

## The Solvent In An Aqueous Solution Is

Non-Aqueous Solutions is a collection of papers presented at the Fourth International Conference on the same subject. One paper presents the application of far- and mid-infra-red, Raman, alkali metal n.m.r. and  $^{13}\text{C}$  n.m.r. techniques to the study of electrolyte solutions in non-aqueous solvents. The paper notes that spectroscopic techniques can be very useful in the elucidation of the structure of electrolyte solutions. Both the vibrational spectroscopy and particularly the alkali metal n.m.r. are very sensitive probes of the immediate chemical environment of ions in solutions. Another paper points out that the energy change associated with the solvation of ions can be represented as the sum of two energy terms; firstly, from the dielectric polarization of the solvent molecules in the continuous dielectric medium; and secondly, due to specific ion-solvent interactions in the inner solvation shells of the ions. The energy contribution of the latter is minimal but can show comparatively large differences in various types of solvents. Another paper describes the chemistry of solutions in highly associated strong protonic acid solvents, including sulphuric acid, oleums, fluorosulfuric acid, and hydrogen fluoride. Organic chemists, analytical chemists, investigators, and scientists whose works involve physical or inorganic chemistry will find the collection truly beneficial. Solubility Data Series, Volume 50: Carbon Dioxide in Non-Aqueous Solvents at Pressures Less Than 200 kPa contains evaluated data for the solubility in non-aqueous solvents of carbon dioxide at a partial pressure not greater than 200 kPa. The Solubility Data Series is a project of Commission V.8 (Solubility Data) of the International Union of Pure and Applied Chemistry (IUPAC). The text has as its goal the preparation of a comprehensive and critical compilation of data on solubilities in all physical systems, including gases, liquids and solids. Chapters are devoted to providing data on the solubility of carbon dioxide in compounds such as alkanes, cyclic alkanes and alkenes, alcohols, solvents, other than alcohols, containing carbon, hydrogen and oxygen, and animal and vegetable oils and fats. Chemists will find the text extremely useful.

The majority of reactions that are of chemical or biological interest occur in solution. A proper understanding of ion-solvent interactions would form the basis of quantitatively explaining the influence of the solvent and the extent of interactions of ions in solvents, thus paving the way for the real understanding of the different phenomena associated with solution chemistry. There has been an increasing interest in the behaviors of electrolytes in non-aqueous and aqueous-organic solvents with a view to investigate ion-ion and ion-solvent interactions under varied conditions. The purpose of this book is therefore, to reveal different thermodynamic and transport properties of electrolytes in non-aqueous and aqueous-organic mixed solvent media. Besides presenting simple facts and concepts, the book also presents the complex nature of ion-solvent interactions. This book intended to provide an appreciation to all those interested in chemical sciences and should be especially useful to the researchers of solution chemistry.

vi the information collected and discussed in this volume may help toward the achievement of such an objective. I should like to express my debt of gratitude to the authors who have contributed to this volume. Editing a work of this nature can strain long established personal relationships and I thank my various colleagues for bearing with me and responding (sooner or later) to one or several letters or telephone calls. My special thanks once again go to Mrs. Joyce Johnson, who bore the main brunt of this seemingly endless correspondence and without whose help the editorial and referencing work would have taken several years. F. FRANKS Biophysics Division Unilever Research Laboratory Colworth/ Welwyn Colworth House, Sharnbrook, Bedford January, 1973

Contents Contents of Volume 1 ..... xv Contents of Volume 3 ..... xvi .  
 . . . Contents of Volume 4 . . . . . xvii . . . . . Chapter 1 The Solvent Properties of Water F. Franks  
 1. Water, the Universal Solvent-the Study of Aqueous Solutions 2. Aqueous Solutions of Nonelectrolytes ..... 5 2.1. Apolar Solutes ..... 6 2.2. Polar Solutes ..... 19 2.3. Ionic Solutes Containing Alkyl Residues-"Apolar Electrolytes" ..... 38 3. Aqueous Solutions of Electrolytes ..... 42 3.1. Single Ion Properties ..... 42 3.2. Ion-Water Interactions ..... 43 3.3. Interionic Effects ..... 47 4. Complex Aqueous Mixtures 48 Chapter 2 Water in Stoichiometric Hydrates M. Falk and O. Knop 1. Introduction. . . . . 55 . . . . . 2. Symmetry and Types of Environment of the  $\text{H}_2\text{O}$  Molecule 2 in Crystals ..... 57 vii Contents viii 2.1. Site Symmetry. . . . . 57 . . . . .

Hydroxide values and associated alkali metal may be recovered from alkaline aqueous solutions using classes of fluorinated alcohols in a water immiscible solvent. The alcohols are characterized by fluorine substituents which are proximal to the acidic alcohol protons and are located to adjust the acidity of the extractant and the solubility of the extractant in the solvent. A method for stripping the extractant and solvent to regenerate the extractant and purified aqueous hydroxide solution is described.

The conductivity behavior of ionomers and ionic liquids in non-aqueous solvents was studied. Ionic liquids (BMIM-PF<sub>6</sub> and EMIM-TF) were dissolved in polar (DMF) and non-polar (THF) solvents and solution conductivity was measured. When dissolved in a polar solvent, ionic groups in ionic liquids stayed as electrolytes, which resulted in the high conductivity of the solution in DMF. The conductivity measurement was also carried out on the systems of polymers (SPS-Na ionomer, PS, and PMMA) and an ionic liquid (BMIM-PF<sub>6</sub>) dissolved in DMF and THF, respectively. Regardless of the types of polymers, all the solutions in DMF showed the same conductivity, which was identical to that of the pure ionic liquid in DMF. However, when the solvent was switched to THF, the conductivity of the solution containing both ionic liquid and ionomer was negligible compared to the other solutions. This change in conductivity was due to the aggregation between ionomer and ionic liquid in a non-polar solvent (THF). In order to further investigate the effect of the solvent polarity on the solution conductivity with both ionic liquid and ionomer, ionomer was dissolved in a series of DMF/THF solvent mixtures and the ionic liquid was added. At the same concentration of the ionic liquid, the solution conductivity increased with increasing the content of DMF. This phenomenon suggests that the ionic groups tend to dissociate in the high-polarity solvent and associate in the low-polarity solvent.

The book starts with an exposition of the relevant properties of ions and continues with a description of their solvation in the gas phase. The relevant properties of prospective liquid solvents for the ions are dealt with. The process of the transfer of ions from the gas phase into a liquid where they are solvated is then taken care of. Various aspects of the solutions of the ions, such as structural and transport ones and the effects of the ions on the solvent dynamics and structure are then described. In cases where the solvent is a mixture selective solvation takes place and is discussed. The interactions of ions with one another that may lead to ion pairing and with other solutes in the solution as well as their dependence on the solvent are also dealt with. The book concludes with applications of the concepts expounded previously in fields such as electrochemistry, hydrometallurgy, separation chemistry, biophysics, and synthetic methods. The book contains a large amount of factual information in the form of extensive tables of critically examined data and illustrations of the points made throughout.

Considerable attention has been focussed on non-aqueous chemistry in the last decade and this situation has arisen no doubt from a realization of the vast application of this branch of chemistry. Within this field much energetic work has been channelled into

the determination of the coordination chemistry of transition metals in these solvent systems. Elaborate experimental techniques have been developed to discover, in particular, the magnetic and spectral properties of complex compounds, and the theoretical background of such systems has been expanded to corroborate, as far as possible, the experimental results. This text has, however, a different bias from many books currently available on this branch of chemistry, and is designed to be a survey of known facts on many of the non-aqueous solvents currently in use mainly in the field of halogen chemistry, together with a discussion of these facts in the light of accepted principles. As such, it is hoped to close a gap in the literature of which many workers and advanced students in this field will be aware. The treatment is meant to be selective rather than completely comprehensive and must inevitably reflect some of the special interests of the author.

Fifty oil soluble amines were screened for possible use as extractants for uranium from sulfuric acid solutions. The most promising of these were studied further to obtain the optimum conditions for operation of such a process. Kerosene was used as the diluent. Arising no doubt from its pre-eminence as a natural liquid, water has always been considered by chemists as the original solvent in which very varied chemical reactions can take place, both for preparational and for analytical purposes. This explains the very long-standing interest shown in the study of aqueous solutions. In this connection, it must be stressed that the theory of Arrhenius and Ostwald (1887-1894) on electrolytic dissociation, was originally devised solely for solutions in water and that the first true concept of acidity resulting from this is linked to the use of this solvent. The more recent development of numerous physico-chemical measurement methods has made possible an increase of knowledge in this area up to an extremely advanced degree of systematization. Thus today we have available both a very large amount of experimental data, together with very refined methods of deduction and of quantitative treatment of chemical reactions in solution which enable us to make the fullest use of this data. Nevertheless, it appears quite evident at present that there are numerous chemical processes which cannot take place in water, and that its use as a solvent imposes 2 INTRODUCTION limitations. In order to overcome these limitations, it was natural that interest should be attracted to solvents other than water and that the new possibilities thus opened up should be explored.

The objective of this dissertation is to consider the hypothesis that there is a necessity for some legal framework in order to make adequate provision for the implementation and operation of consultative procedures in Great Britain. It is hoped to draw conclusions regarding this hypothesis primarily by means of an examination of consultation in Great Britain and the Federal Republic of Germany, the latter country operating a highly legal and formalised system of industrial relations. A description of the way in which one particular company has implemented consultation mechanisms in both the aforementioned countries is used to illuminate the more practical aspects. By way of introduction, the place of joint consultation within the range of possibilities for employee participation in managerial decision-making is noted. Contents: Aqueous Solution Chemistry, Acids and Bases, Solute-Solvent Interactions, Chemistry in Protonic Solvents Liquid Ammonia, Liquid Hydrogen, Fluoride, Sulphuric, Acid, Liquid, Hydrogen, Cyanide, Acetic Acid and Liquid Hydrogen Sulphide, Non- Protonic Solvents Liquid Dinitrogen Tetroxide, Liquid Sulphur, Dioxide and Liquid Halides.

Non-Aqueous Solutions — 5 is a collection of lectures presented at the Fifth International Conference on Non-Aqueous Solutions held in Leeds, England, on July 5-9, 1976. The papers explore reactions in non-aqueous solutions as well as the thermodynamic and kinetic properties of non-aqueous solutions. Examples of the use of spectroscopic techniques are presented, and solutions in molten salts are given. Metals in solution and liquid metal solutions are also considered. This book is comprised of 12 chapters and begins with a review of a general scheme which considers the species formed by cation-electron and electron-electron interactions at dilute to moderate concentrations, along with the influence of the solvent and the metal on these interactions. The discussion then shifts to the application of electron spin resonance spectroscopy to the study of solvation; the influence of solvent properties on ligand substitution mechanisms of labile complexes; and the effect of acidity on chemical reactions in molten salts. Subsequent chapters deal with the chemistry of solutions of salts in liquid alkali metals; preferential solvation in kinetics; and the use of non-aqueous solvents for preparation and reactions of nitrogen halogen compounds. Results of Raman spectroscopic studies of non-aqueous solutions and spectroscopic studies of coordination compounds formed in molten salts are also presented. This monograph will be of interest to chemists.

In this work, we study methyl nonafluorobutyl ether (MFE) and tris(2,2,2-trifluoroethyl) phosphite (TTFP), respectively, as a co-solvent for the non-aqueous electrolyte of Li/air battery. Results show that in certain solvent ratios, both solvents are able to increase the specific capacity of carbon in Li/O<sub>2</sub> and Li/air cells. More interestingly, the improvement in discharge performance of the Li/air cells increases with discharge current density. These results cannot be explained by the ionic conductivity and viscosity data of the electrolytes since the participation of fluorinated co-solvents hardly changes viscosity of the solvent blends while reversely reduces ionic conductivity of the electrolyte. In particular, we find that a 30 wt.% (vs. solvent) addition of TTFP into a 0.2m (molality) LiSO<sub>3</sub>CF<sub>3</sub> PC electrolyte can significantly improve the discharge performance of Li/air cells, and that the resultant electrolyte is able to support long-term operation of Li/air cells in dry ambient environments due to its low volatility. We believe that the observed performance improvement is associated with the increased dissolution kinetics and solubility of oxygen in fluorinated solvent containing electrolyte.

[Copyright: 978efd9e829e50bd512a20a3b72598d7](https://doi.org/10.1002/9781118151222.ch005)