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KINETICS AND CATALYSIS IN MICROHETEROGENEOUS SYSTEMS

edited by
M. Grätzel
K. Kalyanasundaram

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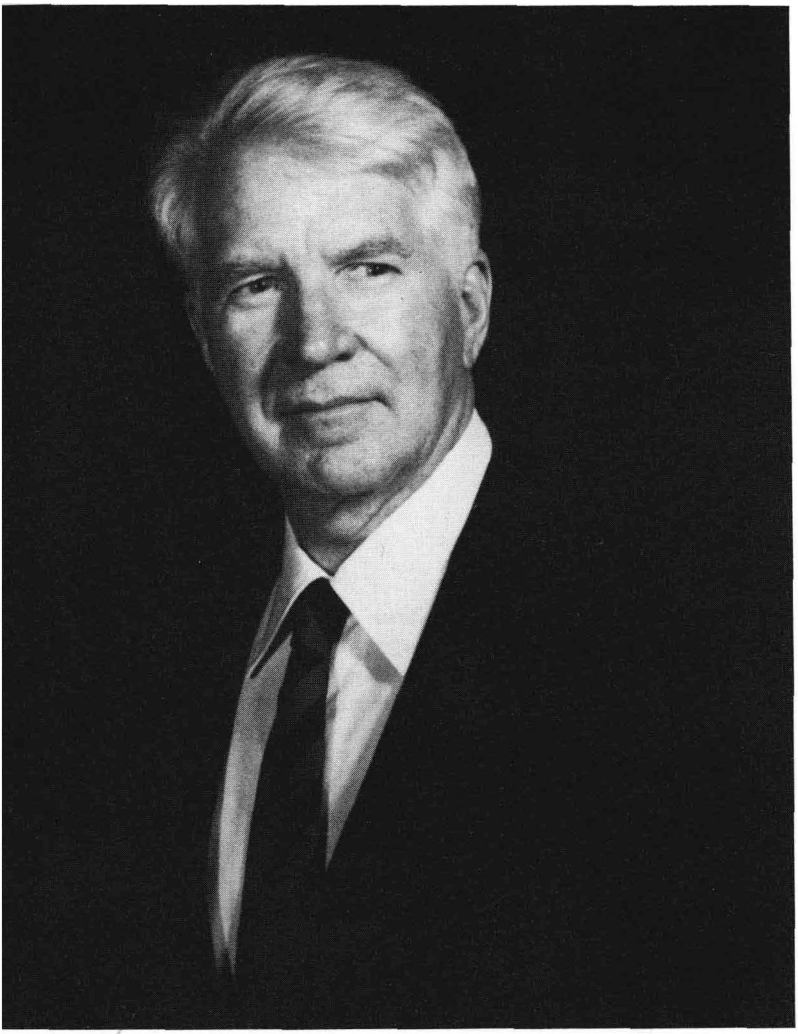

Frederick M. Fowkes (1915-1990)

The sudden death of Frederick M. Fowkes in November 1990 interrupted a life of intense research, teaching and editorial work, ending his leadership of his research group in colloid and surface chemistry at Lehigh University, where he held the position of professor emeritus. He carried out pioneering work in the study of interfacial phenomena in apolar media and on the relevance of acid-base interactions to adhesion science and technology.

Personally I lost my co-editor, an invaluable and ingenious contributor in editing the Surfactant Science Series. Our cooperation started in 1964 and will continue for some time posthumously with volumes in preparation. This volume is devoted to his memory.

Martin J. Schick

Preface

Solubilization of molecules in surfactant-based aggregates of micelles, and its consequences for detergency action, is well known. In addition to empirical efforts to optimize the performance of surfactants in industry, much research has been devoted to characterization of the structure and dynamical properties of the micelles. In the last two decades, a large number of organized assemblies and supramolecular hosts that are capable of solubilizing molecules have been identified: lipid aggregates such as vesicles, liposomes, and monolayer and multilayer assemblies; organic and inorganic polymers; supramolecular hosts such as zeolites, crown ethers, and cyclodextrins; and inorganic colloids such as silica clays and silica. These are broadly known as microheterogeneous systems, because of their colloidal dimensions in spite of the large number of molecules they contain.

As in the micellar hosts, transient residence of solute molecules at or near preferred microdomains in any of this large variety of hosts has important practical consequences. Enhanced yields of products, better product selectivity, and control of reaction rates can be achieved by intervening in the reactant distribution and bimolecular interactions at the microscopic level. The former constitutes the domain of catalysis and the latter kinetics. Catalysis in numerous photochemical, thermal and electrochemical reactions has been demonstrated. The controlled nature of the solute distribution, microenvironments quite different from that of the bulk solvent where the host aggregates are present, and restricted mobility of the reactants in the host cavities and pores render reactions in these organized and confined media unique in many aspects.

In this monograph we have attempted to provide a quantitative assessment of the advances in the area of catalysis and kinetics in microheterogeneous systems. We have been extremely fortunate to have several leading experts to provide a series of overview articles highlighting the progress. In the introductory chapter (Chapter 1), we have elaborated on the importance of these novel host assemblies and the scope of the various presentations. Although some of the chapters have a typical physical chemistry flavor in terms of their rigor, they are written for students at the graduate level. In view of the wide variety of systems and reactions examined, this volume should be of interest to chemists interested in catalysis, colloids, detergency, and reaction kinetics, engineers in chemical and material science, and physicists interested in semiconductors, metal clusters, material aspects and catalysis. It is with immense pleasure that we acknowledge the collaboration with the authors and Dr. Martin Schick, series editor.

M. Grätzel
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Kinetics and Catalysis in Microheterogeneous Systems: An Introduction

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I. INTRODUCTION

For decades chemists have been interested in structure-property relationships and often have examined this at the molecular level in homogeneous solutions or as isolated molecules in the gas phase. The last two decades have shown a growing interest in the study of molecular aggregates of organic and inorganic molecules. This volume deals with microheterogeneous systems of this kind. By microheterogeneous systems one refers to an aggregated system in which the structure of the constituent molecules along with the solvent or other surrounding medium determines the structure of the aggregate. But despite the large number of molecules it contains, the overall aggregate is still small, usually of colloidal dimensions; hence the term microheterogeneous.

The microheterogeneous systems we are dealing with in this volume are composed of either organic or inorganic matter (cf. Fig. 1). The former includes surfactant or lipid molecules dispersed in