

PRIKAZI KNJIGA

BOOK REVIEWS

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Solid – Liquid Interfaces

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Our good acquaintance and frequent guest – lecturer at our Symposia, the distinguished, now emeritus Dutch Professor from the Wageningen University, one of the undoubtedly leading authorities of the world's colloid science, undertook the task to write a capital compendium of surface and colloid chemistry in five volumes. The two first volumes have already appeared.

I have in front of me the second volume of this large undertaking, devoted to the solid/liquid interfaces. I have no intention to analyze the details of this book, rather to take notice of its conceptual basis and the treatment of the subjects. With the author, an expert and a scientist, whose lifework is centered around the subjects of this field of colloid science, it is not difficult to assume the importance and the authoritarianism of this volume. As in all monographs and textbooks we are witnessing the author's viewpoints in the field he is close to and which is, for a scientist at the end of his rich career, a critical hindsight. Lyklema's book is not an exception. If the reader or the student accepts this from the beginning, he will get acquainted with a valuable and important view on this scientific field.

The first chapter is entitled: Adsorption at the gas/solid interface. The author's commentary is interesting. He considers this interface and the techniques developed for the studies of these peripheral for the book, yet an unavoidable need for the understanding of phenomena at the solid/liquid interface. The biggest value of this chapter is in the elucidation of contemporary techniques and methodologies used in studies of solid surfaces in contact with the gaseous phase or in vacuum. I do believe that for a student of liquids, or solid/liquid interfaces the extent and the explanation of modern techniques, particularly of the AFM (the atomic forces microscope) is sufficient for a general information. More can be found in the literature references in the book, both of classical papers and of literature from the beginning of the 1990s. It is interesting to review the author's views of the BET (Brunauer – Emmet – Teller) theory of multilayer adsorption on solid surfaces, supported by a well conceived overview of the most important papers of Polany,

Harkins, Hills, Sing and particularly of the Russian school around Dubinin. In the whole chapter the emphasis is on the thermodynamic approach. Also in the chapter there was room for a treatise on wetting with an appropriate reference to Temkin. The chapter ends, as is the case with others also, with a treatment of IUPAC recommendations.

The solid/liquid interface chapter starts with descriptions of adsorption phenomena from the liquid phase, devoted to uncharged and small molecules. The emphasis is on the basics, in accordance with the title of the book. The author approaches here his own experience shown in the treatment of dynamics of the processes. The chapter is dominated by the views and the references on the work of D. H. Everett and Ron Ottewil from the 1960s and 1970s. A due credit is given to the contributions to this field of Prigogine, Schay and his Hungarian school, but also to the Anglosaxon school of electrochemistry of Bockris, Conway and their associates. For us it is interesting that among the references on the kinetics of adsorption, there are listed those of Ivica Ružić from *Croatica Chemica Acta*.

The third chapter leads us to the electrical double layer. The 232 pages give, in my opinion, a realistic viewpoint of knowledge in this field. The author explicitly states that his approach differs from that usually used in electrochemical literature, specifically on mercury surfaces. The introduction on the varieties of double layers on different materials and in the presence of different solutes is very good. His approach to the understanding of diffuse layers is based on thermodynamics. In addition to the exposition of the well known Overbeek school, which is well known in Croatian colloid circles, a critical review of the accomplishments of the Russian school, to which the author has been exposed in his personal contacts, above all with Stanislav Dukhin. For the student in this field the important part is the introduction to statistical thermodynamics of double layers in the interpretation of Cairns, Torry and others. In the references the work of Sveto Marčelja from 1993 is mentioned. In the treatise on the structure of the double layer the author emphasizes that the Stern model was published at the same time as the Debye – Hückel theory of electrolytes. D. C. Grahame gets the credit for championing of the inner and outer Helmholtz plane in 1941. It would be difficult to mention in this review all the sources, but even a superficial look at the references (these are printed only as footnotes in the text) convinces me that Lyklema has not omitted a single important reference on papers either from colloid science or electrochemistry. I would recommend to every student or novice in this field to read the text on the difference between the point of zero charge and the isoelectric point. The exhaustive references on the Dutch school are complemented with the references on the work by Frumkin, Randles, Eley, and on the more recent work by Trasatti, Parsons, Guidelli, Matsumoto and others.

The unavoidable chemistry of silver halogenides, the bread of colloid chemistry through some 90 years, has been thoroughly treated, but primarily thorough the works of the Dutch school. I have found only one reference on

Egon Matijević, but there is no mentioning of Težak's school. Silica and clays have been treated in the text. The latter were obviously not a subject of great interest of the author, who mentions only one example of a 2 : 1 structure and its phenomenology. Semiconductors have also been treated. In discussing relaxation phenomena in the double layer there is an obvious important influence of the work of Stanislav Dukhin with references to his publications.

The chapter on electrokinetic phenomena is the second by size in the book, and is well written. In the historical hindsight we find all the great names, from Reuss in 1809, and then Smoluchowski, Henry and Lars Onsager. Lyklema's competence is witnessed by the mathematics in this chapter, which requires a fair amount of background knowledge before the reading can be effective. However, the instructive models make the comprehension easier. The work of Derjaguin, Robert J. Hunter, Bickerman and Vincent have been treated in the perspective of applications, with description of techniques, historical and contemporary. The theoretical basis is treated using references to Overbeek's late papers, and along many applications of electrophoresis are described. There is also a discussion on surface conductivity. Unfortunately, I found only a few references on the Petersburg school from the 1950s and 1960s, in that period the most authoritative group on the electrokinetics of dispersed systems. The predominance is of papers of Dukhin, who originated from Derjaguin's school.

There is an interesting opinion in the book on the application of electrophoresis. Lyklema offers his opinion that academic research of basic processes, and that of applied have different approaches, and that using a single technique of measurements is possibly never sufficient. Under applied electrophoretic measurements Lyklema refers only to investigations of interaction between particles and on colloid stability.

There is a lot of room devoted to relaxation phenomena and dielectric dispersion. The influence of Stanislav Dukhin on the writing cannot be overlooked, considering the mathematics and the deductions. The same is true for diffusiophoresis, a field with many publications, but one that did not make an impact, or initiated application in research. The application of electrophoresis in various modes on proteins, a technique of exceptional importance for clinical analyses, has been mentioned, but with no in-depth treatment. This refers also to paper electrophoresis, whose theory and applications was a life-time contribution of Zvonimir Pucar.

The last, 5th Chapter, describes adsorption of polymers and polyelectrolytes. Here Lyklema recurred to the origins of polymer (bio)chemistry, to the papers by Kulm of the 1930s, leaned on the theoretical work of Flory from the mid-1950s, devoting much room to deGennes, ending with papers from his own laboratory, mainly those of Gerald Flerer. Much attention is given to polyelectrolytes in solutions and their adsorption on interfaces. This part is largely descriptive avoiding the use of mathematics. An example to this

is the description of the 9 models of polymer adsorption at interfaces. Once again much latitude is given to Lyklema's collaborator and colleague Gerald Fleer. After an introductory description of models, the attention is given to the theory of adsorption and the use of mathematics in the interpretation, as used by Fleer. It should be mentioned that the paper by Vlado Hlady, Fleer and Lyklema from 1982, on the adsorption of dextrane on AgI, got 6 citations in the chapter, time and again with a full reference in the footnote. The highlight of Fleer's work on the adsorption of polymers on electrically charged and neutral surfaces, illustrates the importance the author gives to the work of his own laboratory.

The book ends with an appendix on the mathematics of the two-dimensional equation of state, then with data on the points of zero charge of metals, the pH for the points of zero charge and free energies for a number of materials. As each number is accompanied with the literature reference of the origin of these data, the appendices, collected in one place, are handy for fast information. The indices in 59 pages add also much value to the book.

The foregoing detailed review of the book indicates its necessity in each laboratory engaged in research on colloid and surface properties of materials. The extent of this review is to induce the reader to accept or not, both of some statements and of the data, theory and models. I do believe that this volume, and well as the whole Lyklema's series, will have in the next ten years the same crucial role in the field, as Kruyt's colloid chemistry from the 1950s had on all of us entering the field at the time. I am also convinced that without Lyklema's book it will not be possible advancing the field and be engaged in research of interfaces.