

ANALYTICAL CHEMISTRY

*Essays in Memory of  
Anders Angström*

WÄNNINEN

# ESSAYS ON ANALYTICAL CHEMISTRY

IN-MEMORY OF PROFESSOR ANDERS RINGBOM

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## PREFACE

Professor Anders Ringbom died in Åbo on December 22, 1972, at the age of 69. Not quite three years earlier he had retired from the position as Professor of Analytical and Inorganic Chemistry at Åbo Akademi. He could then look back on more than forty active years at that University, which he had served as a research and teaching assistant, as a lecturer, and finally as a professor.

Friends and colleagues of Professor Ringbom conceived the idea of collecting papers by analytical chemists into a book in honour of the memory of the highly esteemed researcher and teacher. The editing committee formed for this purpose began soliciting contributions from the world's leading analytical chemists in April 1974. The response was gratifying, about fifty of Professor Ringbom's colleagues and personal friends pledging contributions. The editing committee feels particularly honoured by the participation of Professor I.M. Kolthoff, a highly regarded friend and colleague of Professor Ringbom.

The resulting book provides a very good survey of present research in Analytical Chemistry, several new techniques being treated. The papers have been grouped under the following headings: Chemical Equilibria, Titrations, Photometric Analysis, Electrochemistry, Separations, Trace Analysis, Kinetic Analysis, and Other Analytical Topics.

The editing of the memorial volume has been a pleasant task for the editing committee. We appreciate the valuable help received from many persons to which we wish to express our thanks. In particular, we want to thank Professor Håkan Ringbom who kindly checked the English language of several papers. We are also very grateful to Dr. R.A. Chalmers at the University of Aberdeen, Old Aberdeen, Scotland for valuable advice and for critical examination of the language of many papers. It is also thanks to his efforts that it has become possible to print the memorial volume at Pergamon Press, Oxford, England.

Permission to reproduce some figures in this volume has been granted by several authors and scientific societies. We thank them for this courtesy.

The final manuscript for offset printing has been produced by Mr. Arto Alli at the Copying Center at Åbo Akademi. His experience has been of great value.

Stiftelsen för Åbo Akademi Forskningsinstitut (The Research Institute of the Åbo Akademi Foundation) has provided substantial economic support covering most of the cost of producing the final offset manuscript. We express our sincere thanks for this most valuable help.

Åbo in April 1976

*Erkki Wänninen*

*Leo Harju  
Folke Ingman*

*Bengt Skrifvars  
Ebbe Still*

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Publications by Anders Ringbom

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## CONTENTS

Preface ix

Publications by Anders Ringbom xi

### Chemical Equilibria

#### *Acid-Base Complexes*

- Kolthoff I. M. "Acid-Base Reactions in Nonaqueous Solvents", 1  
Bates R. G. "Measurement of Hydrogen Ion Concentration", 23  
Hakoila E., Meretoja A., and Salvela R. "Acid-Base Equilibria of Dipeptides II. Effect of Hydrolysis", 29  
Sarneski J. E., and Reilley C. N. "The Determination of Proton Binding Sites by NMR-Titrations", 35

#### *Metal Complexes*

- Anderegg G. "Applications of Some Ligands Containing Pyridyl Residues", 51  
Beck M. T. "Determination of Stability Constants of Metal Complexes", 59  
Burger K. "On the Selectivity and Analytical Importance of the Formation of Mixed Ligand Complexes", 81  
Galus M., and Hulanicki A. "Spectrophotometric Study of Mixed Copper Complexes with Bis-(carboxymethyl)dithiocarbamate and Ligands containing Nitrogen Donor Atoms", 89  
Näsänen R., Lindell E., and Tilus P. "Stability Constant Values for the Protonation and Copper(II) Complex Formation of N,N-Di(2-hydroxyethyl)-1,3-Propanediamine in Aqueous Solution", 95  
Österberg R. "Analysis of Multicomponent Equilibria with Potentiostatic Methods", 103  
Perrin D. D. "The Formation and Stability of Mixed-Ligand Complexes", 113  
Petit-Ramel M.M., and Paris M. R. "Use of Spectropolarimetry for Studies of Complex Equilibria", 123  
Tanaka M. "Multidentate Ligand Substitution Reactions as Applied to Analytical Chemistry", 133

#### *Chemical Structure*

- Bjerrum J. "Metal-Ion Complex Formation in Solution and the Soft-Hard Principle of Chemical Interaction", 143  
Högfeldt E. "On the Association of Water in Some Simple Electrolytes", 155  
Ohtaki H., Yamaguchi T., and Maeda M. "The Structures of Hydrated Divalent Transition-Metal Ions in Solution", 163

### Titration

- Budevsky O. "Graphical Method for Construction of Titration Curves", 169  
Harju L., and Skrifvars B. "Application of the Ringbom ECR (Exactly Correct Reference solution) Principle to Titrations", 175

## Contents

- Ingman F., and Still E.** "The Precision of Photometric and Potentiometric Measurements and Titrations, Particularly Gran Titrations", 183
- Johansson A., and Ingman F.** "Photometric Titrations", 189
- Kragten J.** "Photometric Complex-Titrations of Submicromole Amounts of Metals", 205
- Přibil R.** "Titration Reagents in Complexometry", 219
- Svehla G.** "Radiofrequency Titrations", 233
- Zýka J.** "Newer Trends in Redox Titrimetry", 245

## Photometric Analysis

- Flaschka H., and Coulter M. L.** "Investigations in Analytical Photometry. Long-Path Photometry", 253
- Kotrly S., and Vytřas K.** "Colour Changes of Ion-Combination Indicators", 259
- Nakagawa G., and Wada H.** "Effects of Auxiliary Complex-Forming Agents on the Colour Change of Metallochromic Indicator", 281

## Electrochemistry

- Elving P. J., Tsuji K., and Webb J. W.** "Investigation of Chemical Reactions: Examples of Polarographic Approaches", 293
- Laitinen H. A.** "Electrometric Titrations", 305
- Pretsch E., Büchi R., Ammann D., and Simon W.** "Lipophilic Complexing Agents Designed for Use in Ion Selective Liquid Membrane Electrodes", 321
- Pungor E., Tóth K., and Nagy G.** "Ion-Selective Electrodes", 331

## Separations

- Belcher R., Khalique A., and Stephen W. I.** "The Use of Chelate Compounds in Inorganic Analysis by Gas Liquid Chromatography", 343
- Inczédy J.** "Complexing Agents in Ion Exchange Chromatography", 351
- Schmuckler G.** "Complexation in Ion-Exchange Resins", 371
- Schill G., Borg K. O., Modin R., and Persson B.-A.** "Ion-Pair Extraction in the Analysis of Drugs and Related Compounds", 379
- Uesugi K., and Freiser H.** "Di(p-butylphenyl)thiocarbazone, A New Metal Chelating Extractant", 397

## Trace Analysis

- Alimarin I. P., Yakovlev Yu. V., and Dogadkin N. N.** "Activation Analysis of High Purity Substances", 405
- Duyckaerts G., and Gillain G.** "Determination of Cu, Pb, Cd, Zn in Sea Water and Plankton by Anodic Stripping Voltammetry", 417
- Guilbault G. G.** "Fluorescence Analysis on Solid-Surfaces", 435
- Haerdi W., and Monnier D.** "Séparations Rapides de Traces Métalliques en Solution sur Gouttes de Mercure", 453
- Langmyhr F. J.** "Direct Atomic Absorption Spectrometric Analysis of Solid Samples", 461
- Stephens R., and West T. S.** "Sample Atomization in Low Pressure Flames", 477
- West P. W., Shendrikar A. D., and Dharmarajan V.** "Chemical Methods for Analysis of Airborne Particulates", 489

## Contents

### Kinetic Analysis

- Kopanica M., and Stará V.** "Analytical Application of the Rate Phenomena of the Reaction of Metal Chelates", 505
- Ridder G. M., and Margerum D. W.** "Simultaneous Kinetic Analysis", 515
- Yatsimirskii K. B., and Tikhonova L. P.** "Catalytic Methods of Analysis", 529

### Other Analytical Topics

- Bermejo-Martinez F., and Rodriguez-Vazquez J. A.** "Sampling", 537
- Chalmers R. A.** "The Analysis of a Paper on Analytical Chemistry", 551
- Cheng K. L., and Prather J. W. II.** "Photoelectron Spectroscopy in Analytical Chemistry", 559
- Hirsch R. F.** "Statistical Analysis in Analytical Chemistry", 577
- Irving H. M. N. H.** "The Development of Analytical Techniques", 591
- Virtanen R., Kivalo P., Laukkarinen T., and Haimi R.** "Capillary Electrophoretic Method Based on Potentiometric Detection", 601

**Author Index, 607**

# ACID-BASE REACTIONS IN NONAQUEOUS SOLVENTS

I. M. KOLTHOFF

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Minneapolis, Minnesota 55455, U.S.A.*

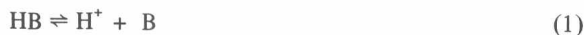
## Contents:

- Concepts of Acids and Bases
- Classification of Solvents
- Amphiprotic Solvents
  - (a) Neutral
  - (b) Protogenic
  - (c) Protophilic
- Aprotic Solvents
  - (a) Protophobic Dipolar
  - (b) Protophilic Dipolar
  - (c) Inert Solvents
- Acid-Base Strength in Different Classes of Solvents
  - Leveling of Acid-Base Strength
- Hydrogen Bonding
  - Homo- and Heteroconjugation
- Analytical Significance of Homo- and Heteroconjugation
  - Conjugation and Solubility
  - Effect of Conjugation on Conductometric Titration Curves
  - Effect of Conjugation on Potentiometric Titration Curves
  - Effect of Hydrogen Bond Donors and Acceptors on pH of Mixtures of an Acid and Its Salt in AN
- Resolution of Acid Strength and Its Relation with Transfer Activity Coefficients
- Diprotic Acids
- Analytical Uses of Dipolar Aprotic Solvents
  - (a) Protophobic Solvents
  - (b) Protophilic Solvents

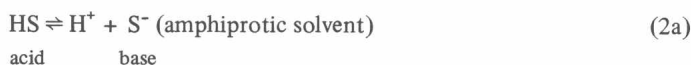
## CONCEPTS OF ACIDS AND BASES

Since more than three centuries a classification of groups of substances as acids or bases has been in vogue. Such a classification was based on properties, such as acid taste, or reactivity, like color of syrup of violets, formation of salts. After Lavoisier (1777) and especially Davy (1810) had proposed to characterize acids on the basis of composition, it was Liebig who in 1838 defined acids as compounds which contain hydrogen (composition) and in which the hydrogen can be replaced by a metal (reactivity). This definition gained wide acceptance. Theoretical concepts of acids and

bases could not be proposed until the birth of theoretical (physical) chemistry. Less than 100 years ago Svante Arrhenius enriched the chemical literature with the theoretical definition that acids, when dissolved in water, dissociate into hydrogen ions and anions, while bases dissociate in water into hydroxyl ions and cations. This theory has played an important role in the quantitative treatment of acid-base titrations in water by Niels Bjerrum<sup>1</sup> in 1914. However, the Arrhenius theory appeared to have several limitations. Acid-base characteristics are not only confined to noncharged compounds. Moreover, to confine acid-base characteristics only to water as a solvent appeared to be too restricted. It was not until 1923 when Brønsted<sup>2</sup> proposed his concept of acids and bases, generally referred to as the Brønsted-Lowry<sup>3</sup> theory, that a quantitative treatment of acid-base reactions in nonaqueous solvent became possible. According to Brønsted, an acid, HB, is a substance which can split off a proton, while a base, B, is a solvent which can combine with a proton:

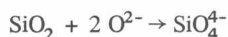
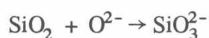


Thus, an acid HB which splits off a proton forms a base B, the system HB–B is called a conjugate system, where B is the conjugate base of the acid HB and *vice-versa*. An acid can have any charge and the conjugate base has a charge one less positive than the acid. Free protons as such do not exist in solution and the solvent, denoted by HS or S, must have basic properties to allow reaction (1) to occur, and it must have acid properties to transform the base into its conjugate acid:



Acid-base reactions also occur in solvents without acid or basic properties (inert solvents). G. N. Lewis<sup>4</sup> objected to the cult of the proton and proposed a classification in which acids are defined as compounds that combine with a base by sharing electrons provided by the base, thus forming a neutralization product which is a coordination compound. The number of compounds (acids) which can share electrons is extremely large. Complexation reactions, a subject to which the late Professor Anders Ringbom<sup>5</sup> has contributed so much, are acid-base reactions in the Lewis sense. On the other hand, Brønsted acids are "neutralization products" of the proton with a base, *e.g.*,  $\text{H}^+ + \text{Cl}^- \rightarrow \text{HCl}$ ;  $\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+$ , etc. To avoid confusion, the author proposed many years ago to distinguish between Brønsted acids and Lewis acids. The present chapter deals with Brønsted acid-base reactions in nonaqueous solvents.

For the sake of completeness, reference only is made to the Lux<sup>6</sup>-Flood<sup>7</sup> concept of acid-base systems in melts containing oxy anions:  $\text{Base} \rightleftharpoons \text{Acid} + \text{O}^{2-}$ . For example:





## CLASSIFICATION OF SOLVENTS

It is logical to base a classification of solvents on their acid-base characteristics. Such a classification is qualitative in nature; the class to which a solvent belongs is determined in a rough qualitative way by its acid-base characteristics. Thus we distinguish between two main classes of solvents, amphiprotic (HS) and aprotic (S) solvents. An amphiprotic solvent has acid (Equation (2a)) and basic (Equation (2b)) properties, forming a stable *lyate* ion ( $S^-$  in Equation (2a)). As the name indicates, aprotic solvents cannot split off a proton; actually they may have extremely weak acid properties, *but they do not form a stable lyate ion*. An important characteristic of an amphiprotic solvent is the value of its autoprotolysis product  $K_s$ :

$$K_s = [HS^+][S^-] \quad (4)$$

For the sake of convenience subclassifications can be made of the two main classes:

## AMPHIPROTIC SOLVENTS

- (a) *Neutral*: Water and compounds which have acid-base characteristics of the same order of magnitude as water has, alcohols, phenols, glycols.
- (b) *Protogenic*: Acetic, formic, sulfuric acids. They are much stronger acids and much weaker bases than water is. Analytically, acetic acid is the most important protogenic solvent.
- (c) *Protophilic*: Ammonia, ethylenediamine, dimethylsulfoxide (DMSO). They are (much) stronger bases and much weaker acids than water is.

## APROTIC SOLVENTS

- (a) *Protophobic dipolar*: Acetonitrile, acetone, sulfolane. They are much weaker bases than water is.
- (b) *Protophilic dipolar*: N,N-dimethylformamide (DMF), pyridine, dimethylsulfoxide\* (DMSO). They are stronger bases than water is.
- (c) *Inert solvents*: Hydrocarbons, halogenated hydrocarbons. These solvents have such weak acid and base properties that they are classified as inert. Their dielectric constant is very small (less than 10).

## ACID-BASE STRENGTH IN DIFFERENT CLASSES OF SOLVENTS

*Leveling of Acid-Base Strength.*

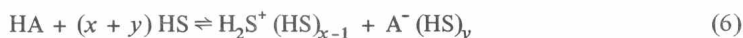
The dissociation of an acid HA into its ions involves an acid-base reaction with the solvent:



In each solvent the hydrogen ion is the proton associated with the solvent. *The transfer of the proton from HA to the solvent is favored by increasing basic strength of the solvent.* Water is strong enough a base to yield in 0.1 M solutions practically complete dissociation of the "strong" acids

\*Dimethylsulfoxide, denoted as DMSO, usually has been considered as an aprotic solvent. However, it has a stable lyate ion, called dimsyl.

perchloric, hydrochloric, sulfuric ( $K_1$ ). In a solvent which is a much weaker base than water, differentiation of strength of these acids is found. For example, in the dipolar aprotic protophobic solvent acetonitrile the order of acid strength is perchloric > sulfuric ( $K_1$ ) > hydrochloric. Water is a much stronger base than acetonitrile and "levels" the strength of these acids. The protophilic solvents have a stronger leveling effect on acids than neutral solvents. In Equation (5a) the proton is solvated with one molecule of solvent. Actually many molecules of solvent may be associated with the proton as a result of hydrogen bonding and ion-dipole interaction. In Equation (5a) the anion  $A^-$  is written as a naked ion, but in reality it is generally solvated by hydrogen bonding, ion-dipole interaction and other types of solvation. Hence Equation (5a) is a simplified presentation of the dissociation of an acid HA:



Truly aprotic solvents are not hydrogen bond donors and, in general, solvation of anions is very much less than in a neutral or protogenic amphiprotic solvent. The "dissociation" of an uncharged base B increases with acid strength of the solvent



Actually the ions again are solvated. In a truly aprotic solvent reaction (7) cannot occur and B can be protonated only by addition of an acid. Again, we observe a leveling effect. For example, carboxylic acids do not exhibit any basic characteristics in water or other neutral solvents, but they are completely ionized in sulfuric acid as a solvent.

From the above discussion it is clear that acid and base strengths in a solvent are not only determined by the tendency of the acid of a given charge type to split off a proton and the tendency of a base of a given charge type to combine with a proton, but that extent of proton transfer from an acid to a base also depends upon the solvation of the reactants and the reaction product in a particular solvent. In addition, the extent of dissociation of an uncharged acid (Equation (6)) or uncharged base (Equation (7)) decreases with decreasing dielectric constants of the solvent, while this constant has virtually no effect on the "dissociation" of a cation acid  $BH^+$  or of an anion base  $A^-$ :



Although solvation may occur in the gas phase, the extent of reaction between an acid and a base in the gas phase, in the absence of solvation, yields quantitative information about the true acid and base strength of the particular system. Especially in the last several years many of such studies have been carried out. Frequently the order of acid or base strength in the gas phase deviates considerably from that in a solvent. For example, in the gas phase toluene is a stronger base than water, while we classify the former as an inert and water as an amphiprotic solvent.

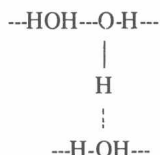
Solvation by hydrogen bonding is very important for an understanding of acid-base equilibria and the effect of various additives on such equilibria in dipolar aprotic solvents. The next section is devoted to this topic.

## HYDROGEN BONDING

### HOMO- AND HETEROCONJUGATION

Hydrogen bonding is an important selfassociation (autocomplexation) reaction of solvent molecules in amphiprotic solvents and association of solute anions or molecules with solvent or solute in all solvents. There exists a very extensive literature on hydrogen bonding.<sup>8,9,10,11</sup> According to the simple valence theory, the hydrogen atom is univalent but in hydrogen bonding it is formally divalent. Atoms in compounds B with electronegativity greater than hydrogen have the capability of forming AH--B hydrogen bonds, in which B has an unshared pair of electrons (base) and is the hydrogen bond acceptor, AH being a Brønsted acid and the donor. AH may also act as a hydrogen bond acceptor, *e.g.*, water and alcohols.

In "neutral" amphiprotic solvents like water and alcohols there is considerable association (polymerization) of solvent molecules by hydrogen bonding, the solvent acting as a hydrogen bond donor and acceptor.



Water is a unique solvent as it has a three-dimensional structure as a result of multiple hydrogen bonding. This structure is quite involved and incompletely understood. In mixtures of water and alcohols hydrogen bonded complexes containing both species are present. Solutions of water in inert solvents contain mainly intermolecular hydrogen bonded water molecules, and to a minor extent, water hydrogen bonded to the solvent if the latter has only very weak basic properties, like benzene.<sup>12</sup> Self-association of alcohols in nonpolar (inert) solvents has been studied by Fletcher and Heller.<sup>13</sup> However, when a solvent is only a poor hydrogen bond donor or/and acceptor, water or alcohols as solutes can be present as monomers. For example, Muney and Coetzee<sup>14</sup> concluded from spectrophotometric studies that in acetonitrile water is monomeric to a concentration of about 1 *M*. Solubility of water in nonmiscible inert and other types of protophobic solvents which also contain a hydrogen bond donor or acceptor can be greatly increased by hydrogen bonding and equilibrium conditions then may become quite involved. For example, the solubility of water in inert solvents is increased by carboxylic acids as a result of formation of hydrogen bonded complexes between water and acid. Salts with a large organic cation (*e.g.*, tetraphenylarsonium) and small anion with a localized charge (*e.g.*, chloride or carboxylate) increase the solubility of water in nonmiscible inert solvents because of hydrogen bonding of water with the anion (hydration). These types of reactions are especially important in the interpretation of extraction analysis and of the effect of water and alcohols on the pH of mixtures of an acid and its salt in dipolar protophobic solvents (*v.i.*).

In all probability the "simple" dissociation of an acid of any charge type in a solvent S (base)

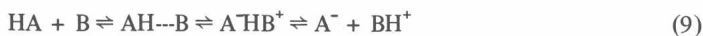
occurs with the intermediate formation of a hydrogen bond complex; e.g., for an uncharged acid:



Especially in an amphiprotic solvent, HS, several molecules of HS can be added to  $\text{SH}^+$  by hydrogen bonding to  $\text{SH}^+ \cdots (\text{SH})_n$ . For example, in water the proton is present mainly in the form of  $\text{H}^+(\text{H}_2\text{O})_4$ .

Quite generally, in amphiprotic solvents (HS) the proton is strongly solvated by hydrogen bonding  $\text{S} \cdots \text{HS}^+$ . In water and alcohols the solvated proton distinguishes itself by a very high mobility. In an oversimplified way this is accounted for by a jumping (transfer) of the proton from one water molecule to another. A lyate ion, like  $\text{OH}^-$  in water,  $\text{OCH}_3^-$  in methanol, is also hydrogen bonded to the solvent and has a high mobility compared to that of other ions. The high mobility of the proton in alcohols is greatly decreased by even very small amounts of water by the formation of  $\text{H}_3\text{O}^+$  (and  $\text{H}^+(\text{H}_2\text{O})_x(\text{ROH})_y$ ). The stability of the solvated proton increases with basic strength of solvent. For example, the stability of the solvated proton in various solvents decreases in the order ammonia, ethylenediamine > pyridine > dimethylsulfoxide > water or alcohol > acetone or acetonitrile > sulfolane or nitromethane.

Hydrogen bonding is especially important in inert solvents and the overall equilibria may become quite involved.



In solvents of low dielectric constant interionic reactions with formation of ion triplets and quadruplets in addition to ion pairs make the equilibria quite complicated. A lucid discussion of acid-base interactions in inert solvents is given by Davis.<sup>15</sup> The equilibria are much simpler in dipolar aprotic solvents with a dielectric constant greater than about 20 than in inert solvents. Even in solvents which are very weak bases, like acetonitrile, acetone, sulfolane, nitromethane, hydrogen bonding with acids is strong enough to make dimerization of acids very small and virtually negligible in dilute solutions. Particularly in these protophobic solvents hydrogen bonding between an anion  $\text{A}^-$  and its conjugate acid  $\text{HA}$  has a large effect on the shape of titration curves:



Hammett and Van Looy<sup>16</sup> were among the first to recognize this type of complexation of anions in a solvent which is or is not a very poor hydrogen bond donor. The complex  $\text{HA}_2^-$  (or  $\text{A}^-(\text{HA})_{n+1}$ ) has been called a homoconjugate, while hydrogen bonding with a nonconjugate acid  $\text{HR}$  has been called heteroconjugation:<sup>17</sup>



Formation constants of homo- and heteroconjugates are much greater in protophobic than in protophilic aprotic solvents. The latter are stronger bases than the former and form stronger hydrogen bond complexes (solvates) with  $\text{HA}$  (or  $\text{HR}$ ) than the protophobic solvents do. Thus in any solvent there is competition between  $\text{A}^-$  and the solvent  $\text{S}$ :



For the sake of simplicity only one  $\text{HA}(\text{HR})$  is written, but more than one molecule  $\text{HA}(\text{HR})$  often