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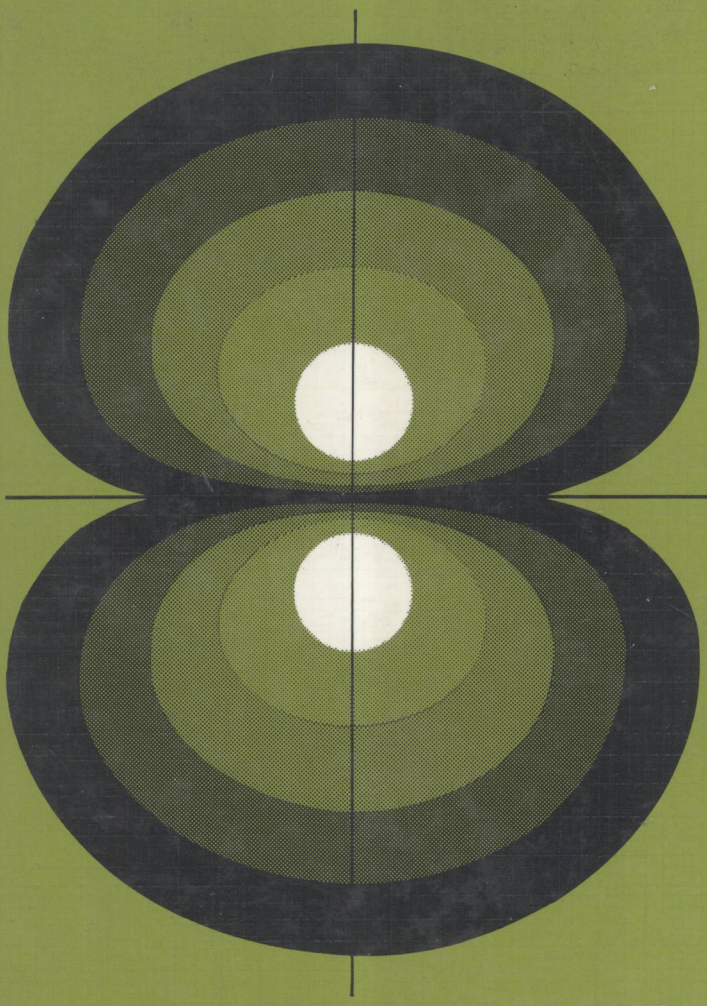

79

STRUCTURE AND DYNAMICS OF SOLUTIONS

Edited by
Hitoshi Ohtaki
and
Hideo Yamatera

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STRUCTURE AND DYNAMICS OF SOLUTIONS

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PREFACE

Since "The Theory of Electrolytic Dissociation" (1833) was proposed by Arrhenius (1859-1927), the chemistry of electrolyte solutions has been extensively studied in Europe as part of physical chemistry, which was established as a new discipline by Ostwald (1853-1932). Arrhenius' theory was based on experimental results derived from osmotic-pressure measurements on electrolyte solutions. The concept of osmotic pressure was first established by van't Hoff (1852-1911) who made significant contributions to the development of chemical thermodynamics. This was further extended by Nernst (1864-1941) and then by Hildebrand (1881-1983), who brought chemical thermodynamics from Berlin to California, by N. Bjerrum (1879-1958), Debye (1884-1966) and Hückel (1896-1980), Onsager (1903-1976), who was one of Debye's students, by Prigogine (1917-) and others in Europe and the U.S.A.

The combination of the chemistry of electrolyte solutions as physical chemistry with inorganic chemistry and analytical chemistry was achieved by Schwarzenbach (1904-1974), J. Bjerrum (1909-), a son of N. Bjerrum, and Sillén (1916-1970). However, in some countries like Japan there were still different streams in solution chemistry without any unification of traditional physical chemistry with other fields of chemistry.

The dawn of solution chemistry in Japan came not too long after that in Europe. Already Sakurai (1858-1939), Ikeda (1864-1935), Osaka (1867-1950), Katayama (1877-1961) and others were attracted by solution chemistry mostly from the viewpoint of physical chemistry and they used thermodynamics and thermochemistry in their studies. However, the development of solution chemistry was not so remarkable when compared with other topics in physical chemistry. Physical chemists in Japan were much more interested in the behavior of individual molecules and spectroscopy was the most important tool for these studies. The trend continued even after the Second World War, and solution chemistry, the term having not been used in the 1940's, was a relatively small area of

chemistry in Japan at the beginning of the 1960's.

After the Second World War the miraculous recovery of Japanese economy provided contacts for young scientists with European and American scientists. These contacts introduced new areas from these countries by introducing subjects which had not been studied previously. Thus traditional studies which existed in Japan were quickly changed by the activities of young chemists who returned from abroad.

The term "solution chemistry" appeared in a booklet of abstracts of papers presented at the national meeting of coordination chemistry of Japan in 1962 as the title of a subject area, although some studies on equilibria of complex formation reactions in solution were presented at the first national meeting of coordination chemistry of Japan in 1951. The amalgamation of chemists from different areas in Japan was not achieved until the beginning of the 1960's.

Efforts were made by the pioneers of Japanese solution chemistry to unite those interested in the chemistry of molecular liquids and electrolyte solutions through various projects under the sponsorship of the Ministry of Education, Science and Culture and other organizations in Japan. The first joint work was carried out by some solution chemists in different areas through the compilation of a review article entitled "Ions and Solvents" published by the Chemical Society of Japan in 1967. The 6th International Symposium on Solute-Solute-Solvent Interactions which was held in Minoo, Osaka in 1982 established a milestone of solution chemistry in Japan. Many world-leading solution chemists attended this symposium from abroad and very fruitful discussions ensued. Since then, solution chemistry in Japan has been accepted as an active research field covering a wide range of chemistry.

A special research project "Microscopic and Dynamical Aspects of Solute-Solvent Interactions" was accepted by the Ministry of Education, Science and Culture of Japan as a three-year project from the 1985 to 1987 fiscal years (Nos. 60129031, 61134043, and 62124039). The project encouraged Japanese solution chemists very much and many interesting results were produced by the members of the project and their colleagues. An international symposium "Molecular and Dynamic Approaches to Electrolyte Solutions" was held in Tokyo in 1988

to summarize the activities of the project. The success of the symposium established the status of solution chemistry in Japan as an indispensable area of chemistry.

At the end of the project we thought that it should be worthwhile to publish a book in which the activities of Japanese solution chemists who collaborated in the project could be presented. Although most results obtained in the project have been published as individual scientific papers in various international journals, it was certainly desirable to summarize the results in a concise manner using an international language.

Solution chemistry is such a broad topic that this book cannot cover the whole area, and thus, this book may not contain a world-wide view of the relevant field in a strict sense. However, readers may still understand recent trends in solution chemistry in the world through this book, because Japan has become one of the world leaders in this field over the last few decades. We hope that this book will give suggestions and ideas to those interested in solution chemistry.

English of the text was checked by Professor H. Chihara, and Professor M. Tanaka. The layout of each chapter was made with the assistance of Professor M. Nakahara.

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November, 1991

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Structure and Dynamics of Solutions
H. Ohtaki and H. Yamatera (eds.)

Chapter 1

INTRODUCTION

Classical solution chemistry was in most cases based on the concept of a continuous medium of solvent having certain characteristic bulk properties which contained neutral or charged solutes of hard sphere. Thermodynamics and statistical thermodynamics were the most useful tools to study solution properties and behavior of solutes in the continuous media. Structures of liquids were discussed by using approaches from two extremes which assumed the liquids as either fluid solids or highly viscous gases.

For electrolyte solutions electrostatic interactions between charged particles in a continuous medium with a characteristic dielectric constant were taken into account and some correction terms were introduced in concentrated solutions where ions behaved non-ideally due to ion-ion interactions. A typical example is the Debye-Hückel theory which has been successfully used for interpreting variations of activity coefficients with concentrations of various electrolytes in very dilute aqueous solutions. Many people examined to extend the theory to concentrated solutions without changing the basic concept of the continuous medium of solvent. The application of the theory to such concentrated electrolyte solutions was tried by introducing adjustable parameters which had little physical meanings. Bjerrum's theory which has been often used to interpret ion-pair formation in solution contains a more or less physicochemically arbitrary quantity of the distance of ion-pairing q. The Einstein-Stokes theory contains the bulk viscosity which loses physicochemical meaning in discussions at the molecular level. In fact ions move in a medium consisting of discrete molecules.

Development of modern solution chemistry definitely does not allow to persist in the simple assumption of continuous media of solvents, and knowledge of interactions between solvent molecules and structures of liquids, as well as ion-solvent and ion-ion interactions, become essentially important to interpret thermodynamic, dynamic and transport phenomena in solutions.

Dielectric constant can be no more characteristic quantity to interpret short range ion-ion interactions and physicochemical quantities based on more or less molecular aspects are required to be introduced in solution chemistry. The donor-acceptor concept of solvent molecules which was first introduced by Gutmann with a well-defined form was very helpful to understand ion-solvent interactions which could not be interpreted from simple electrostatic considerations, although the concept was not a fully molecular one.

The term "structure of liquids" is better accepted by most chemists than before for many nonaqueous solvents. The term is certainly accompanied by the introduction of discontinuity of solvent media and thus establishment of new theories based on the molecular interactions between individual species are necessary. Liquids are regarded as ensembles of molecules having characteristic molecular structure in which inhomogeneous electron distributions must be taken into account. Intermolecular charge transfer interactions should also be taken into consideration. The dielectric constant of the medium between adjacent particles cannot have a value estimated from the bulk properties, because no solvent molecule can exist there. The liquid structure should be changed when solutes are

TABLE 1.

A comparison between interesting points in classical and modern solution chemistry.

Classical Solution Chemistry	Modern Solution Chemistry
Bulk properties of liquids and simple electrolytes solutions	Microscopic behavior of individual molecules and ions
Static properties	Dynamic properties
Liquid structure as extrapolation of knowledge of solids and gases	Direct observations of liquid structure by, for example, the diffraction method
Equilibrium states or ground states	Activated states or excited states