*.

Polydispersity and the averages

The terms *relative molecular mass* and *particle size* can only have well-defined meanings when the system under consideration is *monodispersed* – i.e. when the molecules or particles are all alike.

Colloidal systems are generally of a *polydispersed* nature – i.e. the molecules or particles in a particular sample vary in size. By virtue of their stepwise build-up, colloidal particle and polymer molecular sizes tend to have skew distributions, as illustrated in Figure 1.2, for which the Poisson distribution often offers a good approximation. Very often, detailed determination of relative molecular mass or particle size distribution is impracticable and less perfect experimental methods, which yield average values, must be accepted. The significance of the word *average* depends on the relative contributions of the various molecules or particles to the property of the system which is being measured.

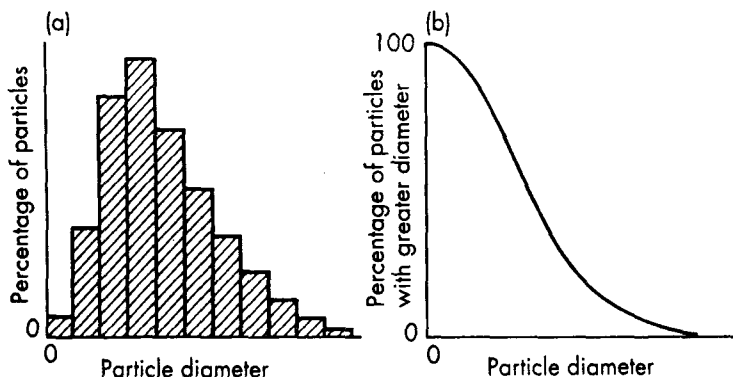


Figure 1.2 Particle diameter distribution for a polydispersed colloidal dispersion expressed (a) in histogram form, and (b) as a cumulative distribution

Osmotic pressure, which is a colligative property, depends simply on the number of solute molecules present and so yields a *number-average* relative molecular mass:

$$M_r \text{ (number average)} = \frac{\sum n_i M_{r,i}}{\sum n_i} \quad (1.1)$$

where n_i is the number of molecules of relative molecular mass $M_{r,i}$.

In most cases the larger particles make a greater individual contribution to the property being measured. If the contribution of

each particle is proportional to its mass (as in light scattering), a *mass-average* relative molecular mass or particle mass is given:

$$M_r \text{ (mass average)} = \frac{\sum n_i M_{r,i}^2}{\sum n_i M_{r,i}} \quad (1.2)$$

For any polydispersed system, M_r (mass average) $>$ M_r (number average), and only when the system is monodispersed will these averages coincide. The ratio M_r (mass average)/ M_r (number average) is a measure of the degree of polydispersity.

Preparation and purification of colloidal systems

Colloidal dispersions

Basically, the formation of colloidal material involves either degradation of bulk matter or aggregation of small molecules or ions.

Dispersion of bulk material by simple grinding in a colloid mill or by ultrasonics does not, in general, lead to extensive subdivision, owing to the tendency of smaller particles to reunite (*a*) under the influence of the mechanical forces involved and (*b*) by virtue of the attractive forces between the particles. After prolonged grinding the distribution of particle sizes reaches an equilibrium. Somewhat finer dispersions can be obtained by incorporating an inert diluent to reduce the chances of the particles in question encountering one another during the grinding, or by wet-milling in the presence of surface-active material. As an example of the first of these techniques, a sulphur sol in the upper colloidal range can be prepared by grinding a mixture of sulphur and glucose, dispersing the resulting powder in water and then removing the dissolved glucose from the sol by dialysis.

A higher degree of dispersion is usually obtainable when a sol is prepared by an aggregation method. Aggregation methods involve the formation of a molecularly dispersed supersaturated solution from which the material in question precipitates in a suitably divided form. A variety of methods, such as the substitution of a poor solvent for a good one, cooling and various chemical reactions, can be utilised to achieve this end.

A coarse sulphur sol can be prepared by pouring a saturated solution of sulphur in alcohol or acetone into water just below boiling point. The alcohol or acetone vaporises, leaving the water-insoluble sulphur colloiddally dispersed. This technique is convenient for dispersing wax-like material in an aqueous medium.

Examples of hydrosols which can be prepared by suitably controlled chemical reaction include the following:

1. *Silver iodide sol.* Mix equal volumes of aqueous solutions (10^{-3} to 10^{-2} mol dm $^{-3}$) of silver nitrate and potassium iodide. Separate the sol from larger particles by decantation or filtration. By arranging for the silver nitrate or the potassium iodide to be in very slight excess, positively or negatively charged particles, respectively, of silver iodide can be formed.
2. *Gold sol.* Add 1 cm 3 of 1% H $\text{AuCl}_4 \cdot 3\text{H}_2\text{O}$ to 100 cm 3 of distilled water. Bring to the boil and add 2.5 cm 3 of 1% sodium citrate. Keep the solution just boiling. A ruby red gold sol forms after a few minutes.
3. *Sulphur sol.* Mix equal volumes of aqueous solutions (10^{-3} to 5×10^{-3} mol dm $^{-3}$) of Na $_2\text{S}_2\text{O}_3$ and HCl.
4. *Hydrous iron(III) oxide sol.* Add, with stirring, 2 cm 3 of 30% FeCl $_3$ (aq) to 500 cm 3 of boiling distilled water. A clear reddish-brown dispersion is formed.

Nucleation and growth

The formation of a new phase during precipitation involves two distinct stages – *nucleation* (the formation of centres of crystallisation) and *crystal growth* – and (leaving aside the question of stability) it is the relative rates of these processes which determine the particle size of the precipitate so formed. A high degree of dispersion is obtained when the rate of nucleation is high and the rate of crystal growth is low.

The initial rate of nucleation depends on the degree of supersaturation which can be reached before phase separation occurs, so that colloidal sols are most easily prepared when the substance in question has a very low solubility. With material as soluble as, for example, calcium carbonate, there is a tendency for the smaller particles to redissolve (see page 68) and recrystallise on the larger particles as the precipitate is allowed to age.