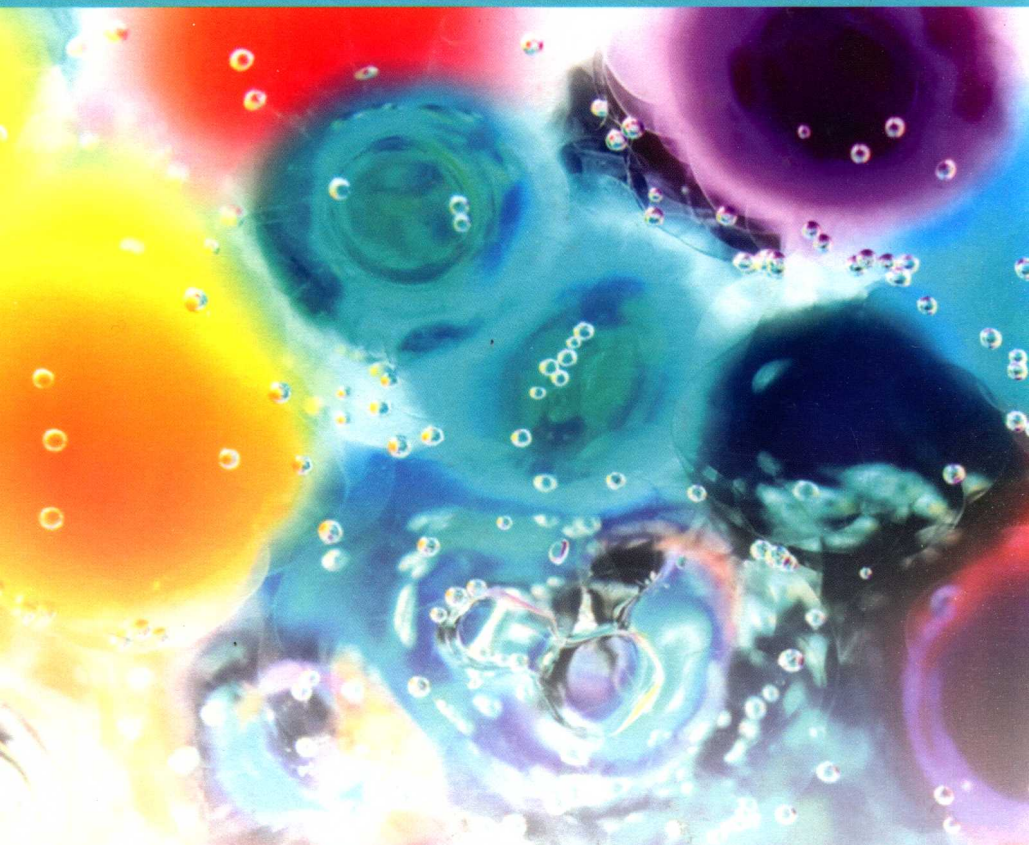


INTRODUCTION TO ELECTRICAL INTERFACIAL PHENOMENA



EDITED BY
K.S. BIRDI



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INTRODUCTION TO
ELECTRICAL
INTERFACIAL
PHENOMENA

Preface

Chemical processes can be characterized in various ways. In one specific case it may concern the presence or absence of electrical charges. This was originally characterized as electrochemistry. Under electrochemistry one finds further subcategories. Electrochemistry is concerned with such simple systems as aqueous solutions of NaCl or more complex systems such as the storage battery. In more complex systems we may add biological cells with charged surfaces. Electrochemistry concerns the charge distribution in the system. The charges near any interface give rise to asymmetric potential. The latter is the subject matter of this book on the electrical interfacial phenomena. The true distance between charges is the main subject of interest.

The text deals with the double layer at the electrode-solution interface. The term *double layer* was used to analyze systems where the charge distribution near interfaces becomes important for the system. Near any interface, there is an asymmetrical charge distribution. This region is where the electrical double layer exists.

The present theory of the double layer depends mainly on dielectric constant concepts, the latter being more typical of 16th- than 20th-century thinking. There are no theories in the double layer that are entirely particulate. The concepts of the double layer deal with the interplay between various layers of electronic charges.

In most physical chemistry textbooks, the subject of electrochemistry is described in its classical fashion. However, due to some major recent developments in surface chemistry, the role of charges at interfaces has become very important (such as batteries, washing processes, adhesion, biological cells (for antibiotics, etc.)). This book presents a picture of the state of an art that is probably on the plateau of further development and stands at a very important stage of application in everyday life.

The subject matter begins with an introduction to the electrical interfacial phenomena, as well as useful examples. Later, more advanced systems are described, and this leads the reader to some comprehensive description of the double layer.

The editor

Professor K. S. Birdi received his undergraduate education in India (B.S., Hons. Chem.) from Delhi University, Delhi, in 1952, and later he traveled to the United States for further studies, majoring in chemistry at the University of California at Berkeley. After graduating in 1957 with a B.Sc., he joined Standard Oil of Richmond, California. Later he joined Lever Brothers in Copenhagen, Denmark, in 1959 as chief chemist in the Development Laboratory. During this period he became interested in surface and colloid chemistry and joined, as assistant professor, the Institute of Physical Chemistry (founded by Professor J. Brønsted), Danish Technical University, Lyngby, Denmark, in 1966. He initially conducted 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, Birdi got 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 the European Union projects. These projects also 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 in 1990 was appointed to the Danish Pharmacy University, Copenhagen, as professor in physical chemistry. Since 1999, Professor Birdi has been actively engaged in consultancy to both industrial and university projects.

Birdi has had continuous involvement with various industrial contract research programs. These projects have been a very important source of information in keeping up with real problems, and have helped in the guidance of research planning at all levels.

Professor Birdi is a consultant to various national and international industries. He is and has been a member of various chemical societies and 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 (1985–1987) of the ACS journal *Langmuir*.

Professor Birdi has been an advisor for about 90 advanced student projects and various Ph.D. projects. He is the author of about 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 of surface and colloid chemistry. His first book on surface science, along with coauthor D. K. Chattorraj, was published in 1984: *Adsorption and the Gibbs Surface Excess* (New York: Plenum Press). This book remains the only one of its kind. The Gibbs theory is described in this book in extensive detail. The interfacial adsorption of all types of systems are analyzed (soaps and detergents; emulsions; colloidal systems; biological cells: ion-transport and channels; antibiotics). Further publications include *Lipid and Biopolymer Monolayers at Liquid Interfaces* (Plenum Press, New York, 1989), *Fractals in Chemistry, Geochemistry, and Biophysics* (Plenum Press, New York, 1994), *Handbook of Surface and Colloid Chemistry*, (Editor; 1st ed., 1997; 2nd ed., 2003; CD Rom, 1999; 3rd ed., 2008; CRC Press, Boca Raton, Florida), *Self-Assembly Monolayer* (Plenum Press, New York, 1999), *Scanning Probe Microscopes* (CRC Press, Boca Raton, Florida, 2002), and *Surface and Colloid Chemistry: Principles and Applications* (CRC Press, Boca Raton, Florida, 2009). Surface and colloid chemistry has remained his major research interest.

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chapter one

Introduction to electrical interfacial phenomena

K. S. Birdi

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Introduction

The subject of *chemistry* is taught in high schools and universities. *Electrochemistry* is characterized as a part of general chemistry that relates to charged ions or macromolecules or particles or solids or liquid drops. Charged ions are also found in various other sciences such as physics and biochemistry and geochemistry. However, one finds that electrical charges behave differently when these are situated at or near interfaces. Therefore the state of charges at *interface* needs some special analyses. In the present book the *electrical interfacial phenomena* will be described using the classical electrochemistry and surface chemistry.

In most simple cases such as aqueous solution of a salt, such as NaCl, the Na^+ and Cl^- ions are analyzed by different thermodynamic theories. The addition of NaCl to water (which is neutral) imparts positive (Na) and negative (Cl) ions. The addition of NaCl to water gives rise to various changes in the physicochemical (colligative) properties of the solution (Appendix). This may be:

- conductivity
- depression of the freezing point
- increase of the boiling point

In such solution, the number of positive ions is always equal to the negative ions (as required by the electro-neutrality criteria).

POSITIVE ION	NEGATIVE ION
NEGATIVE ION	POSITIVE ION

POSITIVE ION	NEGATIVE ION
NEGATIVE ION	POSITIVE ION
POSITIVE ION	NEGATIVE ION

The distance between ions decreases with increasing concentration, as described by the Debye-Huckel (D-H) theory. However, it is found that in small regions the distribution of ions is not equally dispersed. This remarkable observation has given rise to many important consequences, in the simple solution and also in other more complex systems. The distribution of the positive (Na) and negative (Cl) ions throughout the system is found to change with concentration. This means that the distance between a positive and a negative ion decreases with increasing concentration of NaCl (Figure 1.1). Later this will be analyzed and the consequences found to be of much importance in such systems.

It will also be shown that in the case of such solutes as soaps or detergents (surface-active substances or amphiphiles) there is a difference in the adsorption of ions (e.g., positive or negative) at the surface (or interface). The difference in the degree of adsorption would thus give rise to a quantity called surface potential. The monolayers of such surface active substances have been found to be very useful model systems for more complicated systems. In literature one finds a much detailed description related to amphiphiles, since these play a very important role in everyday life (Chattoraj & Birdi, 1984; Adamson, 1999; Birdi, 2003, 2008, 2009; Girault, 2004; Somasundaran, 2006). Another area of interest is where an electrode (metal) is placed in an aqueous solution (Kortum, 1965) (Figure 1.2).

In this case there may be both exchange and adsorption of ions on the electrode. This kind of situation is most important in battery technology. The surface adsorption in such systems has been analyzed by using the Gibbs adsorption theory (Adamson, 1999; Chattoraj & Birdi, 1984; Birdi, 2009). It is found that the concentration of some substances, such as soaps and detergents, is much *higher* at the surface than inside the bulk of solution (as described by the Gibbs adsorption theory). These substances are also called

surface-active agents (substances)
amphiphiles
detergents

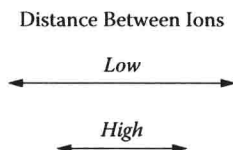


Figure 1.1 Change in distance between Na and Cl ions in an NaCl solution (low concentration; high concentration) (schematic).

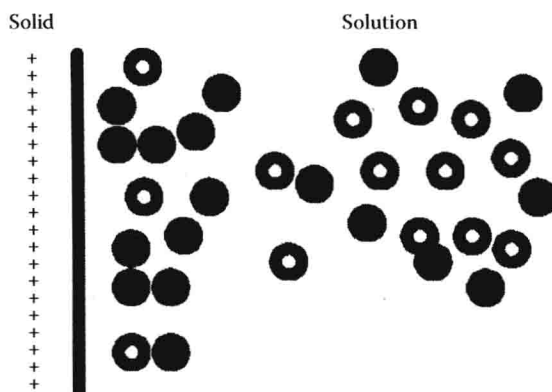


Figure 1.2 Distribution of ions near an electrode with positive charge.

surfactants
emulgators
soaps

Gibbs described the *real system* (which consists of two bulk phases) with an *interphase* between them, by an equivalent system in which the properties of the adjoining phases remain constant up to an interfacial phase, the interface. This is of interest in the case of battery technology. In fact, under the present energy and pollution concern, this technology is expected to expand considerably. Especially, battery technology is related to the application of wind energy and solar energy. Battery can store energy and thus can provide sustained usefulness. Currently one finds a wide range of area where batteries are used (from cars to mobile phones). In fact, battery technology is already well established technology for the CO₂ control and reduction needs in the coming century. In all these systems, the main concern is about how the positive and negative ions are distributed throughout the medium. If one considers an NaCl solution in water, then it is accepted that each positive ion is surrounded by a negative ion (and vice versa) thus giving electroneutrality. The distance between these two different charges will of course depend on the concentration. Based on theoretical derivations, the distance between charges was analyzed by D-H theory (Appendix). The distance (also called the Debye distance), $1/\kappa$, was found to be given as:

$$1/\kappa = 3 / (\text{concentration of NaCl})^{1/2} (10^{-8} \text{ cm})$$

The values of $1/\kappa$ are found to be dependent on concentration and the charge on the ions (Table 1.1).

Table 1.1 Magnitudes of Ionic Atmosphere, $1/\kappa$, as a Function of Salt Concentration and Type

Electrolyte		1:1	1:2	2:2	1:3
		$(1/\kappa \text{ (} 10^{-8} \text{ cm)})$			
Moles/liter	0.0001	304	176	152	124
	0.001	96	56	48	39
	0.01	30	18	15	12
	0.1	9.6	6	5	4

It is thus observed that the *ionic atmosphere* is many times greater in dilute electrolyte solutions than in concentrated systems. However, the differences become lower at higher concentrations. Experiments show that the asymmetry of ions at or near interfaces are of importance in order to understand these systems.

In physics, one describes a capacitor that has two plates of charge separated by some distance. The potential drops linearly from the plate to the other side. However, if a charged metal electrode is placed in a solution, this will not be as simple as a capacitor. This arises from the fact that charges in aqueous media are able to move about and are hydrated ions.

When a solid surface (for example a metal) comes into contact with a solution containing electrolyte, different ionic reactions are found to take place. The solid surface becomes charged due to the difference of ion affinities between the solid and the solution, or the ionization of surface groups. This change in ionic characteristic gives rise to rearrangement of the surrounding ions in the solution. In general, one describes this state of ions by using Gouy–Chapman–Stern (GCS) theory (Appendix). The GCS model gives rise to two layers of specific ions near the surface.

SOLID SURFACE

STERN LAYER DIFFUSE LAYER

The Stern layer is designated the region next to the charged solid surface (Figure 1.3).

Ions are supposed to be bound due to spacially-adsorbing and Coulombic interactions. The electrical double layer (EDL) is the region next to the Stern layer. Ions in the EDL region can move freely about in any direction. EDL is only present under such situations, and different examples will be considered in this book (Lyklema, 1995; Hunter, 2001; Birdi, 2009) (Figure 1.4).

Experiments show that indeed EDL is present at or near any interface.

The significance of the quantify $1/\kappa$ has been found to be important in all kinds of systems:

- NaCl solution properties (conductivity, freezing point, etc.)
- charged particles (colloids, emulsions, suspensions, etc.)

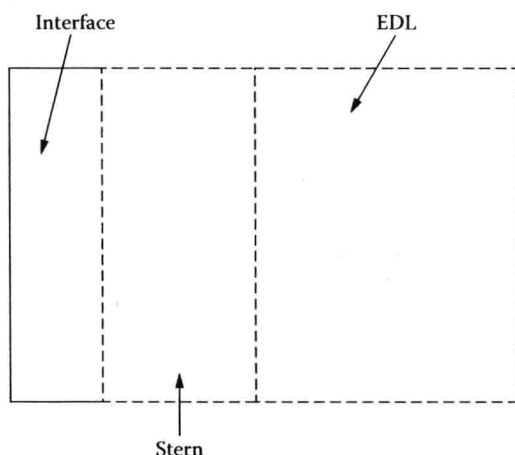


Figure 1.3 Distribution of ions near a charged interface (Stern; Gouy-Chapman) (schematic).

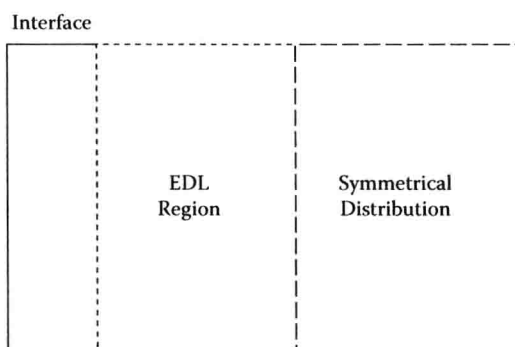


Figure 1.4 Interfacial charge distribution (electrical double layer (EDL)) (schematic).

cement industry
 paper and ink industry
 storage battery (all kinds)
 charged macromolecules (proteins, polymers)
 biological cells

For example, billions of batteries are commercially produced for various uses and applications (telephones, toys, appliances, cars, radios, instruments, microelectronics). In the case of a battery, one has a positive and a negative electrode as placed in an electrolyte (consisting of fluid phase or gel). The electrode with the positive charge, Figure 1.5, and the state of ions in proximity is shown. It is obvious that near the positive electrode

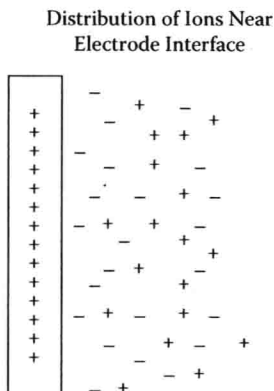


Figure 1.5 Distribution of ions near an electrode surface with a positive charge (schematic).

there will be a large number of negative ions. The situation near the negative electrode will be just the opposite. It is also obvious that the stronger the potential on the battery, the more counter-ions will be attracted. The asymmetry of distribution thus gives rise to many characteristics, which makes such interfaces unique. Analysis shows, however, that the *number of counter-ions* varies with distance from the electrode.

Thus the state of ions suddenly becomes different from when no electrode was present. The interfacial region where the ions are varying and dependent on the potential of the electrode is the **EDL**. It is thus found that the potential characteristics will depend on the variation of the charges near the electrode. In general, this will also be the case for any other system with a charged surface and its surrounding. The adsorption of ions constitutes the underlying phenomenology of the double layer and contributes to the most experimentally-consistent molecular model of the interface.

The *charge-charge* interactions are found in many everyday systems:

- electrolyte solutions
- colloidal suspensions
- cement industry
- paper and ink industry
- storage battery
- emulsions (oil-water)
- biological cells (virus, etc.)
- wastewater treatment and pollution control

The two electrodes are chosen such that each has a different chemical potential. The surface charges thus dictate the battery potential. The

current flows through the connecting wire from the more negative electrode to the more positive electrode (as in the case of a downhill movement!). The electricity produced is balanced by ions transported through the electrolyte inside the cell (Appendix). In lead batteries one used fluids such as strong H_2SO_4 . Nowadays one uses gels so as to stabilize the system on impacts under accidents. In the case of rechargeable batteries the reactions inside the cell are reversed when an opposite potential is applied. Most rechargeable batteries can be cycled more than 1000 times. Battery electrochemistry characteristics are mainly based on the principles of EDL on the electrode (Appendix). In general, ions can also be adsorbed on an electrode surface. This can take place under different conditions. The ions may be *specifically adsorbed*. In addition to the latter, an excess of oppositely charged ions are also found to be attracted close to the charged electrode surface. However, due to solvation of ions, these ions cannot approach the surface as closely as the specifically adsorbed ions. These ions are found to be distributed in a diffuse layer. It is thus found that near the surface of an electrode (Figure 1.5) one has the following ions:

electrode surface with charge
diffuse layer of opposite charges

This state of distribution of ions, in general, is called the EDL. Accordingly, one finds that EDL has been analyzed extensively in the literature.

This book deals with those interfacial phenomena that are related to charges in the liquid phase or the solid phase. As will be shown, the distribution of charges in any given phase (liquid or solid) is not symmetrical around or near a charge. This situation becomes even more asymmetrical near any **interface (air-liquid, liquid-liquid, solid-liquid)**.

The role of electrical interfacial phenomena in various industrial processes and products is well established. Some typical and important areas are as follows:

paint industry (electro-deposition)
aircraft industry
auto industry
agrochemical
photographic
printing ink
detergent and washing
dyestuffs
ceramic
cement

biology
emulsion technology
energy industry
oil production
coal technology
pollution control
wastewater treatment

Typical examples of such systems will be described.

Colloidal systems are found in different areas of everyday life. In the wastewater treatment the colloidal suspension is destabilized through the application of **EDL** science. The Derjaguin-Landau-Verwey-Overbeck (**DLVO**) theory is mainly used in such systems treatment. Since drinking water is becoming a very critical aspect for the survival of mankind, it is obvious that this area of science will need much research in the future. Another area where colloidal particles are involved is the paint and paper industry. In these systems also the understanding of such suspensions is evaluated by applying various surface and colloid science theories. The development of nano-scale particles (nano-technology) is another new application of **EDL** that is of recent origin.

Emulsion technology is one of the most important areas where the *interfacial charges* play an important role. Oil and water do not mix, as is well known. However, if the high interfacial tension (ca. 50 mN/m) at the oil-water phase is considerably reduced (less than 0.1 mN/m) by addition of suitable emulsifiers and so forth, then the system becomes stable for a longer time. Many of these emulsifiers used to stabilize emulsions are ionized so the emulsion droplets exhibit an electric charge. In these oil-water emulsion systems, the presence of such charges at the interface will lead to the formation of an **EDL**.

Emulsion

OIL SURFACE (CHARGE) . WATER SURFACE (CHARGE) .

The nature of **EDL** will determine the stability characteristics of the given emulsion. The stability of the system would then be dependent on:

EDL repulsion
van der Waals attraction

When two charged emulsion droplets approach each other, there is a repulsive interaction when the diffuse layers begin to overlap (as depicted below). The magnitude of this repulsion energy increases as the region of the overlap increases and the kinetic movement of the droplets enhances the movement.