Handbook of

SURFACE and COLLOID CHEMISTRY

表面和胶体化学手册

Edited by

K. S. Birdi

Handbook of

SURFACE and COLLOID CHEMISTRY

Edited by

K.S. Birdi
Royal Danish School of Pharmacy
Copenhagen, Denmark

CRC Press
Boca Raton New York

Library of Congress Cataloging-in-Publication Data

Handbook of surface and colloid chemistry / edited by K.S. Birdi.
p. cm.
Includes bibliographical references and index.
ISBN 0-8493-9459-7 (alk. paper)
1. Surface chemistry. 2. Colloids. I. Birdi, K.S., 1934–
QD508.H36 1997
541.3'3--dc21
97-3758
CIP

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage or retrieval system, without prior permission in writing from the publisher.

All rights reserved. Authorization to photocopy items for internal or personal use, or the personal or internal use of specific clients, may be granted by CRC Press, LLC provided that $.50 per page photocopied is paid directly to Copyright Clearance Center, 27 Congress Street, Salem, MA 01970 USA. The fee code for users of the Transactional Reporting Service is ISBN 0-8493-9459-7/97/$0.00+$.50. The fee is subject to change without notice. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

CRC Press, LLC consent does not extend to copying for general distribution, for promotion, for creating new works, or for resale. Specific permission must be obtained in writing from CRC Press for such copying.

Direct all inquiries to CRC Press, LLC 2000 Corporate Blvd., N.W., Boca Raton, Florida 33431.

© 1997 by CRC Press LLC.

No claim to original U.S. Government works

International Standard Book Number 0-8493-9459-7
Library of Congress Card Number 97-3758
Printed in the United States of America 1 2 3 4 5 6 7 8 9 0
Printed on acid-free paper

书　　名：Handbook of Surface and Colloid Chemistry
作　　者：K.S. Birdi (ed.)
中 译 名：表面和胶体化学手册
出 版 者：世界图书出版公司北京公司
印 刷 者：北京中西印刷厂
发　　行：世界图书出版公司北京公司 (北京朝内大街137号　100010)
开　　本：1/20　787×1245　　印　张：39
出版年代：1999年10月
书　　号：ISBN 7-5062-1476-8/O・281
版权登记：图字 01-1999-2724
定　　价：150.00元

Handbook of

SURFACE and COLLOID
CHEMISTRY

Preface

The science related to the subject of surface and colloid chemistry has been expanding in the past decade at a rapid pace. Especially, this science has been found to be of importance in such new areas as environmental control and bio-technology.

Initially, the subject began some fifty years back when theoretical understanding of surface and colloid systems was found to be of much importance. The amount of information published since then has increased steadily; consider that there are at present some half a dozen different specialty journals related mainly to surface and colloids. The application area of this subject has developed rapidly both in the industrial and biological areas.

During the last few decades, many empirical observations have been found to have basis in the fundamental laws of physics and chemistry. These laws have been extensively applied to the science of surface and colloid chemistry. This development gave rise to investigations based upon 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), food industry, biomembranes, membranes, and pharmaceutical industry. Recently, new areas of applications are developing, one of which is the synthetic transplants and biological monitors. These trends show the importance of this field of science in everyday life.

Accordingly, at this stage there is an urgent need for a *handbook* which should provide easily available theoretical and experimental information on the systems related to surface and colloids. The purpose of the handbook is to bring the reader up-to-date with the most recent developments in this area. In this handbook a unifying theme of information on surface and colloid chemistry is presented by a team of international experts. The subject content is presented in such a manner that the reader can follow through the physical principles which are needed for application, and extensive references are included for understanding the related phenomena.

As the subject area and the quantity of knowledge is 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 bibliographies in excess of 1000.

It is most impressive to find how theoretical knowledge has lead to some fascinating developments in the technology. The purpose of this handbook is also to further this development. The molecular description of liquid surfaces has been obtained from surface tension and adsorption studies. The emulsion formation and stability is described by the 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 is a molecular film and molecular self-assemblies. A description about many questions about monomolecular films on solids is answered with the use of modern scanning microscopes. This has indeed led to such new scientific fields as nano-technology. In the past decade these developments in the increased sensitivity and innovation in instruments has added much knowledge. The colloidal structures and their stability have been found to be of much interest as described extensively in this handbook.

Finally, with great pleasure I thank the staff of CRC Press for their patience and endurance in helping me through this task as editor.

I wish also to thank my wife for providing the right kind of consideration while working through the material for this handbook.

The Editor

Dr. K.S. Birdi received a B.Sc. degree in Chemistry from Delhi University, Delhi, India, in 1952. He then traveled to the U.S. for further studies, majoring in chemistry at the University of California at Berkeley. After graduation in 1957, he joined Standard Oil of California, Richmond.

Dr. Birdi married and moved to Copenhagen in 1959, where he joined Lever Bros., in 1959 as Chief-Chemist, Development Laboratory. During this period he became interested in surface chemistry and joined, as assistant professor, the Institute of Physical Chemistry (founder of institute: Professor J. Brønsted), Danish Technical University, Lyngby, Denmark, in 1966. He initially did research on surface science aspects (e.g. detergents; micelle formation; adsorption; biophysics). During the early exploration and discovery stages of oil and gas in the North Sea, he got involved in 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 the European Common Market projects. These projects also involved extensive visits to other universities and an exchange of guests from all over the world. Dr. 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.

There was continuous involvement with various industrial contract research programs throughout these years. These projects have actually been a very important source of information in keeping up with real problems, and helped in the guidance of research planning at all levels.

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

In order to describe these research observations and data he realized that it was essential to write books on the subject. His first book on surface science was published in 1984: *Adsorption and the Gibbs Surface Excess,* Chatorraj, D.K. and Birdi, K.S., Plenum Press, New York. Further publications include *Lipid and Biopolymer Monolayers at Liquid Interfaces,* K.S. Birdi, Plenum Press, New York, 1989; and *Fractals, in Chemistry, Geochemistry and Biophysics,* K.S. Birdi, Plenum Press, New York, 1994. Surface chemistry has remained his major interest of research throughout these years.

Contributors

K.B. Andersen
Department of Biological Science
Royal Danish School of Pharmacy
Copenhagen, Denmark

K.S. Birdi
Anal. and Pharm. Chemistry
Royal Danish School of Pharmacy
Copenhagen, Denmark

Anne Marit Blokhus
Kjem. Institute
University of Bergen
Bergen, Norway

Steven P. Christiano
Dow Corning Corp.
Midland, Michigan

Krassimir D. Danov
Faculty of Chemistry
Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics
University of Sofia
Sofia, Bulgaria

Tapas K. De
Department of Chemistry
University of Delhi
Delhi, India

Nikolai D. Denkov
Faculty of Chemistry
Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics
University of Sofia
Sofia, Bulgaria

Jacques E. Desnoyers
INRS — Energie et Materiaux
Inst. Nat. Rech. Scient.
Varennes, Canada

H. Yıldırım Erbil
Department of Chemistry
TUBITAK, Marmara Research Center
Gebze, Kocaeli
Turkey

Janos H. Fendler
Department of Chemistry
Center for Membrane Engineering Science
Syracuse University
Syracuse, New York

Harald Førdedal
Kjem. Institute
University of Bergen
Bergen, Norway

Charles M. Hansen
FORCE Institute
Brøndby, Denmark

Harald Høiland
Department of Chemistry
University of Bergen
Bergen, Norway

Thorvald Jakobsen
Kjem. Institute
University of Bergen
Bergen, Norway

Peter A. Kralchevsky
Faculty of Chemistry
Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics
University of Sofia
Sofia, Bulgaria

S. Krishnakumar
Langmuir Center for Colloids and Interfaces
Columbia University
New York, New York

D. Kristensen
Anal. and Pharm. Chemistry
Royal Danish School of Pharmacy
Copenhagen, Denmark

Zdravko I. Lalchev
Laboratory of Model Membranes
Faculty of Biology
Department of Biochemistry
University of Sofia
Sofia, Bulgaria

Wolfgang Littman
Consulting Reservoir Engineering
Wunstof, Germany

Amarnath Maitra
Department of Chemistry
University of Delhi
Delhi, India

B. Markovic
Langmuir Center for Colloids and Interfaces
Columbia University
New York, New York

Clarence A. Miller
Chemical Engineering Department
Rice University
Houston, Texas

L. Moesby
Department of Biological Science
Royal Danish School of Pharmacy
Copenhagen, Denmark

K. Olsen
Department of Biological Science
Royal Danish School of Pharmacy
Copenhagen, Denmark

Gérald Perron
INRS — Energie et Materiaux
Inst. Nat. Rech. Scient.
Varennes, Canada

M.P. Pileni
University P. et M. Curie
Paris, France

Johan Sjöblom
Department of Chemistry
University of Bergen
Bergen, Norway

Tore Skodvin
Kjem. Institute
University of Bergen
Bergen, Norway

P. Somasundaran
Langmuir Center for Colloids and Interfaces
Columbia University
New York, New York

C.M. Sorensen
Department of Physics
Kansas State University
Manhattan, Kansas

D.T. Vu
Anal. and Pharm. Chemistry
Royal Danish School of Pharmacy
Copenhagen, Denmark

Darsh T. Wasan
Department of Chemical Engineering
Illinois Institute of Technology
Chicago, Illinois

X. Yu
Corporate Research Center
International Paper
Tuxedo, New York

Contents

Chapter 12

Chapter 13

Chapter 14

Chapter 15

Chapter 16

Chapter 17

Chapter 18

Chapter 19

1 Surface and Colloid Chemistry

K.S. Birdi

CONTENTS

1.1 INTRODUCTION

Matter exists as gas, liquid, and solid phases, as has been recognized by classical science. The molecules which are situated at the interfaces (e.g., between gas-liquid, gas-solid, liquid-solid, liquid$_1$-liquid$_2$) are known to behave differently than those in the bulk phase.[1-15] It is also accepted that the molecules situated near or at the interface (i.e., liquid-gas) will be situated differently with respect to each other than 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 asymmetrical force field, which gives rise to the so-called surface tension or interfacial tension (Figure 1).

The resultant force on molecules will vary with time because of the movement of the molecules; the molecules at the surface will be pointed downwards into the bulk phase. The nearer the molecule is to the surface, the greater the magnitude of the force due to asymmetry. 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. Analogous case would be when the solid is crushed and surface area increases. Further, molecular phenomena at the surface separating the liquid and the saturated vapor are appreciably more complex than those which occur in the bulk homogeneous fluid phase. Especially, some amphiphiles exhibit the *self-assembly* characteristic. This phenomena 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 and cannot pass through a membrane with a pore size ca. 10^{-6} m (Thomas Graham described this about a century ago). The colloid particles may be spherical, but in some cases one dimension can be much larger than the other two (as in a needle-like shape). The size of particles also determines whether one can see them by the naked eye. Colloids are not visible to the naked eye nor under an ordinary microscope. The scattering of light can easily be used to see such colloidal particles (such as dust particles, etc.). The size of colloidal particles then may range from 10^{-4} to 10^{-7} cm. The units used are as follows:

$$1\ \mu\text{m} = 10^{-6}\ \text{m}$$

$$1\ \text{Å} = 10^{-8}\ \text{cm} = 0.1\ \text{nm} = 10^{-10}\ \text{m}$$

0-8493-9459-7/97/$0.00+$.50

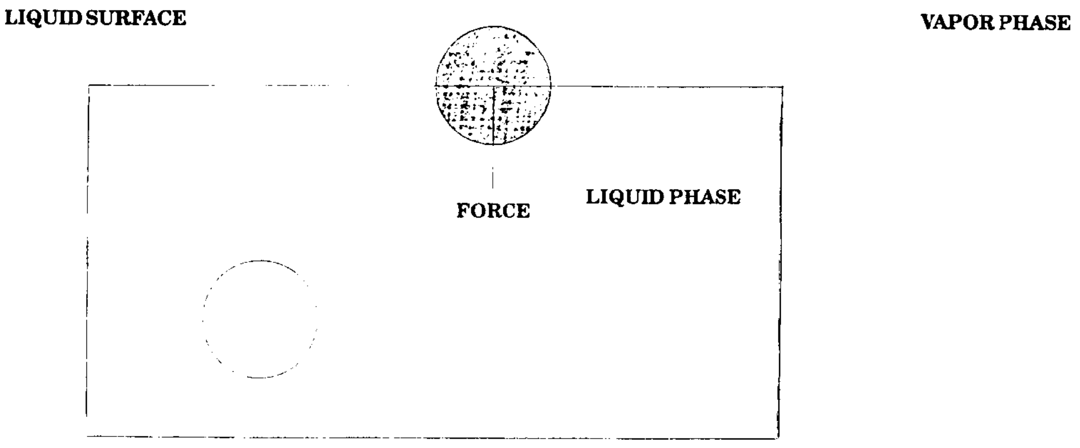

FIGURE 1 Intermolecular forces around a molecule in the bulk liquid and around a molecule in the surface layer.

Since colloidal systems consist of two or more phases and components, the interfacial area-to-volume ratio becomes very significant. There are some very special characteristics which must be considered as regards colloidal particle behavior: size and shape, surface area, and surface charge density. The Brownian motion of the particles is a much-studied field. The fractal nature of surface roughness has recently been shown to be of importance.

The definitions generally employed are as follows. "*Surface*" is a term used when one considers the dividing phase between:

Gas–Liquid

Gas–Solid

"*Interface*" is the term used when one considers the dividing phase:

Solid–Liquid

Liquid_1–Liquid_2

Solid_1–Solid_2

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 those molecules in the bulk phase. The question one may ask, then, is how sharply does the density change from that of being fluid to that of gas. Is this a transition a monolayer deep or many layers deep? Many reports are found where this subject has been investigated. The composition of the surface of a solution with two-components or more would require additional comments.[15] In Table 1 are given typical colloidal suspensions that one finds in everyday life.

The 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. Since the colloid particles move about constantly, their dispersion energy is determined by the Brownian motion. The energy imparted by collisions with the surrounding molecules at temperature $T = 300$ K is $3/2\ k_B T = 3/2 \times 1.38 \times 10^{-23} \times 300 = 10^{-20}$ J (where k_B is the Boltzmann constant). This energy and the intermolecular forces would thus determine the colloidal stability.

TABLE 1
Typical Colloidal Systems

Phases		
Dispersed	**Continuous**	**System name**
Liquid	Gas	Aerosol fog, spray
Gas	Liquid	Foam, thin films, froth
Liquid	Liquid	Emulsion (milk)
Solid	Liquid	Sols, AgI
Suspension		Waste-water
Biocolloids		Blood
Liquid	Solid	Solid emulsion
Solid	Gas	Solid aerosol (dust)
Gas	Solid	Solid foam — expanded (polystyrene)
Solid	Solid	Solid suspension/solids in plastics

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

These considerations are important in regard to the different systems mentioned above: paints, cements, photographic products, water purification, sewage disposal, emulsions, chromatography, catalysts, pharmaceutical products, and biology (cell, virus).

REFERENCES

1. Bakker, G., *Kapillaritat und Uberflachenspannung Handbuch der Eksperimentalphysik*, 3d vi, Leipzig, 1928; Freundlich, H., *Colloid and Capillary Chemistry*, Methuen, London, 1926.
2. Adam, N.K., *The Physics and Chemistry of Surfaces*, Clarendon Press, Oxford, 1930.
3. Bancroft, W.D., *Applied Colloid Chemistry*, McGraw-Hill, New York, 1932.
4. Partington, J.R., *An Advanced Treatise of Physical Chemistry*, Vol. II, Longmans, Green, New York, 1951.
5. Harkins, W.D., *The Physical Chemistry of Surface Films*, Reinhold, New York, 1952.
6. Davies, J.T., Rideal, E.K., *Interfacial Phenomena*, Academic Press, New York, 1963.
7. Defay, R., Prigogine, I., Bellemans, A., and Everett, D.H., *Surface Tension and Adsorption*, Longmans, Green, London, 1966.
8. Gaines, G.L., Jr., *Insoluble Monolayers at Liquid-Gas Interfaces*, Wiley-Interscience, New York, 1966.
9. Matijevic, E., Ed., *Surface and Colloid Science*, Vol. 1–9, Wiley-Interscience New York, 1969–1976.
10. Aveyard, R. and Hayden, D.A., *An Introduction to Principles of Surface Chemistry*, Cambridge, London, 1973.
11. Fendler, J.H. and Fendler, E.J., *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975.
12. Adamson, A.W., *Physical Chemistry of Surfaces*, 5th ed., Wiley-Interscience, New York, 1990; Faraday Symposia of the Chemical Society, No. 16, *Structure of the Interfacial Region*, Faraday Society, London, 1981.
13. Chattoraj, D.K. and Birdi, K.S., *Adsorption and the Gibbs Surface Excess*, Plenum Press, New York, 1984.
14. Birdi, K.S., *Lipid and Biopolymer Monolayers at Liquid Interfaces*, Plenum Press, New York, 1989.
15. Feder, J., *Fractals: Physics of Solids and Liquids*, Plenum Press, New York; 1988; Avnir, D., Ed., *The Fractal Approach to Heterogenous Chemistry*, Wiley, New York, 1989; Birdi, K.S., *Fractals — In Chemistry, Geochemistry and Biophysics*, Plenum Press, New York, 1993.

2

Interfacial Interactions of Liquids

H. Yıldırım Erbil

CONTENTS

0-8493-9459-7/97/$0.00+$.50