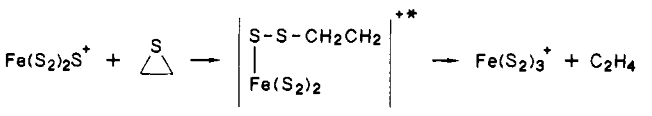
Scheme I



result in multiple S_2 losses, such losses are possible from either type of structure. In addition, the thermochemistry obtained in Tables IV–VII for these species do not distinguish between these two types of structure.

It is interesting to try to rationalize the observed reactivity of these species with ethylene sulfide, summarized in Table I, in terms of the possible structures. Oxidative addition of ethylene sulfide to the metal center should only be facile provided that the intermediate species not exceed the +7 oxidation state of iron. Assuming the structures $Fe(S_2)_n^+$ and $Fe(S_2)_{n-1}S^+$ for $n = 1$–3, this would predict a sharp reduction in reactivity for $Fe(S_2)_2S^+$ and $Fe(S_2)_3^+$ where oxidative addition to the ethylene sulfide would proceed through a +9 intermediate. This, in fact, is what is observed for reaction 1 in Table I. In contrast, the $Fe(S)(S_4)^+$ and $Fe(S_2)(S_4)^+$, representative of possible ring structures for FeS_5^+ and FeS_6^+, respectively, could react with ethylene sulfide by oxidative addition proceeding through an "allowed" +7 oxidation state of iron. Finally, the observed reactivity of FeS_5^+, although substantially reduced, suggests either the presence of a ring structure or that a mechanism not involving oxidative addition can occur as postulated in Scheme I.

Conclusion

Photodissociation, CID, and kinetic methods were used to study various iron sulfides generated from sequential reactions with ethylene sulfide. The kinetic behavior of the sulfides indicates a homogeneous population in each case and, thus, they are believed to be predominantly thermalized and consisting mainly of one isomer. The last two sulfur abstractions were found to be substantially slower than the first four.

CID and photodissociation studies showed predominant loss of S_2 with little or no loss of S atom. While these results are consistent with structures involving coordinated S_2 units, polysulfide ring structures also dissociate by S_2 loss and cannot be ruled out for FeS_n^+, $n = 4$–6. Photodissociation thresholds provided absolute bond energies for the iron sulfides, from which various thermochemical values were calculated. These data yield loss of either S_2 or S_3 as the lowest energy process for these species.

Acknowledgement is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the U.S. Department of Energy (DE-FG02-87ER13766) for supporting this research and to the National Science Foundation (CHE-8612234) for providing funds for the advancement of FTMS methodology. The authors also thank Ian Rothwell for helpful discussions.

Registry No. Fe^+, 14067-02-8; FeS^+, 60173-22-0; ethylene sulfide, 420-12-2.

Time-Resolved Studies of "Salt Effects" on Weak Acid Dissociation

J. Lee

Contribution from the Picosecond and Quantum Radiation Laboratory, P.O. Box 4260, Texas Tech University, Lubbock, Texas 79409. *Received February 8, 1988*

Abstract: Using the photon initiated weak acid 2-naphthol as a probe for local structure on subnanosecond time scales, a variety of specific effects, including quenching of the excited state, and various degrees of enhancement or inhibition of the proton dissociation process have been observed. Both urea and Na_2SO_4 up to molar concentrations are inert toward the proton dissociation reaction. The most common behavior is exhibited by LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$. At different "critical" concentrations, specific for each salt, they totally block the otherwise fast proton dissociation process. The latter result is believed to be caused by hydration of cations and anions and the consequent loss of "free" water molecules necessary for the rapid production of $(H_9O_4)^+$. At lower concentrations there is active competition between the hydrated ions and the proton for available "free" water. A "kinetic solvation number" for each electrolyte system, determined from a random walk matrix analysis, is used to explain the observed results. These experiments are the first that are capable of investigating the "chemical structure" of outer-sphere hydration shells of simple ions.

Picosecond and femtosecond kinetic spectroscopies are changing the way chemical reactions are regarded. Continuum models[1-3] are having to be replaced by molecular-level descriptions. Weak acid processes in aqueous media containing ions or polar solutes is yet another example where these new methods can make an impact. Such processes form a part of a wider class of ionic reactions in aqueous salt solutions that play a major role in chemistry. Understanding chemical reactions in ionic solutions is also important in biology[4] where primary processes such as charge transfer take place in an ionic environment.

Because of the strongly different acidities[5-9] of 2-naphthol in its ground (2-ROH, $pK_a = 9.8$) and electronically excited (2-ROH*, $pK_a^* = 2.6$) states, this molecule can be utilized as a "photon initiated acid".[8,9] When the acid state is formed by an ultrashort light pulse, associated changes in the surrounding liquid medium can be probed on the nanosecond time scale of the 2-ROH* lifetime. Because of this brief lifetime, only the most rapid deprotonation reactions are detected by this technique. For example, it was found[8,9] that proton dissociation from 2-ROH* is immeasurably slow in pure alcohol but can be activated by a water "cluster" having a minimum of four molecules. The proton dis-

---

(1) (a) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold: New York, 1958. (b) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd revised ed.; Butterworths: London, 1965. (c) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum: New York, 1970.

(2) Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973.

(3) Smedley, S. I. *The Interpretation of Ionic Conductivity in Liquids*; Plenum: New York, 1980.

(4) *Water and Ions in Biological Systems*; Pullman, A., Vasilescu, V., Packer, L., Eds.; Plenum: New York, 1985.

(5) Forster, Th. Z. *Electrochem.* **1950**, *54*, 531.

(6) Weller, A. Z. *Electrochem.* **1952**, *56*, 662.

(7) Weller, A. Z. *Physik. Chem.* (*Frankfurt am Main*) **1958**, *17*, 224.

(8) Lee, J.; Griffin, R. D.; Robinson, G. W. *J. Chem. Phys.* **1985**, *82*, 4920.

(9) Lee, J.; Robinson, G. W.; Webb, S. P.; Philips, L. A.; Clark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 6538.

0002-7863/89/1511-0427$01.50/0 © 1989 American Chemical Society

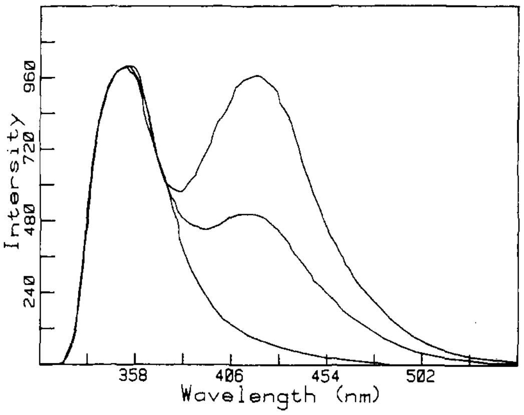


Figure 1. Emission spectra of 2-naphthol in 0.1 M LiF (top), neutral H_2O (middle), and 4 M LiCl (bottom) solutions at 20 °C: λ_{exc} = 305 nm. The spectrum is normalized to its ROH band.

sociation process is thus drastically curtailed in a water/alcohol mixed solvent as the alcohol concentration increases.

More recently, we have become interested in applying these techniques to the study of weak acid dissociation in salt solutions. In this paper, we will (1) illustrate the various salt effects that can occur with the deprotonation of 2-naphthol (2-ROH*) in aqueous solutions, (2) discuss the inadequacy of using water activity for explaining the observed results, and (3) propose a kinetic model to analyze the data for the purpose of revealing relevant ionic structures of electrolyte solutions.

Experimental Section

LiCl, LiBr, NaCl, NaBr, KCl, $MgCl_2$, and $CaCl_2$ were purchased from Sigma. Na_2SO_4, $NaClO_3$, urea, and LiF (gold label) were purchased from Aldrich. 2-Naphthol, purchased from Kodak, was 99% pure. All the above chemicals were used without further purification. Water used in the experiment was triply distilled. Absorption and emission spectra of pure salt solutions were checked between 260 and 600 nm. No spectrum that could be attributed to impurity or contamination was detected. The concentration of 2-naphthol was maintained below 5×10^{-5} M. The emission spectra and the lifetimes of 2-naphthol were measured in various salt solutions (0–9 m) at 0, 20, 40, 60, and 80 °C. The detailed experimental apparatus for lifetime measurements has been published elsewhere.[8]

Results

The three emission spectra in Figure 1 are from 2-naphthol in pure water, LiF, and LiCl solutions. The intensity behavior of 2-naphtholate (2-RO^{-}*) emission at 423 nm indicates that proton dissociation is enhanced in LiF solution and retarded in LiCl solution. The enhancement in LiF comes about because F^- is a weak base. Termination of the 2-ROH* deprotonation process by addition of NaCl has already been reported.[10-12] The degree of retardation is dependent on the salt concentration and was attributed to the "rupture of the water structure" upon the addition of salt.[11,12] A detailed investigation of this group of salts will be described later in this paper.

The same straightforward spectroscopic techniques show that Na_2SO_4, $MgSO_4$, and urea at molar concentrations have no effect whatsoever on the deprotonation of 2-ROH*. The inert character of Na_2SO_4 has also been observed[11] for 1-naphthol and is probably caused by the weak ionic dissociation of the sulfates.[13] The case of urea is particularly interesting, since it has long been considered a strong "structure breaker" in water.[14] However, the 2-ROH* dissociation results show that for proton hydration, urea does not even behave as a diluent (statistical structure breaker).[15] Clearly, the structure making/breaking concept must depend on the specific property or experiment in question. Apparently, every water molecule bound to urea can participate in the rapid formation of $(H_9O_4)^+$. Hydration of the proton simply overwhelms the much weaker urea/water interactions. Furthermore, temperature measurements show that no additional activation barrier is contributed by the presence of urea or the sulfates.

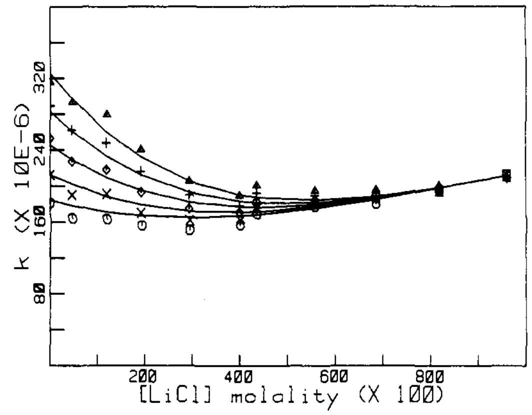


Figure 2. Total decay rates (k) of protonated 2-naphthol as a function of LiCl concentration and temperature: ○ = 0 °C, × = 20 °C, ◇ = 40 °C, + = 60 °C, △ = 80 °C. Solid curves are fitted data.

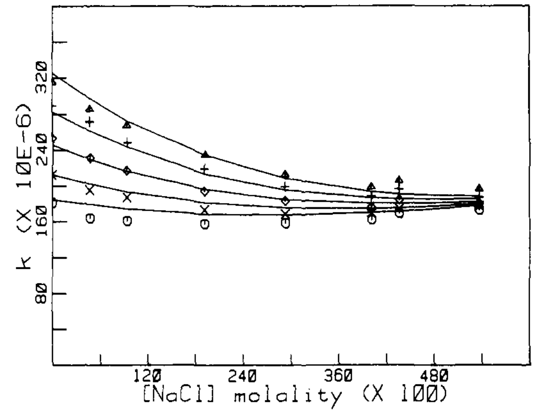


Figure 3. Total decay rates (k) of protonated 2-naphthol as a function of NaCl concentration and temperature: ○ = 0 °C, × = 20 °C, ◇ = 40 °C, + = 60 °C, △ = 80 °C. Solid curves are fitted data.

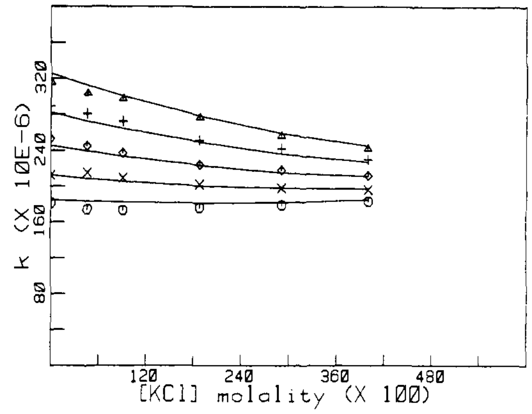


Figure 4. Total decay rates (k) of protonated 2-naphthol as a function of KCl concentration and temperature: ○ = 0 °C, × = 20 °C, ◇ = 40 °C, + = 60 °C, △ = 80 °C. Solid curves are fitted data.

Solutions of LiBr and NaBr were found to quench 2-ROH* completely. The effective quencher is the Br^- ion, and the

---

(10) Harris, C. M.; Selinger, B. K. *J. Phys. Chem.* **1980**, *84*, 891.

(11) Webb, S. P. *Picosecond Studies of Excited State Proton Transfer Reaction*; Ph.D. Thesis, University of California, Berkeley, CA, 1985.

(12) Shizuka, H.; Ogiwara, T.; Narita, A.; Sumitani, M.; Yoshihara, K. *J. Phys. Chem.* **1986**, *90*, 6708.

(13) Sillen, L. G. *Stability Constants of Metal-Ion Complexes. Suppl. No. 1 Part I. Inorganic Ligands*; Special Publ. 25; The Chemical Society: London, 1971; pp 135–136.

(14) Frank. H. S.; Franks, F. *J. Chem. Phys.* **1968**, *48*, 4746.

(15) Franks, F. In *Hydrogen-Bonded Solvent Systems*; Covington, A. K., Jones, P., Eds.; Taylor and Francis: London, 1968; pp 31–47.

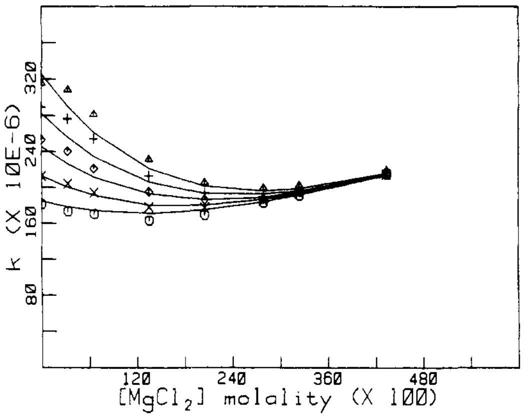


Figure 5. Total decay rates (k) of protonated 2-naphthol as a function of $MgCl_2$ concentration and temperature: ○ = 0 °C, × = 20 °C, ◊ = 40 °C, + = 60 °C, △ = 80 °C. Solid curves are fitted data.

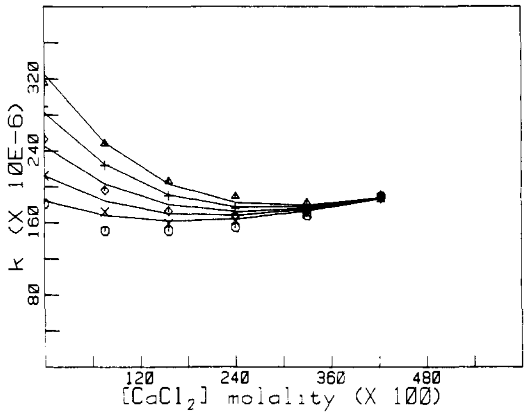


Figure 6. Total decay rates (k) of protonated 2-naphthol as a function of $CaCl_2$ concentration and temperature: ○ = 0 °C, × = 20 °C, ◊ = 40 °C, + = 60 °C, △ = 80 °C. Solid curves are fitted data.

quenching rate constant was measured to be 0.274 ns^{-1} M^{-1}.

Salts that retard the 2-ROH* deprotonation process deserve further investigation. By using such salts, the ionic structure of electrolyte solutions can be probed through a study of different degrees of ion-induced retardation on the deprotonation process. The results of time-resolved studies of 2-ROH* emission as a function of [LiCl], [NaCl], [KCl], [$MgCl_2$], and [$CaCl_2$] are shown in Figures 2–6. In addition to retardation, a weak quenching of 2-ROH* is also observed at high salt concentrations. The quenching rate k_q can be determined from the slope of the straight line drawn from the high concentration end to the pure water end at 0 °C. The proton dissociaton rate k_{dis} can then be obtained by subtracting this background value from the total rate. Because of an activation energy (2.6 kcal/mol) for 2-ROH* deprotonation,[8,9] the emission is temperature dependent but less so as salt is added and the deprotonation component decreases. All five figures should be compared with Figure 2 of ref 8 for water/alcohol mixtures, and differences in curvature as a function of concentration and temperature should be noted for different electrolyte solutions.

Discussion

In spite of its failure to explain the LiF, LiBr, $MgSO_4$, Na_2SO_4, and urea results, a decrease in water activity (a_w) has been used rather successfully to explain the retardation of the deprotonation process in other salts.[16,17] It was found that the deprotonation rate correlates reasonably well with the water activity of the salt solutions

$$k_{dis} = k^{\circ}_{dis} a_w^{\,n} \qquad (1)$$

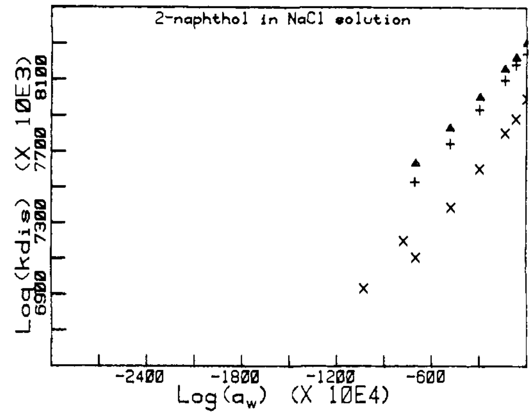


Figure 7. Log (k_{dis}) vs log (a_w) for NaCl solutions at 20 °C (×), 60 °C (+), and 80 °C (△). The data for water activity are obtained from ref 21.

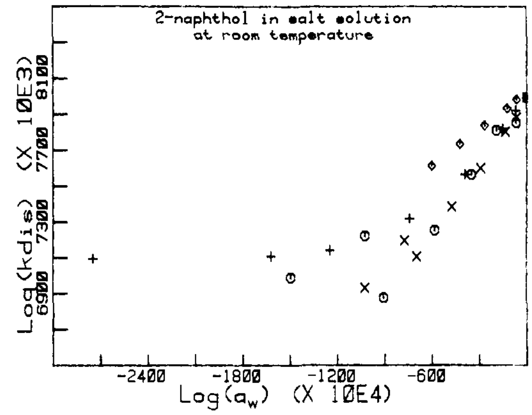


Figure 8. Log (k_{dis}) vs log (a_w) at 20 °C for LiCl (○), NaCl (×), KCl (◊), and $MgCl_2$ (+). The data for water activity are obtained from ref 21.

where k_{dis} and k°_{dis} are proton dissociation rates in water with and without salt. The constant n, which depends on the characteristics of the parent molecule, varies from 6 to 10.[18] Equation 1 can be rewritten[19,20]

$$k_{dis} = k^{\circ}_{dis} \exp[-nh\textstyle\sum m_i\nu_i/55.56] \qquad (2)$$

in terms of the osmotic coefficient h of the solutions, where m_i and ν_i are molality and stoichiometric number, respectively, of the ions. The constant n was rationalized as the number of water molecules required for hydration of a proton.[16] Such a simple relation, if correct, would indicate that the hydration structure of an ion in an electrolyte solution can be fully represented by its osmotic coefficient. To test the validity of these relationships, a systematic test of eq 2 as a function of proton donors, salt types, salt concentrations, and temperatures is desired.

Figure 7 shows plots of log (k_{dis}) of 2-ROH* in NaCl solutions as a function of log (a_w) at 20, 60, and 80 °C.[21] The results agree with previous room temperature measurements.[16] Moreover, the validity of eq 2 is seen to extend to high temperatures and gives a constant n (=10) for NaCl solutions.

Despite the success of eq 2 for NaCl solutions, this formulation using different salts (Figure 8) or proton donors becomes un-

---

(16) Huppert, D.; Kolodney, E.; Gutman, M.; Nachliel, E. *J. Am. Chem. Soc.* **1982**, *104*, 6949.

(17) Politi, M. J.; Chaimovich, H. *J. Phys. Chem.* **1986**, *90*, 282.

(18) Gutman, M.; Huppert, D.; Nachliel, E. *Eur. J. Biochem.* **1982**, *121*, 637.

(19) (a) Conway, B. E. In *Activity Coefficients in Electrolyte Solutions*; Pytkowicz, R. M., Ed.; CRC Press, Inc.: Boca Raton, FL, 1979; Chapter 5. (b) Johnson, K. S.; Pytkowicz, R. M. In *Activity Coefficients in Electrolyte Solutions*; Pytkowicz, R. Mm., Ed.; CRC Press, Inc.: Boca Raton, FL, 1979; Vol. II, Chapter 1.

(20) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd revised ed.; Butterworths: London, 1965; pp 29–30.

(21) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd revised ed.; Butterworths: London, 1965; pp 476–495.

satisfactory. In comparison to $n = 10$ for NaCl, the fitted n for KCl is 6. Furthermore, for $MgCl_2$, instead of a linear relationship between log (k_{dis}) and log (a_w), the plot is very nonlinear. Although termination of k_{dis} is apparent at 9.6 m LiCl (Figure 2) and 5 m $MgCl_2$ (Figure 5) and $CaCl_2$ (Figure 6), eq 2 gives a substantially larger k_{dis} than the observed one for these electrolyte solutions and thus contradicts the experimental findings.

Preliminary work using a proton abstraction molecular probe[22] have also confirmed the failure of eq 2 and, as in the present experiments, has revealed distinct differences of the electrolytes studied. Hence, it becomes apparent that some other model must be used to analyze these results.

Ion Solvation

The solvation environment of an ion is generally divided into three regions: (1) the primary solvation shell, where the solvent molecules are tightly bound to the ion; (2) the bulk region, where the properties of the pure solvent are preserved; and (3) the intermedium region, which bridges the other two regions and dynamically participates in the interaction between them.[1] It is important to realize, however, that, in accordance with gas-phase cluster studies,[23] the hydration energy per water molecule probably does not fall into a discrete set of regions such as this but rather decreases monotonically with the addition of water molecules. We will therefore retain this terminology only in a general sense.

The primary solvation shell has been studied by conventional, static spectroscopic techniques. The intermedium region, because of its dynamic character, is inaccessible by steady-state techniques and is not well characterized.[24] The problem was recognized many years ago by Taube and co-workers,[25] who made a careful distinction between a "kinetic solvation number" and a "primary solvation number". The experimental method described in this paper, using an ultrafast response photon initiated acid as a probe, is capable of examining the structure of an electrolyte solution in the region near the ion. Consequently, our experimental results should closely relate to the intermedium region and Taube's "kinetic solvation number".

The slow down of proton-transfer rates of 2-ROH* as the salt concentration increases is mainly caused by the water molecules being bound to the salt in the manner of the two innermost hydration shells described above. The most loosely attached water molecules comprising the intermedium region may be able to detach from the ion and reorient to hydrate the proton on the time scale governed by the excited state lifetime of the photon initiated acid. Strongly bound, primary shell water cannot participate in the proton-transfer process on this time scale. The number n_0 of such strongly bound water molecules attached to an ion and incapable of entering into the proton hydration process depends not only on the characteristics of the ion, such as charge and polarity, but also on the characteristics of the probe molecule, such as lifetime and pKa*. Consistent with the concept of the "kinetic solvation number", n_0 is the result of dynamical competition between proton dissociation/hydration and ion hydration processes in the quasiequilibrium state reached during the excited state lifetime of the photon-initiated acid.

A Kinetic Model

Since the electrolyte problem and the previously studied water/alcohol problem (ref 8) resemble each other in their effect on 2-ROH* deprotonation, a similar kinetic explanation was sought. Taking N as the number of water molecules required for forming the proton acceptor, i.e., $N = 4$ for $H_9O_4^+$, there are $N + 1$ possible microscopic configurations for the photon-initiated acid: N or more free water molecules, $N - 1$ free waters, $N - 2$ free waters, ... zero free waters. Only in the first case is proton dissociation possible during the lifetime of the excited state acid. The random walk feature of the problem enters since these structures, and thus the number of free waters, fluctuate during the time scale set by this lifetime. This picture is similar to that in the alcohol/water mixed solvent experiments, where water molecules are physically displaced by the presence of the alcohol.

Table I. Ionic Quenching Constant (k_q), Critical Concentration (m_0) and Kinetic Solvation Number (n_0) for Electrolytes

electrolyte	k_q (/ns/m)	m_0 (mol/kg)	n_0
LiCl	0.011	11.11	5.00
NaCl	0.011	11.11	5.00
KCl	0.011	21.00	2.65
$MgCl_2$	0.023	6.00	9.25
$CaCl_2$	0.017	6.00	9.25

New features enter, however, for the electrolyte solutions, since, instead of being inert toward the photon-initiated acid, as alcohol molecules are, the added ions may (1) tie up water in their primary hydration shells and reduce the population of free water for accepting protons and (2) interact with and quench the excited state acid to varying degrees. An extreme case of the quenching effect was seen to occur for added Br^- ions, where quenching is so rapid that proton dissociation from the acid does not occur. The presence of quenching can be clearly seen in Figures 2, 3, 5, and 6 from the variations of rates with salt concentration and salt type at the highest concentrations. Table I indicates that Cl^- probably dominates this weak quenching effect.

To proceed with the analysis, we first consider high salt concentrations. A "critical" concentration m_0 is assumed for each electrolyte solution. At this concentration proton dissociation during the lifetime of the excited state acid is no longer capable of competing with the ion for water. Thus, n_0 (= $55.56/m_0$) water molecules are so firmly bound to each ion at the temperature of the experiment that they are incapable of participating as proton acceptors. With this assumption, the fraction of free water $[H_2O]_f$ can be established for different electrolyte concentrations

$$[H_2O]_f = 1 - m/m_0 \qquad (3)$$

where $[H_2O]_f = 0$ for $m \geq m_0$.

Next, an ionic quenching rate parameter k_q is assumed for each electrolyte. This quenching constant can be easily determined from the slope of the 0 °C curve at high electrolyte concentrations ($m > m_0$), where deprotonation is blocked. The total decay rate at these concentrations is simply the sum of the intramolecular decay rate of the probe molecule k_0 in the absence of proton dissociation and the quenching rate mk_q. These values of k_q, along with m_0 and n_0, are summarized in Table I.

We would expect the linear dependence of the quenching rate on m to remain valid below m_0 despite the presence of the deprotonation rate k_{dis}. In order to satisfy this requirement for an ensemble of microscopic configurations, the decay rate of the ith configuration is written as follows

$$k(i \neq 0) = k_0 + (i/N)m_0k_q \qquad (4)$$

where $i = 1, 2, ...N$. In the case where $i = 0$, the probe molecule is situated in a free water environment. Proton dissociation is possible, but there is no quenching. Thus,

$$k(i = 0) = k_0 + k_p \exp(-\Delta E/k_BT) \qquad (5)$$

In the case of 2-naphthol, $\Delta E = 2.62$ kcal/mol and $k_p = 8.89$ ns^{-1}. Finally, a cluster of at least four water members is assumed to be the proton acceptor. This assumption is based on the results from previous water/alcohol studies.[8,9] In fact, the cluster size of 4 will be seen to give the most reasonable fit of the experimental data.

By using the above description, we now note that, as before,[26] a 6 × 6 random walk matrix can be used to describe the dynamics of the problem. The system may remain in its original state

---

[22] Pines, E.; Huppert, D.; Gutman, M.; Nachliel, N.; Fishman, M. *J. Phys. Chem.* **1986**, *90*, 6366.

[23] Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466.

[24] Hunt, J. P. *Metal Ions in Aqueous Solutions*; W. A. Benjamin, Inc.: New York, 1963; Chapter 3.

[25] Swinehart, J. H.; Rodgers, T. E.; Taube, H. *J. Chem. Phys.* **1963**, *38*, 398.

[26] Moore, R. A.; Lee, J.; Robinson, G. W. *J. Phys. Chem.* **1985**, *89*, 3648.

(diagonal matrix elements), interchange randomly ($i \pm 1$ off-diagonal matrix elements) between any of the five excited state microscopic configurations, or irreversibly decay to the ground state from any one of these excited state configurations (off-diagonal matrix elements connecting the ground state). The ith decay rates are given by eq 4 or 5, while the other off-diagonal rates are diffusional. In this way, a simulated lifetime can be calculated and compared with the experimental data. The calculated data are indicated by solid curves in Figures 2–6. The m_0 and n_0 values used for each electrolyte solution are those given in Table I and thus are assumed in this lowest approximation not to be appreciably affected by the temperature 0–80 °C. Using a matrix size greater or smaller than 6 does not fit the experimental data well. As seen in Figure 2 of ref 8, this is in complete agreement with the previous findings.

Despite the overly simple picture, the calculated results agree pretty well with the experimental data. No distinct difference in m_0 is found between LiCl and NaCl solutions nor between $MgCl_2$ and $CaCl_2$ solutions. The variations of m_0 are in agreement with the fact that Mg^{2+} and Ca^{2+} carry twice the charge of Li^+ and Na^+, while K^+, being much larger, is less polar. A larger "kinetic solvation number" n_0 is expected for ions having more charge and a smaller size.

Calculated rates sometimes lower than the observed ones are noticeable at high temperature, while the reverse is seen at low temperature. This is caused by the assumption of constant m_0 for all temperature data. As the temperature increases, water molecules in the intermedium region become less strongly bound to the ion and become more capable of participating in the proton-transfer process. Hence, m_0 should increase as the temperature increases, and n_0 should decrease. Although the temperature dependence of m_0 and n_0 is not clear for the 2-ROH* experiments, where the deprotonation process itself has a strong temperature dependence, it becomes much clearer using the 1-naphthol (1-ROH*) probe where deprotonation in pure water is independent of temperature. The deprotonation of 1-ROH* becomes dependent on temperature in the electrolyte solutions, giving clear evidence that an activation energy exists for removing water molecules from the intermedium region of the ion for participating in the proton hydration process. These results are consistent with the temperature trends found in this paper and will be reported in a separate paper.[27]

The complete separation of effects caused by cations or anions is not possible at present. However, a comparison of results using NaCl and $NaClO_3$ shows no apparent difference except for the value of k_q. Consequently, the cation plays a more significant role in 2-ROH* deprotonation than the anion. A similar finding was also observed in a proton abstraction system.[22] In fact, the residence time for the "bound" water around Cl^-, estimated to be a few picoseconds from MD simulations[28] and magnetic resonance data,[29] is compatible with the orientation time of bulk water molecules. This time is sufficiently short so that it does not impede the participation of Cl^- bound waters in proton hydration. On the other hand, a residence time of a few milliseconds is found for Mg^{2+} and Ca^{2+}. Another reason for the cation effect on proton hydration may be that the cation is competing for the same negative part of the water molecule that the proton is. This view is consistent with the ideas expressed in earlier papers that proton hydration requires *four properly oriented water molecules*, not any four water molecules having unspecified orientations. Hence, the "kinetic solvation number" n_0 listed in Table I for different electrolyte solutions is most likely associated with the cation.

Conclusions

Using a photon initiated weak acid probe, we have been able to study the molecular level ionic structure of an electrolyte solution. We find that the "intermedium region" situated between bulk solvent and the primary solvation shell is not a rigidly defined region but rather depends on dynamic competition between local environmental factors. As a result, the observed "kinetic solvation number" of each electrolyte, is more relevant than the water activity for explaining various salt effects on weak acid deprotonation.

Acknowledgment. I thank Professors G. Wilse Robinson and P. K. DasGupta for valuable discussions. Support by the Robert A. Welch Foundation (D-0005 and D-1094) and the National Science Foundation (CHE8611381) is acknowledged.

Registry No. LiCl, 7447-41-8; NaCl, 7647-14-5; KCl, 7447-40-7; $MgCl_2$, 7786-30-3; $CaCl_2$, 10043-52-4; $(H_9O_4)^+$, 12501-73-4; 2-naphthol, 135-19-3.

---

(27) Lee, J.; Robinson, G. W., manuscript in preparation.

(28) Hertz, H. G. *Water, a Comprehensive Treatise*; Franks, F.; Ed.; Plenum: New York, 1973; Vol. 3.

(29) Impey, R. W.; Madden, P. A.; McDonald, I. R. *J. Phys. Chem.* **1983**, *87*, 5071.