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ARE MODELS OF ANION HYDRATION OVERBOUND? THE SOLVATION OF THE ELECTRON AND CHLORIDE ANION COMPARED**M. SPRIK***IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland*

Abstract. By means of a fully polarizable model for the chloride ion-water interaction we show that the modelling of anion solvation suffers from a similar inconsistency as the current electron-solvent potentials. Either the bulk hydration enthalpies are correct with the first hydration shell overbound, or the potential is adapted to describe the local environment of the solute at the expense of a major loss of solvation enthalpy. It is argued that boundary effects in the simulation are at least partly responsible for this dilemma. A further parallel between a polarizable aqueous halide ion and the solvated electron is the anisotropy in the surrounding solvent, which is reflected in an asymmetry in the electronic excitation spectrum.

1 The excess electron in water

The solvated electron is of fundamental importance in many chemical processes in solution. In particular the excess electron in polar solvents has been the subject of intensive experimental and theoretical investigation (for a review of the computer simulation work see Refs. [1,2]). The picture that emerged from these studies is that the excess electron in the solvated state resembles in many respects an anion of moderate size such as Cl^- . Computer simulation allows us to compare the structure of the solvent around the electron and anion in detail. It was found that the electron is localized in a cavity with a diameter of 4 to 5 Å. [2]. The first solvation shell shows less structure compared to the Cl^- ion but is qualitatively similar. Strong evidence that the cavity model is essentially correct comes from the excitation spectrum of the solvated electron. The lowest excitation energy corresponds to a transition from the s-like ground state to a manifold of p-like states, which remain localized in the unrelaxed cavity [2]. This explains the well-known peak in the light absorption spectrum which in the case of the hydrated electron is located at 1.75 eV. The position of this maximum is largely determined by the cavity radius.

All computer studies agree on these rough features despite substantial differences in the interaction potentials. However, there appears to be a systematic disagreement as to experimental results. We will restrict the discussion in this short contribution to the hydrated electron. Many of the observations and conclusions are also valid for the electron in ammonia [3]. The enthalpy ΔH for solvation in bulk water is approximately 1.7 eV [4]. The majority of potential models gives a value of ΔH close to this number. Unfortunately, the predicted excitation energy ΔE is 0.5 – 0.6 eV too large [2]. In Ref. [5] the effect of the introduction of variable electronic polarization in the model for the solvent was investigated. The result was an increase of the cavity size and a reduction of the excitation energy. However, this was achieved at the expense of an unacceptable loss of binding energy (more than 1 eV).

The conclusion seems to be that the current models are not able to account for both the binding and excitation energy with the same set of parameters. A possible explanation may be that the electron solvent interaction potential, being a pseudo-potential, is different in the ground and excited state [6]. In this communication we will pursue another explanation, namely that the numerical procedures for evaluating the solvation enthalpies are not sufficiently accurate for the purpose of a quantitative comparison to experiment. The proposition is that the commonly used solvent samples of several hundred molecules are too small and that as a result ΔH in the bulk liquid is underestimated. That

perturbations by finite system effects might complicate simulations in the bulk is supported by studies of excess electrons in clusters, which are not subject to this limitation. In Ref. [7] the binding energies of internal (solvated) states in clusters of a varying number of molecules are calculated. Recent experiments [8] seem to indicate that these energies may be too large by as much as 0.5 to 1 eV.

If our conjecture is correct, then these difficulties are not specific to the solvated electron and should also affect the simulation of classical ions. In the next section we will argue that this is indeed the case for the Cl^- in water. We will introduce a polarizable potential, both for the water molecules and the anion, and show that the problem is only aggravated by including the polarization, as was also the case for the electron. In the last section we summarize the similarities between a hydrated electron and a halide ion in solution, thereby emphasizing the role of polarizability.

2 The chloride anion in water

We start with the observation that in the conventional models for ion-water interaction such as TIP4P [9] the cohesion in gas-phase clusters is too strong. The parameters of TIP4P have been carefully optimized to reproduce the experimental value of the binding energy of a Cl^- ion and a single water molecule [10]. However, if more molecules are added, the decrease in energy is consistently larger than the experimental enthalpy change for this reaction [10]. For $\text{Cl}^-(\text{H}_2\text{O})_4$ the integrated enthalpy deviates already by 38 kJmol^{-1} . On the other hand, the ΔH for the bulk liquid is calculated as 340 kJmol^{-1} in Ref. [9], i.e. within a few kJmol^{-1} of the experimental values. This result is somewhat fortuitous and only holds for a system with $N = 125$ solvent molecules. If the sample size is increased from $N = 125$ to $N = 216$, ΔH is lowered by about 10 percent. Another 5 percent is gained by going from $N = 216$ to $N = 512$.

These size effects, though not negligible, are no reason for major concern. However, these simulations were performed under periodic boundary conditions applying a spherical cutoff of half the box length. If instead an Ewald summation technique is used to evaluate the electrostatic long-range interactions, a rather different set of enthalpies is obtained. The results of the two methods show a systematic shift of about 70 kJmol^{-1} virtually independent of N . Neither Ewald summation or spherical cutoff can claim to be significantly better for the calculation of ΔH of single ions. However, from the discrepancy of almost 1 eV it can be inferred that boundary effects are likely to be more serious than is apparent from the N dependence of ΔH in samples of a few hundred particles. This point is also discussed in Refs. [11] and [12], where a similar conclusion is drawn.

In view of the uncertainty in the determination of ΔH , we can, therefore, not disregard the possibility that similar to ions in clusters, ions in solution are also overbound in the conventional models like TIP4P. Structural data from neutron scattering experiments [13] also point in this direction. The coordination number $n = 5.8$ in the first hydration shell is found to be 1 to 2 molecules less than what most models predict. Moreover, as can be seen in Fig. 1, the radial distribution function is less structured. These considerations have motivated us to redesign the $\text{Cl}^- \text{H}_2\text{O}$ potential by fitting it to properties which can be unambiguously determined both in experiment and simulation. For these quantities we choose the gas phase hydration enthalpies and the structure of the first coordination shell in the bulk liquid. The ab initio $\text{Cl}^- \text{O}$ distance in the dimer [9] is used as a further criterion. On the other hand, we will compromise on the value for ΔH in the liquid.

We have implemented the empirical scheme sketched above for a fully polarizable model in which both the water molecules and the Cl^- have variable dipole moments. This potential is based on the polarizable model for pure water we have recently developed [14] (see also [15]). This model gives a good description of key liquid properties, such as the radial distribution functions, the static dielectric constant and the self-diffusion coefficient. Also the binding energy and the structure of the gas phase dimer are acceptable. We adopt this model here without modification. The polarization of the chloride ion is represented in exactly the same manner as for the oxygen in the water [15]. The crucial parameter is the characteristic length controlling the short-range damping of the induction. This parameter and the other coefficients in the $\text{Cl}^- \text{H}_2\text{O}$ interaction are optimized with respect to the selected quantities. The details of this procedure and the precise parameter set will be published elsewhere. Here we will summarize the results relevant for the discussion of the solvated electron.

Figure 1. Neutron weighted sum of the radial distribution functions of the O and H atoms with respect to the Cl^- ion. Shown are the results for the TIP4P model [9] (dashed), a model with both the water and chloride ion polarizable (dotted) and experiment (solid) [13].

As anticipated, good agreement with experiment can only be achieved by a less tightly bound first hydration shell. The final result for the distributions of the O and H sites with respect to Cl^- ion is shown in Fig. 1. The coordination number is 5.8. The loss of solvation enthalpy in the standard size liquid sample of $N = 216$ is substantial. ΔH is reduced to 240 kJ mol^{-1} compared to 340 kJ mol^{-1} in experiment. This is clearly a very unsatisfactory situation, which we have decided to accept for the moment in lieu of a reliable method for the calculation of ΔH . It should be mentioned here that, despite the low ΔH in the liquid, the hydration enthalpies for the cluster are still somewhat overestimated.

3 The electron and chloride ion compared

The previous section demonstrates that the modelling of the chloride ion is troubled by a similar inconsistency as the solvated electron. It is possible to obtain the correct solvation enthalpy but not without other observables showing signs of overbinding. These observables include for the electron the excitation spectrum, for the ion the coordination number and the cluster enthalpies for both. The alternative, as we have attempted here, is to adapt the model to reproduce the experimental findings for these properties with the consequence of a major decrease of the (absolute) bulk liquid ΔH . In our opinion boundary effects are at least partly responsible for this dilemma and numerical values of ΔH should be viewed with some suspicion.

To conclude we would like to point out another parallel between the aqueous halide ions and the electron. While the average induced dipole moment of the Cl^- vanishes in the liquid, the r.m.s. value is $1.35D$ with a relaxation time of several picoseconds. Figure 2 shows the distribution of the orientation of the induced dipole moment with respect to the Cl^- -O radius vector of the water molecules in the first hydration shell. For comparison the orientational distribution of the coordinated permanent solvent dipole moments is also given. The induced dipole moment of the ion has a slight preference for the direction opposite the bond vector. This correlation has a double interpretation. It also gives the angular distribution of the positions of the water molecules with the induced moment as a reference. This implies that the environment of an ion is anisotropic with the result that degenerate manifolds of excited electronic states are split. Measurements of the electronic excitation of aqueous Cl^- seem not to be feasible but the first line in the UV spectrum of I^- [16] exhibits a small high-frequency tail resembling the more pronounced tail in the absorption spectrum of the electron. This asymmetry is likewise explained by a mechanism of anisotropic fluctuations in the liquid [2].

Figure 2. Distribution of the orientation of the permanent dipole moments of the coordinated water molecules (solid) and the induced moment of the chloride ion (dashed). The orientation is measured by the cosine of the angle of the dipole moment with respect to the radius vector pointing from the ion to the oxygen.

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