Handbook of Surface and Colloid Chemistry 2nd Ed

HANDBOOK OF Surface and Colloid Chemistry

Second Edition

Edited by

K.S. Birdi

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Dedication

To Lilian

Preface

The science related to the subject of surface and colloid chemistry has expanded in the past decade at a rapid pace. This area of science has been especially important in such new areas as environmental control, wastewater processing, nanotechnology, pharmacy, and biotechnology. The applications of nanoparticles in pharmacy products are very significant. Initially, the subject arose over 50 years ago when theoretical understanding of surface and colloid systems developed. The amount of information published since has increased steadily; consider that there are at present some half a dozen different specialty journals related mainly to surface and colloid chemistry. The applications of this subject have developed rapidly in both the industrial and biological areas.

During the last few decades, many empirical observations have been found to be based in the fundamental laws of physics and chemistry. These laws have been extensively applied to the science of surface and colloid chemistry, which gave rise to investigations based on molecular description of surfaces and reactions at interfaces. Especially during the last decade, theoretical analyses have added to the understanding of this subject with increasing molecular detail. These developments are moving at a much faster pace with each decade.

The application area of surface and colloid science has increased dramatically during the past decades. For example, the major industrial areas have been soaps and detergents, emulsion technology, colloidal dispersions (suspensions, nanoparticles), wetting and contact angle, paper, cement, oil recovery, pollution control, fogs, foams (thin liquid films), the food industry, biomembranes, drug delivery (vesicles), membrane technology, and the pharmaceutical industry. Recently, new areas of applications are developing, two of which are synthetic transplants and biological monitors. These trends show the importance of this field of science in everyday life.

Thus, a group of experts from the United States, Europe, and worldwide wrote a handbook that covered this subject extensively in 1997 (*Handbook of Surface and Colloid Chemistry,* CRC Press, Boca Raton, FL). However, since 1997 the number of publications related to surface and colloid science has grown exponentially. Accordingly, a new group of experts decided that at this stage there is an urgent need for a second edition of the handbook, which should make theoretical and experimental information on the systems related to surfaces and colloids readily available. The purpose of this second edition of the handbook is to bring the reader up-to-date with the most recent developments in this area. The second edition of this handbook both updates the first edition and includes new areas of research. Hence, the two editions combined cover an extensive range of research subjects. In this edition of the handbook a unifying theme of information on surface and colloid chemistry is presented by a team of international experts. The subject content is presented such that the reader can follow through the physical principles that are needed for applications, and extensive references are included for understanding the related phenomena. Thus, the two editions together become a gateway to a vast number of literature references. This is unique in the current literature.

As the subject area and the quantity of knowledge are immense, there is always a need for a team of experts to join together and compile a handbook. It is therefore an honor for me to be able to arrange and present to the reader chapters written by experts on various subjects pertaining to this science, with bibliographical references well in excess of 2000.

It is most impressive to discover how theoretical knowledge has led to some fascinating developments in the technology. The purpose of this handbook is also to further this development. The scope of the second edition of this handbook is consciously different from that of any existing volume on the same subject. The molecular description of liquid surfaces has been obtained from surface tension (under static and dynamic conditions) and adsorption studies. Thin-film formation and emulsion formation and stability are described by interfacial film structures. The surfaces of solids are characterized by contact angle and adsorption studies. Foams are described by the bilayer arrangement of the detergent and other amphiphile molecules in the thin films. The ultimate in interfaces are molecular films and molecular self-assemblies. Many questions about monomolecular films on solids are answered with the use of modern scanning probe microscopes (SPMs). The impact of the scanning tunneling microscope (STM) and the atomic force microscope (AFM) is delineated. This has indeed led to such new scientific fields as nanotechnology. In the past decade developments in increased sensitivity and innovation in instruments have added much knowledge. Colloidal structures and their stability have been found to be of much interest, as described extensively in this second edition of the handbook. The theoretical basis of colloids and their stability is thoroughly described.

The chapters are arranged such that the information is basically needed for the whole handbook. The organization allows the reader to follow the subject area smoothly, with the extensive data provided in the form of tables and figures supporting this aim.

The Editor

Professor K. S. Birdi received his undergraduate education (B.Sc. Hons. Chem.) from Delhi University; Delhi, India, in 1952. He also majored in chemistry at the University of California at Berkeley. After graduation in 1957, he joined Standard Oil of California, Richmond.

In 1959, Dr. Birdi became chief chemist at Lever Brothers in Denmark. He became interested in surface and colloid chemistry and joined the Institute of Physical Chemistry as an assistant professor. He initially did research on surface science aspects (e.g., thermodynamics of surfaces, detergents, micelle formation, adsorption, Langmuir monolayers, biophysics). During the early exploration and discovery stages of oil and gas in the North Sea, Dr. Birdi became involved in Danish Research Science Foundation programs, with other research institutes around Copenhagen, in the oil recovery phenomena and surface science. Later, research grants on the same subject were awarded from European Union projects. These projects involved extensive visits to other universities and an exchange of guests from all over the world. Professor Birdi was appointed Research Professor in 1985 (Nordic Science Foundation), and was then appointed, in 1990, to the School of Pharmacy, Copenhagen, as professor in physical chemistry. Since 1999, Professor Birdi has been actively engaged in consultancy to both industrial and university projects.

Professor Birdi is a consultant to various national and international industries. He is and has been a member of various chemical societies, and a member of organizing committees of national and international meetings related to surface science. He has been a member of selection committees for assistant professor and professor, and was an advisory member (1985 to 1987) of the ACS journal *Langmuir.*

Professor Birdi has been an advisor for some 90 advanced student projects and various Ph.D. projects. He is the author of some 100 papers and articles (and a few hundred citations).

To describe these research observations and data he realized that it was essential to write books on the subject of surface and colloid chemistry. His first book on surface science was published in 1984: *Adsorption and the Gibbs Surface Excess,* Chattorraj, D.K. and Birdi, K.S., Plenum Press, New York. This book remains the only one of its kind in the present decade. Further publications include *Lipid and Biopolymer Monolayers at Liquid Interfaces,* K.S. Birdi, Plenum Press, New York, 1989; *Fractals — In Chemistry, Geochemistry and Biophysics,* K.S. Birdi, Plenum Press, New York, 1994; *Handbook of Surface and Colloid Chemistry,* CRC Press, Boca Raton, FL, 1997 (CD-ROM, 1999), and *Self-Assembly Monolayer,* Plenum Press, New York, 1999. Surface and colloid chemistry has remained his major research interest throughout these years.

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Contents

1 Introduction to Surface and Colloid Chemistry

K. S. Birdi

Matter exists as gas, liquid, and solid phases, as has been recognized by classical science. The molecules that are situated at the interfaces (e.g., between gas–liquid, gas–solid, liquid–solid, $liquid_1$–$liquid_2$, $solid_1$–$solid_2$) are known to behave differently from those in the bulk phase.[1-17] It is also well known that the molecules situated near or at the interface (i.e., liquid–gas) are situated differently with respect to each other than are the molecules in the bulk phase. The intramolecular forces acting would thus be different in these two cases. Furthermore, it has been pointed out that, for a dense fluid, the repulsive forces dominate the fluid structure and are of primary importance. The main effect of the repulsive forces is to provide a uniform background potential in which the molecules move as hard spheres. The molecules at the interface would be under an asymmetric force field, which gives rise to the so-called surface tension or interfacial tension (Figure 1.1).[16]

The resultant force on molecules varies with time because of the movement of the molecules; the molecules at the surface will be pointed downward into the bulk phase. The nearer the molecule is to the surface, the greater the magnitude of the force due to asymmetry. The region of asymmetry plays a very important role. Thus, when the surface area of a liquid is increased, some molecules must move from the interior of the continuous phase to the interface. The surface of a liquid can thus be regarded as the plane of potential energy. An analogous case would be when the solid is crushed and the surface area increases per unit gram. Further, molecular phenomena at the surface separating the liquid and the saturated vapor are appreciably more complex than those that occur in the bulk homogeneous fluid phase. Especially, some amphiphiles exhibit the *self-assembly* characteristic. This phenomenon is known to be the basic building block of many natural assemblies.

The designation *colloid* is used for particles that are of some small dimension that cannot pass through a membrane with a pore size ~10^{-6} m (= μm) (Thomas Graham described this about a century ago). The nature and relevance of colloids are among the main current research topics.[16]

Colloids are an important class of materials, intermediate between bulk and molecularly dispersed systems. The colloid particles may be spherical, but in some cases one dimension can be much larger than the other two (as in a needle shape). The size of particles also determines whether they can be seen by the naked eye. Colloids are not visible to the naked eye or under an ordinary optical microscope. However, the scattering of light can be used to see such colloidal particles (such as dust particles, etc.) easily. The size of colloidal particles then may range from 10^{-4} to 10^{-7} cm. The units used are as follows:

1 μm = 10^{-6} m
1 Å (angstrom) = 10^{-8} cm = 0.1 nm = 10^{-10} m

The angstrom unit is named for the famous Swedish scientist, and currently the nm (10^{-9}) unit is mainly used. Because colloidal systems consist of two or more phases and components, the interfacial area-to-volume ratio becomes very significant. Colloidal particles have a high ratio of surface area to volume compared with bulk materials. A significant proportion of the colloidal

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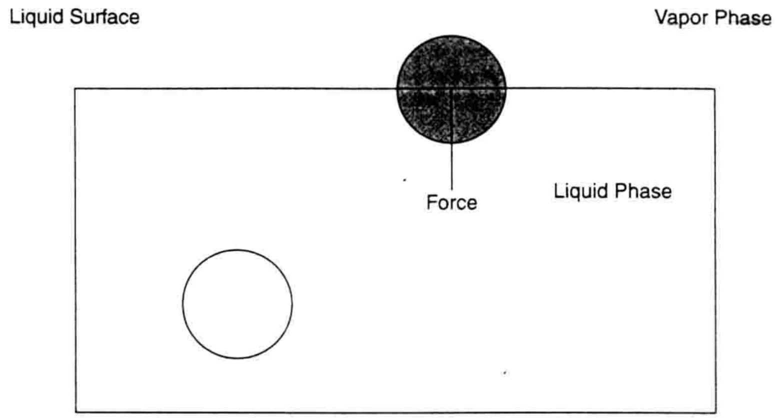

FIGURE 1.1 Intermolecular forces around a molecule in the bulk liquid and around a molecule in the surface layer (schematic).

molecules lie within, or close to, the interfacial region. Hence, the interfacial region has significant control over the properties of colloids. To understand why colloidal dispersions can be either stable or unstable, we need to consider the following:

- The effect of the large ratio of surface area to volume
- The forces operating between the colloidal particles

There are some very special characteristics that must be considered regarding colloidal particle behavior: size and shape, surface area, and surface charge density. The *Brownian motion* of the particles is a much-studied field, and the fractal nature of surface roughness has recently been shown to be important. Recent applications have been reported employing nanocolloids.

The definitions generally employed are as follows. *Surface* is a term used when considering the dividing phase between

Gas–Liquid
Gas–Solid

Interface is the term used when considering the dividing phase:

Solid–Liquid
Liquid_1–Liquid_2
Solid_1–Solid_2

In other words, surface tension may be considered to arise because of a degree of unsaturation of bonds that occurs when a molecule resides at the surface and not in the bulk. The term *surface tension* is used for solid–vapor or liquid–vapor interfaces. The term *interfacial tension* is more generally used for the interface between two liquids, two solids, or a liquid and a solid.

It is, of course, obvious that in a one-component system the fluid is uniform from the bulk phase to the surface, but the orientation of the surface molecules will be different from the molecules in the bulk phase. The question we may ask, then, is how sharply the density changes from that of being fluid to that of gas. Is this transition region a monolayer deep or many layers deep?

TABLE 1.1
Typical Colloidal Systems

Phases		
Dispersed	**Continuous**	**System Name**
Liquid	Gas	Aerosol fog, spray
Gas	Liquid	Foam, thin films, froth, fire extinguisher foam
Liquid	Liquid	Emulsion (milk), mayonnaise, butter
Solid	Liquid	Sols, AgI, photography films, suspension wastewater, cement
Biocolloids		
Corpuscles	Serum	Blood
Hydroxyapatite	Collagen	Bone
Liquid	Solid	Solid emulsion (toothpaste)
Solid	Gas	Solid aerosol (dust)
Gas	Solid	Solid foam — expanded (polystyrene), insulating foam
Solid	Solid	Solid suspension/solids in plastics

Many reports are found where this subject has been investigated.[13,14] The Gibbs adsorption theory considers the surface of liquids to be monolayer. The experiments that analyze the spread monolayers are also based on one molecular layer. The subject related to self-assembly monolayer (SAM) structures has been treated extensively.[14,16] However, there exists no procedure that can provide information by a direct measurement; this subject is described later in this handbook. The composition of the surface of a solution with two components or more requires additional comments.[15] In Table 1.1 are given typical colloidal suspensions that are found in everyday life.

Colloidal systems are widespread in their occurrence and have biological and technological significance. There are three types of colloidal systems:[16]

1. In simple colloids, clear distinction can be made between the disperse phase and the disperse medium, e.g., simple emulsions of oil in water (o/w) or water in oil (w/o).
2. Multiple colloids involve the coexistence of three phases of which two are finely divided, e.g., multiple emulsions of water in oil in water (w/o/w) or oil in water in oil (o/w/o).
3. Network colloids have two phases forming an interpenetrating network, e.g., polymer matrix.

Colloidal stability is determined by the free energy (surface free energy or the interfacial free energy) of the system. The main parameter of interest is the large surface area exposed between the dispersed phase and the continuous phase. Because the colloid particles move about constantly, their dispersion energy is determined by Brownian motion. The energy imparted by collisions with the surrounding molecules at temperature $T = 300$ K is $\frac{3}{2} k_B T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 = 10^{10-20}$ J (where k_B is the Boltzmann constant). This energy and the intermolecular forces would thus determine the colloidal stability. The idea that two species should interact with one another, so that their mutual potential energy can be represented by some function of the distance between them, has been described in the literature.

Furthermore, colloidal particles frequently adsorb (and even absorb) ions from their dispersing medium. Sorption that is much stronger than expected from dispersion forces is called *chemisorption,* a process that is of both chemical and physical interest.

These considerations are important in regard to many different systems: paints, cements, adhesives, photographic products, water purification, sewage disposal, emulsions, chromatography, oil recovery, the paper and print industry, microelectronics, soap and detergents, catalysts, food products, pharmaceutical products, and biology (cell, virus).

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2 Hydrogen Bonding in Solutions: The Equation-of-State Approach

Costas G. Panayiotou

CONTENTS

2.1 INTRODUCTION

Hydrogen bonding is a subject of remarkable diversity as it is present in and dictates the behavior of an enormous number of systems including aqueous solutions, systems of biological/biomedical interest, pharmaceuticals, colloids and surfactants, physical networks and gels, adhesives and pastes, extractives and binders, polymer alloys and blends. There are many reviews of the subject in the

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