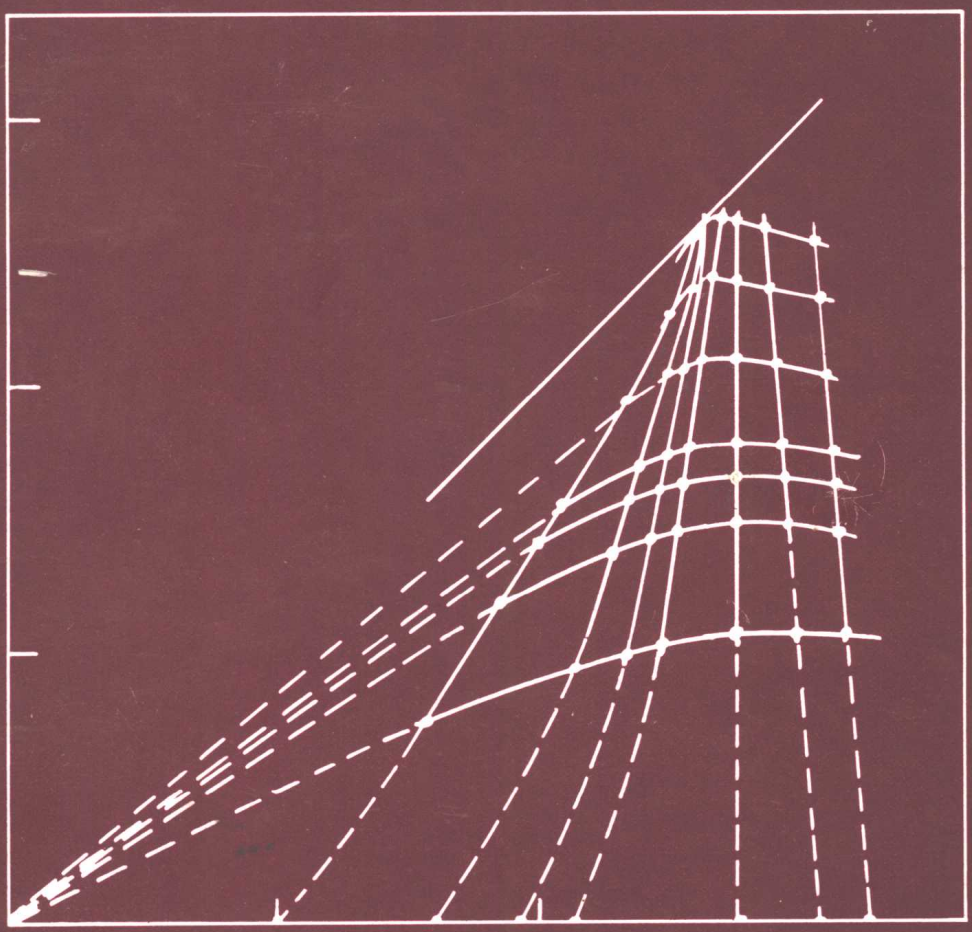
ADSORPTION AND THE GIBBS SURFACE EXCESS



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ADSORPTION AND THE GIBBS SURFACE EXCESS

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PREFACE

The subject matter of this book is not entirely new in that much has been written about the state of the interfacial chemistry in other textbooks. However, the authors have found that there is really a need for a book which can lead an investigator, a student, or a beginner through the in-depth understanding and descriptions involved in the derivations and usage of the adsorption equations based on the unified concept of the Gibbs surface excess. The derivation of the original Gibbs equation for the liquid interface has been amplified with reformulations and criticisms. Attempts have been frequently made to relate the surface excess quantities with the thermodynamic properties of the physically defined interfacial phase. In the last two decades, useful applications of the Gibbs equations have been made for the study of adsorption at solid–liquid as well as liquid–gas interfaces formed in the presence of the multicomponent solutions in the bulk. These recent treatments become useful for the experimental studies of the adsorption of electrolytes and interfacial properties related to neutral and charged monolayers. The consistency of the experimental results with those to be expected from the theories of the electrical double layer needs careful examination. An attempt has been made to present in a single volume all these developments based on the unified concept of the Gibbs surface excess.

The study of the adsorption from solution is of considerable importance in the field of biology and in many other branches of applied science. The discussion of the concept of the Gibbs surface excess in this book for the interpretation of the hydration and binding phenomena in the biopolymer system is relatively new. It is hoped that this will initiate further research work in the various important fields of physical biochemistry, biophysics, and biology in general. Relevant discussions on the adsorption at biosurfaces, model biomembranes, etc., have been included in this book to demonstrate that the concept of the Gibbs excess is very useful to the life sciences in general.

The treatment in different parts of the book is based on the fundamental concept of classical thermodynamics. A large amount of experimental results have been included throughout the book for the critical examination of the theoretical treatments. Results based on statistical thermodynamics have been discussed in a few sections to clarify certain basic aspects of the adsorption phenomena. The notations used in the mathematical treatment have been kept uniform as far as possible.

The references are as up-to-date as is technically possible. The book does not cover all other aspects of surface science where the Gibbs surface excess concept is not essential since these are well covered by the existing textbooks. The aim of this book is to point out those specific areas of surface phenomena where the application of the Gibbs surface excess concept is essential or not yet fully appreciated. Topics of great controversy are also mentioned in brief with comments at the end of each chapter in order to provide a basis for future research for a newcomer in the field.

More than two hundred illustrations have been included in the eleven chapters of this book. We express our thanks and gratitude to the following publishers and societies for permitting us to use the figures first published in their journals and books:

The Chemical Society, London; The American Chemical Society, Washington, D.C.; The Chemical Society of Japan, Tokyo; The Council of Scientific and Industrial Research, New Delhi; F. A. Davis Company, Philadelphia; Dr. Dietrich Steinkoff Verlag, Darmstadt; Academic Press Inc., New York; Wiley-Interscience Publications and John Wiley and Sons, New York; Elsevier Biomedical Press and Elsevier Scientific Press, Amsterdam; Marcel Dekker Inc., New York; Pergamon Press, London; Butterworth Scientific Ltd., Borough Green, England.

In addition, many authors have given their consent to the use of their illustrations in our book for which we express our sincere thanks. The appropriate references for these illustrations in specific journals and books have been mentioned in the figure captions. Many of these figures have been redrawn with major or minor changes to suit the system of notation used in this book.

The authors would like to thank their many colleagues, friends, and students for helpful suggestions and discussions during the course of writing this book. They are particularly grateful to Professor S. K. Mukherjee and Dr. K. P. Das, who read the complete manuscript of the book and made valuable comments. The authors had many discussions with the late Professor J. Koefoed which were very useful and important. The technical assistance received from Dr. B. K. Sadhukhan, Mr. Subrata Basu, and Mr. D. Thakurta is also acknowledged with thanks. One of the authors (DKC) expresses his indebtedness to the Danish Natural Science Research Council for the award of a travel grant and would also like to acknowledge the hospitality offered by the staff of the Fysisk Kemisk Institute during his stay in Denmark from 1979 to 1980 as the Guest Professor of the Danish Technical University.

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CHAPTER 1

INTRODUCTION

1.1. ADSORPTION FROM SOLUTION

Adsorption at various types of interfaces will take place when a liquid phase is in contact with another immiscible phase which may be solid, liquid, or gas. For adsorption to occur in excess, one or both of the phases should contain more than one component. Two immiscible bulk phases must be in contact with each other so that some of these components are accumulated in excess at the interfacial region and the process of transfer of the component from the bulk to the surface will continue until a state of adsorption equilibrium is reached. The component which is preferentially accumulated at the interface is frequently termed an adsorbate. The term adsorbent is also used for the powdered solid on the surface of which adsorbates from the liquid phase are accumulated in excess. The types of the interfaces are usually designated by names of the bulk phases in contact with each other such as air–water, benzene–water, mercury–water, or alumina–water interfaces.

The adsorption of a gas by powdered solid materials has been extensively studied from the experimental and theoretical standpoints. The kinetic and thermodynamic interpretations of the process are relatively simple because the concentration of the gas can be altered by change of pressure. The adsorption of gases has been extensively reviewed by Adamson[1] and others,[2] and this will not be discussed here in further detail. The water vapor adsorption by biopolymers will be discussed in Chapter 9 in brief to show some aspects of adsorption which appear to be similar when it takes place either in the gas or the solution phases.

The adsorption from the solution depends on its composition. Unlike the gaseous system, the concentration of the solute component in the solution can be reduced only by increasing the amount of the solvent component in the bulk. Further both solute and solvent components in the bulk medium compete with each other for excess accumulation at the interfacial region. The surface region between two bulk phases is thin and its property is very sensitive to the change in properties of the bulk. In fact, the properties of the surface region can be altered to a significant extent by the change in the properties of the bulk system. The thermodynamics of adsorption at the fluid interface were elaborately considered by Gibbs[3] and an attempt will be made in this book to treat different types of adsorption phenomena from the unified concept of "the Gibbs surface excess."

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1.2. NATURE OF THE INTERFACE

The gas–liquid and liquid–liquid systems are mobile so that the interfaces attain an equilibrium shape quickly. Because of this, thermodynamic treatment of the adsorption for such systems becomes simple.

The boundary region between a liquid and a solid is distinctly different in this respect since the surface structure and shape for this system are mostly controlled by the arrangement of the molecules in the crystal lattice at the interfacial region of the solid. The shape of the surface therefore is not smooth like the liquid–gas interface. In most cases, the solid–liquid interface is highly heterogeneous in structure in multiple directions.[1] Further, the solid surface possesses a tendency to assume minimum surface area after rearrangement of the crystal forces. For the attainment of equilibrium shape therefore at the solid interface, a large amount of time may be needed. A true state of thermodynamic equilibrium is usually not attained at the solid–liquid interface. The extent of adsorption of a component at the solid–liquid interface usually changes with time but it reaches a constant value within a period varying between a few hours and few days depending on the nature of the system. A state of adsorption equilibrium is thus reached so that the application of the thermodynamic principles appears to be justified. However, it is not clear how far this state of equilibrium is dependent on the dynamic structure of the underlying solid surface.

Adsorption and desorption phenomena frequently occurring at a biosurface are of considerable interest in the field of biology. Cell-membrane, liposome, ribosome, proteins, carbohydrates in insoluble forms, bones, etc. are examples of biosurfaces. In living systems, the biosurfaces are frequently formed due to the complex mixing of biopolymers and lipids. These surfaces are in contact with water containing organic solutes and inorganic salts so that the phenomenon of adsorption occurs in the biological systems. Because of the extensive interaction of the biosurface with the adjacent bulk-water phase, the biosystem in many cases becomes swollen gel so that the phase boundary region is difficult to detect even qualitatively. Many workers in their thermodynamic treatment assume the whole biogel system as a single phase without an interface. Further, the structure of the biosurface in many cases becomes flexible due to the conformational alterations of the partly rigid and partly flexible biopolymers present in the system. The adsorption sites on the biosurfaces are also highly heterogeneous since the chemical structures of different monomers forming the biopolymers are widely different from each other. The adsorption of solutes from the solution by synthetic polymers and textile fibers also possesses many of the complexities which may occur in the case of the biosurfaces just discussed.

Many biopolymers like proteins, nucleic acids, and carbohydrates actually dissolve in the aqueous medium, apparently forming a single phase system.

However, small solute as well as water molecules forming the aqueous phase may accumulate close to the boundary region of the biocolloid particle due to the binding interaction. In fact the binding phenomena may be identified with the phenomena of adsorption if one assumes that there exists a physical boundary between the aqueous and biocolloid phases.

1.3. NATURE OF THE ADSORBATE

There exists a large number of organic compounds called the surfactants which lower the surface tension of water significantly. These solutes accumulate at the liquid interface in large excess. The surfactants are frequently adsorbed at various types of solid–liquid, gas–liquid, liquid–liquid interfaces and also at the biosurfaces. More recently a surfactant is termed an amphiphile[4] since its molecule contains an elongated hydrocarbon chain (termed a hydrophobic tail) and an ionic or polar group (termed a polar head group). When the concentration of the surfactant in the aqueous medium exceeds a critical value (called the critical micelle concentration or cmc), the amphiphile molecules aggregate forming colloidal micelles.[4,5] The amphiphiles may be cationic, anionic, or nonionic in nature. A list of few surfactants and their cmc values are given in Table 1.1.

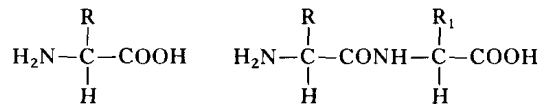
There exist many organic compounds such as alcohols, acids, urea, dyes, etc., a molecule of which contains a polar head group attached to a short-chain hydrophobic tail. Because of this, the affinities of these substances for various surfaces are relatively low. In many systems, these short-chain compounds compete with water solvent for excess accumulation at the interface.

Many organic macromolecules soluble in water may accumulate at various types of interfaces provided the monomeric units contain hydrophobic and hydrophilic groups in a balanced form. Globular proteins soluble in water

TABLE 1.1. Critical Micelle Concentrations (cmc) of Some Amphiphiles in Aqueous Medium at 25°C

Amphiphiles	Name	cmc (M)
$C_8H_{17}OCH_2CH_2OH$	Octyl glycol ether	4.9×10^{-3}
$C_8H_{17}-C_6H_4-O(CH_2CH_2O)_{10}OH$	Triton X100	2×10^{-4}
$C_8H_{17}N^+(CH_3)_2CH_2COO^-$	Octyl N-beatine	2.5×10^{-1}
$C_8H_{17}OCHC_5H_{10}O_5$	β-D-octylglucoside	2.5×10^{-2}
$C_{16}H_{33}N^+(CH_3)_3Br^-$	Cetyltrimethyl ammonium bromide	7.6×10^{-4}
$C_{12}H_{25}SO_4^-Na^+$	Sodium dodecyl sulphate	8.0×10^{-3}
$C_{12}H_{25}NH_3^+Cl^-$	Dodecyl ammonium chloride	1.38×10^{-2}
$C_8H_{17}COO^-K^+$	Potassium nonanoate	2.0×10^{-1}

possess surface-active properties. The formulas of an amino acid and a dipeptide, respectively, may be written as



The side-chains represented by R, R_1 etc. of many amino acids contain hydrophobic groups. Sometimes many hydrophilic groups are also incorporated in the side-chain of an amino acid. Two amino acids are linked with each other by a —CONH— or "peptide bond" whereby a dipeptide is formed.[6,7] During protein synthesis within the living system, the polypeptide chains are formed in perfect sequence.[7] The number of the amino acids in a polypeptide chain may vary between 50 to 200 or more depending on the nature of the protein. The sequence of amino acids in the polypeptide chain of a particular protein is thus fixed and this represents the primary structure of the biopolymer. The globular proteins egg albumin, bovine serum albumin, and ribonuclease each contain only one polypeptide chain. The proportion of hydrophobic and hydrophilic groups in this chain will control the surface-active property of a protein with respect to a particular interface.

A polypeptide chain in a protein can undergo helical or planar folding due to the intrachain or interchain hydrogen bonding between —NHCO— groups.[6,8,9] This is sometimes regarded as the secondary structure. A polypeptide can also fold further due to the interaction between side-chain groups within the chain whereby a relatively rigid globular structure of a protein molecule is formed.[6] This is termed the tertiary structure of the protein. Various forces responsible for the globular structure have been discussed elsewhere.[10] Many proteins such as hemoglobin contain more than one polypeptide chain and these remain associated due to the specific forces present thus forming quaternary structure in a protein molecule.

Conformation of globular protein molecules of rigid structure has been discussed in several reviews.[10,11] When an aqueous solution of a globular protein is heated, the forces responsible for the compact structure are affected by thermal agitation until a stage is reached when the biopolymer molecule unfolds extensively and the phenomenon is known broadly as denaturation.[6,12] Denaturation of protein also occurs at ordinary temperature due to the addition of acid, alkali, urea, guanidine hydrochloride, etc. in sufficient amount. Many soluble proteins such as gelatin, histone, etc. are flexible in structure at ordinary temperature and these are regarded as denatured proteins.

A globular protein adsorbed at an interface may undergo denaturation in various degrees due to the impact of the boundary forces on its structure. This alteration of the structure at the interface is time dependent[13] and the phenomenon itself is of considerable biological interest.

The nucleic acids are also biopolymers which control the genetic properties of the living systems. The monomer unit of deoxyribonucleic acid (DNA) is called deoxyribonucleotide or simply nucleotide which contains a deoxyribose unit attached to a purine or pyrimidine base on one side and a phosphate group on another side. The polymerization of nucleotides takes place through the formation of phosphodiester bonds.[7] The nucleotide unit occurring in DNA polymer is anionic because of the presence of a negative charge on the phosphate group. The sodium salt of DNA polymer thus behaves as a polyelectrolyte. The purine and pyrimidine bases attached to two DNA chains are hydrogen bonded with each other, whereby a double helix structure is formed. This rigid structure is extremely important in controlling the genetic properties within the living system.[7] The nucleotide unit of ribonucleic acid (RNA) contains a ribose sugar attached to an organic base and a phosphate group. Soluble RNA behaves as a flexible polyelectrolyte and is single stranded in structure.

1.4. NATURE OF THE BULK PHASE

For preferential or the excess adsorption to occur from the solution, at least one of the bulk phases must remain in the liquid state. The adsorbate should be soluble to some extent in this liquid solvent. The common solvent widely used in the study of adsorption is water. For the study of adsorption of an organic electrolyte, the aqueous solvent sometimes contains inorganic neutral salt whose affinity for the surface is negligible. Many important properties of the organic and inorganic solutes dissolved in water are already known. These known properties (such as activity coefficients, solubilities, cmc) are very useful in dealing with thermodynamic treatment of the adsorption phenomena. The study of adsorption from an aqueous solution to the biosurface is of considerable biological importance.[4,13] In this book also, we shall discuss mostly the results of the adsorption from the aqueous phase.

The second bulk phase in the adsorption system may be gas (air, vapor, etc.), organic liquid practically insoluble in water (e.g., benzene, heptane, etc.), powdered solid (e.g., alumina, glass, etc.), or insoluble biopolymers. The role of this second bulk phase has been neglected apparently in dealing with the theories of adsorption from the aqueous solution. The effect of the second phase has, however, been implicitly included in the experimental data.

1.5. THERMODYNAMICS OF THE BULK PHASE

We have previously pointed out that the thermodynamic properties of the interfacial region are controlled to a large extent by the thermodynamic functions related to the adjacent bulk phases. The chemical thermodynamics

of the system containing the bulk phase or phases at equilibrium have been developed quantitatively. We shall discuss some relevant points of this subject in concise form. For details, the readers are referred to books dealing with chemical thermodynamics.[14–16]

Let us assume that the bulk phase α is composed of $n_1, n_2, \ldots, n_i$ moles of components so that the differential change in internal energy dE due to the change in heat, dQ, and work, dW, in a reversible process can be expressed from the first and second laws of thermodynamics by the equation

$$\begin{aligned} dE &= dQ - dW + \sum_i \mu_i dn_i \\ &= TdS - pdV + \sum_i \mu_i\, dn_i \end{aligned} \tag{1.1}$$

Here dS and dV represent the differential change in entropy and volume, respectively, and T and p are the temperature and pressure in the system under consideration undergoing mechanical work only. The last term in equation (1.1) takes into account the variation in the moles $n_1, n_2, \ldots, n_i$ of components during the differential change occurring in the open system. From equation (1.1), the chemical potential μ_i of the ith component can be defined thus:

$$\mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j} \tag{1.2}$$

Except n_i, moles of all other components represented by n_j remain constant on the right-hand side of equation (1.2). If there is no variation in the mass in phase α, $\sum_i \mu_i\, dn_i$ becomes zero in equation (1.1), and the relation for the closed system will be obtained.

If H, F, and G stand for the enthalpy, the Helmholtz free energy, and the Gibbs free energy of the system, respectively, these are defined by the equations

$$H = E + pV \tag{1.3}$$

$$F = E - TS \tag{1.4}$$

$$\begin{aligned} G &= H - TS \\ &= E + pV - TS \end{aligned} \tag{1.5}$$

Differentiating these equations and then combining with the fundamental equation (1.1), one finds[15]

$$dH = TdS + Vdp + \sum_i \mu_i dn_i \tag{1.6}$$

$$dF = -SdT - pdV + \sum_i \mu_i dn_i \tag{1.7}$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i \tag{1.8}$$

From these equations and also from equation (1.1), it can be shown that

$$\mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \tag{1.9}$$

It may also be noted that V, n_i, E, H, F, G represent the functions of the state whose magnitudes will depend on the amount of the material of the system. These are termed extensive state properties of the system. On the other hand, the state functions T, p, μ_i etc. do not depend on the amount of the substance and these are regarded as intensive properties. The ratio of two extensive properties is regarded as an intensive state function for a system.

Keeping the intensive properties T, p, μ_i constant, the system containing phase α can undergo a reversible process such that the extensive properties S, V, and n_i are altered to KS, KV, Kn_i, etc. Here K is a proportionality constant. Integration of equation (1.1) under this situation[15] leads to the following relation:

$$E = TS - pV + \sum_i \mu_i n_i \tag{1.10}$$

so that one can write also in the light of equations (1.3), (1.4), and (1.5)

$$H = TS + \sum_i \mu_i n_i \tag{1.11}$$

$$F = -pV + \sum_i \mu_i n_i \tag{1.12}$$

$$G = \sum_i \mu_i n_i \tag{1.13}$$

Equation (1.13), on general differentiation and then in combination with

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