

Microhydration: Understanding Solute-Solvent Interactions at Molecular Level

*D.K. Maity^{1,2}

¹Director's Office, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India

²Homi Bhabha National Institute, Mumbai-400094, India

ABSTRACT

Structure, molecular properties and energy parameters of microhydrated clusters of a few chemical systems are reported. Ground and excited state calculations are carried out applying sophisticated electronic structure theory to account dispersion interactions accurately. Dissociation of acid molecules in water, understanding of photoacidity and solubility of halogen gases are discussed following studies on microhydrated clusters.

Keywords: Cluster, molecular property, solute-solvent interaction, microhydration, photoacid, first principle calculation.

Introduction

In recent years, the study on microhydration of neutral and charged chemical species has been a subject of intense research both from experimental and theoretical points of view to understand the structural, energetic, spectroscopic, and dynamic aspects of hydration at molecular level.¹⁻⁹ This is mainly because of the strong dependency of the properties on size and geometry of the hydrated clusters of these species. When a solute is added to a solvent water medium, the water molecules those are in immediate vicinity of the solute get rearranged to allow the solute going through the hydration process. The electron distribution pattern of the added solute plays the key role to shape up the structure of the water network around the solute. The properties of these solute embedded water clusters provide basic understanding of the fundamental interactions those are responsible for hydration process at molecular level and thus it is important not only to chemists but also to physicists, biologists and researchers in material science. Microhydrated clusters are formed by the step-

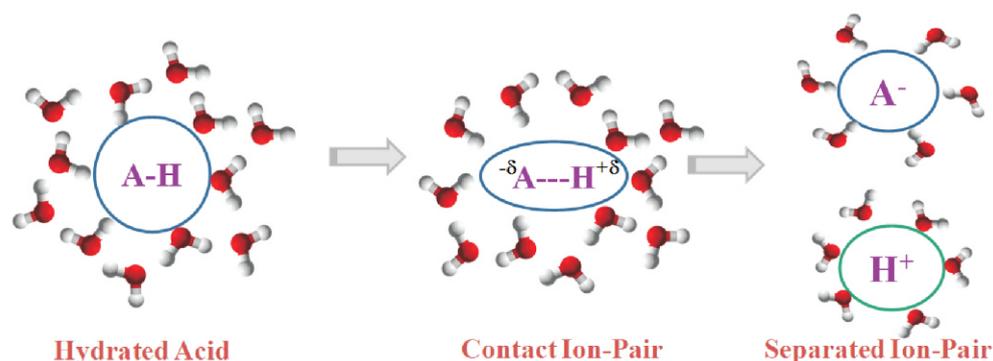
wise addition of water molecules to a chemical species. These clusters are stabilized by hydrogen bonding. Hydrogen bonds play a key role in determining the three dimensional structures of the cluster. It is known that implicit macroscopic solvation models fail to accurately describe the effect of hydration on the structure and properties of molecules in many cases. Thus, consideration of explicit solvent water molecules is very essential to understand the effect of hydration.

In what follows, computed results of microhydrated clusters of certain interesting systems are presented focusing on three selected molecular properties. Calculations are carried out applying high level electronic structure theory.

Results and Discussion

Acid Dissociation

Acids (AH) are ubiquitous in nature. Acidic solutions play a major role in a wide range of fields. A plethora of chemical, physical and biological phenomena involves acid-water interactions. Be it an enzyme catalysed reaction in a biological system or the formation of cloud condensation nuclei in the atmosphere, it all depends on the proton transfer process between the acid and water molecules, that is, acidity of the acid. Further, acid-water molecular clusters provide an ideal system to study the relation between solvation and reactivity, as ionization of the acid molecule occurs during the progress from molecular clusters to aqueous solution. In macroscopic description, a strong acid signifies an acid that ionizes completely in an aqueous solution whereas a weak acid does not ionize fully in such an environment. Thus, the ability to transfer a proton to a water molecule is the answer to differentiate an acid based on its strength. In the context of the microscopic or molecular level description of the strength of an acid, one may ask a



Scheme 1: Schematic representation of hydration of acids. AH represents the acid molecule and the red and grey balls represent oxygen and hydrogen atoms of the water molecule respectively. The reorientation of the water molecules around the acid molecule, the weakening of the A-H bond and formation of solvent separated ion pair is shown.

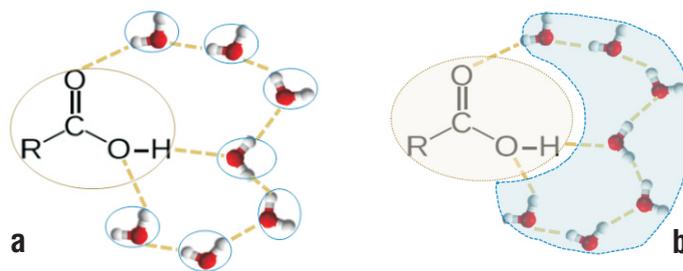
fundamental question: How much water is required to ionize an acid? The answer to this question involves a microscopic study of the hydration of acids. In acid-water clusters ($\text{AH}\cdot n\text{H}_2\text{O}$), solute acid molecule forms hydrogen bonds with the solvent water molecules present in the immediate neighbourhood. As a result of intermolecular interactions between the acid molecule and solvent water molecules, the A-H bond of the acid molecule weakens and proton transfer from the acid molecule to solvent water molecules occurs, leading to dissociation of the acid molecule, as depicted in Scheme 1.

The process of hydration of an acid molecule involves formation of contact ion pair followed by solvent separated ion pair, and yields hydrated protons in either Eigen ($\text{H}_3\text{O}^+\cdot 3\text{H}_2\text{O}$) or Zundel ($\text{H}_3\text{O}^+\cdot \text{H}_2\text{O}$) forms. Thus, determining the number of water molecules needed to stabilize the hydrated ion pair will tell us the number of water molecules that are needed to ionize an acid. A few recent theoretical studies report the number of water molecules needed to ionize H_2SO_4 , HCl , HNO_3 and HClO_4 . Experimental reports of proton transfer in hydrated acid molecules are mainly based on matrix isolation and thin-film IR studies. Based on the study of amorphous thin films of HNO_3 and water, it is reported that three solvent water molecules are required to stabilize ionized HNO_3 . Gas-phase ultra-fast pump-probe experiments on HBr -water clusters led to the conclusion that five water molecules are needed to induce ionization of HBr .⁵ High resolution mass-selective infrared laser spectroscopy are also employed to observe the formation of hydronium ion in the tetra-hydrated cluster of HCl , within superfluid He cluster, at a temperature of 0.37 K. Ab initio molecular dynamics simulations technique used to explore the free energy surface of the HCl -water system and to explain how the proton transfer barrier is surmounted under the cryogenic conditions of the experiment. The addition of a fourth water molecule to the unionized tri-hydrate is predicted to yield a "partially aggregated" complex which then transforms into the structure containing Cl^- and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$.

The A-H bond length is an indicator for ionization of acid molecules in hydrated acid clusters. Upon hydration, due to hydrogen bonding between the proton of the acid molecule and O atom of the nearest water molecule, weakening of the A-H bond occurs. This leads to elongation of A-H bond. With increase in size of the hydrated acid cluster, the A-H bond length also increases and finally after dissociation of the acid, the A-H bond distance would be in the range of H-Bond lengths. There is a corresponding decrease in the H...O H-bond distance, which finally reduces to O-H covalent bond length of the hydronium ion, upon acid dissociation. These distances are usually determined computationally, as their experimental measurement is difficult because the increase is usually a few hundredths of an angstrom.

Stabilization and interaction energy

Based on the geometry of the most stable conformers of free and hydrated molecules, energy parameters are defined to understand the molecular interactions existing within the molecular clusters. Solvent-induced stabilization energy of hydrated clusters of the molecule, $\text{M}\cdot n\text{H}_2\text{O}$, is defined as $E_{\text{stab}} = E_{\text{M}\cdot n\text{H}_2\text{O}} - (n \cdot E_{\text{H}_2\text{O}} + E_{\text{M}})$, where, $E_{\text{M}\cdot n\text{H}_2\text{O}}$ refers to the energy of the hydrated cluster, $\text{M}\cdot n\text{H}_2\text{O}$, $E_{\text{H}_2\text{O}}$ and E_{M} correspond to the energy of a single water and molecule, respectively. By definition, E_{stab} represents stabilization of the molecule due to its interactions with the solvent water molecules. E_{stab} gives the stabilization of the molecule on account of addition of solvent water molecules, which includes both solute-solvent as well as solvent-solvent interactions, as depicted in Scheme 2a for



Scheme 2: a) Schematic diagram depicting the solvent stabilization energy, E_{stab} , for a hydrated carboxylic acid system, $\text{RCOOH}\cdot n\text{H}_2\text{O}$. This energy parameter includes solute-solvent as well as solvent-solvent interactions. The red and white balls represent oxygen and hydrogen atoms respectively of water molecule. b) Schematic diagram depicting the interaction energy, E_{int} , for a hydrated carboxylic acid system, $\text{RCOOH}\cdot n\text{H}_2\text{O}$. This energy parameter contains only solute-solvent interactions. The red and white balls represent oxygen and hydrogen atoms respectively of water molecule.

carboxylic acid system. To isolate the solute-solvent interactions from the solvent stabilization energy, excluding any solvent-solvent stabilization, interaction energy, E_{int} is defined as $E_{\text{int}} = E_{\text{M}\cdot n\text{H}_2\text{O}} - (E_{(\text{H}_2\text{O})_n} + E_{\text{M}})$. $E_{(\text{H}_2\text{O})_n}$ and E_{M} correspond to the energy of the water cluster and the acid molecule, respectively, in the same geometry as is present in the hydrated acid cluster.

For evaluation of $E_{(\text{H}_2\text{O})_n}$, solute part RCOOH is removed from the optimized geometry of the cluster, followed by a single-point energy calculation. Following a similar procedure for the evaluation of E_{M} , the $(\text{H}_2\text{O})_n$ part is removed from the optimized geometry of the hydrated cluster, followed by a single-point energy calculation. Thus, the interaction energy includes only solute-solvent interactions, removing all solvent-solvent interactions as depicted in Scheme 2b. The calculations are done at $\omega\text{B97X-D/ aug-cc-pVDZ}$ level of theory.

The plot of calculated interaction energy (E_{int}) vs. n , number of water molecules for $\text{HCOOH}\cdot n\text{H}_2\text{O}$ clusters are also displayed in Fig. 1a. Calculated stabilization and interaction energy is very close for a few small size clusters. But when inter molecular hydrogen

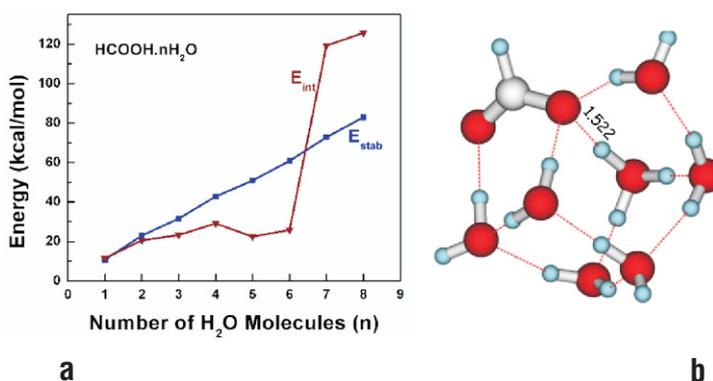


Fig. 1: a) Plot of calculated stabilization energy, E_{stab} and interaction energy, E_{int} at B97XD/aug-cc-pVDZ level in kcal/mol vs. n , number of water molecules for $\text{HCOOH}\cdot n\text{H}_2\text{O}$ clusters. A minimum of seven water molecules are needed to dissociate formic acid molecule; b) Optimized minimum energy structure of $\text{HCOOH}\cdot 7\text{H}_2\text{O}$ cluster showing bond distance of the dissociating O-H bond.

bond among water molecules starts to build up; solvation energy surpasses the interaction energy. The variation of solvent stabilization energy with size of the cluster (n) is observed to be linear. Interaction energy calculated for cluster size ($n=4-6$) is much smaller than solvent stabilization energy for same size clusters. Note that interaction energy is much higher for charged system. Thus, variation of interaction energy with size of the cluster (n) shows sharp increase for hepta- and octa- hydrated cluster as these represents charge separated state of formic acid. The interaction energy (E_{int}) is the measure of the interaction between formic acid and solvent water units. Interaction energy of these clusters is decomposed into different components and electrostatic interaction is observed to be the major contributor.⁷

The structure of a hydrated acid cluster depends on the delicate balance between the hydrogen bond stabilization, coulombic attraction and proton transfer energy. An interesting point noted is the extra stability of hydrogen bonded closed ring conformers of the hydrated acid clusters, relative to open chain conformers. This is not surprising as the number of stabilizing hydrogen bonds are more in case of the closed ring conformers. An elongation is seen in the acidic O-H bonds of the hydrated acid clusters, in all cases, with increase in number of water molecules. This is expected as the hydrogen bonds between the acid molecule and the water molecules causes weakening of the acidic hydroxyl bonds. It is observed that a minimum of six water molecules are needed to dissociate trifluoroacetic acid molecule while eight water molecules are needed for the dissociation of benzoic acid molecule. In case of oxalic acid molecule, the dissociation of the first acidic proton requires the presence of at least seven water molecules. The structure of the ionized acid-water cluster resembles that of the Eigen cation interacting with the carboxylate anion surrounded by the remaining water molecules. The proton transfer in $\text{CH}_3\text{COOH}\cdot n\text{H}_2\text{O}$ and second proton transfer in $(\text{COOH})_2\cdot n\text{H}_2\text{O}$ are not observed even when $n=8$. The proton transfer from an acid molecule to the solvent water molecules in a hydrated acid cluster can be explained by the stronger stabilization of the contact ion pairs upon hydration, compared to the neutral acid molecule.

Photoacids

Photo acids undergo significant enhancement in their acidity upon electronic excitation. This leads to excited state proton transfer to the solvent. The change in electron density distribution of a photo acid can be determined from its excited state acidity constant. This information is of much interest to both photo chemists, who can study the differences in reactivity of molecules in ground and excited state, and theoretical chemists, who can calculate the excited state electronic structure and the nature of the transitions involved. The significant change in acidity of these molecules makes them an ideal system to probe solute-solvent interactions and solvent polarities. Photo acids can be used as molecular probes for determining the structural transitions of proteins under various conditions. Water accessibility in biological surfaces can also be probed using photo acids. The excited state pKa of a photo acid is generally determined from the Farster cycle, based on absorption and emission data. It can also be determined using photo-potentiometry.

In aqueous solution, aromatic compounds like phenol and 2-naphthol have ground state pKa values of 10.0 and 9.2 respectively, while their excited state pKa values are just 3.6 and 2.8 respectively. Theoretical calculations to explain excited state proton transfer in phenols has been reported. Two different explanations

have been proposed for the increase in acidity in the first excited singlet state. One proposition attributes the increase in acidity to a charge transfer in the photo acid. According to the other proposition, the enhanced excited state acidity is largely determined by the deprotonated photo acid.

It is reported that the acidity constants of ground and first excited triplet states of 2-naphthol are comparable while that of the first excited singlet state differ by a factor of $\sim 10^6$. The studies were based on flash photolysis, fluorescence and phosphorescence measurements. They provide a qualitative explanation for this observation based on electron density. The difference in the pKa value of ground state and excited states of 2-naphthol could be reflected in the number (n) of water molecules needed for their ionization. Studies on microhydration of 2-naphthol (nap) at ground (nap_{S_0}), first excited triplet (nap_{T_1}) and first excited singlet (nap_{S_1}) states is carried out applying DFT based electronic structure method considering a suitable functional for excited state calculations. It is seen that even in the presence of four water molecules, proton transfer from naphthol to water molecules is not observed for either ground or first excited triplet state. However, proton transfer becomes a barrier-less process for first excited singlet state of tetra-hydrate of naphthol.⁸

A rigid potential energy scan of the acidic O-H bond of $\text{nap}\cdot 4\text{H}_2\text{O}$ at the first excited singlet state reveals that in the presence of four water molecules, the acidic proton transfer from nap to the neighbouring water molecule becomes a barrier-less process, as shown in Fig. 2. In fact, in the first excited singlet state, the tetra-hydrate becomes unstable at O-H bond distances less than 1.4 Å. The potential energy profiles show that a barrier exists for proton transfer from nap to solvent water molecules in all cases except the tetra-hydrate of nap at the first excited singlet state. In case of first excited singlet state spontaneous dissociation of the O-H bond is observed for the tetrahydrate cluster of 2-naphthol. This is in line with the experimentally observed fact that first excited singlet state is

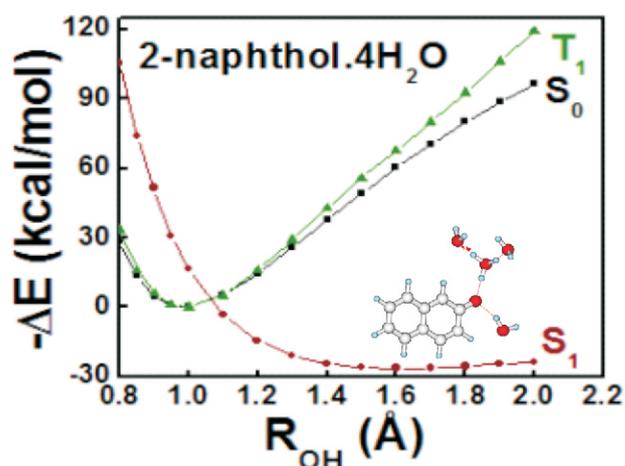


Fig.2: Rigid potential energy scan carried out applying TD-DFT at CAM-B3LYP/ aug-cc-pVDZ level for O-H bond of 2-naphthol.4H₂O, at ground, first excited triplet and singlet state. ΔE gives the relative energy of the system at each point of the scan of the dissociating O-H bond, with respect to the energy of the equilibrium geometry. Curves marked as S_0 , T_1 and S_1 represent potential energy surfaces of ground, first excited triplet and singlet states respectively of 2-naphthol.4H₂O, upon increasing the bond distance of dissociating O-H bond of the acid.

Species $X_2 \cdot nH_2O$	Stabilization energy of $X_2 \cdot nH_2O$ clusters (kcal/mol)		Interaction energy of $X_2 \cdot nH_2O$ clusters (kcal/mol)	
	X=Cl	X=Br	X=Cl	X=Br
$n = 1$	2.85	3.86	3.07	4.11
$n = 2$	9.85	5.52	4.36	5.76
$n = 3$	9.88	13.53	3.91	7.74
$n = 4$	25.82	27.68	7.42	9.58
$n = 5$	28.24	30.23	8.49	11.02
$n = 6$	45.66	47.87	9.31	11.66
$n = 7$	65.00	60.03	4.55	11.32
$n = 8$	73.25	71.26	6.57	13.73

Table 1. Calculated stabilization and interaction energy in kcal/mol for $X_2 \cdot nH_2O$ systems (X=Cl, Br; $n=1-8$) at MP2/6-311++G(d,p) level of theory.

more acidic than the ground and first excited triplet state. It is worth mentioning that no such bond dissociation is predicted in water medium when the computation is performed considering macroscopic solvent model.

Solubility of Cl_2 / Br_2 gas in water

Solubility of bromine gas is 14.9 gm compared to 0.729 gm for chlorine gas in 100 gm of water at room temperature. As these molecular species (Cl_2 / Br_2) are having zero dipole moment, one has to apply explicit solvation model to study the solvent effect rather than taking a macroscopic solvation model like Onsager's continuum reaction field model. The molecular interaction between a neutral solute and solvent water molecules as well as the hydrogen bonding interactions among the solvent water molecules can be examined in such studies placing explicit solvent molecules around a solute. Such studies provide information on the evolution of hydration motifs of X_2 (X=Cl & Br) systems in water. Electronic polarization in condensed phase can guide to evolve polarizable point charge model in studying various properties and processes including solvent effect. Thus, a systematic study in halogen-water clusters are of considerable interest to understand solute-solvent and solvent-solvent intermolecular interactions in water medium and hence for molecular modelling in aqueous phase. Calculated structures suggest that Br_2 exists as a charge separated ($Br^{+\delta}-Br^{-\delta}$) entity in the hydrated clusters but Cl_2 does not exist as a charge separated ion pair in presence of solvent water units.⁹ Table 1 presents calculated stabilization and interaction energy of Cl_2 and Br_2 hydrated clusters. One can see from the table that solvent stabilization energy increases steadily for both Cl_2 and Br_2 hydrated clusters. However, interaction energy profiles show different features for the two different gases. In case of $Br_2 \cdot nH_2O$ clusters the said energy increases and for $Cl_2 \cdot nH_2O$ clusters it increases slowly showing fluctuations and finally reaches to a lower value. The numerical values are smaller than those for hydrated clusters of Br_2 . Calculated higher interaction energy for $Br_2 \cdot nH_2O$ clusters than that for $Cl_2 \cdot nH_2O$ cluster is able to explain the higher solubility of bromine gas over chlorine gas in bulk water.

Conclusion

Implicit macroscopic solvation models fail to describe the effect of hydration on the structure and properties of several class of molecules. Explicit hydration (microhydration), leading to dissociation of acid molecules are studied. Calculated stabilization energy increases linearly on successive addition of solvent water molecules whereas sudden increase in interaction energy is predicted for the hydrated clusters of acid indicating dissociation of the acid molecules. Rigid potential energy scan for O-H bond of $RCOOH \cdot nH_2O$ cluster maybe used as an indicator to study microhydration in acid molecules to track proton transfer and formation of contact ion pairs. Microhydration studies of 2-naphthol at ground, first excited triplet and singlet states are carried out using TD-DFT. It is seen that even in the presence of four water molecules, proton transfer from 2-naphthol to water molecules is not observed for either ground or first excited triplet state. However, proton transfer becomes a barrier-less process for first excited singlet state of tetra-hydrate cluster of 2-naphthol. Higher solubility of Br_2 gas over Cl_2 gas in water could be explained based on studies of microhydrated clusters of Br_2 and Cl_2 . Overall, studies on microhydration is very important to understand several properties of molecules and ions (including metal ions) in water medium and has far reaching consequences including extraction behaviour.

Acknowledgement

Author wishes to thank the co-workers, A.K. Pathak and Parvathi K., for their significant contributions during their doctoral research.

Corresponding Author*

D.K. Maity (dkmaity@barc.gov.in)

References

- [1] X. Wang, X. Yang, J.B. Nicholas, L. Wang, *Science*, 2001, **94**, 1322.
- [2] M. Miyazaki, A. Fujii, T. Ebata, Mikami, *N. Science*, 2004, **304**, 1134.
- [3] J.M. Headrick, E.G. Diken, R.S. Walters, N.I. Hammer, R.A. Christie, J. Cui, E.M. Myshakin, M.A. Duncan, M. A. Johnson, K.D. Jordan, *Science*, 2005, **308**, 1765.
- [4] A. Gutberlet, G. Schwaab, Ö. Birer, M. Masia, A. Kaczmarek, H. Forbert, M. Havenith, D. Marx, *Science*, 2009, **324**, 1545.
- [5] K.R. Leopold, *Annu. Rev. Phys. Chem.* 2011, **62**, 327.
- [6] D.B. Millet, *Nature Geoscience*, 2012, **5**, 8.
- [7] D.K. Maity, *J. Phys. Chem. A*, 2013, **117**, 8660.
- [8] K. Parvathi, R. Kar, D.K. Maity, *J. Phys. Chem. A*, 2018, **122**, 929.
- [9] A.K. Pathak, T. Mukherjee, D.K. Maity, *J. Phys. Chem. A* 2008, **112**, 744.