The Application of the Hydrogen Bond Theory to Some Questions of Nomenclature

Sven Arrhenius[a]

[a] Department of Medical Chemistry, Royal Veterinary College, Stockholm, Sweden

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SVEN ARRHENIUS

Department of Medical Chemistry
Royal Veterinary College
Stockholm, Sweden

SUMMARY

The hydrogen bond is considered to be a special case of the oscillating ion bond (OIB bond).

An OIB solvent is described as one built up by smaller, rapidly oscillating ions, X^+, and more stationary ions, stator ions, St^{m-}. Solvents with ions of the opposite charge, X^- and St^{m+}, are not discussed.

An idealized OIB solvent, $(XSt)_a$, with linear OIB aggregates formed as long, curled chains, is constructed. The mean aggregation value, $M_T(a)$, is their fundamental parameter. The linear OIB medium is suitable for deductions.

From the conditions at rupture of the linear OIB chain, the apparent dissociation into X^+ and St^- ions is demonstrated.

The more natural medium is that of net or cage aggregates, (X_mSt). For them, the fundamental parameter is the percentage of oscillation possibilities not used, denoted $M_T(b)$.

It is impossible to determine which of the X^+ and St^{m-} ions form the molecule (X_mSt). It is so unstable that it must be called a pseudo molecule.

Polar solvents containing single molecules with parts of electrical asymmetry (local dipole moments) or their association products behave differently from OIB media. In this paper they are called dipolar solvents.

Common salt ions, denoted B^+ and A^-, are oriented and associated to local dipoles in dipolar as well as in OIB solvents.

The ions of the OIB medium itself, X^+ and $(X_nSt)^{(m-n)-}$, behave differently from the ions B^+ or A^-. These medium ions change the structure of the medium itself.

Chemical individuals which increase the apparent X^+ ion content without introduction of other kinds of cations and without destroying (X_mSt) pseudomolecules are called acids.

Correspondingly, an alkali is a chemical individual which increases the $(X_nSt)^{(m-n)-}$ ion content.

If X^+ reacts to form a complex ion, AoX^+, the apparent content of $(X_nSt)^{(m-n)-}$ ions will increase. Thus, Ao is said to be a pseudoalkali.

In the same way, $(X_nSt)^{(m-n)-}$ ions may be involved with complexes such as $/BoP^+(X_nSt)/^{(m-n-p)-}$. As the apparent content of St^--containing ions decreases, the medium is acidified. Hence, a chemical individual such as BoA_p may be called a pseudoacid.

The formation of solvent ions is characteristic of OIB media; it does not occur in pure dipolar solvents. The extraordinarily high electrical conductivity for solvent ions characterizes a solvent with net or cage aggregates.

The model for the OIB solvents is built up on the X^+ ions. $pX = -\log_{10}/X^+/$ is an expression for the description of the medium. It corresponds to the use of pH in aqueous systems.

The number of H^+ ions calculated from the pH value denotes the number of chains ending in H^+.

A pH scale for description of OIB solutions with (X_mSt) as dominating pseudomolecule cannot be used for solutions of another OIB medium (X_nV). If both solvents are miscible in all proportions, there will be one proportion, giving the critical mixture, where the pX scale has to be shifted.

INTRODUCTION

The theory of hydrogen bonding has had a marked influence on physical chemistry in the last few decades. There is hardly any property of aqueous solutions that cannot be better explained by taking this theory into consideration [1, 2]. Also, some questions of nomenclature, which plays such an important role in elementary chemistry, ought to be treated on the basis of this theory.

According to the hydrogen bond theory, water is built up by ice clusters of very different shapes and magnitudes and with very short lifetimes. In

these clusters the structure is the same as in solid ice, with a distance between oxygen atoms of 2.76 Å. On their four valence bonds, in tetrahedral arrangement, hydrogen ions are moving between two turning points, indicated in this paper as $(H^+)_1$ and $(H^+)_2$. The distance $O\text{-}(H^+)_1$ is 0.99 Å, and hence the distance $(H^+)_1\text{-}(H^+)_2$ is 0.78 Å [3]. (In the following discussion the exact magnitude of these figures is not involved.) An element of the cluster may thus be drawn:

$$\ldots\ldots\ O^{2-}\ \ldots\ldots\ (H^+)_1\ \ldots\ (H^+)_2\ \ldots\ldots\ O^{2-}\ \ldots\ldots$$
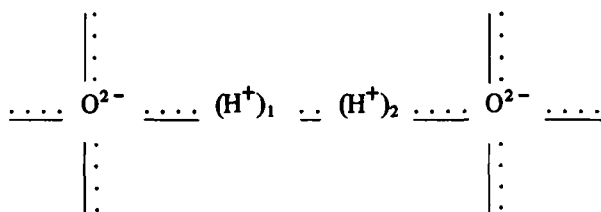
In the diagram, a two-dimensional representation of the three-dimensional tetrahedral structure is used. The notation for the bond, ... , will in itself include both the common electron envelope from oxygen to hydrogen marked by the "valence line," _____ , and the oscillation denoted with the dotted line, ...

GENERALIZATION OF THE HYDROGEN BOND

The hydrogen bond is found in media other than water, e.g., sulfuric acid and alcohols. In the water formula O^{2-} is thus to be exchanged for complex ions like SO_4^{2-}, $H_5C_2O^-$, etc. The essential condition is stability in the O^{2-} position, or that of the complex ions compared to the rapidly varying distances for the oscillating H^+ ions. Hence, a common name for O^{2-}, SO_4^{2-}, etc. ions is proposed: "stator ions," abbreviated here to St^{m-}. Since the H^+ ion is considered to be interchangeable with other ions, the name "oscillator ion" would be convenient. It is here symbolized as X^+. Any theoretical hindrance to extend the hydrogen bond from water to a medium of the general type X_nSt_m apparently does not exist. The oscillator is first considered to be a single ionized atom. To treat the idealized case with monovalent stator . . . . St^- . . . . and oscillator ions X^+, the element in our aggregate formula hence will be:

$$\ldots\ldots\ St^-\ \ldots\ldots\ (X^+)_1\ \ldots\ (X^+)_2\ \ldots\ldots\ St^-\ \ldots\ldots$$

and after adding the terminal parts, the formula of our chain-like aggregates will be:

$$(X_aSt_a) \dots (X^+)_1 \dots (X^+)_2 \dots St^- \dots (X_bSt_b)$$
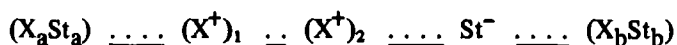
This aggregate can now be broken between the two turning points, $(X^+)_1$ and $(X^+)_2$, in two different ways: The normal situation for X^+ at the rupture is in position $(X^+)_2$ or close to it. In this case the result of the rupture will be two smaller aggregates, $(X_aSt_a) = (XSt)_a^O$ and $(X_{b+1}St_{b+1}) = (XSt)_{b+1}^O$. The smaller aggregates are neutral. The more unusual rupture will be with X^+ close to or in the position $(X^+)_1$. The result will then be $(X_{a+1}St_a)^+ = (XSt)_aX^+$ and $(X_bSt_{b+1})^- = (XSt)_bSt^-$, or two ionic aggregates.

Polyvalent stator ions, St^{m-}, will give rise to net or cage aggregates. They are clusters of chains. Only a few of them will be broken at the same time, giving holes in the aggregates held together by the unbroken residue of chains. Considering the rupture only, we may describe two types:

$$(X_mSt)_{a+b}^O = (X_mSt)_a^O + (X_mSt)_b^O$$
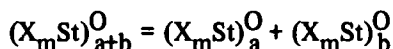
for normal rupture with X^+ in or close to the position $(X^+)_2$. For the rupture close to position $(X^+)_1$ it follows:

$$(X_mSt)_{a+b}^O = (X_mSt)_aX^+ + (X_{mb-1}St_b)^-$$
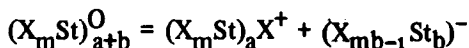
It is now to be noted that the unbroken chains, $(X_mSt)_a$ and $(X_mSt)_b$, and their ionized products may still belong to the same aggregate, $(X_mSt)_{a+b}$. This aggregate will only be limited by the surface of the liquid. Our assumptions of normal or ionic rupture of oscillating ion bonds can be extended to all kinds of liquids where these types of bonds occur. Thus, we may also apply them to water:

for normal rupture: $(H_2O)_{a+b} = (H_2O)_a + (H_2O)_b$
and for ionic rupture: $(H_2O)_{a+b} = (H_2O)_aH^+ + (H_2O)_{b-1} \cdot OH^-$
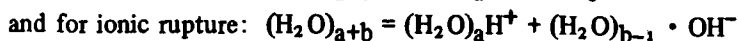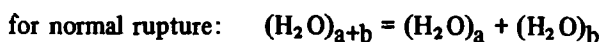
According to the classical theory, the latter may be abbreviated to give:

$$H_2O = H^+ + OH^-$$
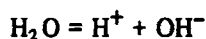
This is the simplest way of expressing the dissociation of water. According to Brönsted and Lowry, the ionic rupture is described by the statement:

$$2\,H_2O = H_3O^+ + OH^-$$

THE POLAR SOLVENTS

There are two extremes for polar solvents: The oscillating ion bond solvent ("OIB solvent") described here, and solvents for molecules with finite dipole moments. The latter will be denoted here as "dipolar solvents." Both kinds of liquids may transport alternating current by electrical displacement. From the dielectric constants of dipolar solvents measured at different frequencies, two fundamental properties of the solute molecules may be calculated: the dipole moments and the relaxation times. They may also be calculated from the molecular structures, combined with the viscosity of the medium. Differences between dipolar moments and relaxation times obtained by the two methods of determination are explained by association. The dipolar molecules may form quadrupoles, chains, or other combinations. Such aggregates may also split up and recombine. But ionized molecules or aggregates will not occur. The abnormal rupture giving ionized aggregates is characteristic of the oscillating ion bond.

The alternating electric current is transported through the OIB medium by the ions, mainly by the oscillating ions, X^+. If we denote the central point between positions $(X^+)_1$ and $(X^+)_2$ by $(X^+)_3$, this point is brought closer to the cathode during that phase for the alternating current. From dielectric constant data for an OIB medium, it is not possible to calculate any molecular dimensions. The description of these media from the formula $(X_mSt)_a$ corresponds to the formula for polymers, $-(ABC \ldots)_n-$. Whatever may be involved in the symbols A, B, C, etc., an electrical alternating current will not change the constitution of the group $(ABC \ldots)$. On the other hand, if we create a model for an ice cluster or any other OIB aggregate, we cannot tell which ions, X^+, belong to a special stator ion, St^{m-}. The expression for an OIB medium as a polymeric molecule is confusing. Thus, it is necessary to have a special name for such a nonexisting part of an OIB chain or net. Here, the name "pseudomolecule" is proposed.

Extremes must always be considered as ideal conditions rather than as actual situations. Thus, in pure water all "molecules" are not built into the ice clusters. There will always be some monomers, $(H_2O)_1$, that can

orient in an electrical field in the same manner as does a chlorobenzene molecule, $C_6H_5 \cdot Cl$, dissolved in benzene, C_6H_6.

In dissolving a neutral salt, $BA = B^+ + A^-$, in a polar solvent, a new chemical individual may be formed. At first, we will not take these kinds of reaction into consideration. Common salt ions, e.g., Na^+, Cl^-, etc., may orient and associate to molecules in dipolar solvents. If we disregard the rather improbable straight linear aggregate $(XSt)_a$, there will always be details of local electric asymmetry along the chains. The local dipole moments thus created may be oriented in the same manner as free polar molecules by small ions B^+ or A^-. The effect of neutral salts will be of the same kind on all polar solvents.

THE SOLVENT IONS

Salts or molecules containing or causing solvent ions like X^+, St^{m-}, $(XSt)^{(m-1)-}$, or, in general, $(X_nSt)^{(m-n)-}$, behave quite differently. We will denote these units as XA and B_mSt. The solvent ions introduced in the medium X^+, St^{m-} will be added instantly to the aggregates and will become a part of the OIB system. For the linear system $(XSt)_a$, all neutral aggregates have a positive end, X, and a negative end, St. The time for rupture of a chain will be the same as for the recombination, and hence we have a characteristic constant for this OIB solvent at a definite temperature, T, the "mean value for aggregation," $M_T(a)$. Many of the physical properties will depend upon this value. They may be described by $f(M_T(a))$. In adding XA to the medium, ionic aggregates ending with two X:$-(X \ldots (StX)_a \ldots St \ldots X)^+$—will be formed. They will always repel each other, and hence the recombination into bigger aggregates is hindered. The value for aggregation, $M_T(a)$, will decrease. We can apply the same reasoning for the addition of BSt to the solvent forming $(St \ldots (XSt)_a \ldots X \ldots St)^-$ ions. If we construct the functions $M_T(a) = f(St^-)$ or $f(X^+)$, these functions will be congruent. For this idealized OIB medium, any physical property depending on $M_T(a)$ will have a maximum or minimum at the neutral point where $/X^+/ = /St^-/$ and will behave symmetrically about this point.

For the more complicated net or cage aggregates, a or $M_T(a)$ has no meaning. Instead, we will use b to denote a rupture in an oscillating bond chain to form a breakage in the chain and a hole in the network, or any increase in size of an old one. If the total number of St^{m-} ions in a solution is known, the number of possible oscillating ion connections can

be calculated. Thus, b is the number of unused possibilities for a single St^{m-} ion, and $M_T(b)$ symbolizes the number of breakages taken per mole (X_mSt). This expression will describe this medium and its physical properties in the same way as $M_T(a) = f(X^+)$ did for the linear OIB medium. The same notion about adding XA or BSt to this medium applies, and the same objections about functions of b as for a for physical properties of the solvent are relevant. However, functions $f(X^+) = M_T(b)$ and $f(St^{m-}) = M_T(b)$ cannot be assumed to be congruent since a number of different negative ions, $(X_{m-1}St)^-$, $(X_{m-2}St)^{2-}$, etc., may be added.

The net or cage aggregates have another characteristic property. If one single X^+ ion is added, there will be a break at one spot in the network. However, this rupture will be translated to quite another place in the network by ionic movements in the OIB system only. The same kind of ion transport may also occur for the negative ions, $(X_{m-1}St)^-$, etc. Thus, the equivalent electric conductance for these ions cannot be ascertained from their ion radii and the viscosity of the solvent.

THE GENERAL NOMENCLATURE FOR ACIDS AND ALKALIS

From the point of view of nomenclature, we will summarize these ideas by proposing another name for XA or BSt molecules. All molecules (or more correctly, all chemical individuals, in the sense of the phase rule, that will increase the number of X^+ ions in an OIB medium without changing the pseudomolecules of that medium or without introducing any other positive "ballast ions," B^+, into the medium) will be named "acids." They are here symbolized by $XA = X^+ + A^-$. The opposite molecular species are called "alkalis," and are denoted by $BSt = B^+ + St^-$. Alkalis are defined as chemical individuals which are capable of increasing the content of negative ions of an OIB solvent without introducing other negative (nonsolvent) ions at the same time.

With water, these definitions would be as follows: Acids are molecules or ionic crystals, $H_nA = H^+ + (H_{n-1}A)^-$, and alkalis are $BSt_m = B^+ + m St^-$. In St^- are included O^{2-} and OH^-. The chemistry of inorganic complexes [4] is rendered more difficult because of complex formation with H_2O, H^+, OH^-, or O^{2-}. Considering the possibility of generalizing the hydrogen bond into an oscillating ion bond, the complexes formed with OIB ions or (pseudo-) molecules must be discussed. The most simple case is the solution of Ao or Bo molecules in the linear OIB solvent (XSt):

$$Ao^O + (XSt) = AoX^+ + St^-$$
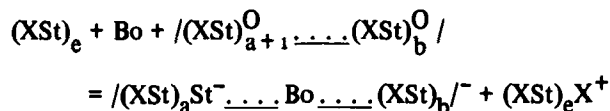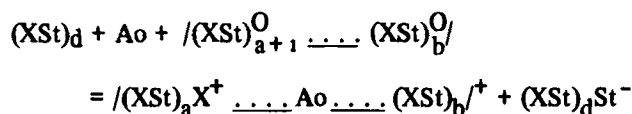
$$Bo^O + (XSt) = BoSt^- + X^+$$
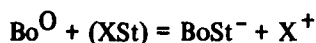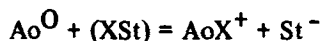
The first reaction makes the OIB medium alkaline. Thus, Ao may be called a "pseudoalkali." A translation for alkali-like is alkaloid. The name is ordinarily used for a group of pseudoalkalis of plant origin characterized by their pharmacological activities. Chemically they are amines, $N(R_1, R_2, R_3)$, giving the reaction for Ao with water:

$$N(R_1, R_2, R_3)^O + H_2O = N(R_1, R_2, R_3)H^+ + OH^-$$
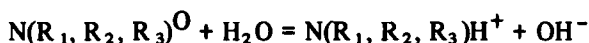
Bo makes the medium acid, and will consequently be called "pseudo-acid." A typical aqueous pseudoacid is carbon dioxide, CO_2:

$$(CO_2)^O + H_2O = HCO_3^- + H^+$$
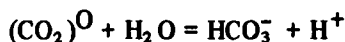
The theoretical issue behind the nomenclature is: "Do the AoX^+ and $BoSt^-$ ions behave as Na^+ or Cl^- ions, do they orient and associate to local dipole moments in the OIB chains, or will they form links in the OIB chains?" The reactions for the last alternative may obey the formulas:

$$(XSt)_d + Ao + /(XSt)^O_{a+1} \ldots (XSt)^O_b/$$

$$= /(XSt)_a X^+ \ldots Ao \ldots (XSt)_b/^+ + (XSt)_d St^-$$

$$(XSt)_e + Bo + /(XSt)^O_{a+1} \ldots (XSt)^O_b /$$

$$= /(XSt)_a St^- \ldots Bo \ldots (XSt)_b/^- + (XSt)_e X^+$$

If the complex constants are equal to 1.00 (and hence also the dissociation constants for the complexes), the bond $Ao \ldots X^+$ (or $St^- \ldots Bo$) will be broken and recombined as easily as the $St^- \ldots X^+$ bond. The fundamental part of the mixed OIB chain, $Ao \ldots (X^+)_1 \ldots (X^+)_2 \ldots St^-$, will be built up symmetrically with the distances $Ao-(X^+)_1$ equal to that of $St^--(X^+)_2$.

In the complexes taken into account, the constants are greater than 1.00. The forces are stronger and the distances $Ao-(X^+)_1$ are shorter than between $(X^+)_2$ and St^-. The result of this asymmetrical rupture will be Ao in an end position. The same kind of position in the chain will be given to Bo.

In adding Ao to solvents with the more complicated cage aggregates, we will find AoX^+ in positions where we used to find ions like Na^+, B^+, etc. The characteristic property of these cage aggregates is the rapid transport of solvent ions through the chain system by displacements of the oscillating ions. The X^+ ion of the AoX^+ complex cannot oscillate like other X^+ ions in the OIB system. Since the complex AoX^+ behaves like an ion and not like an acid, the name "pseudoalkali" for reactants like Ao is necessary. The same kind of reasoning will show the name "pseudo-acid" for Bo to be reasonable.

THE pX (pH) SCALE

Careful attention should be given to the "dissociation formula" for water, $H_2O = H^+ + OH^-$, or to the more generalized expression for all OIB media, $(X_mSt) = X^+ + (X_{m-1}St)^-$. From the logarithmic expression pH + pOH $= pK_w = 14.00$ and other logarithmic equilibrium formulas for the solutes, the pH value is obtainable. From the antilogarithm of pH, the actual concentration of H^+ ions can be calculated. But this is not at all correct. Except for those few molecules which are in the monomeric form $(H_2O)_1$, the hydrogen atoms are in the bonded form as oscillating ions. The concentration of such H^+ ions would be about 100 N. For the idealized linear OIB system, pX gives the concentration of aggregates with X endings. For cage aggregates, and thus also for water, pX (pH) represents the number of X^+ breakages where X^+ ions (H^+ ions) are limiting.

The confusingly high content of H^+ ions is explained by the electron cloud surrounding the jumping ions. In our deduction for the OIB bonds, $St \ldots (X^+)_1 \ldots (X^+)_2 \ldots St^-$, the coordinative bond marked ___ has been omitted and only the ionic bond . . . . considered. In chemical terms this may be rectified by assuming that only $\mathcal{A}$ % of the oscillating ions are true X^+ ions. The rest, $(100 - \mathcal{A})\%$, are conceived to be neutral atoms, X^0. Such a symbolization would apparently not be very enlightening.

So, pH should be viewed as an expression for the conditions in an aqueous solution only. For the OIB medium the mean aggregate value $M_T(a)$ could be appraised; it would provide a better expression than pX. However, the description of aqueous solutions by using the pH scale is so convenient that it can hardly be replaced. This scale is based on the equation pH + pOH = 14.00 and is only strictly correct for the temperature of 24.00°C. By agreement, the scale is extended for use at other temperatures. In using the expression $p(H^+ : OH^-) = pH - pOH$ as an

independent variable for the description of aqueous solutions, we could eliminate pK = 14.00. The variation of the dissociation constant for water is thus eliminated. Any discussion of what is really meant by dissociation of an OIB pseudomolecule would thus be superfluous.

MISCIBLE OIB SOLVENTS

The pH scale is sometimes used for the description of mixtures of water with substances which are miscible with water in all proportions. Let us discuss systems of mixtures of two linear OIB solvents, $(XSt)_a$ and $(XV)_e$. For the pure solvents, $M_T(a)$ and $M_T(e)$ will be at a maximum. (N.B. The pure solvents are acids.) In mixing $(XSt)_a$ and $(XV)_e$, aggregates symbolized by the structure . . . . St^-. . . . $(X^+)_1$. . $(X^+)_2$ . . . . V^-. . . . may be formed. If the forces between St^- and X^+ are as strong as those between V^- and X^+, the mixed aggregates will behave as an ideal linear OIB system. If the forces are of different magnitude, such intermediates will not be permanent. In adding $(XSt)_a$ to $(XV)_e$, ions like $(XV)_eX^+$ are formed, and $M_T(e)$ decreases. The addition of $(XV)_e$ to $(XSt)_a$ gives exactly the same effect; $M_T(a)$ decreases. In the ideal case without intermediates, a point on the mixing axis, called the "critical mixture," will be obtained where $M_T(a)$ = $M_T(e) = 1$. The most frequent aggregates in the critical mixture are $(X_2St)^+$, $(X_2V)^+$, $(XSt_2)^-$, and $(XV_2)^-$.

For small concentrations of (XV) in (XSt), pX may be described by pX = pK_{XSt} - pSt. By agreement, this pX calculation may be extended until the critical mixture. For solvents with fewer (XSt) than (XV) pseudomolecules, the pX scale ought to be built up on the equation: pX + pV = pK_{XV}. In mixed media of cage aggregates (X_mSt) and $X_nV)$, we are obliged always to figure with intermediates. Also, here we have to consider $pK_{XSt} \neq pK_{XV}$. At least two different pX scales must be used. The point where the ions $(X_{m+1}St)^+$ and $(X_{n+1})^+$ reach their maximal concentration may also be called here the critical mixture. For water, $(X_{m+1}St)^+ = (H_3O)^+$.

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