

Acid–Base Titrations in Nonaqueous Solvents and Solvent Mixtures

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The use of nonaqueous solvents has many advantages in analytical chemistry, especially in acid–base titrations (1–5). The number of methods based on redox reactions in nonaqueous solutions (2, 4) is negligible relative to that of acid–base determinations, and the chelatometric titrations (e.g., those of metal ions in dimethylformamide with EDTA; ref 5) are of little practical importance.

Since several organic bases and acids (as well as their salts) can be found in pharmaceuticals, nonaqueous titrations are generally used for their determination. These methods are some of the most popular quantitative pharmaceutical analyses. The determination of these substances by nonaqueous titrations is highly preferred in different pharmacopoeias since the method is quantitative, exact, and reproducible. There are over a hundred assays based on this method in the *European Pharmacopoeia* 2000 (6) and a similar order of magnitude can be estimated in *USP 24* (7) (in spite of the fact that HPLC and similar methods are sometimes preferred).

At the same time, the interpretation of these reactions is rather inconsistent; the theories and suppositions of the 1920s and 1930s are applied and sometimes confused. For example, one of the most popular textbooks on analytical chemistry (8) discusses the topics of nonaqueous media on the grounds of the so-called solvent theory. As it will be treated in this paper, this theory can be easily understood, explains the promoting (and leveling) effects, but is not applicable to the differentiating effect. The following discussion tries to address these issues.

Background

The concepts of acids and bases is relatively old. Their connection to special materials and the study of their aqueous solutions was established during the 19th century. The theory, attributed generally to Arrhenius, differentiates between acids and bases well, but it is insufficient for nitrogen-bases or salts producing acidic or basic solutions. (The auxiliary idea of “hydrolysis” for these kind of interactions has been a troublesome one until now.)

The year 1923 was a very important year for chemical sciences, especially for the physical chemistry of solutions. The “Theory of Electrolytes” published in 1923 by P. Debye and E. Hückel (9) was tremendously successful. Physical-chemical research was influenced by their theory for a long time. Some researchers thought that all phenomena experienced in solution could be explained by the electrostatic interactions of the ions, and there was no need to assume other specific interactions. Coordination-chemistry research, while started earlier, came to a standstill, and this stop can be also considered as a consequence of the Debye–Hückel theory (10). (Coordination-chemistry research was reinvigorated nearly two decades later after the excellent dissertation of J. Bjerrum; ref 11)

The paper of J. N. Brønsted on “The Conception of Acids and Bases” (12) was also published in 1923, as well as T. M. Lowry’s work about the “Uniqueness of Hydrogen” (13). The basis for the Brønsted–Lowry theory was laid in these publications. Considering further developments, Brønsted’s concept was proven more useful in analytical chemistry for the explanation of acid–base reactions.

Brønsted’s Acid–Base Theory

The essence of an acid–base reaction is the transfer of a proton from the acid, HA, to a base, B, in an equilibrium reaction, where a new acid and a new base are formed



Pairs HA, A[−] and B, BH⁺ are coupled by the transfer of a proton and are called conjugate (connected or corresponding) acid–base pairs. Equation 1 gives a common description for any species producing an acidic or basic aqueous solution (independent of whether the species was a compound or an ion) since water is able to react either as an acid or as a base (i.e., it can act both as HA or B, depending on the properties of the partner).

Brønsted’s theory perfectly describes the fact that water can form two conjugate acid–base pairs: the H₂O, OH[−] and H₃O⁺, H₂O. The H₃O⁺ and OH[−] species represent the strongest possible acid and base in aqueous solutions and characteristic acid–base reactions in the water. The autoprotolysis of water (or its autodissociation),



describes the ionic product of water

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (3)$$

(the [H₂O] can be taken as constant) and the concept of pH, as well as the well-known connection of dissociation constants of conjugated acid–base pairs

$$\begin{aligned} K_a \times K_b &= \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{OH}^-][\text{BA}]}{[\text{A}^-]} \\ &= [\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad (= K_w) \end{aligned} \quad (4)$$

where K_w is the ion-product constant (K_w) of water.

Lewis’ Acid–Base Theory

Lewis’ booklet, *Valence and Structure of Atoms and Molecules* (14), where Lewis’ acid–base concept was first outlined, was also published in 1923 (15). The central idea of Lewis’ theory is that the base is able to donate its free electron pair

Nonaqueous Solvents

Evgeny N. Vulfson



Nonaqueous Solvents:

The Chemistry of Nonaqueous Solvents VA J.J. Lagowski, 2012-12-02 The Chemistry of Nonaqueous Solvents Volume V A Principles and Basic Solvents provides the theoretical aspects of nonaqueous solution chemistry independent of solvent and information on individual solvent systems This volume contains chapters on solvation and complex formation in protic and aprotic solvents solvent basicity ion selective electrodes in nonaqueous solvents nonaqueous solvents in organic electroanalytical chemistry and anhydrous hydrazine and water hydrazine mixtures Chemists researchers and students of chemistry and chemical engineering will find the book a good reference material Electrochemistry in Nonaqueous Solutions Kosuke Izutsu, 2009-09-22 An excellent resource for all graduate students and researchers using electrochemical techniques After introducing the reader to the fundamentals the book focuses on the latest developments in the techniques and applications in this field This second edition contains new material on environmentally friendly solvents such as room temperature ionic liquids **Characterization of Solutes in Nonaqueous Solvents** Mamantov, 2012-12-06 This book consists of contributions by participants in the Symposium Spectroscopic and Electrochemical Characterization of Solute Species in Non Aqueous Solvents which took place at the American Chemical Society Meeting Division of Analytical Chemistry August 31 and September 1 1976 San Francisco California The manuscripts were submitted to the editor during the first half of 1977 and in most cases represent reviews of selected research topics in the broad area of characterization of solute species in non aqueous solvents In organizing this Symposium I attempted to bring together a significantly large group of research workers involved in spectroscopic and electrochemical studies in the three large classes of non aqueous solvents organic solvents covalent inorganic solvents and molten salts The experimental approaches and problems such as avoidance of traces of moisture and oxygen are frequently similar for all types of non aqueous solvents It is hoped that this volume will be useful to all concerned with chemistry in non aqueous solvents Gleb I lamantov Contents 1 IDENTIFICATION AND SYSTEMIZATION OF SOLVENT PROPERTIES INVOLVED IN THE LIGAND SUBSTITUTION KINETICS OF LABILE COMPLEXES OF NICKEL II J F Coetzee D Frollini C G Karakatsanis E J *The Chemistry of Nonaqueous Solvents V4* J J Lagowski, 2012-12-02 The Chemistry of Nonaqueous Solvents Volume IV Solution Phenomena and Aprotic Solvents focuses on the chemistry of nonaqueous solvents with emphasis on solution phenomena and aprotic solvents such as tetramethylurea inorganic acid chlorides cyclic carbonates and sulfolane This book is organized into seven chapters and begins with an overview of the theory of electrical conductivity and elementary experimental considerations along with some of the interesting research on nonaqueous solvents It then turns to a discussion on hydrogen bonding phenomena in nonaqueous systems as probed by four spectroscopic techniques the different methods used in studying redox systems in nonaqueous solvents such as potentiometry and steady state diffusion methods and the use of tetramethylurea as a nonaqueous medium for chemical reactions and chemical investigations The reader is also introduced to inorganic acid chlorides of high dielectric

constant with special reference to antimony trichloride and preparation methods for cyclic carbonates including vinylene carbonate ethylene carbonate propylene carbonate and butylene carbonate The book concludes with a chapter on sulfolane focusing on its preparation and purification physical properties and toxicology This book will be of interest to chemists who want to know more about nonaqueous solvents Nonaqueous Solvents Ralph A. Zingaro,1968 **The Dissociation of Electrolytes in Non-aqueous Solvents as Determined by the Conductivity and Boiling-point Methods ...** Henry Royer Kreider,1911 *Inorganic Chemistry* James E. House,2012-12-31 *Inorganic Chemistry* Second Edition provides essential information for students of inorganic chemistry or for chemists pursuing self study The presentation of topics is made with an effort to be clear and concise so that the book is portable and user friendly The text emphasizes fundamental principles including molecular structure acid base chemistry coordination chemistry ligand field theory and solid state chemistry It is organized into five major themes structure condensed phases solution chemistry main group and coordination compounds with several chapters in each There is a logical progression from atomic structure to molecular structure to properties of substances based on molecular structures to behavior of solids etc The textbook contains a balance of topics in theoretical and descriptive chemistry For example the hard soft interaction principle is used to explain hydrogen bond strengths strengths of acids and bases stability of coordination compounds etc Discussion of elements begins with survey chapters focused on the main groups while later chapters cover the elements in greater detail Each chapter opens with narrative introductions and includes figures tables and end of chapter problem sets This new edition features new and improved illustrations including symmetry and 3D molecular orbital representations expanded coverage of spectroscopy instrumental techniques organometallic and bio inorganic chemistry and more in text worked out examples to encourage active learning and to prepare students for their exams This text is ideal for advanced undergraduate and graduate level students enrolled in the Inorganic Chemistry course This core course serves Chemistry and other science majors The book may also be suitable for biochemistry medicinal chemistry and other professionals who wish to learn more about this subject area Concise coverage maximizes student understanding and minimizes the inclusion of details students are unlikely to use Discussion of elements begins with survey chapters focused on the main groups while later chapters cover the elements in greater detail Each chapter opens with narrative introductions and includes figures tables and end of chapter problem sets

Acid-base Titrations in Nonaqueous Solvents James Sherwood Fritz,1973 **Inorganic Chemistry in Nonaqueous Solvents** Arthur Kenneth Holliday,A. G. Massey,1965 *Non-Aqueous Solvents in Inorganic Chemistry* A. K. Holliday,2013 *Non Aqueous Solvents in Inorganic Chemistry* gives a concise treatment of the important inorganic non aqueous solvents emphasizing why they do in fact exhibit solvent power how they are prepared and handled experimentally how they can be used as media for the synthesis or analysis of inorganic and organometallic compounds and how far the various acid base concepts can be useful in accounting for many but not all of the reactions observed This book is intended primarily for the

undergraduate reader both for the intending Chemistry Honours or R I C graduate and the non specialist student **An Investigation of the Existence of Colloidal Electrolytes in Nonaqueous Solutions** S. S. Kistler,1929 The Chemistry of Nonaqueous Solvents VB J.J. Lagowski,2012-12-02 The Chemistry of Nonaqueous Solvents Volume V Acidic and Aprotic Solvents Part B covers the theoretical aspects of individual solvents in nonaqueous solution chemistry This volume is divided into five chapters The first two chapters discuss the purification structure physical properties electrochemistry solubilities and reactions of specific solvents including trifluoroacetic and halosulfuric acids Chapter 3 deals briefly with the preparations and properties of the interhalogens principally in the liquid state This chapter emphasizes their uses as nonaqueous solvents especially through extensive study of their acid base reactions Spectroscopic data and their contribution to the understanding of their solution chemistries are also considered Chapter 4 surveys the autoionization purification methods solubilities solvolytic reactions conductivity conductometric potentiometric spectrophotometric and visual titrations as well as the isolation of solid complexes in inorganic halides and oxyhalides Chapter 5 describes the solubility reactivity and spectroscopic data of molten salts This book is of value to analytical chemists and analytical chemistry teachers and students Study of Macrocyclic Complexes in Nonaqueous Solvents Gholamhossein Rounaghi,1980

The Chemistry of Non-aqueous Solvents: A. Principles and basic solvents. B. Acidic and aprotic solvents. 2. v J. J. Lagowski,1978 **The Chemistry of Nonaqueous Solvents III** J.J. Lagowski,2012-12-02 The Chemistry of Nonaqueous Solvents Volume III Inert Aprotic and Acidic Solvents is a compilation of critical surveys of specific solvent systems The compendium contains discussions on the solution chemistry of sulfur dioxide and acyl halides the solvent properties of hydrogen sulfide and carboxylic acids and the Bronsted acid base behavior in inert organic solvents Chemists researchers and students of chemistry and chemical engineering will find the book a good reference material *Non-aqueous Solvents* John R. Chipperfield,1999 Solvents other than water are used in chemical analysis chemical manufacturing and in specialized syntheses This book covers the principles and uses of non aqueous solvents at a level suitable for first or second year undergraduates The book first discusses the general properties of solvents and introduces the necessary concepts for making rational choices of solvents for different applications There is a discussion of the various chemical interactions between solvents and the substances dissolved in them and how solvents change the course of reactions The chemistry of 16 common solvents is discussed emphasizing the advantages and disadvantages of each The book concludes with an account of the chemistry of molten salts and discusses the use of low melting temperature compounds as synthetic media The book expands on the brief treatment of non aqueous solvents given in many textbooks while avoiding the complexities introduced in research treatises It is the only book currently available that provides an in depth treatment accessible to undergraduates

Advances in Protein Chemistry ,1963-01-01 *Advances in Protein Chemistry* *Enzymes in Nonaqueous Solvents* Evgeny N. Vulfson,2008-02-05 Enzymatic catalysis has gained considerable attention in recent years as an efficient tool in the

preparation of natural products pharmaceuticals fine chemicals and food ingredients The high selectivity and mild reaction conditions associated with enzymatic transformations have made this approach an attractive alternative in the synthesis of complex bioactive compounds which are often difficult to obtain by standard chemical routes However the majority of organic compounds are not very soluble in water which was traditionally perceived as the only suitable reaction medium for the application of biocatalysts The realization that most enzymes can function perfectly well under nearly anhydrous conditions and in addition display a number of useful properties e.g. highly enhanced stability and different selectivity has dramatically widened the scope of their application to the organic synthesis Another great attraction of using organic solvents rather than water as a reaction solvent is the ability to perform synthetic transformations with relatively inexpensive hydrolytic enzymes It is worth reminding the reader that in vivo the synthetic and hydrolytic pathways are catalyzed by different enzymes However elimination of water from the reaction mixture enables the reversal of hydrolytic enzymes and thus avoids the use of the expensive cofactors or activated substrates that are required for their synthetic counterparts

Conductivity and Viscosity in Mixed Solvents Containing Glycerol ... Maurice Roland Schmidt, 1909 *Journal of the American Chemical Society*
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