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# PRACTICAL APPLICATION OF BASIC RESEARCH IN HYDROGEN BONDING

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## Introduction

It has become common in recent years for non-scientists to react rather disdainfully toward research projects that address what appear to them to be highly specialized areas of interest and which, from their titles, offer little good for mankind. Those of us who spend great portions of our waking hours engrossed in these studies tend to over-react in the other direction by holding our endeavors in an exaggerated esteem that tends to preclude an appropriate assessment of their essential merit. As is usually the case, the proper perspective lies somewhere in between.

Sound basic research must proceed with a minimal amount of hindrance placed upon it by practical demands but it still must not consume inordinate amounts of resources (including the scientist's time and the society's funds) if it does not hold a glimmer of hope for bettering the predicament of mankind. This paper describes the experience of a physical chemist who happily discovered a very practical use for his background and research of some ten years in the area of hydrogen bonding. The essential motivation for this decade of devotion has stemmed from a curious need to understand how molecules hold themselves together and how they interact with one another. The territory is so extensive in relation to this interest that the necessity of selecting an area that was manageable, but which had a direct bearing upon the general area of molecular interaction, was obvious.

Hydrogen bonding studies offer a unique opportunity to obtain a glimpse at the entire panorama of molecular interactions, because the phenomenon of hydrogen bonding sits on the border between what are normally regarded as the strong interactions related to chemical bonding and the weak type of interactions that cause molecules to line their dipoles up and stick to one another but not really form any lasting alliances. These "middle of the road" interactions are not only of an esoteric interest to those of us who examine them but also play an important role in how the substances on this planet and elsewhere behave.

The crucial insight that occurred to James Watson in wrestling with the helical structure of the DNA molecule came from an examination of accurate molecular models that suggested that hydrogen bonding between amino acid groups along the polypeptide chains could give rise to the observed structure of this protein. The strange behavior of water (see following papers) is directly attributable to the ubiquitous presence of strong hydrogen bonding between its molecules. Among other things, it leads to its abnormally high boiling point in comparison to other molecules of similar molecular weight.

The particular application of hydrogen bonding studies described in this paper has little to do with living creatures or water solutions but it does serve

to further the claim that an understanding of the hydrogen bonding phenomenon can lead to practical results. It is highly unlikely that the author would have maintained much interest in his research if its sole purpose was to apply the results to a practical problem. Even if the author would have been aware of the particular practical problem described in this paper, it is unlikely that he would have gained the appropriate insights and mental imagery that were required to develop the thinking that eventually brought about a meaningful solution if he had only examined this one problem.

### Hydrogen Bonding and Molecular Interactions

An extensive literature has developed through the years concerning a wide variety of areas in which hydrogen bonding is important. Two sources for a general survey of research in these areas are books by Pimentel and McClellan (1) and Vinogradov and Linnell (2). There are also other good sources available.

A "hydrogen bond" is formed in the following way:



In this reaction, "A" represents a highly electronegative atom (F, O, or N, although other atoms could be involved), "B" represents a "base" with a pair of electrons available, and "R" represents the rest of the molecule to which the AH group is attached. The product of the reaction is a molecular complex that is held rather tenuously by the H atom between A and B. The energy of the H-B bond is only a few kcal/mol in comparison to "true" chemical bonds which have energies in the tens to hundreds of kcal/mole. This means that these bonds are easily shaken apart by the thermal motions of molecules, which involve kinetic energies also of a few kcal/mol. Thus, the bonds are continually being formed and broken under normal conditions of temperature and pressure in liquid solutions.

One of the curious aspects of describing this interaction as a "bond" is that this demands that the H atom exceed its normal bonding capacity (which allows for the formation of one bond). This has given rise to controversy as to whether or not this should be described as chemical bonding. The alternative is to describe the attraction between H and B as a coulombic one (positive H attracting the negative electron pair on B) in the same category as dipolar interactions. Evidence has accrued, however, which indicates that there is electron sharing between H and B, one of the criteria for chemical bonding.

To better understand the types of molecular interactions, it is useful to consider the magnitude of energies associated with the forces involved in the interactions as well as the character of the forces themselves. The weakest interactions involve energies of 1 kcal/mol or less and are related to what are called *dispersion forces* and are essentially of a quantum mechanical nature. They arise from instantaneous dipole moments in molecules that interact between the molecules over very short distances. These forces are responsible

for holding molecules of a nonpolar nature in the liquid phase of a substance. Hydrocarbons offer an example of liquids that are essentially held together by these forces. The extreme volatility of gasoline (a mixture of hydrocarbons) is an indication of the weakness of these forces. Even He gas becomes a liquid at very low temperatures (approx.  $4^0$  K) because of these forces.

A step up in energy to a few kcal/mol is involved in the next category of interactions, those involving molecules with dipole moments (unsymmetric charge distributions) that interact with one another by a mutual alignment of the dipoles. This reduces the energy of a system and stabilizes liquid and solid phases of substances. If molecules have strong enough dipoles, these can induce dipoles in nonpolar molecules and this type of interaction involves energies of a kcal/mol.

Hydrogen bonding and the formation of so-called *charge transfer complexes* are in the next category of interactions and these involve energies of a few to 15 or 20 kcal/mol. The hydrogen bonding interaction has been described previously and the charge transfer process can be typified by weak complexes formed when  $I_2$  is mixed with benzene. Actual transfer of electron density occurs in both of these cases and while it is not as large in magnitude as the electron shifts in true chemical bonding situations, the onset of electron density shift signals the beginning of the range of interaction energies associated with chemical bonding.

The normal notions of chemical bonding involve either complete transfer of electron density between atoms (ionic bonding) or the mutual shift of electron density to the region between atoms (polar covalent and pure covalent bonding). These interactions are quite energetic, ranging from 50 to several hundred kcal/mol. Since these lead to changes in the character and make-up of substances, they are not directly concerned with the particular problem described in this paper.

### **Solubility of Polymers in Solvents**

The problem to which the author applied his background in hydrogen bonding research involves a practical matter. There are numerous examples in the world of practical chemistry in which certain substances must be dissolved in solvents in order for them to be used in a practical manner. One such example is ordinary paint which is a solution of polymeric molecules in organic solvents (or water). The Shell Development Company in Houston, Texas is a part of the research division of the Shell Oil Corporation which is involved in the business of providing solvents to a wide variety of industries including the paint industry. Recent air pollution regulations that are being implemented across the country have given rise to a problem for the solvent industry. Older formulations of solvent blends, while being very suitable for dissolving polymers, have been designated as air pollutants that are not allowed by these regulations. In order to find substitute blends that satisfy these regulations and that still dissolve polymers, a more fundamental understanding of molecular interactions became necessary.

The problem of determining good solvent blends is related to the molecular interactions described previously. Dispersion, dipole, and hydrogen bonding interactions are the determining factors in the formation of a solution of a polymer in a solvent or a blend of solvents. It has become customary in the industry to quantitatively identify parameters for solvents and polymers that are associated with each type of interaction. These parameters have been derived from consideration of the heat of vaporization of liquids and the experimentally observed solubility behavior of polymers. Two solvents tend to form homogeneous mixtures if their dispersion, polar, and hydrogen bonding parameters are very similar. It has been assumed that polymers with parameters similar to those of a solvent, or a solvent blend, will form solutions with the solvent or solvent blend. A discussion of the details of this approach can be found in several references (3, 4, 5).

The particular contribution that the author has made to this problem involves an improved technique for estimating the hydrogen bonding energies in mixtures of solvents and polymers. The technique involves two mathematical models that utilize hydrogen bonding parameters for substances that allow for the prediction of whether a solvent or blend of solvents will prefer to interact with itself through hydrogen bonding or with a polymer when it is mixed with the solvents. These models were developed from considerations of hydrogen bonding theory based upon experimentally measured interaction energies, some of which the author and his students have studied for the past several years.

When hydrogen bonding is present, it becomes the determining factor in whether or not a solution will form. The author spent two summers in Houston developing these models and implementing their use on a computer in order to allow the computer to select solvents that meet pollution regulations, that are cost effective and that dissolve the particular polymers of interest. Using the models, it has become possible to predict solution or non-solution behavior with better than 80% accuracy. This is a marked improvement over earlier methods that were not based upon theoretical considerations but instead were derived from empirical approaches.

The computer method of using the models also provides industry with a means of selecting appropriate solvent combinations for specific polymers without resorting to exhaustive laboratory experimentation using a trial and error approach.

### Conclusion

The ultimate success of these models from the standpoint of their practicality and utility will be measured by how well they stand the critical test of practical use by the solvents industry. It is the author's belief that they will serve the industry well and they represent a contribution of a theoretical scientist to the real world of practical chemistry.

This unexpected but happy marriage of an academician with a chemical industry was made possible originally by a grant from the National Science Foundation. Subsequent work on the project has been supported by the Shell Development Company and not only has this resulted in benefits for Shell but it has also added a dimension to the author's research interest that could not have come in any other way.

It is quite rewarding when one finds his efforts to be of use, even if these efforts were made merely for the joy of discovery.

### Literature Cited

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### Two New NSTA Publications

The following publications were recently introduced at the 25th Annual National Science Teachers Association's Convention held in Cincinnati.

*Hunger: The World Food Crisis* (\$2.50), an annotated bibliography by Kathryn Mervine Fowler, contains reviews of publications, lists of curriculum materials, films, and organizations involved in food and hunger issues. Produced under a grant from the U.S. Office of Environmental Education, *Hunger: The World Food Crisis* was developed to facilitate the introduction of food topics into the K-12 classroom.

*Games for the Science Classroom* (\$3.75), by Paul B. Hounshell and Ira R. Trollinger, has been designed to enhance the learning environment through the use of instructional games. Containing all the information necessary for choosing, ordering, and preparing over 100 games in the biological, physical, earth/space, and general sciences, this guide also includes a brief summary of their rules.

Both publications may be ordered directly from NSTA; write: National Science Teachers Association, 1742 Connecticut Avenue, N.W., Washington, D.C. 20009. All orders must be prepaid except those on official purchase order forms. Add 50 cents postage and handling on all prepaid orders. Shipping and handling charges will be added to all billed purchase orders.