

# Applied Colloid and Surface Chemistry

Richard M Pashley  
Marilyn E Karaman

An abstract artistic photograph featuring numerous translucent blue bubbles and droplets of various sizes. Some bubbles are in sharp focus, showing internal reflections, while others are blurred in the background, creating a sense of depth. The bubbles appear to be floating or moving, with some showing thin films and others more solid-looking. The overall composition is dynamic and visually appealing, set against a light, slightly textured background.

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# Applied Colloid and Surface Chemistry

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# Preface

This book was written following several years of teaching this material to third-year undergraduate and honours students in the Department of Chemistry at the Australian National University in Canberra, Australia. Science students are increasingly interested in the application of their studies to the real world and colloid and surface chemistry is an area that offers many opportunities to apply learned understanding to everyday and industrial examples. There is a lack of resource materials with this focus and so we have produced the first edition of this book. The book is intended to take chemistry or physics students with no background in the area, to the level where they are able to understand many natural phenomena and industrial processes, and are able to consider potential areas of new research. Colloid and surface chemistry spans the very practical to the very theoretical, and less mathematical students may wish to skip some of the more involved derivations. However, they should be able to do this and still maintain a good basic understanding of the fundamental principles involved. It should be remembered that a thorough knowledge of theory can act as a barrier to progress, through the inhibition of further investigation. Students asking ignorant but intelligent questions can often stimulate valuable new research areas.

The book contains some recommended experiments which we have found work well and stimulate students to consider both the fundamental theory and industrial applications. Sample questions have also been included in some sections, with detailed answers available on our web site.

Although the text has been primarily aimed at students, researchers in cognate areas may also find some of the topics stimulating. A reasonable background in chemistry or physics is all that is required.

# Contents

<b>Preface</b>	<b>xi</b>
<b>1 Introduction</b>	<b>1</b>
Introduction to the nature of colloidal solutions	1
The forces involved in colloidal stability	4
Types of colloidal systems	5
The link between colloids and surfaces	6
Wetting properties and their industrial importance	8
Recommended resource books	10
Appendices	11
<b>2 Surface Tension and Wetting</b>	<b>13</b>
The equivalence of the force and energy description of surface tension and surface energy	13
Derivation of the Laplace pressure equation	15
Methods for determining the surface tension of liquids	17
Capillary rise and the free energy analysis	21
The Kelvin equation	24
The surface energy and cohesion of solids	27
The contact angle	28
Industrial Report: Photographic-quality printing	33
Sample problems	35
Experiment 2.1: Rod in free surface (RIFS) method for the measurement of the surface tension of liquids	37
Experiment 2.2: Contact angle measurements	42
<b>3 Thermodynamics of Adsorption</b>	<b>47</b>
Basic surface thermodynamics	47
Derivation of the Gibbs adsorption isotherm	49
Determination of surfactant adsorption densities	52

Industrial Report: Soil microstructure, permeability and interparticle forces	54
Sample problems	55
Experiment 3.1: Adsorption of acetic acid on to activated charcoal	56
<b>4 Surfactants and Self-assembly</b>	<b>61</b>
Introduction to surfactants	61
Common properties of surfactant solutions	63
Thermodynamics of surfactant self-assembly	65
Self-assembled surfactant structures	68
Surfactants and detergency	70
Industrial Report: Colloid science in detergency	74
Sample problems	75
Experiment 4.1: Determination of micelle ionization	75
<b>5 Emulsions and Microemulsions</b>	<b>79</b>
The conditions required to form emulsions and microemulsions	79
Emulsion polymerization and the production of latex paints	81
Photographic emulsions	84
Emulsions in food science	85
Industrial Report: Colloid science in foods	85
Experiment 5.1: Determination of the phase behaviour of microemulsions	87
Experiment 5.2: Determination of the phase behaviour of concentrated surfactant solutions	90
<b>6 Charged Colloids</b>	<b>93</b>
The formation of charged colloids in water	93
The theory of the diffuse electrical double-layer	94
The Debye length	99
The surface charge density	101
The zeta potential	102
The Hückel equation	103
The Smoluchowski equation	106
Corrections to the Smoluchowski equation	108
The zeta potential and flocculation	110
The interaction between double-layers	112
The Derjaguin approximation	116
Industrial Report: The use of emulsions in coatings	117
Sample problems	119
Experiment 6.1: Zeta potential measurements at the silica/water interface	120
<b>7 Van der Waals forces and Colloid Stability</b>	<b>127</b>
Historical development of van der Waals forces and the Lennard-Jones potential	127

Dispersion forces	131
Retarded forces	132
Van der Waals forces between macroscopic bodies	133
Theory of the Hamaker constant	134
Use of Hamaker constants	140
The DLVO theory of colloid stability	140
Flocculation	142
Some notes on van der Waals forces	148
Industrial Report: Surface chemistry in water treatment	148
Sample problems	150
<b>8 Bubble coalescence, Foams and Thin Surfactant Films</b>	<b>153</b>
Thin-liquid-film stability and the effects of surfactants	153
Thin-film elasticity	156
Repulsive forces in thin liquid films	157
Froth flotation	158
The Langmuir trough	159
Langmuir–Blodgett films	166
Experiment 8.1: Flotation of powdered silica	168
<b>Appendices</b>	<b>173</b>
1 Useful Information	173
2 Mathematical Notes on the Poisson–Boltzmann Equation	175
3 Notes on Three-dimensional Differential Calculus and the Fundamental Equations of Electrostatics	179
<b>Index</b>	<b>181</b>

# 1

## Introduction

Introduction to the nature of colloids and the linkage between colloids and surface properties. The importance of size and surface area. Introduction to wetting and the industrial importance of surface modifications.

### Introduction to the nature of colloidal solutions

The difference between macroscopic and microscopic objects is clear from everyday experience. For example, a glass marble will sink rapidly in water; however, if we grind it into sub-micron-sized particles, these will float or disperse freely in water, producing a visibly cloudy 'solution', which can remain stable for hours or days. In this process we have, in fact, produced a 'colloidal' dispersion or solution. This dispersion of one (finely divided or microscopic) phase in another is quite different from the molecular mixtures or 'true' solutions formed when we dissolve ethanol or common salt in water. Microscopic particles of one phase dispersed in another are generally called *colloidal solutions* or *dispersions*. Both nature and industry have found many uses for this type of solution. We will see later that the properties of colloidal solu-



tions are intimately linked to the high surface area of the dispersed phase, as well as to the chemical nature of the particle's surface.

Historical note: The term 'colloid' is derived from the Greek word 'kolla' for glue. It was originally used for gelatinous polymer colloids, which were identified by Thomas Graham in 1860 in experiments on osmosis and diffusion.

It turns out to be very useful to dissolve (or more strictly disperse) solids, such as minerals and metals, in water. But how does it happen? We can see why from simple physics. Three fundamental forces operate on fine particles in solution:

- (1) a gravitational force, tending to settle or raise particles depending on their density relative to the solvent;
- (2) a viscous drag force, which arises as a resistance to motion, since the fluid has to be forced apart as the particle moves through it;
- (3) the 'natural' kinetic energy of particles and molecules, which causes Brownian motion.

If we consider the first two forces, we can easily calculate the terminal or limiting velocity,  $V$ , (for settling or rising, depending on the particle's density relative to water) of a spherical particle of radius  $r$ . Under these conditions, the viscous drag force must equal the gravitational force. Thus, at a settling velocity,  $V$ , the viscous drag force is given by:  $F_{\text{drag}} = 6\pi r V \eta = 4\pi r^3 g (\rho_p - \rho_w)/3 = F_{\text{gravity}}$ , the gravitational force, where  $\eta$  is the viscosity of water and the density difference between particle and water is  $(\rho_p - \rho_w)$ . Hence, if we assume a particle–water density difference of  $+1 \text{ g cm}^{-3}$ , we obtain the results:

$r \text{ (Å)}$	100	1000	10 000	$10^5$	$10^6$
$r \text{ (μm)}$	0.01	0.1	1	10	100
$V \text{ (cm s}^{-1}\text{)}$	$2 \times 10^{-8}$	$2 \times 10^{-6}$	$2 \times 10^{-4}$	$2 \times 10^{-2}$	2

Clearly, from factors (1) and (2), small particles will take a very long time to settle and so a fine dispersion will be stable almost indefinitely, even for materials denser than water. But what of factor (3)? Each particle, independent of size, will have a kinetic energy, on average, of around  $1 kT$ . So the typical, random speed ( $v$ ) of a particle (in any direction) will be roughly given by:

$$mv^2/2 \cong 1kT \cong 4 \times 10^{-21} \text{ J} \quad (\text{at room temperature})$$

Again, if we assume that  $\rho_p = 2 \text{ g cm}^{-3}$ , then we obtain the results:

$r \text{ (Å)}$	100	1000	10 000	$10^5$	$10^6$
$r \text{ (μm)}$	0.01	0.1	1	10	100
$v \text{ (cm s}^{-1}\text{)}$	$10^2$	3	0.1	$3 \times 10^{-3}$	$1 \times 10^{-4}$

These values suggest that kinetic random motion will dominate the behaviour of small particles, which will not settle and the dispersion will be completely stable. However, this point is really the beginning of 'colloid science'. Since these small particles have this kinetic energy they will, of course, collide with other particles in the dispersion, with collision energies ranging up to at least  $10 kT$  (since there will actually be a distribution of kinetic energies). If there are attractive forces between the particles – as is reasonable since most colloids were initially formed via a vigorous mechanical process of disruption of a macroscopic or large body – each collision might cause the growth of large aggregates, which will then, for the reasons already given, settle out, and we will no longer have a stable dispersion! The colloidal solution will coagulate and produce a solid precipitate at the bottom of a clear solution.

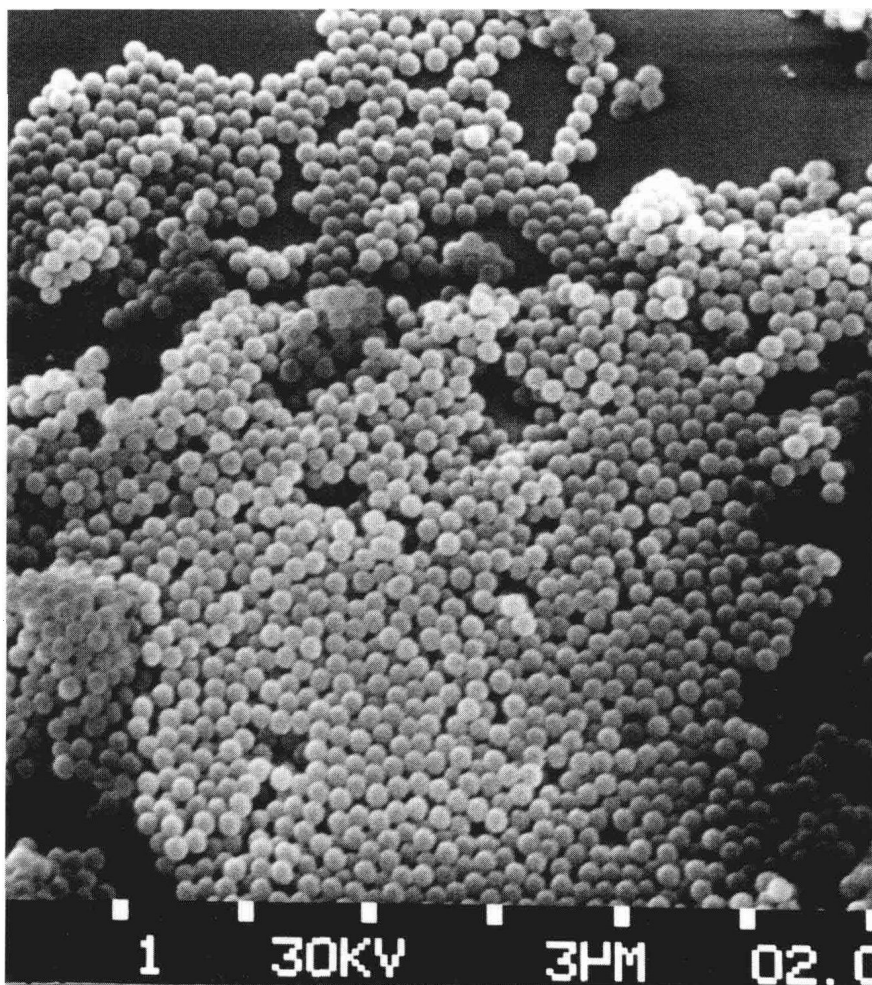
There is, in fact, a ubiquitous force in nature, called the *van der Waals force* (vdW), which is one of the main forces acting between molecules and is responsible for holding together many condensed phases, such as solid and liquid hydrocarbons and polymers. It is responsible for about one third of the attractive force holding liquid water molecules together. This force was actually first observed as a correction to the ideal gas equation and is attractive even between neutral gas molecules, such as oxygen and nitrogen, in a vacuum. Although electromagnetic in origin (as we will see later), it is much weaker than the Coulombic force acting between ions.

## **The forces involved in colloidal stability**

Although van der Waals forces will always act to coagulate dispersed colloids, it is possible to generate an opposing repulsive force of comparable strength. This force arises because most materials, when dispersed in water, ionize to some degree or selectively adsorb ions from solution and hence become charged. Two similarly charged colloids will repel each other via an electrostatic repulsion, which will oppose coagulation. The stability of a colloidal solution is therefore critically dependent on the charge generated at the surface of the particles. The combination of these two forces, attractive van der Waals and repulsive electrostatic forces, forms the fundamental basis for our understanding of the behaviour and stability of colloidal solutions. The corresponding theory is referred to as the DLVO (after Derjaguin, Landau, Verwey and Overbeek) theory of colloid stability, which we will consider in greater detail later. The stability of any colloidal dispersion is thus determined by the behaviour of the surface of the particle via its surface charge and its short-range attractive van der Waals force.

Our understanding of these forces has led to our ability to selectively control the electrostatic repulsion, and so create a powerful mechanism for controlling the properties of colloidal solutions. As an example, if we have a valuable mineral embedded in a quartz rock, grinding the rock will both separate out pure, individual quartz and the mineral particles, which can both be dispersed in water. The valuable mineral can then be selectively coagulated, whilst leaving the unwanted quartz in solution. This process is used widely in the mining industry as the first stage of mineral separation. The alternative of chemical processing, for example, by dissolving the quartz in hydrofluoric acid, would be both expensive and environmentally unfriendly.

It should be realized, at the outset, that colloidal solutions (unlike true solutions) will almost always be in a metastable state. That is, an electrostatic repulsion prevents the particles from combining into their most thermodynamically stable state, of aggregation into the macroscopic form, from which the colloidal dispersion was (artificially) created in the first place. On drying, colloidal particles will often remain separated by these repulsive forces, as illustrated by Figure 1.1, which shows a scanning electron microscope picture of mono-disperse silica colloids.



**Figure 1.1** Scanning electron microscope image of dried, monodisperse silica colloids.

## **Types of colloidal systems**

The term 'colloid' usually refers to particles in the size range  $50\text{\AA}$  to  $50\mu\text{m}$  but this, of course, is somewhat arbitrary. For example, blood could be considered as a colloidal solution in which large blood cells are dispersed in water. Often we are interested in solid dispersions in aqueous solution but many other situations are also of interest and industrial importance. Some examples are given in Table 1.1.

**Table 1.1**

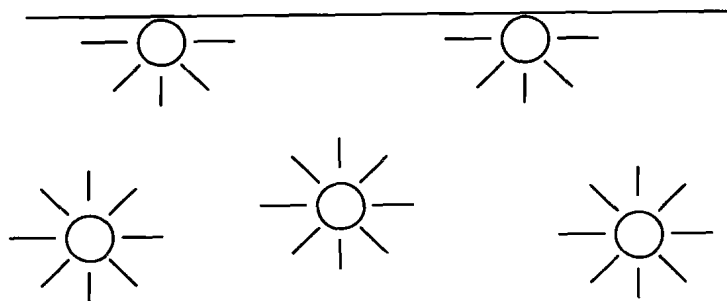
Dispersed phase	Dispersion medium	Name	Examples
Liquid	Gas	Liquid aerosol	Fogs, sprays
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Liquid	Foam	Foams
Liquid	Liquid	Emulsion	Milk, Mayonnaise
Solid	Liquid	'Sol' or colloidal solution	Au sol, AgI sol
		Paste at high concentration	Toothpaste
Gas	Solid	Solid foam	Expanded polystyrene
Liquid	Solid	Solid emulsion	Opal, pearl
Solid	Solid	Solid suspension	Pigmented plastics

The properties of colloidal dispersions are intimately linked to the high surface area of the dispersed phase and the chemistry of these interfaces. This linkage is well illustrated by the titles of two of the main journals in this area: the *Journal of Colloid and Interface Science* and *Colloids and Surfaces*. The natural combination of colloid and surface chemistry represents a major area of both research activity and industrial development. It has been estimated that something like 20 per cent of all chemists in industry work in this area.

## The link between colloids and surfaces

The link between colloids and surfaces follows naturally from the fact that particulate matter has a high surface area to mass ratio. The surface area of a 1 cm diameter sphere ( $4\pi r^2$ ) is  $3.14\text{ cm}^2$ , whereas the surface area of the same amount of material but in the form of  $0.1\text{ }\mu\text{m}$  diameter spheres (i.e. the size of the particles in latex paint) is  $314\,000\text{ cm}^2$ . The enormous difference in surface area is one of the reasons why the properties of the surface become very important for colloidal solutions. One everyday example is that organic dye molecules or pollutants can be effectively removed from water by adsorption onto particulate activated charcoal because of its high surface area. This process is widely used for water purification and in the oral treatment of poison victims.

Although it is easy to see that surface properties will determine the stability of colloidal dispersions, it is not so obvious why this can also



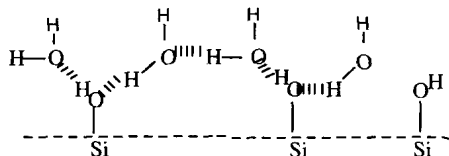
**Figure 1.2** Schematic diagram to illustrate the complete bonding of liquid molecules in the bulk phase but not at the surface.

**Table 1.2**

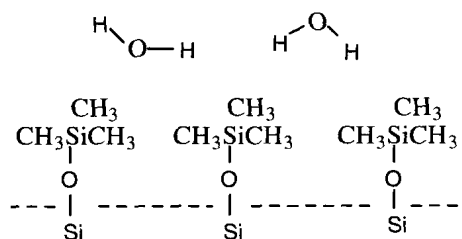
Liquid	Surface energy in $\text{mJm}^{-2}$ (at $20^\circ\text{C}$ )	Type of intermolecular bonding
Mercury	485	metallic
Water	72.8	hydrogen bonding + vdW
<i>n</i> -Octanol	27.5	hydrogen bonding + vdW
<i>n</i> -Hexane	18.4	vdW
Perfluoro-octane	12	weak vdW

be the case for some properties of macroscopic objects. As one important illustration, consider Figure 1.2, which illustrates the interface between a liquid and its vapour. Molecules in the bulk of the liquid can interact via attractive forces (e.g. van der Waals) with a larger number of nearest neighbours than those at the surface. The molecules at the surface must therefore have a higher energy than those in bulk, since they are partially freed from bonding with neighbouring molecules. Thus, work must be done to take fully interacting molecules from the bulk of the liquid to create any new surface. This work gives rise to the surface energy or tension of a liquid. Hence, the stronger the intermolecular forces between the liquid molecules, the greater will this work be, as is illustrated in Table 1.2.

The influence of this surface energy can also be clearly seen on the macroscopic shape of liquid droplets, which in the absence of all other forces will always form a shape of minimum surface area – that is, a sphere in a gravity-free system. This is the reason why small mercury droplets are always spherical.



**Figure 1.3** Water molecules form hydrogen bonds with the silanol groups at the surface of clean glass.



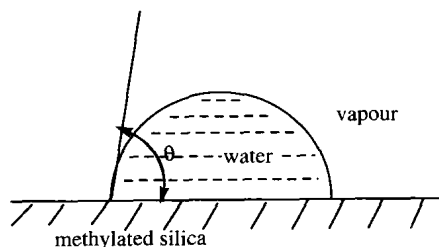
**Figure 1.4** Water molecules can only weakly interact (by vdw forces) with a methylated glass surface.

## Wetting properties and their industrial importance

Although a liquid will always try to form a minimum-surface-area shape, if no other forces are involved, it can also interact with other macroscopic objects, to reduce its surface tension via molecular bonding to another material, such as a suitable solid. Indeed, it may be energetically favourable for the liquid to interact and ‘wet’ another material. The wetting properties of a liquid on a particular solid are very important in many everyday activities and are determined solely by surface properties. One important and common example is that of water on clean glass. Water wets clean glass (Figure 1.3) because of the favourable hydrogen bond interaction between the surface silanol groups on glass and adjacent water molecules.

However, exposure of glass to Me<sub>3</sub>SiCl vapour rapidly produces a 0.5 nm layer of methyl groups on the surface. These groups cannot hydrogen-bond and hence water now does not wet and instead forms high ‘contact angle’ ( $\theta$ ) droplets and the glass now appears to be hydrophobic, with water droplet beads similar to those observed on paraffin wax (Figure 1.5).

This dramatic macroscopic difference in wetting behaviour is caused by only a thin molecular layer on the surface of glass and clearly demonstrates the importance of surface properties. The same type of



**Figure 1.5** A non-wetting water droplet on the surface of methylated, hydrophobic silica.

effect occurs every day, when dirty fingers coat grease onto a drinking glass! Surface treatments offer a remarkably efficient method for the control of macroscopic properties of materials. When insecticides are sprayed onto plant leaves, it is vital that the liquid wet and spread over the surface. Another important example is the froth flotation technique, used by industry to separate about a billion tons of ore each year. Whether valuable mineral particles will attach to rising bubbles and be 'collected' in the flotation process, is determined entirely by the surface properties or surface chemistry of the mineral particle, and this can be controlled by the use of low levels of 'surface-active' materials, which will selectively adsorb and change the surface properties of the mineral particles. Very large quantities of minerals are separated simply by the adjustment of their surface properties.

Although it is relatively easy to understand why some of the macroscopic properties of liquids, especially their shape, can depend on surface properties, it is not so obvious for solids. However, the strength of a solid is determined by the ease with which micro-cracks propagate, when placed under stress, and this depends on its surface energy, that is the amount of (surface) work required to continue the crack and hence expose new surface. This has the direct effect that materials are stronger in a vacuum, where their surface energy is not reduced by the adsorption of either gases or liquids, typically available under atmospheric conditions.

Many other industrial examples where colloid and surface chemistry plays a significant role will be discussed later, these include:

- latex paint technology
- photographic emulsions
- soil science
- soaps and detergents



- food science
- mineral processing.

## **Recommended resource books**

Adamson, A.W. (1990) *Physical Chemistry of Surfaces*, 5th edn, Wiley, New York

Birdi, K.S. (ed.) (1997) *CRC Handbook of Surface and Colloid Chemistry*, CRC Press, Boca Raton, FL

Evans, D.F. and Wennerstrom, H. (1999) *The Colloidal Domain*, 2nd edn, Wiley, New York

Hiemenz, P.C. (1997) *Principles of Colloid and Surface Chemistry*, 3rd edn, Marcel Dekker, New York

Hunter, R.J. (1987) *Foundations of Colloid Science*, Vol. 1, Clarendon Press, Oxford

Hunter, R.J. (1993) *Introduction to Modern Colloid Science*, Oxford Sci. Publ., Oxford

Israelachvili, J.N. (1985) *Intermolecular and Surface Forces*, Academic Press, London

Shaw, D.J. (1992) *Introduction to Colloid and Surface Chemistry*, 4th edn, Butterworth-Heinemann, Oxford, Boston