A SYMPOSIUM ON NON-AQUEOUS SOLUTIONS[1]

INTRODUCTION

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Any survey of chemical literature impresses the reader again with the fact, long recognized, that water is indeed the "universal solvent." As Conant says, "Much important chemistry has been obscured by our slavish devotion to water." Of the work on non-aqueous solvents, the major part has had to do with the physical constants, to the neglect of the nature and type of the reactions and the products formed. It has become increasingly evident, however, that a sound understanding of both the chemistry and the physics of these solutions is essential to a basic and more inclusive knowledge of chemistry.

After the successful application of the ideas of Arrhenius to electrolytic dissociation in aqueous solutions, it appeared reasonable that the results obtainable with other solvents should be capable of similar interpretation. In the early investigations of non-aqueous solutions, however, serious difficulties were encountered. Much of the earlier work is of questionable accuracy and later work has revealed such startling discrepancies, when any attempt was made to reconcile results with the accepted theories, that at the present time few of the desired generalizations can be made.

The simple relations between conductance and concentration found for aqueous solutions do not in general appear when other solvents are used. For certain solutions with dielectric con-

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stants approaching that of water, the conductance varies with concentration in a way analogous to that observed in aqueous solutions. This is particularly true of ammonia and the amines. In other cases the conductance decreases with increasing concentration and becomes constant at high concentrations. When the solvent has a very low dielectric constant, the conductance increases with concentration until the solution is about molar and then begins to decrease. It is generally stated that the value of Λ_∞ is greater in aliphatic than in aromatic solutions of the same type. In the case of alcoholic solutions the results obtained are more or less similar to the results obtained with water solutions, and diverge with the increasing complexity of the alkyl group. Numerous measurements have been made in formic acid, acetic acid, ammonia and the amines. Liquid halogens, halogen hydrides, glycerol, benzene, chloroform, hydrogen peroxide, sulphur dioxide, aluminum bromide, sulfuric acid, hydrocyanic acid and many other non-aqueous solvents have been examined.

The classical researches are those of Walden, who examined a large number of substances. Many attempts have been made, particularly by Kraus and Walden, to reconcile the data obtained with the classical dilution laws; the success of these attempts is questionable.

The temperature coefficient of conductivity in non-aqueous solutions is again a function that does not conform to classical laws. In some work done in this laboratory it was found that for the alkyl magnesium bromides in ether solution the equivalent conductivity increases with temperature between 20° and $-10°$, while for phenyl magnesium bromide in the same range it passes through a maximum.

The dielectric constant of many solvents is known at present with considerable accuracy. The Nernst-Thompson rule relating ionizing power to dielectric constant has been broadly confirmed by experiment. However, we have discovered in recent years other influences promoting ionization, and these appear most markedly when the dielectric constant is small. The dielectric constants of hydrogen bromide and hydrogen iodide, for example, are low, yet these solvents give excellent conducting media with certain organic acids.

Originally the assumption was made that all reactions are ionic. The curious arrest of many reactions in carefully dried solutions lent support to this generalization. Careful experiments, however, have shown that reactions can take place in non-aqueous solutions that show no conductance. The question of the application of the mass action law to non-aqueous solutions has been studied in detail. In some cases where the solvent is water-like, Ostwald's dilution law is followed. Concentrated solutions of ammonium formate in anhydrous formic acid obey the law. In other cases the Rudolphi dilution law is followed. The equation of Kraus and Bray has been applied to non-aqueous solutions with some success. In many solutions in ammonia the mass action law holds good, and the smaller the ionization the higher the concentration to which the law is applicable.

Little accurate work is on hand relative to the solvated compounds formed when various salts are dissolved in different solvents. Transport numbers in solvents other than water have been determined, but little work has been done here. This field would possibly give us much information as to the type of ionization and the compounds formed. Electrolysis can be carried out in non-aqueous solvents and the results have both scientific and practical value, yet this is a phase of chemistry that until recently has been almost entirely neglected.

Such is the present situation so far as the physical aspects of non-aqueous solutions are concerned. If we are to free ourselves from our thralldom to water and enlarge our conception of chemistry, some detailed study of the chemical reactions taking place in non-aqueous media is required. In such a study the nature of the solvent cannot be neglected, as was formerly done in the study of aqueous solutions.

In recent years many new and brilliant workers have entered this field, stimulated, no doubt, by the newer theoretical considerations and the successful application of interionic attraction theories to strong electrolytes in aqueous solution. It was entirely impossible to reconcile strong electrolytes with van't

Hoff's law of dilute solutions or to the classical mass action law; therefore the original theory has had to be revised. Some of the difficulties have been overcome by considering strong electrolytes as completely ionized and assuming that the electrical forces between the ions account quantitatively for the observed deviations. By far the most successful, although certainly not the first of these interionic theories, we owe to Debye and Hückel. They showed that it was possible to explain in a purely theoretical manner the change in the activity coefficient of ions with concentration. This change can be represented by a square root law when the solution is dilute enough to be regarded as completely ionized. This theory, applied recently to non-aqueous solutions, is promising. We have learned that the ionizing power does not depend entirely on the dielectric constant, but that other factors are perhaps more important. We find that we can classify solvents in four groups: acid solvents such as hydrofluoric acid; basic solvents like ammonia; amphiprotic solvents such as water; and aprotic solvents such as benzene.

One of the main contributions to the chemistry of non-aqueous solvents, certainly from a scientific point of view, has been the enlarging of our conception of acids and bases. Kraus and Franklin have defined acids and bases in an ammonia system. Conant, Hall and Davidson in their work on acetic acid have defined an acid and a base in an acid medium, while Brönsted has perhaps formulated the best definition of these substances for all solvents.

Hall's excellent paper reviews the efforts made to formulate a general definition of an acid and a base. The various methods of obtaining quantitative data on acidity in various solvents are discussed, and the discrepancies in acid strength, as obtained by the different methods, are pointed out. Definite conclusions have been drawn regarding the rôles played by the acidic and basic groups in general. Reactions catalyzed by hydrogen ion are catalyzed by all acid molecules. Likewise all basic molecules have the same properties. The possibility of reducing acidity data, when various solvents are considered, to a quantitative basis seems remote. The establishment of a definite acidity scale is doubtless the goal of this work but if, as Taylor has pointed out, electric potential difference in different solvents is without meaning, we are still a long way from this "absolute activity."

Davidson points out that our knowledge of the chemistry of acetic acid is quite recent. Although acetic acid is an excellent solvent and is easy to investigate, for years its chemistry was a mystery. He finds that metathetical reactions in this solvent parallel those in water solutions to a great extent in spite of a very different dielectric constant. The main difference is in the solubility relations. Many substances quite soluble in water are insoluble in acetic acid. Acids such as perchloric, sulfuric and hydrochloric are shown to be strongly acid in acetic acid, while the metal acetates are bases and can be used to titrate the acids. The acetate ion in this case shows an avidity for the proton similar to that exhibited by hydroxyl ion. The hydrogen ion activity at the neutral point is, of course, vastly different from a similar neutral point in water solution. The solubility of bases in different solvents varies greatly, just as does that of the metallic bases in water. For example, there is extreme variation in the solubility of the metallic acetates in acetic acid, the acid sulfates in sulfuric acid and the fluorides in hydrofluoric acid. An exception is the case of the metallic sulfides which (excepting NH_4HS) are insoluble in liquid hydrogen sulfide.

Ammonia in acetic acid solution exhibits strong basic properties, whereas ammonia in water does not. This is no doubt due to the instability of NH_3H_2O and the weak basic nature of water, incapable of uniting with proton. Davidson's work points to an explanation of the weak basic nature of water in terms of the instability of oxonium acetate. The formation of sodium zincate when zinc hydroxide is treated with excess of base has a perfect analog in the compound formed when excess sodium acetate is added to precipitated zinc acetate in acetic acid. Copper acetate likewise seems to be amphoteric.

Another neglected acid solvent is hydrogen fluoride, similar to water in its dielectric constant but vastly different in most other particulars. The alkaline hydroxides and the alkaline earth hydroxides in this solvent increase in solubility with molecular weight, which is analogous to the behavior of similar compounds in water; but in other respects the solvent does not parallel water. Simons has used the acceptor theory of Sedgwick, coupled with the strong acid nature of the solvent, to explain the abnormalities encountered in hydrofluoric acid solutions of salts, acids and alcohols. In the light of the theory here reviewed solvents can be classified according to their ability to accept protons. A strong base accordingly represents one extreme, with hydrofluoric acid at the other extreme, and water intermediate between them. Water would give up protons to ammonia but accept them from hydrofluoric acid, forming an oxonium ion. Hydrochloric acid would give up protons to both ammonia and water but not to hydrofluoric acid, while acetic acid, which is a weaker acid in water, would give up protons to ammonia and water but receive them from hydrofluoric acid. In this solution it would be basic; thus it is evident that the properties of a polar solvent depend not only upon its dielectric constant but also upon its donor and acceptor powers.

Hydrogen sulfide as a potential solvent is placed between water and acetic acid. Its conductance is about 20,000 times less than that of pure water. Most substances give poorly conducting solutions in this solvent. Some substances that are hydrolyzed in water and soluble in liquid hydrogen sulfide are not thiohydrolyzed. No explanation is advanced for this fact, although many esters hydrolyzed in water form analogous sulfur compounds in liquid hydrogen sulfide.

Ammonia solutions have been well studied by numerous workers. Kraus discusses liquid ammonia as a medium for reduction reactions. Ammonia and the amines are unique in their power to dissolve alkali metals. The metals behave as salts, giving, as the negative ion, the electron which is very active chemically. We have in these metallic solutions the strongest type of reducing media. Since water solutions cannot contain a stronger reducing agent than hydrogen, the realm of strong reduction has remained heretofore unexplored. Its investigation shows many spectacular results. When a salt is added to these metallic solutions, rich in an ammoniated electron, the reaction direction depends on the insolubility of possible reaction products, as well as on the position of the metals in the electromotive series. Here magnesium and aluminum reduce sodium. Metallic alloys of an alkali and an amphoteric metal change to polysalts that are very soluble and excellent conductors. Positive radicals become free radicals and are then reduced. Metallic and electrolytic conductance exist in the same solution. From the many new types of compounds that appear, it seems that we have veritably discovered a new chemistry.

The application of the Debye-Hückel interionic electrical force theory to non-aqueous solutions is still in the early empirical stage. Probably the best way to attack this problem would be by testing the activities of various types of salts in water-like solvents such as the alcohols. Williams has made such tests and finds that the difference between water and alcohol as solvents is one of degree only. The data, however, reveal the inadequacy of the two premises of Debye and Hückel when applied to non-aqueous solvents. Williams indicates the nature of additional assumptions necessary to reconcile experiment and theory.

Williams also discusses the application to conductance of the Debye-Hückel theory, as modified by Onsager, showing that it can be applied to non-aqueous solutions just as the activity theory was applied, but with less exact results. Deviations from this theory are found in even the simplest types of electrolytes in dilute solutions of methyl alcohol. The results demonstrate the same inadequacies in the assumptions underlying the conductance theory as were found in the activity theory and are to be accounted for chiefly by association and solvation. In effect they limit the applicability of the square root law to the expression of interionic forces. This association also renders it impossible to account for changes in conductance with concentration through changes in ionic mobilities.

Scatchard reviews the different theories of non-electrolytic solutions. He then proposes a modification of Hildebrand's treatment for use quantitatively. The properties of liquid mixtures can be calculated from certain general assumptions and it is shown that the theory is capable of rather broad application.

Audrieth's paper criticizes the lack of work done on electrolytic deposition in non-aqueous solutions. He reviews the work that has been done in this field with various solvents and points to the need of a generalization for predicting the solvent to be employed in the electrolysis of any given element.