Journal of Solution Chemistry, Vol. 34, No. 2, February 2005 (© 2005)
DOI: 10.1007/s10953-005-5840-z

Erratum

"History of Solution Chemistry of Japan" [J. Solution Chem. 33(6/7) (2004) 575–606]

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The publisher regrets that due to an error in the production process the uncorrected version of the above article was published without Table 1 on page 593. The full text, along with this table and other corrections not previously carried out, is being reproduced in the below.

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History of Solution Chemistry of Japan

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Received August 21, 2003; revised May 20, 2004

A historical view of the solution chemistry of Japan is described for a wide range of fields of solution chemistry, which relates to physical chemistry, inorganic chemistry, analytical chemistry, biochemistry and bioinorganic chemistry, and colloid and polymer chemistry. The works by pioneers of Japanese solution chemistry are introduced, some of which are not well recognized internationally. The influences of Japanese solution chemistry on the world and *vice versa* are discussed on the basis of a rather personal viewpoint. Recent activities of Japanese solution chemists at the national and international levels are also reviewed.

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1. INTRODUCTION

The history of solution chemistry in Japan is both long and short. From the end of the 19th Century to the beginning of the 20th Century, physical chemistry represented solution chemistry in Europe in the present sense. J. H. van't Hoff (The Netherlands, 1852–1911), who received the first Nobel Prize for Chemistry in 1901 owing to his contribution to the discovery of the laws of chemical dynamics (1883–1885) and osmotic pressure (1887) in solution, was certainly a physical chemist and a solution chemist. His contribution to solution chemistry was recognized most significantly to organic stereochemistry through his proposal of the tetrahedral tetravalent carbon atom in 1874. The theory of electrolytic dissociation (1883) proposed by S. A. Arrhenius (Sweden, 1859–1927) was the starting point for studies of the solution chemistry of electrolytes. He was awarded the third Nobel Prize for Chemistry in 1903. F. W. Ostwald (Germany, 1853–1932) investigated the chemistry of solutions and established physical chemistry as a new field of chemistry and published the *Zeitschrift für physilalische Chemie*, together with van't Hoff, and thereby created a new scientific medium in 1887. He received the Nobel Prize for Chemistry in 1909 for his contribution to catalytic reactions, chemical equilibria, and rates of reactions. Pioneers of chemistry in Japan, who thought that they should introduce the chemistry of advanced countries, rushed to Europe in order to study modern physical chemistry and follow these new methodologies and concepts.

2. DAWN OF SOLUTION CHEMISTRY IN JAPAN

We may say that the person who first studied chemistry in Japan was Yoan Udagawa (1798–1846) (Photo 1), who was influenced by the books written by A. L. Lavoisier (translated into Dutch) and W. Henry (in English, translated into German and then Dutch). In 1837, he published the first textbook of chemistry in Japan, entitled "Sei-mi Kaiso" (Opening of Chemistry: "Sei-mi" comes from the pronunciation of Chemie in Dutch). At that time, however, Japan was far behind Europe in chemistry and was unaware of advances made in atomic theory developed by J. Dalton and J. J. Berzelius due to the National Isolation Policy of the Japanese Government.

Chemistry was brought into Japan by European scientists around the 1860s as was also seen in the other scientific and technological fields of Japan. The names of W. Van den Broek (a Dutchman in Nagasaki: his specialties were chemistry, physics, mathematics, *etc*.), G. Wagener (a German who moved from Nagasaki to Tokyo and Kyoto; chemistry and ceramics), Pompe van Meerdervoort (a Dutchman in Nagasaki: medical science), A. F. Bauduin (a Dutchman in Nagasaki: medical science) and K. M. Gratama (a Dutchman in Nagasaki and Tokyo: chemistry and physics), H. Ritter (a German in Tokyo: chemistry and physics), W. H. Griffis (an American in Fukui: chemistry), W. H. Clark (an American in Shizuoka: mathematics, physics, and chemistry), R. W. Atkinson (an Englishman in Tokyo: chemistry)

Photo 1. Yoan Udagawa (supplied from the Library of Waseda University, Tokyo).

(Photo 2), E. Divers (an Englishman in Tokyo: chemistry) (Photo 3), F. F. Jewett (an American in Tokyo: chemistry), G. Martin (a German in Tokyo: pharmacy and chemistry), J. F. Eijkman (a Dutchman in Tokyo: pharmacy and chemistry) appeared in the history of chemistry in Japan as teachers of chemistry and related sciences. They were invited by the central and local governments of Japan during the period from the middle to the end of the 19th century.

After the pre-university period, The University of Tokyo was established in 1877. The Chemical Society of Japan was born in 1878, but the name was changed to "The Chemical Society of Tokyo" the next year, and then, the name was again changed to "The Chemical Society of Japan" in 1921. The number of members in the beginning was only 28, but membership has increased to about 38,000 in 2003.

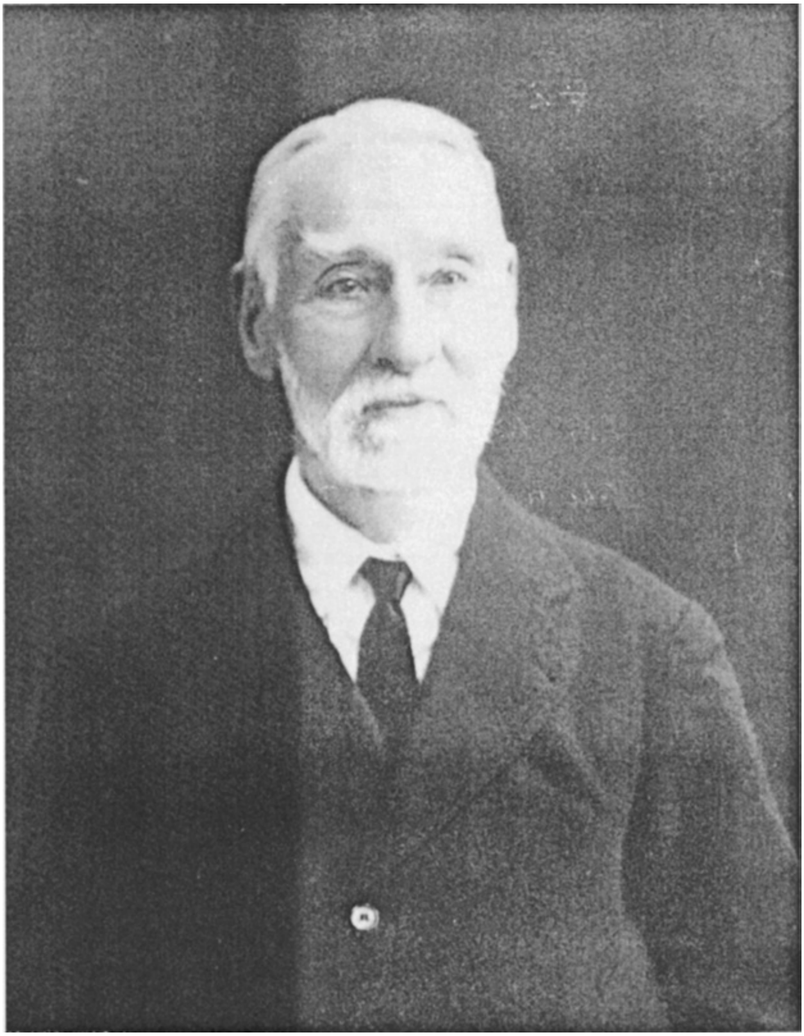

Photo 2. Prof. Robert W. Atkinson (supplied from the Library of the Department of Chemistry, Faculty of Science, The University of Tokyo).

Chemistry was taught at The University of Tokyo, which also incorporated the Faculties of Law, Literature, Science, and Medicine. Joji Sakurai (1858–1936) (Photo 4) was one of the teachers at the university. He was selected as the second government student sent abroad from Japan to study chemistry under the supervision of A. W. Williamson (1824–1904) in London in 1878 and returned in 1881. He became a Lecturer immediately after his return and was promoted as a Professor of the Imperial University of Tokyo (formerly The University of

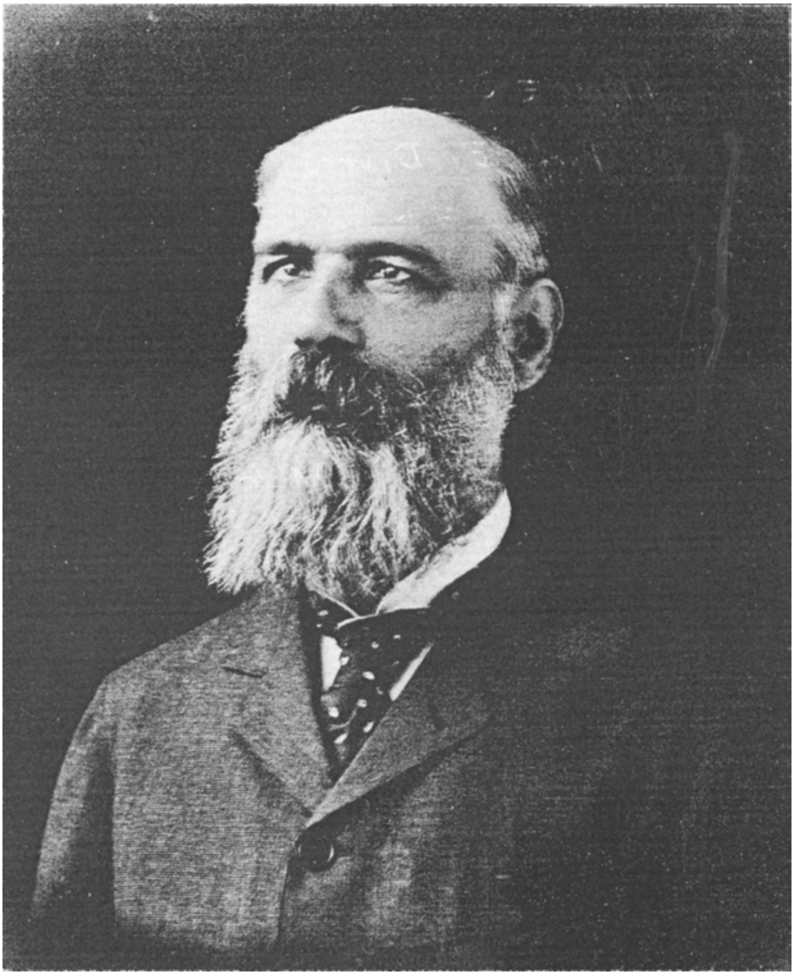

Photo 3. Prof. Edward Divers (supplied from the Library of the Department of Chemistry, Faculty of Science, The University of Tokyo).

Tokyo) the next year. He published some papers on solution chemistry, one of which was a paper concerning an improvement for the method of measurement of the boiling point of liquids (improved Beckmann method)[(1)] and another was the measurement of the molar conductivities of aminosulfonic acids.[(2)]

He was not simply a physical chemist but an all-round player in chemistry who could teach various fields of chemistry at that time, and as such, Sakurai taught both physical and organic chemistry at the university. Therefore, it is understandable that a leading chemist of Japan like him would be interested in modern chemistry, such as solution chemistry, which had been developing rapidly in Europe.

Photo 4. Prof. Joji Sakurai (supplied from the Library of the Department of Chemistry, Faculty of Science, The University of Tokyo).

Sakurai was elected three times as the President of the Chemical Society of Japan from 1883 through 1885, from 1903 to 1904, and from 1909 to 1910. Finally, he became the President of the Japan Academy and a Privy Councilor. His contribution to the establishment of the Institute of Physical and Chemical Research, now often referred to as RIKEN, should also be noted.

Kikunae Ikeda (1864–1936) (Photo 5) first studied analytical chemistry and stayed in the laboratory of Ostwald in Germany from 1899 to 1901 to learn catalytic

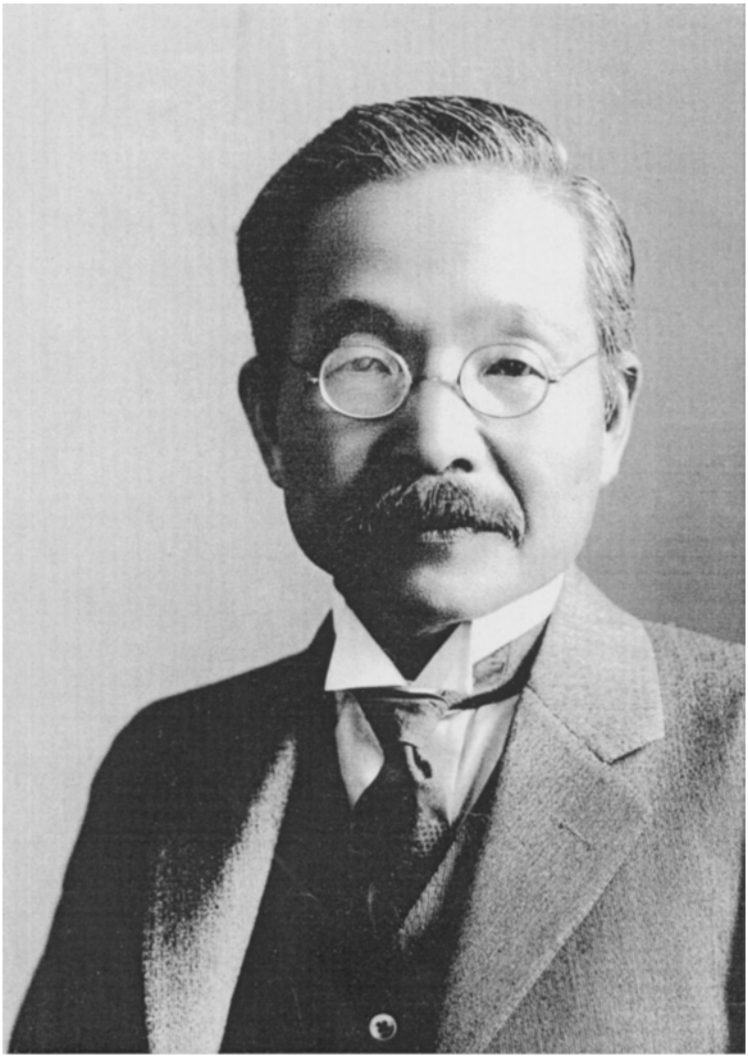

Photo 5. Prof. Kikunae Ikeda (supplied from the Library of the Department of Chemistry, Faculty of Science, The University of Tokyo).

chemistry. His wife was the younger sister of the wife of Sakurai, who was the supervisor of Ikeda during his research work for graduation. Ikeda became an Associate Professor at The Imperial University of Tokyo in 1896, and then he was appointed professor of the newly established Laboratory of Physical Chemistry in 1901 after coming back from Germany. His main emphasis during this period at The Imperial University of Tokyo was on studies of the osmotic and vapor pressures of solutions. He published 22 scientific papers, among which 13 papers were devoted to the chemistry of solutions. Some of his investigations included: "A Simple Experiment in Chemical Kinetics,"(3) "A Relation between the Color of Iodine Solutions and Chemical Properties of Solvents,"(4) and "Studies on the Chemical Theory of Solutions. Part I."(5) After 1907 his interest shifted to the taste of foods and he found that sodium glutamate is the origin of the good taste. He introduced a new category of taste, which is called "Umami" (savory) after sweet, sour, bitter, and salty. He took out more than 50 patents for the production of sodium glutamate and sold it as "Aji-no-Moto" (the name means "The Origin of Taste"). There is a famous anecdote that during his stay in London in 1901, he stayed at an apartment house with Mr. Soseki Natsume, a writer, whose face is now printed on the 1,000 Yen banknote of Japan.

Masao Katayama (1877–1961) (Photo 6) was the successor to Sakurai at the physical chemistry laboratory of The Imperial University of Tokyo. After graduation from the university in 1900, he became a professor of the Tokyo Technical High School (presently the Tokyo Institute of Technology) and taught electrochemistry. He studied chemical equilibria and reaction kinetics in Zurich and Berlin, and became a professor of the Tohoku Imperial University in Sendai in 1909. After the retirement of Sakurai, he was appointed as a professor of The Imperial University of Tokyo in 1919. His most remarkable achievement in physical chemistry related to solution chemistry is the formulation of Katayama's equation,(6) which is a modified Eötvös equation(7) for the change in surface tension with temperature. His book "Kagaku Honron" (The Discourse of Chemistry) was well accepted by Japanese students as an excellent textbook at that time. He criticized Ostwald's physical chemistry based on his Energy Theory. Katayama became a member of the Japan Academy.

Yukichi Osaka (1867–1950) (Photo 7) is one of the students of Sakurai. In 1899 he was sent to Europe by the Japanese Government and stayed in the laboratory of Ostwald in Leipzig for three years. He investigated the optical rotation of d-glucose and the effect of H^+ and OH^- ions on rates of the reaction. After Leipzig he moved to London, Amsterdam, and Göttingen, where he studied chemistry under W. Nernst (1864–1941). After coming back from Europe in 1902, he was appointed as a lecturer at The Imperial University of Tokyo and taught physical chemistry. In 1903 he was promoted to a position of professor of the Kyoto Imperial University. At Kyoto University he studied electrolyte solutions, phase equilibria, reaction kinetics, and colloid chemistry, among which studies of phase equilibria were the most interesting for him. He educated many students, who became leaders in chemistry in the Kansai (Western part) area of Japan. He could be said to be one of the founders of the Kyoto School of Physical Chemistry. One of his students was Shinkichi Horiba, who became a member of the Japan Academy and a Person of Cultural Merits. Osaka's younger sister married Takeshi Takei, who discovered ferrite and later also became a Person of Cultural Merits.

Photo 6. Prof. Masao Katayama (supplied from the Library of the Department of Chemistry, Faculty of Science, The University of Tokyo).

A noteworthy contribution was made by a young Japanese chemist in the field of calorimetric studies. His name was Hajime Hirobe (1883–1914) (Photo 8). In 1913 he was a lecturer at the Imperial University of Tokyo and set up a calorimeter based on his original idea and design for measurements of the heats of mixing of liquids. His work was published in 1926 after his death,[8] but he has been recognized as the pioneer of the thermochemistry of solutions in Japan.

In the 1910s to 1920s many important findings appeared in the field of solution chemistry in Europe. One of them was the Theory for Electrolyte Solutions by

Photo 7. Prof. Yukichi Osaka (supplied from Kyoto University Archives).

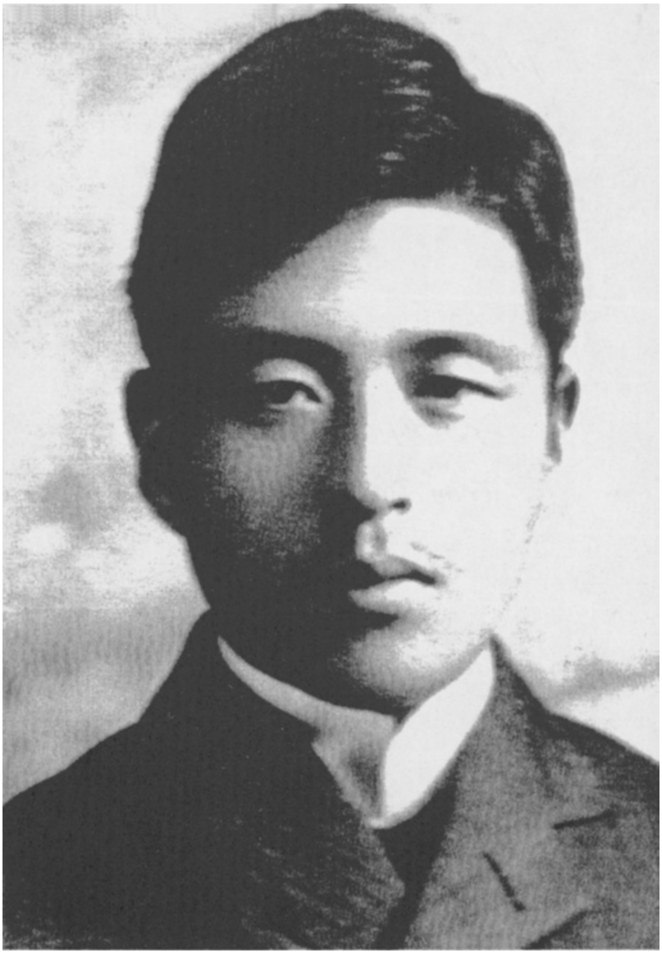

Photo 8. Dr. Hajime Hirobe (supplied from Prof. Masaaki Hirobe, The President of Shizuoka Prefectural University).

P. J. W. Debye (1884–1966) and E. Hückel (1896–1980)[9] that was followed by the Theory of Ion-Pair Formation by N. J. Bjerrum (1879–1958).[10] The concept of pH had already been proposed by S. P. L. Sørensen (1868–1939) in 1909.[11] Raman and infrared spectroscopic methods for solutions were developed in that period and the main stream of physical chemistry in Japan turned from the behavior of ions and molecules in solution to studies of molecular structure in the gas phase and in crystals.

In Japan, new leaders of chemistry were appearing as the front runners of modern chemistry. The leadership of Isamu Nitta (1899–1984) (Photo 9) of

Photo 9. Prof. Isamu Nitta (supplied from "Various Profiles of Chemistry; Posthumous Works of Prof. Isamu Nitta," published from Kashokai in Kansei Gakuin University, published by Kagaku Dojin Publ.)

Osaka Imperial University and San-ichiro Mizushima (1899–1983) (Photo 10) of the Imperial University of Tokyo was so remarkable that X-ray crystallographic studies and molecular spectroscopic studies became the main subjects of physical chemistry in Japan and classical solution chemistry was thinning to a small stream in the field of physical chemistry. Nitta determined the crystal structure of pentaerythritol by X-ray diffraction in 1926[(12)] and from his school Yoshihiko Saito first determined the absolute configuration of optically active coordination compounds, tris(ethylenediamine)cobalt(III), $[Co(en)_3]$.[(13)] Another new leader of physical chemistry from Sakurai's school, S. Mizushima, discovered

Photo 10. Prof. San-ichiro Mizushima (supplied from the Library of the Department of Chemistry, Faculty of Science, The University of Tokyo).

an intermediate form of molecular rotation of 1,2-dichloroethane in 1934[14] and named it the *gauche form* in 1940.[15]

3. INTRODUCTION OF COORDINATION CHEMISTRY TO JAPAN AND ITS DEVELOPMENT BEFORE WORLD WAR II

Solution chemistry of Japan consists of two streams of studies; one is the chemistry of solutions as a part of physical chemistry and the other is the chemistry studied by inorganic and analytical chemists in order to elucidate chemical reactions in solution. Inorganic chemists in the latter area are mainly coordination chemists.

Coordination chemistry was first introduced by Yuji Shibata (1882–1980) (Photo 11), who worked with Alfred Werner (1866–1919) in Zurich. Shibata first

Photo 11. Prof. Yuji Shibata (supplied from author's collection).

stayed in the laboratory of Arthur R. Huntzch (1857–1953) in Leipzig in 1910 and then he moved to the laboratory of Werner in Zurich. Then, he went to G. Urbain in Paris to study coordination chemistry and spectroscopy. He is the only Japanese scientist who worked with Werner.

After coming back from Zurich in 1913, Shibata became a professor of The Imperial University of Tokyo. He bought by himself a spectrometer made by Adam Hilger Co. in England and brought it back to Japan upon his return. He used the spectrometer to study the stereochemistry of coordination compounds. Shibata's spectrometric studies were focused on the structure and composition of coordination compounds dissolved in water. He found a method for determining the composition of coordination compounds formed in solution[(16)] that was the same as that later called Job's continuous variation method,[(17)] but the discovery of the method by Shibata was significantly before that by Job. Nevertheless, Shibata's work was not commonly recognized by chemists around the world, because his report was written in Japanese.

Yuji Shibata was the second son of Shokei Shibata, who was a medical doctor and a pharmacist. Yuji Shibata received the award of the Japan Academy in 1927 and became a member of the Academy and then became the president of the Academy from 1962 until 1970. He was the first Dean of the Faculty of Science of Nagoya Imperial University, and then, the president of Nagoya Imperial University (1949–1957), and he was recognized as a Person of Cultural Merits. His elder brother, Keita Shibata (1877–1949), was a leading scientist of botanical science and biochemistry and became a professor of The Imperial University of Tokyo in 1918 and received the Award of the Japan Academy in 1918. Yuji Shibata was not only a coordination chemist and a spectroscopist, but he was also a pioneer of geochemistry in Japan. He was also interested in investigations of the ancient cultural assets of Japan through his studies of the analytical chemistry of pigments, alloys and glasses. The spectroscopy of coordination compounds was subsequently investigated by Ryutaro Tuchida (1903–1962) (Photo 12) of Osaka Imperial University and others, and studies of ancient cultural assets were continued by Kazuo Yamasaki (1911–) (Photo 13) at Nagoya Imperial University. He received the Award of the Japan Academy and the Membership of the Academy. He was the supervisor of the author.

Spectroscopic studies of coordination compounds in water by Tuchida resulted in the spectrochemical series,[(18)] which was later explained in terms of the ligand field theory. These studies should be a part of solution chemistry, but Tuchida and his students were interested in the structural investigations of complexes. However, interactions between solute and solvent molecules were fully ignored and water was considered to be a simple medium dissolving coordination compounds, which were usually inert. Therefore, Tuchida was highly respected as a coordination chemist, but not recognized as a solution chemist.

Photo 12. Prof. Ryutaro Tuchida (quoted from "Kagakusha, Tsuchida Ryutaro no Iken" (The Opinion of a Chemist, Ryutaro Tsuchida) by A. Tsuchida and T. Tsuchida), Kagaku Dojin Publ. Co., Kyoto, 1975.

Electrochemical methods are strong tools for investigating solution chemistry even at the present time. Polarography was discovered by Jaroslav Heyrovsky (1890–1967) of Czechoslovakia in 1923. He received the Nobel Prize for Chemistry in 1959 and was introduced to Japan by one of his coworkers, Masuzo Shikata (1895–1964) (Photo 14). Shikata came back to Japan in 1924 and was appointed a professor at Kyoto Imperial University. The first paper, which described the discovery of polarography, appeared in 1923.[19] Shikata read his own paper on polarography in 1924 at the 47th Annual Meeting of the Chemical Society of Japan and published a paper together with Heyrovsky in the 1925.[20] He set up

Photo 13. Prof. Kazuo Yamasaki (left) and the author (right) (supplied from author's collection).

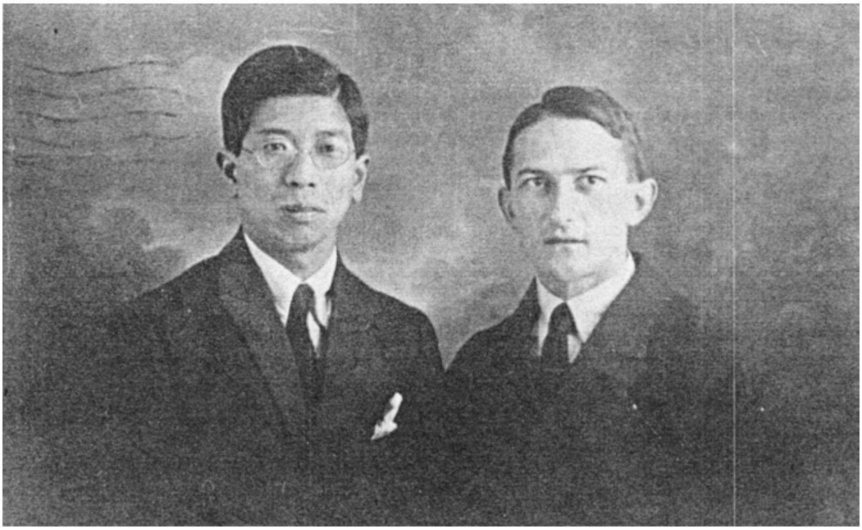

Photo 14. Prof. Masuzo Shikata (left) and Prof. Jaloslav Heyrovsky (right) (supplied from the Chemical Society of Japan).

the first polarographic apparatus in Japan in 1925 at the Faculty of Agriculture of Kyoto Imperial University. Since then, a number of chemists in Japan have studied polarography in various areas of chemistry and established the Association of Polarographers, which involves electrochemists who are interested in studies of electrode potentials, current-voltage relations, and analytical chemists who study ion-pair and complex formation reactions in solution by means of polarography.

The Imperial Universities were dissolved after World War II and renewed as national universities and the title “Imperial” was deleted from all national universities.

4. DEVELOPMENT OF SOLUTION CHEMISTRY IN JAPAN AFTER WORLD WAR II. PART 1. PHYSICAL CHEMISTRY

After the sterile period in Japan caused by World War II between 1941 and 1945, a rapid recovery of activities was achieved in all the areas of science and technology in Japan.

A study of physical chemistry was one of the main streams of solution chemistry in Japan, although the term “Solution Chemistry” was not introduced until the beginning of the 1960s. Solution chemistry may be conventionally classified into three categories: (1) structure, (2) reaction mechanisms, and (3) properties.

1. Structure: Structural studies in physical chemistry were focused mainly on molecular structure in the gas phase and in crystals. Investigations of the molecular structures in liquids were also carried out in various systems, but attention was focused on the structure of single molecules and liquid structures, as ensembles of molecules, did not attract the interest of Japanese physical chemists at that time. Structures of molecules and complex ions in solution were studied by various methods, *e.g.*, NMR, Raman, and IR spectroscopies, and others, but discussions were mostly focused on the structure of solute species as if they existed as isolated species in a continuum medium and solute-solvent interactions on a molecular basis were not generally taken into consideration in explanations of these studies.
2. Reaction Mechanisms: Studies of reaction mechanisms in physical chemistry were highly developed with the introduction of quantum mechanics. The Frontier Electron Theory established by Kenichi Fukui (1918–1998) is a landmark in the success of physical chemistry in this field. In the period after World War II, however, studies of reaction mechanisms by physical chemists in Japan were mainly carried out for homogeneous and heterogeneous catalytic reactions. Photochemistry in solution is one of the important fields of studies on reaction mechanisms in physical chemistry. However, although this work is well accepted as being excellent,

investigators in this field were not categorized as solution chemists, but were rather considered as being purely physical chemists.

3. Properties: Studies of the properties of gases, liquids and solids are certainly important parts of physical chemistry. Colloid chemistry, which covers a large area of physical chemistry, can be regarded as a part of solution chemistry. The thermodynamics of solutions are an indispensable tool for studies of reactions and properties of liquids and solutions. The pioneers of chemistry in Japan from the end of the 19th Century to the beginning of the 20th Century were concerned with thermodynamic studies.

Isamu Nitta and his student, Shuzo Seki, developed thermochemistry in Japan after World War II. Seki's contribution to IUPAC through his studies on thermochemistry should be noted.

Electrolyte solution chemistry was highly developed in Europe and many important results have been reported from the 1920s to the present day. However, the contribution of Japan to this field was not remarkable until the 1960s and the number of publications from Japan during the period from 1925 to 1960 was very limited.

Theoretical investigations of liquids and solutions in Japan were not very significant compared with experimental and theoretical studies on molecular structures in the gas phase.

As described above, many physical chemists in Japan studied the chemistry of solutions, but most of them understood that their works were carried out within their own disciplines of physical chemistry and colloid chemistry, *etc*., and solute-solvent interactions were not properly taken into consideration in their studies. Solvents were regarded as a simple continuum to disperse solutes. Therefore, they did not think that they were contributing to solution chemistry in the world and they never thought to establish solution chemistry of Japan under their leadership.

5. BOOKS RELATED TO SOLUTION CHEMISTRY WRITTEN BY THE PHYSICAL CHEMISTS OF JAPAN

Following World War II a number of books concerning the chemistry of solutions have been published in Europe and the USA. Some of them have been introduced to Japan and translated into Japanese by Japanese chemists. Scientific papers, which could be read by Japanese chemists during World War II, were imported to be kept in libraries of Japanese universities as sources of new scientific results. By learning these modern sciences, some Japanese wished to show their recent results to Japanese chemists through books. Some of the books written in Japanese are listed in Table I (Ia). Books published in other countries were also translated into Japanese and some of those related to solution chemistry in the field

Table I. Books Related to Solution Chemistry and Published in Japan

Author	Title in Japanese (Mean in English)	Publisher (year)
(1) Solution chemistry related to physical chemistry		
a) Books related to solution chemistry by Japanese chemists		
M. Toda	Ekital Kozo-Ron (Structure of Liquids)	Kyoritsu Shuppan Publ. Co., Tokyo (1947)
M. Toda	Ekital Riron (Theories of Liquids)	Kawaide Shobo Publ. Co., Tokyo (1954)
S. Hatashima	Ekital Ron (Theories of Liquids)	Iwanami Zensho, Iwanami Book Co., Tokyo (1954)
M. Toda	Ekital Ron (Theories of Liquids), Iwanami Series of Modem Physics, 4	Iwanami Book Co., Tokyo (1955).
A. Ishihara	Yocki Ron (Theories of Solutions), Iwanami Series of Modem Physics, 5	Iwanami Book Co., Tokyo (1955).
M. Nakagaki and H. Inokuchi	Kagaku-sha no tame no Ekitai-Ron oyobi Kotai-Ron (Theories of Liquids and Solids for Chemists)	Nankodo Publ. Co., Tokyo (1955).
I. Oshida	Ekitai to Yoeki (Liquids and Solutions), Iwanami Series of Modem Chemistry,	Iwanami Book Co., Tokyo (1956).
K. Shinoda	Yoeki to Yokaido (Solution and Solubility)	Maruzen Book Co., Tokyo (1966).
R. Fujishiro and M. Kuroiwa	Yoeki no Scishitsu (Properties of Solutions) I, Series of Modem Physical Chemistry 7	Tokyo Kagaku Dojin Publ. Co., Tokyo (1967)
R. Fujishiro, G. Wada, and R. Taisiamushi	Yoeki no Seishitsu (Properties of Solutions) II, Series of Modem Physical Chemistry 8	Tokyo Kagaku Dojin, Publ. Co., Tokyo (1968)
M. Toda, H. Matsuda, Y. Hiwatari, and M. Wadachi	Yoeki no Kozo to Seishitsu (The Structure and Properties of Solutions)	Iwanami Book Co. Ltd., Tokyo (1976).
K. Amkawa	Mizu Sulyoekl no Kozo to Bussel (The Structure and Properties of Water and Aqueous Solutions)	Hokkaido Univ. Publ., Sappoto (1989).
S. Okazaki and I. Sakamoto	(Solvents and Ions-Chemistry of Non-Aqurous Electrolyte Solutions)	Taniguchi Printing Co., Marsue (1990).

Table I. Continued

Author	Original book	Publisher (year)	Translator	Japanese Title	Publisher (year)
b) Books related to solution chemistry translated into Japanese					
O. Ya Samoilov	The Structure of Aqueous Electrolyte Solutions and the Hydration of Ions	Academii Nauk, Moscow, USSR (1957)	H. Uedaim	Ion no Suiwa (Hydration of Ions)	Chijin Shokan Publ. Co., Tokyo (1967)
E. A. Moclwyn-Hughes	Physical Chemistry, 3 and 4; 2nd ed.	Pergamon Press, London, UK (1961)	Y. Miyahara (Chief Translator)	Busshitsu no Jotai (States of Materials) and Kagaku Heiko to Hanno Sokudo (Chemical Equilibria and Reaction Rates	Baihukan Publ. Co., Tokyo (1968)
D. Eisenberg and W. Kauzmann	The Structure and Properties of Water	Clarendon Press, Oxford, UK (1969)	S. Seki and T. Matsuo	Mizu no Kozo to Bussei (The Structure and Properties of Water)	Misuzu Publ. Co., Tokyo (1975)
Y. Marcus	Introduction to Liquid State Chemistry	John Wiley & Sons, Ltd., New York (1977)	S. Seki (Chief Translator)	Ekitai Kagaku Nyumon (Introduction to Liquid State Chemistry)	Dojin Kagaku Publ. Co., Kyoto (1982)
J. N. Mumel and E. A. Boucher	Properties of Liquids and Solutions	John Wiley & Sons, Ltd., New York (1982)	K. Nakanishi, M. Iida, and S. Okazaki	Ekitai to Yoeki (Liquids and Solutions)	Wiley Japan Inc., Tokyo (1984)

Table I. Continued

Author	Title in Japanese (Mean in English)	Publisher (Year)
(2) Solution chemistry related to inorganic and analytical chemistry		
a) Books related to solution chemistry written by Japanese chemists		
K. Yamasaki, N. Matsuura, N. Tanaka, and R. Tamamushi, ed.	Muki Yoeki Kagaku (Inorganic Solution Chemistry)	Nankodo Publ. Co., Tokyo (1968)
T. Sekine, S. Hamada, and Y. Hasegawa	Kagaku Heiko no Keisan (Calculations for Chemical Equilibria)	Rigaku Shoin Book Co., Tokyo (1974)
H. Ohtaki, M. Tanaka, and S. Funahashi	Yoeki Hanno no Kagaku (Chemistry for Reactions in Solution)	Gakkai Shuppan Center, Co., Tokyo (1977)
H. Ohtaki	Yoeki Kagaku (Solution Chemistry)	Shokabo Publ. Co., Tokyo (1985)
H. Ohtaki	Yoeki no Kagaku (Chemistry of Solutions)	Dainippon Tosho Publ. Co., Tokyo (1987)
H. Ohtaki	Ion no Suiwa (Hydration of Ions)	Kyoritsu Shuppan Publ. Co., Tokyo (1990)
S. Funahashi	Muki Yoeki Hanno no Kagaku (Chemistry for Inorganic Reactions in Solution)	Shokabo Publ. Co., Tokyo (1998)

Table I. Continued

Author	Original book	Publisher (year)	Translator	Title in Japanese	Publisher (year)
b) Books related to solution chemistry and translated into Japanese					
J. O. Edwards	Inorganic Reaction Mechanisms	W. A. Benjamin Inc., New York (1964)	S. Kawaguchi	Muki Hanno no Kikou (Mechanisms of Inorganic Reactions)	Kagaku Dojin Publ. Co., Kyoto (1965)
G. M. Fleck	Equilibria in Solution	Holt, Rinehart and Winston, Inc., New York (1966)	K. Mizumachi	Yoeki-nai no Kagaku Heiko (Chemical Equilibria in Solution)	Maruzen Book Co., Tokyo (1968)
H. H. Sisler	Chemistry in Non-Aqueous Solvents	Reinhold Publ. Corp., New York (1961)	K. Toei and Y. Yamamoto	Hi-Suiyoeki no Kagaku (Chemistry in Non Aqueous Solvents), Selected Topics in Modern Chemistry, 18	Kyoritsu Shuppan Publ. Co., Tokyo (1969)
G. Charlot and B. Trémillon	Les Réactions chimiques dans les Solvents et les sels Foundus	Gauthier-Villars, Paris (1963)	T. Fujinaga and M. Sato	Yobai-nai no Kagaku Hanno to Heiko (Chemical Reactions and Equilibria in Solvents)	Maruzen Book Co., Tokyo (1975)
A. J. Bard	Chemical Equilibria	Harper & Row, Publ., Inc., New York (1966)	Y. Matsuda and K. Ogura	Yoeki-nai Ion Heiko (Ionic Equilibria in Solution)	Kagaku Dojin Pub. Co., Kyoto (1975)
V. Gutmann	The Donor-Acceptor Approach to Molecular Interactions	Plenum, New York (1978)	H. Ohtaki and I. Okada	Donor to Acceptor	Gakkai Shuppan Center Publ., Tokyo (1983)
J. Espenson	Chemical Kinetics and Reaction Mechanisms	McGraw-Hill Inc., New York (1981)	H. Ogino	Kagaku Hanno no Sokudo to Kikou (Kinetics and Mechanisms of Chemical Reactions)	McGraw-Hill Book Co., Tokyo (1984)
K. Burger	Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents - Experimental Methods for their Investigation	Akadémiai Kiadó, Budapest, Hungary (1983)	H. Ohtaki and S. Yamada	Hi-Suiyoeki no Kagaku - (Solvation and Complex Formation Reactions)	Gakkai Shuppan Center Publ., Tokyo (1988)

Table I. Continued

Editor	Name of review book	Publisher (year)
c) Review books of solution chemistry		
H. Ohtaki, N. Tanaka, S. Nakahara, Y. Miyahara, H. Yamatera, and Y. Yamaoto	Ion to Yobai (Ions and Solvents), Kagaku Sosetsu (Chemical Reviews) No. 11, Chemical Society of Japan, ed.	Gakkai Shuppan Center Publ., Tokyo (1976)
H. Ohtaki, H. Nomura and M. Nakahara	Yoeki no Bunshi-Ron-Teki Byozo (Molecular Pictures of Solutions), Kagaku Sosetsu (Chemical Reviews) No. 25, Chemical Society of Japan, ed.	Gakkai Shuppan Center Publ., Tokyo (1995)
d) Collections of classical papers of solution chemistry (Kagaku no Genten Series)		
K. Kuchitsu and K. Higashi	Kozo Kagaku (Structural Chemistry) I, Series 1. Chemical Society of Japan, ed.	Tokyo University Publ. Co., Tokyo (1974)
H. Ohtaki	Denkaishitsu no Yoeki Kagaku (Solution Chemistry of Electrolytes), No. 2, Series II, Chemical Society of Japan, ed.	Gakkai Shuppan Center, Publ., Tokyo (1984)
e) Books of chemistry of ion exchange resins		
M. Honda	Ion Kokan (Ion Exchange)	Nankodo Publ. Co., Tokyo (1954)
M. Honda, H. Kakihana, and Y. Yoshino, ed.	Ion Kokan Jushi (Ion Exchange Resins)	Hirokawa Book Co., Tokyo (1955)
T. Yamabe and M. Seno	Ion Kokan Jushi Maku (Ion Exchange Resin Membrans)	Gihodo Printing Co., Tokyo (1964)
f) Books for Solvent Extraction		
M. Tanaka	Yobai Chushuta (Solvent Extraction), Series of Lectures of Analytical Chemistry, 23, Ed. Japan society for Analytical Chemistry (Editor-in-Chief; H. Okuno)	Kyoritsu Shuppan Publ. Co., Tokyo (1965)
H. Akaiwa	Chushutsu Buri Bunseki-Ho (Methods for Separation and Analysis by Extraction), A Series of Monographs Modern Trends in Chemistry of Kodannsha, No. 15	Kodansha Publ. Co., Tokyo (1972)
M. Tanaka	Yobai Chushutsu no Kagaku (Chemistry of Solvent Extraction)	Kyoritsu Shuppan Publ. Co., Tokyo (1977)
M. Tanaka and H. Akaiwa	Yobai Chushutsu Kagaku (Chemistry of Solvent Extraction)	Shokabo Publ. Co., Tokyo (2000)

Table I. Continued

Author	Name of Book	Publisher (Year)
g) Books for chelate chemistry		
K. Ueno	Kireito Tekitei-Ho (Chelate Titration Methods)	Nankodo Publ. Co., Tokyo (1956)
B. Sakaguchi and K. Ueno	Kinzoka Kireito (Metal Chelates)	Nankodo Publ. Co., Tokyo (1965)
(3) English Books of Solution Chemistry Published in Japan		
N. Tanaka, H. Ohtaki and R. Tamamushi, ed.	Ions and Molecules in Solution; Studies in Physical and Theoretical Chemistry 27	Elsevier, Amsterdam (1983)
N. Ise and I. Sogami, ed.	Ordering and Organizing in Ionic Solutions	World Sci. Publ. Co. Ltd., Singapore, and Yamada Science Foundation, Osaka (1988)
H. Ohtaki and H. Yamatera, ed.	Structure and Dynamics of Solutions; Studies in Physical and Theoretical Chemistry 79	Elsevier, Amsterdam (1992)
H. Nomura and F. Kawaizumi, ed.	Structure, Fluctuation, and Relaxation in Solutions; Yamada Conference XXXXII	Elsevier Sci. Publ., Amsterdam and Yamada Science Foundation, Osaka (1995)
H. Ohtaki, ed.	Crystallization Processes; Wiley Series in Solution Chemistry, Vol. 3	John Wiley & Sons, Chichester, UK (1998)

of physical chemistry are also given in Table I (Ib). The compilation in Table I is not very comprehensive, but we can see some trends in how Japanese scientists have been interested in solution chemistry. The introduction of Samoilov's book[21] through a translation into Japanese by Hisashi Uedaira helped Japanese solution chemists to understand Samoilov's concept of "negative hydration,"[22] because it is difficult for most Japanese to read Russian.

6. DEVELOPMENT OF SOLUTION CHEMISTRY IN JAPAN AFTER WORLD WAR II. PART 2. INORGANIC AND ANALYTICAL CHEMISTRY

Although we see the subjects of inorganic chemistry, organic chemistry and preparatory chemistry in the curriculum of the Tokyo Kaisei School (one of the antecedents of The University of Tokyo), together with general chemistry, qualitative and quantitative analytical chemistry in experimental courses in 1874, chemistry in Japan was not well separated into individual disciplines before 1877 until The University of Tokyo was established. In the curriculum of The University of Tokyo in 1880, students in the Department of Chemistry could study inorganic chemistry, analytical chemistry (qualitative and quantitative), organic chemistry, and preparatory chemistry, as well as physics, geology, epigraphy, and languages.

It is recorded in his book that Yoan Udagawa investigated the water from hot spas in Japan and it was suggested that he analyzed the composition of spa water. Due to industrial and practical requirements, inorganic and organic analytical chemistry have been extensively applied to studies of the pigments of plants, metals, and various inorganic and organic substances. When Yuji Shibata returned from Europe in 1913, he introduced spectroscopy to analytical chemistry and established coordination chemistry and geochemistry in Japan. Therefore, it seems reasonable that inorganic chemistry and analytical chemistry in Japan have a very close relationship to each other, like brothers.

In analytical chemistry in the "old days" in Japan, people were mainly focusing their attention on the determination of the concentration of elements as low and as accurate as possible. Most interests of analytical chemists in Japan were paid to the improvement of classical analytical procedures to fulfill such requirements. After World War II, many new techniques were introduced from the USA and chemistry using ion-exchange resins and solvent extraction was among them and this stimulated analytical chemists to look at solutions in more detail to determine the composition and amounts of species existing in solution.

Ion-exchange resins were made by B. A. Adams and E. H. Holmes in 1935 in the USA and were used for the separation of uranium from other metal ions and the mutual separation of lanthanide ions. The discovery of promethium by J. Marinsky, L. E. Glendenin, and C. D. Corell (1947) from the fission products of ^{235}U is an example of the success of the use of ion-exchange resins. The pioneer of ion-exchange resin chemistry in Japan is Masatake Honda. His first work was published in 1943. Hidetake Kakihana and others contributed to the development of ion-exchange resin chemistry through fundamental studies and separation technologies for inorganic and organic materials, including biomaterials. Honda already published a book on ion-exchange resins in 1954. Since then, many books dealing with ion-exchange resins and membranes have been published. However, chemists who were working in these areas met difficulties in their theoretical considerations due to the lack of thermodynamic data on the resin phase. Following this experience, some inorganic chemists who studied ion-exchange resin chemistry turned their attention to other fields. Ion-exchange resin chemistry was developed for industrial purposes and many chemists who were interested in fundamental chemistry moved to the industrial and applied chemistry fields.

Solvent extraction has further application in the separation and coordination chemistries of metal ions in aqueous and non-aqueous solutions. The first study of the solvent extraction of inorganic ions in Japan was undertaken by Isaburo Wada in 1934 by using ether and metal halides. After World War II, a book written by G. H. Morisson and H. Freiser was translated into Japanese in 1959[(23)] and then, solvent-extraction chemistry became quite popular with Japanese chemists. A Russian book written by Yu. A. Zolotov and his colleagues was translated by Tanaka's school.[(24)] Motoharu Tanaka published many books and played a leading role in the chemistry of solvent extraction in Japan. The most recent book on solvent-extraction chemistry was written by M. Tanaka and Hideo Akaiwa in 2000 [see Table I, (2f)].

Development of methods of analysis for chemical equilibria and stability constants of metal complexes in solution accelerated studies of the solution chemistry in the areas of analytical chemistry and inorganic chemistry. Knowledge of solution equilibria became indispensable in the treatment of data obtained in homogeneous and heterogeneous systems. pH-metry was developed by: Jannik Bjerrum in Denmark for monomeric complex formation reactions, Lars-Gunnar Sillén in Sweden for polynuclear complex formation reactions, Gerold Schwatzenbach in Switzerland for chelation compounds, and Arthur E. Martell in USA for biochemically related complexes in homogeneous solutions. David Dyrssen in Sweden, Yizhak Marcus and A. Steven Kertes in Israel, and many others, applied the methods of data treatment in homogeneous systems to heterogeneous systems, such as ion-exchange and solvent-extraction equilibria.

The main emphasis of coordination chemistry in Japan was the synthesis of various coordination compounds, mostly cobalt(III) complexes, and determination of their structures by using X-ray crystallography and spectrophotometry following the tradition of Y. Shibata. However, some young chemists who were influenced by the new waves of inorganic solution chemistry arising from European schools in the 1960s were interested in the behavior of reactive, labile species rather than inert complexes. The method of potentiometry for determining stability constants of complexes in solution attracted the interest of chemists, not only in Japan, but also in other countries in the world at that time.

There is another group of chemists who were interested in the kinetic properties of chemical reactions rather than static, equilibrium studies in solution. Henry Taube's work for electron-transfer mechanisms between coordination compounds and the labile-inert classification of chemical reactions in solution (he received the Nobel Prize for Chemistry in 1983) stimulated chemists to investigate reaction kinetics in solution. The work by Manfred Eigen on fast reactions (he received the Nobel Prize for Chemistry in 1967) provided important information on the dynamic properties of hydrated water molecules around ions that led to a better understanding of the kinetic and dynamic properties of ions in solution from studies of chemical reactions.

Polarography, introduced by J. Heyrovsky and M. Shikata, is a useful technique for investigating chemical reactions in solution. Many electrochemists and analytical chemists employed this method in their studies. Among them, Nobuyuki Tanaka, who worked with I. M. Kolthoff, studied ionic association and complex formation reactions by polarography and received the Prize of the Chemical Society of Japan in 1964 for his achievements with chemical reactions in solution. He is the first chemist in Japan to receive the Prize of the Chemical Society of Japan for the study of complex formation in solution.

The accumulated results from various subfields of inorganic and analytical chemistry in Japan stimulated chemists to consider establishing their own society of solution chemistry in order to provide a community where they could freely discuss solution chemistry issues.

7. BOOKS RELATED TO SOLUTION CHEMISTRY WRITTEN BY THE INORGANIC AND ANALYTICAL CHEMISTS OF JAPAN

Books on inorganic solution chemistry have been written by many authors. Some books by Japanese inorganic and analytical chemists stored in author's bookcase are listed in Table I (2a). Some books published in other countries were translated into Japanese. Some of them are summarized in Table I (2b). Review books have also been published under the sponsorship of the Chemical Society of Japan [Table I (2c)]. The Chemical Society of Japan planned to publish a series of classic scientific papers with strong emphasis on the various fields of chemistry. A book, which includes papers dealing with solution chemistry, appeared as the 2nd volume of the series II [Table I (2d)]. The famous paper by J. D. Bernal and R. H. Fowler published in 1933[(25)] was cited in the volume on structural chemistry I in series I translated into Japanese. Books on ion-exchange resins, solvent extraction, and chelate chemistry have also been published [Table I (2e–g)]. Most of the ion-exchange resin chemists went into the field of industrial applications. Studies of the solvent extraction of metal ions showed us the importance of understanding reactions in non-aqueous solutions. Those who were interested in chelate chemistry extended their fields to complex formation reactions involving investigations of reaction equilibria, kinetics and structural chemistry of complexes. Books related to solution chemistry written in English and published in Japanese are summarized in Table I (3).

8. THE START OF A NATIONAL SYMPOSIUM ON SOLUTION CHEMISTRY

The term "solution chemistry" was first officially used at the 13th National Conference on Coordination Chemistry of Japan in 1963. Activities of solution chemists in Japan were not remarkable from the 1960s to the middle of the 1970s. Work related to the physical chemistry of solutions was mainly presented at national conferences on physical chemistry, but they did not attract the attention of a wide audience. The chemistry of solutions related to inorganic chemistry was even better accepted in the community of coordination chemists in the 1960s than by those related to the physical chemical community due to efforts of young chemists who returned from mostly European countries in waves. However, they could only maintain a small part of one session at national conferences on coordination chemistry.

In April 1978, H. Ohtaki organized a two-day symposium on the Chemistry of Electrolyte Solutions as a session of the Annual Meeting of the Electrochemical Society of Japan, which was held at the Nagatsuta Campus of the Tokyo Institute of Technology in Yokohama. On this occasion he created a group of chemists interested in electrolytic solutions under the sponsorship of the Electrochemical Society of Japan (later, the group became the Commission on Solution Chemistry of the Electrochemical Society of Japan). At this initial symposium 22 papers were presented together with a panel discussion and a large audience attended the session. In the next year Ohtaki obtained a Scientific Research Fund from the Ministry of Education of Japan and organized a research group of solution chemists that consisted of 14 members, who were physical chemists, inorganic chemists, coordination chemists, analytical chemists, and bioinorganic chemists. Most of them later became leaders of individual research areas in Japan.

In December of 1979, a meeting of the research group was held at the Nagatsuta Campus of the Tokyo Institute of Technology by inviting eminent Japanese scientists as guest speakers as well as group members. Twenty-five presentations were given at this meeting. The third meeting on solution chemistry was held again as a session of the Annual Meeting of the Electrochemical Society of Japan in October, 1980 at the Okayama Campus of the Tokyo Institute of Technology. Subsequently, the symposium on solution chemistry was held every year at various places as an activity of the commission on solution chemistry and the organization became independent from the Annual Meeting of the Electrochemical Society of Japan. The symposium was enlarged and the number of papers presented increased year by year. Currently, the symposium is a three-day conference and more than 100 papers are presented as special lectures, contributed oral presentations and posters, and about 200 people always attend. In 2003 the symposium will have the 26th meeting at the Ritsumeikan University. To celebrate Ohtaki's retirement (his second retirement after his retirement from the Institute for Molecular Science in 1993), an international symposium named the "OHTAKI SYMPOSIUM" was jointly organized with the 26th National Symposium on Solution Chemistry by inviting eminent scientists from abroad, Lean-Marie Lehn (France, Nobel Laureate in 1987), Josef Barthel (Germany), Ivano Bertini (Italy), and Kim A. Burkov (Russia), and eight selected speakers from Japan. About 230 participants attended the symposium.

9. ESTABLISHMENT OF THE ASSOCIATION OF JAPANESE SOLUTION CHEMISTS

Around 1982–1983, some Japanese solution chemists wanted to have their own society of solution chemistry after some successful experience with the series of National Symposia on Solution Chemistry since 1978. Subsequently, the Association of Japanese Solution Chemists was established. H. Ohtaki was appointed as Chairman (later, the Chairman was changed to the President in 1993) in 1983. The Association consists of the President, Chairperson of the Steering Committee, Secretary, Steering Committee Members, and Ordinary Members. After Ohtaki, Hiroyasu Nomura of Nagoya University succeeded the Presidency. In 2002, the Chairperson of the Steering Committee was Masaru Nakahara of Kyoto University. The total number of members of the Society is about 250. The National Symposium on Solution Chemistry is organized under the auspices of the Association.

10. PROJECTS ON PRIORITY AREAS

Epoch-making events occurred in the community of solution chemists of Japan in the periods of 1985–1988 and 1990–1993. In 1985–1988 a research project team entitled "Microscopic and Dynamic Analyses of Solute-Solvent Interactions" was accepted by the Ministry of Education as one of the small projects of the Priority Areas. The team consisted of 23 solution chemists who were divided into five subgroups of "Molecular Dynamics Simulations of Solution," "Local Structures and their Fluctuations," "Dynamic Structure of Intermolecular Interactions," "Mechanisms of Formation of Ion-pairs and Complexes," and

"The Structure of Solutions at High Temperatures and Pressures" under the chairmanship of Hideo Yamatera of Nagoya University. During these three years, the team received 179 million Japanese Yen (∼1.7 million US$) from the Ministry of Education.

In 1990–1993, a larger team of the Project on Priority Areas was established under the sponsorship of the Ministry of Education of Japan. The project was named "Molecular Approaches to Non-Equilibrium Processes in Solution," which consisted of three groups, "Fluctuation of Micro-assemblies," "Dynamics of Diffusion Processes," and "The Structure of Reaction Intermediates." The sum of the financial aid by the Japanese Government within these three years was 369.1 million Japanese Yen (∼3.5 million US$). The project leader was Ohtaki at the Institute for Molecular Science and he was also the head of group 3. Nomura of the Nagoya University and Nakahara of Kyoto University were the heads of groups 1 and 2, respectively. These two projects stimulated the studies of Japanese solution chemists and activities in the field of solution chemistry in Japan were strongly promoted. Fifty-six scientists were involved in the Priority project team. In the evaluation team of the project, well-known international solution chemists, Josef Barthel in Germany, Peter Rossky in USA, and George Neilson in UK contributed. Kazuo Saito, Shuzo Seki, Keiji Morokuma, and Hideo Yamatera were the members of the national evaluation committee of the project. The progress on studies of solution chemistry in Japan was very much enhanced in these six years.

11. INTERNATIONAL ACTIVITIES OF THE SOLUTION CHEMISTS OF JAPAN

In 1978 Ohtaki attended the 4th International Symposium on Solute-Solute-Solvent Interactions (IV ISSSI) in Vienna, Austria, where many interesting topics related to solution chemistry were discussed. Ohtaki was inspired by the symposium and he made up his mind to invite the symposium to Japan. After coming back to Japan, he asked Nobuyuki Tanaka of the Tohoku University to chair the VI ISSSI, which was held in Minoo, Osaka in 1982. The symposium was very successful and we believed that the society of solution chemistry of Japan could be a member of international community of solution chemistry after the symposium.

In January, 1988, the International Symposium on Molecular and Dynamic Approaches to Electrolytic Solutions was held at the Okayama Campus of the Tokyo Institute of Technology in Tokyo under the sponsorship of the Ministry of Education and the Tokyo Institute of Technology. The Chairman was Ohtaki. The three-day conference included 30 papers, of which 15 papers were read by invited speakers from abroad and 33 posters were shown. More than 100 participants filled the conference hall and the symposium was very successful. From the abstract booklet, we see many names of well-known chemists, I. Bertini (Italy), U. Mayer (Austria), N. D. Yordanov (Bulgaria), R. van Eldik (Germany),

D. E. Irish (Canada), P. H. Bopp (Germany), W. A. P. Luck (Germany), S. O. Taniewska-Osinska (Poland), P. W. Wolynes (USA), S. Dhabanandana (Thailand), P. Rienvatana (Thailand), R. Heyrovska (Czechoslovakia), K. Burger (Hungary), B. Holmberg (Sweden), and D. R. Williams (UK). This demonstrates that Japan can be seen as an active member of the international solution chemistry community by the success of this international symposium. After the symposium the number of Japanese participants who attended international conferences on solution chemistry (International Symposium on Solute-Solute-Solvent Interactions (ISSSSI) and International Conference on Solution Chemistry (ICSC)) drastically increased and they almost always occupied about 10% or more of the total number of participants of the conferences.

The movement of Ohtaki from the Tokyo Institute of Technology to the Institute for Molecular Science (IMS) in Okazaki in 1988 created another opportunity to have an international conference under the sponsorship of IMS. He jointly organized the 45th Okazaki Conference on the Chemistry of Intra- and Intermolecular Charge Transfer of Metal Complexes together with Akira Nakamura (Osaka University, later he became the Director of Coordination Chemistry Laboratories of IMS after Ohtaki) and Koji Tanaka (IMS) in December 1993. This conference was somewhat different from other pure solution chemistry conferences but it represented studies in an interdisciplinary area between solution chemistry and coordination chemistry.

In 1994 the Yamada Science Foundation gave financial support to a group of solution chemists in Japan for organizing an international conference, called the Yamada Conference, on the subject of Structure, Fluctuation, and Relaxation in Solutions. The conference was organized by H. Nomura of Nagoya University, and S. Seki, who is a member of Japan Academy and a member of Yamada Science Foundation, and Ohtaki as Advisory Committee Members. We were able to invite 112 scientists including 18 world-leading scientists from outside Japan. The success of the conference gave us a lot of material for a book, "Structure, Fluctuation, and Relaxation in Solutions," published from Elsevier in 1995.

The 30th International Conference on Coordination Chemistry (34 ICCC) held in Kyoto in 1994 was a big event for solution chemists in Japan, because solution chemistry is always an important part of ICCCs. The most noticeable occasion for the solution chemists of Japan was the 26th International Conference on Solution Chemistry (26-ICSC) held in Fukuoka in July, 1999, where the chairman was Ohtaki and the secretary was Shin-ichi Ishiguro of Kyushu University. The conference was sponsored by the Science Council of Japan, the Chemical Society of Japan, and the Association of Japanese Solution Chemists. The International Union of Pure and Applied Chemistry (IUPAC) was also a sponsor of the conference. More than 350 people from 25 countries participated in the conference. The conference was continued for six days with nine sessions and six mini-symposia.

Five satellite symposia were organized at various places in Japan before and after the main conference. A forum for the public was also held during the conference. About 100 citizens including junior and senior high school students and women enjoyed lectures by Japanese scientists.

12. EURASIA CONFERENCE ON CHEMICAL SCIENCES

In relationship to the history and international activities of solution chemistry in Japan, the author would like to briefly mention about the Eurasia Conference on Chemical Sciences ($EuAsC_2S$).

Around 1985–1986, Bernd M. Rode of Innsbruck University, Austria, asked Ohtaki, who is a member of Steering Committee of International Conference on Solution Chemistry, about the possibility of inviting the ICSC to Thailand. Unfortunately the schedule of the conference at that time had been fixed until 1991. Ohtaki suggested that Rode organize another international conference related to solution chemistry in Thailand and he also suggested that a series of conferences should be held in developing countries in Asia or Europe with the idea of supporting the development of their chemistry programs, especially solution chemistry, by inviting eminent scientists from Europe, USA and Japan to the developing countries. Young scientists can rarely participate in international conferences, which are usually held in developed countries far from the developing countries. Rode agreed with Ohtaki and Ivano Bertini of the University of Florence, Italy, joined us to organize the Eurasia Conference on the Chemistry of Solution ($EuAsC_2S$: This logo was created by Sunt Techakumpuch of Chulalongkorn, University of Thailand). The first $EuAsC_2S$ was held in Bangkok in January, 1988 in the presence of HRH Princess Maha Chakri Sirindhorn. The Chairperson of the Local Organizing Committee was Salag Dhabanandana of the Chulalongkorn University. Since then, the $EuAsC_2S$ Conference was held basically every two years in various countries in the Asian area and the 10th $EuAsC_2S$ was held in Hanoi, Vietnam in 2003. The total number of participants of the joint conference was about 780. The name of the conference was changed to the Eurasia Conference on Chemical Sciences, without changing the logo, due to the expansion of the area covered by the conference from only solution chemistry to chemistry including various areas. However, solution chemistry is still an important part of the conference as a basic science and a traditionally accepted subject. The author wanted to mention that a Japanese chemist played an essential role in the establishment of an international conference and that one of the founders of it was a solution chemist.

13. CONTRIBUTION OF THE JAPANESE COMMUNITY TO SOLUTION CHEMISTRY IN THE WORLD

As described above, Japanese solution chemists have contributed to the development of solution chemistry in the world in various ways. The proportion of

Japanese chemists at each international conference on solution chemistry usually exceeded 10% of the total participants during these decades.

It may be said that one of the most significant contributions by Japanese solution chemists is to the exploration of the structural chemistry of aqueous and non-aqueous electrolyte solutions by X-ray diffraction studies. X-ray diffraction studies of liquids were explored almost immediately after the discovery of X-ray diffraction of crystals by P. Debye in 1915.(26) The first examination of non-crystalline substances was made by P. Debye and P. Scherrer(27) in 1916 with paraffin, and then, a number of amorphous substances and liquids were investigated. One of the well-known examples is the structural investigation of water by means of X-ray diffraction by H. H. Meyer,(28) G. W. Stewart(29) and E. Amaldi(30) carried out in 1930–1931 that provided the experimental basis for the theoretical consideration by Bernal and Fowler(25) in 1932. More advanced studies on water structure by the X-ray diffraction method have been made by J. Morgan and B. E. Warren in 1938.(31) An historical survey of these studies is given in an excellent review by R. F. Kruh.(32) More recent studies on the structure of water by A. H. Narten and his colleagues should also be mentioned.(33) Reviews related to the structure of water under normal and extreme conditions described by Japanese chemists can be mentioned where the authors concluded that supercritical water still maintains hydrogen bonds and exists by forming small size clusters, probably together with monomeric dispersed gas-like water molecules.(34,35)

Studies on ionic solvation and complexes in solution have also been summarized in the review by Kruh,(32) but studies before the 1960s have been criticized by many solution chemists. Interpretations given by the authors in this period did not fit well with our knowledge of coordination chemistry and experimental data were not accurate enough to discuss the hydration (coordination) numbers of ions in water. Due to the improvement of electronic devices and equipment, X-ray diffraction studies are well developed.

Most of the investigations of electrolyte solutions by X-ray diffraction until the 1960s (at that time, the EXAFS method had not been employed in the structural studies of electrolyte solutions and the neutron diffraction method for liquids and solutions had not been commonly used) were originated by X-ray crystallographers. The considerations and assumptions introduced in the structural analyses were usually based on crystallographic experiences and very limited consideration has been given to account for reaction equilibria between ions and solvent molecules, and between cations and anions in solution. Work by Georg Johansson in Sweden was well accepted by most solution chemists due to his accurate measurements and reliable explanation of the results. He was a crystallographer, but since he was working in the laboratory of L. -G. Sillén, he had a good understanding of reaction equilibria in electrolyte solutions. Ohtaki worked with him in 1969 and extended the studies to the structure of solvated ions and metal complexes in aqueous and non-aqueous solvents. In Sweden, Ingmar Persson

(Swedish University of Agricultural Science, Uppsala; a pupil of Sten Ahrland of the University of Lund) and Magnus Sandström (Stockholm University; a pupil of G. Johansson of the Royal Institute of Technology) maintain a close cooperation in their research and they are producing a number of good results for the structure of solvated ions in aqueous and non-aqueous solution, and metal complexes in solution.

After Ohtaki, many chemists in Japan studied the structure of ions and complexes in solution by X-ray and neutron diffraction, and EXAFS methods. They are Toshio Yamaguchi of the Tokyo Institute of Technology/Fukuoka University, Hisanobu Wakita of Fukuoka University and Haruhiko Yokoyama of Yokohama City University and their coworkers. They spent some months in Sweden to collaborate with people in Göteborg and Stockholm.

The study of the structure of the hexahydrated copper(II) ion in water by means of X-ray diffraction provided the first experimental evidence of the Jahn-Teller distorted octahedral structure of the d^9 copper (II) ion, whose metal-water bond lengths in the equatorial and axial positions were determined experimentally.[36] An X-ray diffraction study of a series of hydrated transition metal ions[37] can also be mentioned as one of the most interesting subjects in solution chemistry and coordination chemistry in solution investigated by Japanese solution chemists during an early period in the history of X-ray diffraction studies in Japan.

A number of structures of solvated ions in aqueous and non-aqueous solutions have been studied, and the results of these studies are summarized in various reviews.[38–40] In a review by Y. Marcus,[38] results by Ohtaki and his group covered more than 10% of all the references cited by the author. In his review Marcus praised the excellent cooperation among different groups in this field in various countries.

X-ray diffraction studies of solvated ions provided good experimental evidence for molecular dynamics simulation investigations. Therefore, a combination of diffraction studies and MD simulations was employed by various research groups. Most of these groups did not belong to the same laboratory or to the same university and were even located in different countries. The research group of Karl Heinzinger (Germany) and Gabor Palinkas (Hungary) was one of the most active in the 1980s However, the H. Ohtaki – Isao Okada group at the Tokyo Institute of Technology of Japan was working in the same laboratory and thus a closer cooperation could be achieved compared with other cooperative groups in the world.

Studies of supercritical water and liquids may be another important contribution of Japanese solution chemists to the world. High-pressure, high-temperature (HTHP) NMR studies by Nakahara and his groups are now well accepted by the international community of solution chemists as one of the principal techniques for studying the structure and dynamics of supercritical liquids. Work by

T. Yamaguchi using X-ray and neutron diffraction methods is also often cited by various researchers of HTHP solution chemistry (see Ref. [35]).

The stopped-flow-EXAFS method involves another combination of two different experimental techniques. In the course of the Priority Project in 1990–1993, a project team consisting of the groups of H. Ohtaki of the Institute for Molecular Science, S. Funahashi of Nagoya University, and M. Tabata of Saga University tried to develop a new method for the determination of the structure of reaction intermediates in the metal substitution reactions of the mercury (II) porphyrin complex by copper(II) ion.[41] This was the first result for determining the structure of a reaction intermediate in solution. This method employed a reaction similar to that of the mercury(II) porphyrin complex with cobalt(II) ion, which was oxidized by oxygen in solution doing the course the metal substitution reaction.[42]

14. CLOSING REMARKS

Activities of solution chemists in Japan drastically changed during the last 30 years after the historical period from the end of the 19th to the middle of the 20th century. Introduction and catch-up of culture developed in Europe was usually adopted in most fields of the sciences and technologies of Japan, and solution chemistry was not an exception. Consequently, solution chemistry in Japan was able to create something new after the 1970s and Japan became one of the most active countries in solution chemistry research in the world. A language barrier in this field can still be seen to some extent in discussions, but it does not seem to be so serious compared with how it was in the past. Participation by Japanese scientists at international conferences held outside Japan is almost always more than 10% of the total number of participants. Contributions by young Japanese scientists to the international community of solution chemistry have become increasingly significant. There is even a possibility for the establishment of a leadership role in the community of solution chemistry in the world with the creation of new methodologies and new theories by Japanese solution chemists. We are hoping that the 21st century will be a brilliant century for solution chemists in the world, especially Japanese solution chemists, by deepening fundamental research and by extending it to applied sciences such as oceanography, environmental sciences, material sciences, bioscience and biotechnology, and others with continuing the efforts made in the past centuries on many frontiers in this field.

ACKNOWLEDGMENTS

The author referred to “The 100 Years History of Chemical Society” published in an edition of the Chemical Society of Japan and the Tokyo Kagaku Dojin Publishing Co. (1978), “The 100 Years History of the Tokyo Institute of Technology” by the Tokyo Institute of Technology and the Toppan Printing Co., Ltd. (1985), "Chemists in Meiji Era" and "Chemist Kikunae Ikeda" by Kozo Hirota, published by Tokyo Kagaku Dojin Publishing Co. in 1988 and 1994, respectively, and the book written by the sons of Prof. Ryutaro Tsuchida published by Kagaku Dojin in 1975 (Photo 12). The photographs were supplied by courtesy of the Libraries of Waseda University (Photo 1), the Department of Chemistry of Faculty of Science, the University of Tokyo (Photos 2–6, 10), Kyoto University Archives (Photo 7), Faculty of Science, Osaka University (Photo 9), and The Chemical Society of Japan (Photo 14). The author thanks Prof. Hiroyasu Nomura (Emeritus of Nagoya University, and Tokyo Denki University at present for Photo 8), Prof. Masaru Nakahara (Kyoto University), and Prof. Hisao Morisaki (Ritsumeikan University) for their kind help.

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