Stabilization energies of Cl⁻, Br⁻, and I⁻ ions in water clusters

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Molecular dynamics computer simulations were performed on clusters of $Cl^-(H_2O)_n$ ($n=2,...,15$). From the simulations we calculated the stabilization energies of the anion in the cluster. These energies were compared with the values of stabilization energies obtained from the photodetachment spectra of $X^-(H_2O)_n$ clusters ($X=Cl^-$, Br^-, or I^-). The comparison confirms the hypothesis that the anion is attached to the water cluster.

INTRODUCTION

Recent experimental[1-12] and theoretical[13-21] work performed to study solvation in water clusters demonstrates a rich dynamical and structural behavior characteristic for this problem. Among new experimental techniques that play an important role in probing the energetics and structures of ionic clusters one finds the photoelectron spectroscopy, which previously was successfully used to study electron solvation in water clusters.[9] Recently, this technique was used by Cheshnovsky and his collaborators to obtain a photoelectron spectra (PES) of I^- ion solvated in water clusters of up to 15 water molecules.[10] From these spectra they calculated the electrostatic stabilization energy E_{stab} which is the difference between the vertical photodetachment energy of the ion in the cluster and the electron affinity of the bare ion. They observed that the increase in E_{stab} in clusters containing more than six water molecules leveled off and this was considered to be a strong indication that six water molecules form the first solvation layer around the iodide ion.[10] It was therefore proposed in Ref. 10 that the iodide assumes a central position in the cluster. The same assumption about the position of the anion embedded into a cluster of polar solvent is made in a recent theoretical analysis of ion solvation in polar clusters.[18]

At the same time, recent molecular dynamics computer simulations performed on aqueous ionic clusters of $Cl^-(H_2O)_n$ ($n=4,5,6,7,8,14,20$) indicated that the anion in these clusters is not solvated but instead is attached to the cluster.[20-22] Does that mean that the structures of aqueous clusters with Cl^- are different from the structures observed in clusters with I^-? Or if the structures are similar, then what structure is dominant: the one with the ion solvated by water molecules or the one with the ion outside the cluster? To answer these questions one should compare the experimental data with the molecular dynamics calculations performed on the same clusters for which the experimental data are available. Very recently, the photoelectron spectra of Cl^- ion in water clusters were obtained, but due to experimental difficulties these spectra were obtained only for clusters with up to seven water molecules.[23] We could try to resolve the problem of comparison in another way: calculate the PES for I^- ion and compare it with the experiment. For this we need to know the I^-/water interaction potential in fine details, but we do not know it at the present time. As it turns out, a more careful analysis of the

experimental data [the recently obtained PES from $Cl^-(H_2O_2)_n$ ($n=1,2,...,7$) clusters, and from $Br^-(H_2O)_n$ ($n=1,2,...,15$) clusters which were made available to us,[23] and PES from $I^-(H_2O)_n$ ($n=1,2,...,15$) clusters that were reported in the literature[10] permits the resolution of the problem. From the experimental spectra for Cl^- and Br^- we were able to extract the stabilization energies for these ions, while the stabilization energies of I^- are given in Ref. 10. If the environment of Cl^-, Br^-, and I^- in small water clusters ($1 \leqslant n \leqslant 15$) is similar, the PES from these clusters should also be similar. Therefore, one should be able to appropriately scale the values of the stabilization energies, plot these scaled stabilization energies as a function of a number of water molecules in a cluster and get a universal curve. Indeed, we observe that if we multiply all the values of the stabilization energies of I^- by a factor 1.54, the values of stabilization energies of Br^- by a factor 1.23, while leaving the stabilization energies for Cl^- unchanged and plot the values of all stabilization energies as a function of the number of water molecules in a cluster, the data fall on a universal curve, as it is shown in Fig. 1. Therefore to compare the experimental data obtained for Cl^-, Br^-, and I^- with the computer simulation data, one does not have to do separate simulations for every ion. Since the data are scaled to the values of stabilization energies of Cl^- ion, we compare the experimental scaled data with the stabilization energies we calculate from our molecular dynamics simulations performed on clusters with Cl^-.

MOLECULAR DYNAMICS

We used molecular dynamics computer simulations to investigate the structure and dynamics of small clusters made up of one Cl^- ion and $n=2,3,...,15$ water molecules. The simulations with one ion and one water molecule displayed a large uncertainty in the stabilization energy, due to locking in a certain configuration for a long time.

The details about the potential fields used in the simulations and the way we solved the equations of motion and self-consistent equations for the polarization were described in our previous work.[20,21] Each cluster was initially prepared in a configuration where the ion was in the center of the cluster. After a few picoseconds of molecular dynamics the ion spontaneously moved to the surface of the cluster. Then, we continued to perform molecular dynamics for 25 ps to achieve the equilibration of the cluster. This
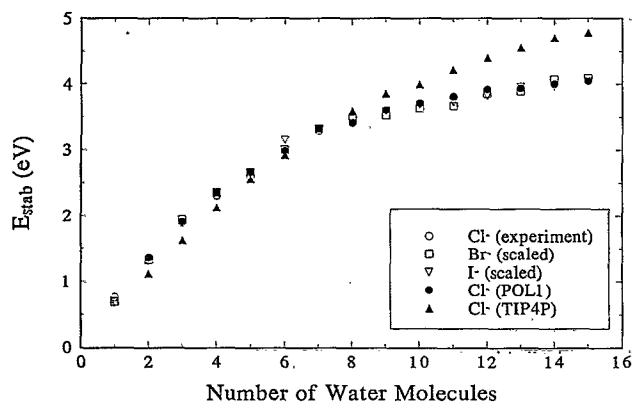
FIG. 1. Electrostatic stabilization energies (E_{stab}) as a function of the cluster size.

TABLE I. Electrostatic stabilization energies (in eV) of $X^-(H_2O)_n$ clusters. Values of E_{stab} directly obtained from experiment for Br^- and I^- ions are given in parentheses.

X^- n	Cl^- Expt.[a]	Br^- (Expt.)[a]	scaled	I^- (Expt.)[b]	scaled	Cl^- POL1 model	Cl^- TIP4P model
1	0.76	(0.57)	0.70	(0.45)	0.69	...	...
2	1.36	(1.08)	1.33	(0.86)	1.32	1.36	1.12
3	1.89	(1.58)	1.94	(1.23)	1.89	1.91	1.63
4	2.31	(1.91)	2.35	(1.53)	2.36	2.35	2.13
5	2.60	(2.17)	2.67	(1.71)	2.63	2.68	2.56
6	2.97	(2.45)	3.01	(2.05)	3.16	2.99	2.92
7	3.30[c]	(2.71)	3.33	(2.14)	3.30	3.33	3.33
8	...	(2.83)	3.48	(2.22)	3.42	3.42	3.60
9	...	(2.87)	3.53	(2.34)	3.60	3.61	3.86
10	...	(2.96)	3.64	(2.40)	3.70	3.72	4.00
11	...	(2.99)	3.68	(2.43)	3.74	3.82	4.23
12	...	(3.14)	3.86	(2.49)	3.83	3.92	4.40
13	...	(3.17)	3.90	(2.57)	3.96	3.94	4.56
14	...	(3.32)	4.08	(2.58)	3.97	4.01	4.70
15	...	(3.33)[c]	4.10	(2.63)	4.05	4.05	4.79

[a]Reference 23.
[b]Reference 10.
[c]The values for these stabilization energies cannot be obtained very accurately from the spectra. We present here our best estimates.

equilibration was followed by 1 ns of the production run. The time step of the trajectory was kept at 1 fs and the total linear and angular momenta of the system were removed. During the trajectory calculations the energy was conserved within the fifth significant digit. Configurations from every tenth step of the trajectory were saved for further analysis. The average kinetic energy of the cluster corresponded to a temperature of 250 K. The value of the experimental temperature is not available to us, but as long as the cluster is able to explore the configuration space, we believe that the temperature should not have an influence on the value of E_{stab}. The temperature in the simulations was chosen to be high enough to eliminate possible trapping of the cluster in a certain configuration for long times.

RESULTS

We performed our cluster calculations using the POL1 potential[24,25] (we called this potential SPCE/POL in our previous work[20,21]) and using the TIP4P potential.[26] As in our previous work,[20,21] we have observed that in the simulations where we used the POL1 potential, the ion is always located on the surface of the cluster for all cluster sizes. This is not the case for the simulations with the TIP4P potential, where the ion becomes solvated in clusters that contain more than six water molecules. The two different arrangements of the ion in water clusters are expected to result in different photoelectron spectra and therefore provide different stabilization energies upon excitation of the cluster. To calculate the stabilization energy E_{stab}, from a molecular dynamics trajectory we carried out the following procedure: (a) the energy of the ion/water cluster was calculated as an average over all saved configurations. (b) in every saved configuration, we instantaneously removed the charge on the ion retaining the configuration of the water molecules. (c) the energy of the cluster created in the previous step was calculated. The difference in the energies calculated in steps (c) and (a) is the stabilization energy. In Fig. 1 we present the comparison between the calculated E_{stab} and the measured E_{stab}. The experimental data on this figure were brought to a common scale as was explained above. (The measured val-

ues of the stabilization energies, the scaled values of these energies, and the values calculated from the molecular dynamics simulations with the POL1 and TIP4P potentials which are used to create Fig. 1 are also given in Table I.) Note, that for $Cl^-(H_2O)_n$ ($n=2,...,7$) clusters the comparison between the experiment and the calculations does not involve any scaling. As Fig. 1 shows, the experimental data and the data calculated from the simulations with the POL1 potential are in good agreement. However, this is not the case when stabilization energies calculated from the simulations using the TIP4P potential are compared with the experimental data.

Figure 1 provides a direct comparison between the experimental and molecular dynamics data on stabilization energies of ions in aqueous clusters. Based on the ideal of similarity and the fact that a good agreement is observed between the experimental E_{stab} and E_{stab} calculated from the simulations with the POL1 model we conclude that I^- and Br^- ions are not solvated in small water clusters, but instead are attached to the water cluster.

As far as the clusters with Cl^- are concerned we observe the following: (a) Our calculated stabilization energies for $Cl^-(H_2O)_n$ ($n=2,...,7$) clusters are in a good agreement with the experiment. (b) The experimental E_{stab} (for all the available experimental data) in $Cl^-(H_2O)_n$ ($n=1,2,...,7$) clusters fit the universal curve. (c) The quantum mechanical calculations performed on $Cl^-(H_2O)_{14}$ cluster indicate the preference for the Cl^- ion to be on the surface of the water cluster.[27]

All these factors, in our opinion, provide a support to our previous conjecture that the Cl^- ion is also located on the surface of the water cluster. Nevertheless, the final judgment on the location of Cl^- in water clusters for up to 15 water molecules should be given only after the photo-

detachment experiment on these clusters will be performed.

As Fig. 1 indicates the structure of the small aqueous clusters with such anions as Cl^-, Br^-, and I^- are similar. What is happening in the larger size clusters and when does a complete solvation occur are some questions to be answered in future experimental and theoretical work.

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