A STUDY OF ASSOCIATION ENERGIES OF SEQUENTIAL $(H_2O)_n$ ($n = 2 - 10$) POLYMERS BY A LOCALIZED ACCEPTOR-DONOR ELECTROSTATIC MODEL

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ABSTRACT

The total and incremental association energies for the process $nH_2O \rightarrow (H_2O)_n$ *and* $(H_2O)_{n-1} + H_2O \rightarrow (H_2O)_n$ ($n = 2 - 10$) *are computed based on a simple localized acceptor(a)-donor(d) electrostatic model. The analysis is performed on a, da, ..., da, d sequential n-mer clusters. The total and incremental association energies and the average association energies per water molecule predicted by the model agree very well with observed values for n = 2 and those obtained from ab initio SCF MO many body calculations [J. Chem. Phys., 1994,* ***100****, 7523] for n = 2 - 6. Overall, the study provides a simple but quantitative theoretical model needed to describe the structures and energetics of small water clusters that can aid in the development of a balanced description of the global potential for these systems.*

INTRODUCTION

The importance of water as a universal solvent has resulted in a notable amount of research towards the development of interaction potentials for water clusters[1-25] as a vehicle to model the properties of bulk water. However, most of these efforts were concentrated on water dimer[1-25], theoretically[1-14] because of its small size and experimentally[15-25] because it seems very difficult to characterize clusters larger than dimers. Actually no measurements of the thermodynamics of polymers larger than the dimers were reported prior to the mid nineties[26]. Furthermore, for water clusters larger than the dimers, the ions $(H_2O)_n^+$ have not been observed[26] by conventional ionization techniques. Although some phenomena can only manifest in trimers or larger n-mers, there has only been a few reported cases[26-30] on the calculations of the binding energies and structures of even water trimer. To date, the work of Xantheas[31] and Xantheas and Dunning[32] appears to be one of the few cases in which the calculation of the binding energies of water polymers, specifically $(H_2O)_n$ ($n = 2 - 6$), are done. These authors considered cyclic $(H_2O)_n$ polymers only.

Because of the failure of the electrostatic multipole expansion in predicting the van der Waals potential minimum[33-38], the hydrogen bond in $(H_2O)_n$ clusters, especially the dimer, has been studied extensively by the *ab initio SCF delocalized molecular orbital method* both at the Hartree-Fock (HF) level and beyond[1-14, 26, 31, 32]. For a cluster made up of *n* monomers[39,40], a total n-mer cluster binding energy ΔE is defined as the total energy of the n-mer cluster minus the sum of the energies of the isolated constituent monomers

$$\Delta E = E(AB\cdots\cdots N) - \sum_{I}^{N} E_I^0 \quad ...(1)$$

At the HF level, ΔE is calculated using $\Phi^{SCF}_{AB......N}$ wave function viz:

$$\Delta E_{SCF} = \int \Phi^{SCF*}_{AB...N} H_{AB...N} \Phi^{SCF}_{AB...N} d\tau - \sum_{I}^{N} E_I^0 \quad .....(2)$$

where $H_{AB......N}$ is the Hamiltonian of the cluster which is expressed as a sum of single-monomer (H_I) and bi-monomer (H_{IJ}) contributions and electron delocalization over the entire cluster is implied. To incorporate the effect of nonpairwise additive interactions in the n-body cluster, the n-mer cluster energy (E(AB······N)) was written[41] as the sum of one-, two-, three-, ..., n-body energy terms

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according to

$$E(AB\cdots N) = \sum_{I}^{N} E(I) + \sum_{I}^{N-1}\sum_{J>I}^{N} \Delta^2 E(IJ) + \sum_{I}^{N-2}\sum_{J>I}^{N-1}\sum_{K>J}^{N} \Delta^3 E(IJK) + \cdots + \Delta^n E(123\cdots N) \quad \text{(3)}$$

where E(I) is the energy of a relaxed monomer molecule in the cluster and the individual two-, three-, ..., n-body terms are expressed in terms of relaxed monomer, dimer, trimer, tetramer, ..., n-mer energies. For example,

$$\Delta^2 E(IJ) = E(IJ) - (E(I) - E(J) \quad \text{.. (4)}$$

$$\Delta^3 E(IJK) = E(IJK) - (E(I) + E(J) + E(K)) - (\Delta^2 E(IJ) + \Delta^2 E(IK) + \Delta^2 EJK)) \quad \text{..(5)}$$

and so on.

However, it has been traditionally accepted[40] to consider the binding energy, ΔE, as made up of various perturbation terms which have defined physical meanings,

$$\Delta E = \Delta E_{ES} + \Delta E_{EX} + \Delta E_{PL} + \Delta E_{EX-PL} + \Delta E_{MIX} + \cdots\cdots \quad \text{..............................(6)}$$

where ΔE_{ES} is the electrostatic energy of interaction between the undistorted charge distributions of the A, B, ······, N monomers at long-range; ΔE_{EX} is the overlap or exchange repulsion energy which results from the inter-penetration of the charge clouds of the monomers at short-range; ΔE_{PL} as the polarization energy; and ΔE_{EX-PL} and ΔE_{MIX} being the exchange-polarization and coupling energy terms respectively.

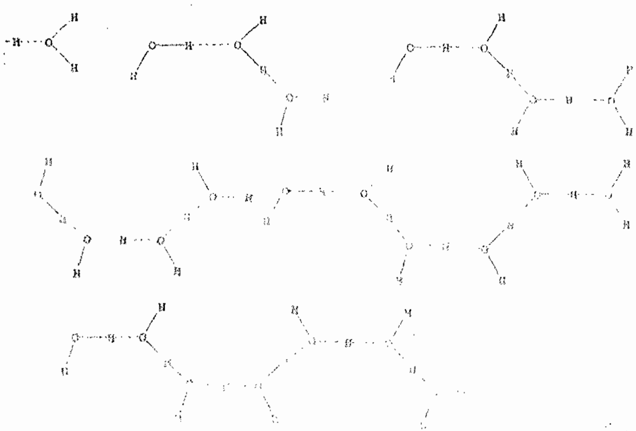
Although one acknowledges the sophistication of the *ab initio SCF MO* method, its 'ability' not to generate values that would agree with experimental data but describe 'correctly' the mode of intermolecular binding in $(H_2O)_n$ systems is unsatisfactory in some respect. Firstly, the $(H_2O)_n$ cluster energy E(AB······N) is calculated in principle with all the *electrons delocalized over the entire cluster* such that electrons loose their monomer identities and move in *whole-cluster delocalized MOs*. The whole-cluster delocalized MOs form 'bridges' between the monomers through which electrons move from one monomer to another. In essence the method treats the interactions between the n H_2O monomers of $(H_2O)_n$ cluster as *chemical interactions*, the intermolecular hydrogen bonds as *chemical bonds* and the $(H_2O)_n$ cluster, in principle, as a *new chemical compound* or species. (The $(H_2O)_n$ (n = 2, 3, ······, n) clusters exist in water vapour, liquid water and in ice). Would the *ab initio SCF MO* description be plausible eventhough bulk water (a stable aggregation of large numbers of H_2O molecules) is essentially no different from isolated H_2O in chemical behaviour? In other words, is the 'stability' of the aggregation of the H_2O molecules due to chemical bond connectedness between the H_2O moieties rather than simple physical interactions? Beside these unanswered questions, the method is unnecessarily complicated; the computations involved are very difficult, time consuming and become practically impossible for large clusters. One question that might even be asked is whether that amount of computational expenditure is really necessary in order to study the intermolecular hydrogen bond in $(H_2O)_n$ clusters. Won't a simpler method that is based on a more realistic physical model predict the properties of such a bond that would also agree with experimental data? This work gives an affirmative answer to this last question.

However, the hydrogen bond in water was extensively studied by Morokuma and his colleagues[42-44] using the energy decomposition (6). The hydrogen bonded complexes they considered includes $(H_2O)_2$, $(NH_3)_2$, etc. and the results of their study showed that, at equilibrium geometry, the exchange repulsion term ΔE_{EX} is nearly compensated by the ΔE_{PL} and ΔE_{EX-PL} attractive terms ($\Delta E_{MIX} \approx 0$ for accurate calculations). This appears to justify the assumptions that the stability of hydrogen bond in water is essentially *governed by electrostatic (i.e. physical) interactions*.

But it is well known that the intermolecular electrostatic interaction cannot give a potential minimum or electrostatic binding[33-38]. However, we have previously reported[45] a simple model for electrostatic interaction that leads to a stable equilibrium or binding at large distances between a pair of molecules *a* and *b*. The model assumes the electrons of molecule *a* to perceive, at long-range, molecule *b* as made up of point-multipoles and vice versa . A potential energy of interaction between the electrons of *a* and the point-multipoles of *b* derived from a single theory has both attractive and repulsive terms for each point-multipole moment on molecule *b*. When applied to linear $(H_2O)_2$ dimer, the model predicts hydrogen bond energy and O ······ O equilibrium distance in good agreement with experimental values. Given the good agreement between theory and experiment for the linear water dimer, a similar calculation on the $(H_2O)_n$ (n = 2 - 10) polymers is expected to give a quantitative understanding of the bonding as well as yielding reliable prediction of the total and incremental association energies for the $nH_2O \rightarrow (H_2O)_n$ and $(H_2O)_{n-1} + H_2O \rightarrow (H_2O)_n$ (n = 2 - 10) processes.

EXPERIMENTAL

Since calculations[31] yield only ~0.01 kcal mol^{-1} relaxation energy per water molecule in cyclic $(H_2O)_n$ clusters (which is a measure of average distortion of water molecules in the cluster from their gas phase optimal structure), the geometry of the water monomers is assumed to be fixed in these calculations. The optimal structures of the *a, da,* ·······; *da, d* sequential $(H_2O)_n$ clusters are shown in Fig. 1.



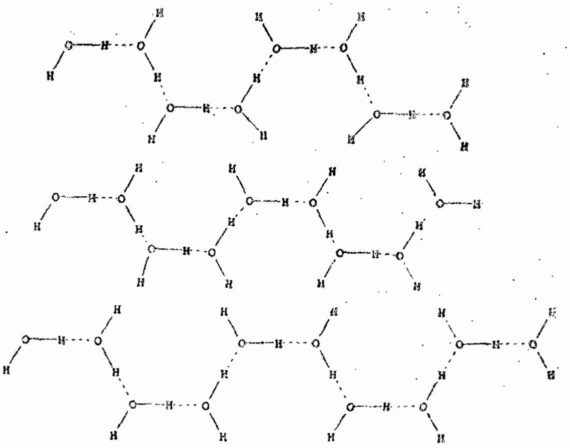


Fig. 1. Optimal structures of *a, da,* ······; *da, d* $(H_2O)_n$ polymers

Then each acceptor-donor pair in the *a, da,* ······; *da, d* $(H_2O)_n$ chain is assumed to present *local characteristics* similar to those of the stable water dimer. Furthermore, each donor H_2O of the acceptor-donor pair in the chain is assumed to be *perceived* by the electrons of the acceptor H_2O as made up of point-multipoles. Finally, the hydrogen bond energy of each acceptor-donor pair in the chain is computed over a (2, 1/1) minimal basis of the acceptor molecule as reported[45] for the case of linear acceptor-donor water dimer.

RESULTS AND DISCUSSION

The results for the total interaction energy of the clusters are summarized in Table 1, part A. These values correspond to the association energies for the polymerization

$$nH_2O \quad \rightarrow \quad (H_2O)_n, \qquad n = 2 - 10. \quad .....(7)$$

The total interaction energies were found to vary linearly with *n*. The average association energies per water molecule for process (7) are also listed in Table 1, part B. It increases faster for *n* = 4 - 10 and extrapolates to a value of -5.5697 kcal mol^{-1} per water molecule for the decamer. Since the water molecules act both as proton donors and acceptors in the *a, da,* ······; *da, d* sequence (except the first and last), the total number of hydrogen bonds in a sequential *n*-mer cluster is (*n* - 1). The experimental estimate for the intermolecular energy of liquid water at 25 °C and 1 atm ranges[46-47] from -9.9 to -10.5 kcal mol^{-1}. On the average each of the water molecules in the liquid water participates in two hydrogen bonds (as we also have in sequential *n*-mer clusters). Assuming that most of the average

Table 1. Total and average association energies for the *process:* $n\mathrm{H_2O} \rightarrow (\mathrm{H_2O})_n$, $n = 2 - 10$

n	Ours	Others(HF)[31]	Experimental[49]	O⋯⋯O chain length
	kcal mol^{-1}			Å
		A. Total association energies (E_n)		
2	-6.1886	-3.71	-6.2 ± 1.5	2.727
3	-12.3772	-11.00	-	4.400
4	-18.5658	-19.51	-	7.127
5	-24.7544	-25.93	-	8.800
6	-30.9430	-32.40	-	11.527
7	-37.1316	-	-	13.200
8	-43.3202	-	-	15.927
9	-49.5088	-	-	17.600
10	-55.6974	-	-	20.327
		B. Average association energies per water molecule		
2	-3.0943	-1.86	-3.1 ± 0.75	
3	-4.1257	-3.67	-	
4	-4.6415	-4.88	-	
5	-4.9509	-5.19	-	
6	-5.1572	-5.40	-	
7	-5.3045	-	-	
8	-5.4150	-	-	
9	-5.5010	-	-	
10	-5.5697	-	-	

intermolecular energy is due to hydrogen bonding, we obtain an upper limit of -5.0 to -5.3 kcal mol^{-1} for the average per hydrogen bond in liquid water. This energy totally agrees with our estimated -5.0 to -5.6 kcal mol^{-1} average association energy per water molecule of the pentamer through decamer. This agreement suggests that water molecules exist in large aggregates.

The incremental association energies $\Delta E_{n-1,n}$ and O⋯O distances $\Delta(O\cdots\cdots O)CL$ of the process

$$(H_2O)_{n-1} + H_2O \rightarrow (H_2O)_n \quad .....(8)$$

for n = 2 -10 are also listed in Table 2. Because the hydrogen bond is localized between each two moieties in the *a, da,* ⋯⋯, *da, d* sequential $(\mathrm{H_2O})_n$

cluster similar to that of the stable water dimer, the incremental association energy is constant. However, it agrees with the experimental value of first incremental association energy and with the higher incremental association energies obtained by Xantheas[31]. The incremental association energies are of the order of the experimental hydrogen bond energy. This suggests that very large $(H_2O)_n$ clusters of the order of *macromolecular* or *supermolecular* size are possible in liquid water. These are of course present in ice. This is further supported by the fact that both our results and those of Xantheas[31] predict the average association energy per water molecule for the process (8) to increase linearly with *n*.

Table 2. Incremental association energies and O······O chain length for the process: $nH_2O \rightarrow (H_2O)_n$, $n = 2 - 10$

n	Ours ($E_{n-1,n}$)	Others(HF)[31]	Experimental	Δ(O······O) CL
		kcal mol^{-1}		Å
2		-3.91	-6.2 ± 1.5	
3		-7.76	-	1.673
4		-8.91	-	2.727
5	-6.1886 all *n* values	-6.73	-	1.673
6		-6.80	-	2.727
7		-	-	1.673
8		-	-	2.727
9		-	-	1.673
10		-	-	2.727

Because of the difficulty of characterizing larger water clusters, there are no experimental $(H_2O)_n$ polymerization energies with which to compare, except for the dimerization. The polymerization energy values reported in the literature[10,21,31,32] come from quantum calculations (Table 1, part A for cyclic $(H_2O)_n$ ($n = 2 - 6$) polymers). Although experimental $(H_2O)_n$ polymerization energies, association energies per water molecule and additive association energies are not yet available for $n > 2$, the values we got for these quantities are in agreement with experimental data for $n = 2$ and those obtained by Xantheas[31] from *ab initio SCF MO* many-body calculations for $n = 3 - 6$, which supports the consistency of our results for $n = 7 - 10$. Lastly, the 2.727Å O······O chain length for the water dimer obtained in this study agrees well with the 2.97 - 2.98Å experimental values[20,48], which also supports the quality of the O······O chain lengths for $n > 2$.

CONCLUSION

The total and incremental association energies and the average association energies per water molecule for the $nH_2O \rightarrow (H_2O)_n$ and $(H_2O)_{n-1} + H_2O \rightarrow (H_2O)_n$ processes have been studied using a simple electrostatic model. The values computed for these quantities agree very well with experimental data and *ab initio* SCF MO results. The study provides both quantitative and qualitative description of the bonding, structure and properties of sequential $(H_2O)_n$ clusters. Lastly, the scheme can be generally and easily extended to even *macro-size* $(H_2O)_n$ sequential clusters, which is practically impossible at the moment with *ab initio* SCF MO method.

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