Quasi-chemical study of Be\(^{2+}\)(aq) speciation

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Abstract

Be\(^{2+}\)(aq) hydrolysis can lead to the formation of multi-beryllium clusters, but the thermodynamics of this process has not been resolved theoretically. We study the hydration state of an isolated Be\(^{2+}\) ion using both the quasi-chemical theory of solutions and ab initio molecular dynamics. These studies confirm that Be\(^{2+}\)(aq) is tetra-hydrated. The quasi-chemical approach is then applied to the deprotonation of Be(H\(_2\)O)\(_4\)\(^{2+}\) to give BeOH(H\(_2\)O)\(_3\)\(^{+}\). The calculated pK\(_a\) of 3.8 is in good agreement with the experimentally suggested value around 3.5. The calculated energetics for the formation of [Be \(\cdot\) OH \(\cdot\) Be]\(^{3+}\) are then obtained in fair agreement with experiments.

Key words: beryllium, ab initio molecular dynamics, deprotonation, speciation, quasi-chemical theory

1 Introduction

Beryllium metal has properties that make it technologically very attractive[1], but these advantages are severely counterbalanced by the high toxicity of inhaled beryllium dust, which causes chronic beryllium disease in a subset of exposed individuals [2]. The etiology of this autoimmune disease [3] is poorly understood, but the final disease state is characterized by lung failure.

Aqueous beryllium chemistry is also incompletely understood. Experiments suggest that beryllium mediated hydrolysis of water leads to the formation of multi-beryllium clusters [1,4]. This same mechanism is likely involved in the dissolution of Be\(^{2+}\)(aq) and of importance in environmental clean-up strategies. Such mechanisms likely underlie deposition of beryllium in biomaterials,

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and thus perhaps in the development of chronic beryllium disease. Thus a molecular understanding of Be\(^{2+}\)(aq) and formation of multi-beryllium species would provide a foundation for addressing these issues of wide importance. This letter takes an initial theoretical step in understanding the aggregation/disaggregation of beryllium clusters in water.

Early electronic structure calculations on beryllium hydration were performed on small clusters [5,6] and some attempted to include the second hydration shell in terms of the reaction field approach [7] or explicitly [8]. Molecular dynamics simulation [9] showed that assuming pair-wise intermolecular interactions lead a hydration number was six (6) whereas including three-body effects brought the hydration number down to four (4) consistent with solution X-ray diffraction experiments.

Be\(^{2+}\) hydration has also been considered within the Car-Parrinello approach [10,11,12]. There a hexa-hydrate cluster quickly dissociated to give a tetra-hydrate structure [10]. The \textit{ab initio} molecular dynamics approach for a Be\(^{2+}\) atom in a box of 31 water molecules also showed that the ion was tetra-hydrated [12]. That work also suggested an effect of the second hydration shell water molecules on some of the bond lengths for the central Be(H\(_2\)O)\(_4\)\(^{2+}\) structure, noted further below.

Those earlier works have addressed important issues about Be\(^{2+}\) solvation, but the thermodynamical aspect of solvation has not been considered specifically. We address the solvation thermodynamics by employing two distinct
theoretical approaches. We study the solvation structure of Be\textsuperscript{2+} using \textit{ab initio} molecular dynamics methods and confirm a stable tetra-coordination. The quasi-chemical theory of solutions then provides a further analysis why the tetra-hydrate is the most stable species. This approach has been used before to address Fe\textsuperscript{3+}(aq) speciation \cite{13}, and the hydration of H\textsuperscript{+} \cite{14}, HO\textsuperscript{-} \cite{15}, Li\textsuperscript{+} \cite{16}, and Na\textsuperscript{+} \cite{17} ions. As mentioned above, beryllium solution chemistry holds the particular challenge of the formation of multi-beryllium clusters. The present studies on Be(H\textsubscript{2}O)\textsubscript{4}\textsuperscript{2+} deprotonation and on formation of [Be·OH·Be]\textsuperscript{3+} provide first steps in describing that aggregation process on a molecular basis, as suggested by Fig. 1.

2 \textit{Ab initio} molecular dynamics

The \textit{ab initio} molecular dynamics (AIMD) simulations were performed with the VASP program \cite{18,19}. The simulation system comprises 32 water molecules and one Be\textsuperscript{2+} ion. The box length was set to 9.71 Å based on the experimental partial molar volume of Be in water \cite{20}. Vanderbilt ultrasoft pseudopotentials \cite{21,22} were used to describe the core-valence interactions for all the atoms. The valence orbitals were expanded in plane waves with a kinetic energy cutoff of 29.1 Ry. All the hydrogen atoms were replaced by deuterium and an integration timestep of 0.5 fs was chosen.

The initial configuration was obtained by placing a Be\textsuperscript{2+} ion in a bath of water molecules. That configuration was energy minimized before initiating the AIMD simulations. At the end of the classical energy minimization, the Be\textsuperscript{2+} ion was found to be penta-hydrated (based on R(\text{BeO}) ≤ 2.5 Å). In an exploratory AIMD run (data not reported), the initial configuration for the AIMD simulation was obtained from a classical molecular dynamics simulation. In that case the ion was hexa-hydrated, but it too quickly reverted to the tetra-hydrated form.

In the first 1.0 ps of the AIMD simulation the temperature was maintained at 300 K by scaling the velocities. After this initial phase, a microcanonical (NVE) ensemble simulation was performed for about 2.5 ps.

Within the first 160 fs of the ca. 3.5 ps of the AIMD simulation, the coordination number changed to four (4) and stayed so for the rest of the simulation. The energy in the NVE simulation was -472.25±0.08 (2\textsigma) eV, suggesting good energy conservation. The mean temperature was 316.2±21.6 K.

Fig. 2 shows the oxygen(water) radial distribution around the beryllium ion. Observe that the inner shell is physically sharply defined and the hydration number is four (4). Further structural characterization of Be\textsubscript{[H\textsubscript{2}O]\textsubscript{4}\textsuperscript{2+}} solvation
Fig. 2. Radial distribution of oxygens around Be$^{2+}$. The right ordinate (dashed line) gives the coordination number, $n(r)$.

is collected in table 1. Earlier[12] it was suggested that the second hydration

Table 1
Solvation structure of Be[1H$_2$O]$_4^{2+}$. Inner: Results for the inner-shell hydration; Outer: Results for the outer-shell hydration. Cluster: Results pertaining to a gas-phase cluster (or isolated molecule) obtained with the methods in section III. All lengths are in Å and angles are in degrees. Values in parentheses are for the isolated H$_2$O molecule.

|                | AIMD Inner   | AIMD Outer  | AIMD Cluster |
|----------------|--------------|-------------|--------------|
| R(BeO)         | 1.64±0.06    | —           | 1.64         |
| ΩOBeO          | 109.3±5.9    | —           | 111.4±5.9    |
| ROH            | 1.02±0.04    | 1.00±0.03   | 0.98±0.01 (0.97) |
| ΩHOH           | 108.5±5.6    | 106.5±5.5   | 111.4 (105.7) |

shell has a significant influence on the OH bond length of the inner shell water molecule. In the present case, we do find a slight lengthening of the OH bond in the inner-shell water, but the statistical uncertainties here and in the earlier study [12], suggest that the difference between the inner-shell and outer-shell water is subtle. The increase in the HOH angle for the inner shell water is similar to the earlier study [12] and is in line with the values obtained for an isolated Be(3H$_2$O)$_4^{2+}$ cluster. Also notice that the oxygen atoms in the inner-shell are nearly tetrahedrally distributed around the central Be$^{2+}$ ion, but that structure does fluctuate somewhat.
3 Quasi-chemical Theory

In the quasi-chemical theory [23], the region around the solute of interest is partitioned into inner and outer shell domains. In the present study, the inner shell, where chemical effects are important, is treated quantum mechanically. The outer shell contributions have been assessed using a dielectric continuum model. In principle, a variational check of this partition is available (see [17]).

Hydration state of Be\(^{2+}\): The inner shell reactions pertinent to Be\(^{2+}\) hydration are:

\[
\text{Be}^{2+} + n\text{H}_2\text{O} \rightleftharpoons \text{Be(}\text{H}_2\text{O})_n^{2+}
\]

The free energy change for these reactions were calculated using the Gaussian programs [24]. The Be \(
\cdot\text{(H}_2\text{O})_n^{2+} \) (\(n = 0 \ldots 6\)) clusters were geometry optimized in the gas phase using the B3LYP hybrid density functional[25] and the 6-31+G(d,p) basis set. Frequency calculations confirmed a true minimum, and the zero point energies were computed at the same level of theory. Single point energies were calculated using the 6-311+G(2d,p) basis set. A purely inner-shell \(n = 5\) cluster could not be obtained; the optimization gave structures with four (4) inner and one (1) outer sphere water molecule. For \(n = 6\) both a purely inner-shell configuration, and a structure with four (4) inner and two (2) outer shell water molecules were obtained. The quasi-chemical theory here utilizes only the inner-shell structure.

For estimating the outer shell electrostatic contribution, the ChelpG method [26] was used to obtain partial atomic charges. Then with the radii set developed by Stefanovich et al.[27], surface tessera were generated [28], and the solvation free energies of the clusters were calculated using a dielectric continuum model [29]. With this information and the binding free energies for the chemical reactions, a primitive quasi-chemical approximation to the excess chemical potential of Be\(^{2+}\)(aq) in water is:

\[
\beta \mu_{\text{Be}^{2+}\text{(aq)}}^{\text{ex}} \approx -\ln \left( \tilde{K}_n \rho_{\text{H}_2\text{O}}^{-n} \right) \]

where \(\tilde{K}_n = K_n^{(0)} \exp \left[ -\beta \left( \mu_{\text{Be(H}_2\text{O})_n^{2+}}^{\text{ex}} - n\mu_{\text{H}_2\text{O}}^{\text{ex}} \right) \right] \). \(K_n^{(0)}\) is the equilibrium constant for the reaction in an ideal gas state, with \(n\) of Eq. 1 the hydration number of the most stable inner shell cluster, and \(\beta = 1/\kappa\text{B}T\). The density factor \(\rho_{\text{H}_2\text{O}}\) appearing in eq. 1 reflects the actual density of liquid water and its effect is accounted for by including a replacement contribution of \(-n\kappa\text{B}T \ln(1354)\). A detailed statement on standard states and this replacement contribution can be found in Grabowski et al. [14].
Fig. 3. Quasi-chemical contributions of the solvation free energy of Be$^{2+}$(aq). Specifically, the plot (left ordinate) is $-k_B T \times \ln \left( K_n \mu_{H_2O}^n \right)$ vs. $n$ predicted by the primitive quasi-chemical approximation; see Ref. [16]. $n$ is the number of inner shell water molecules surrounding the anion. $\Delta$: $-RT \ln K_n^0 - nRT \ln(1354)$; $\times$: $\mu_{\text{ex}}^{Be(H_2O)_n^{2+}} - n\mu_{H_2O}$. An observation volume of radius 2.0 Å centered on the cation defined the inner shell. Using a smaller radii did not make an appreciable difference.

From figure 3 it is clear that the tetra-aquo cation is the most stable form in solution. This is also consistent with the predictions of the AIMD simulations. As fig. 3 indicates, neglecting solvation effects would have forced us to conclude that both the tetra- and hexa-hydrates should be observed. However, it is the substantial unfavorable solvation of the hexa-hydrate that precludes its presence in the solvent. The calculated solvation free energy of -567.7 kcal/mole is in the right range and is in good agreement with the value (-574.6 kcal/mole) cited in [20]. Solvation free energy values for these highly charged species may have significant uncertainties, and the agreement here should not mask the real difficulties facing ion-solvation thermodynamics. The agreement in inner-shell hydration number between AIMD simulations and quasi-chemical calculations is, however, a non-trivial result.

In table 2 some of the energies relevant to the $n = 4$ case above is collected in addition to other free energy values that we will use in analyzing the $pK_a$ of the tetra-aquo cluster.

$pK_a$ of Be$(H_2O)_4^{2+}$: The acidity of Be$(H_2O)_4^{2+}$ is described by the

$$K_a = \frac{[\text{BeOH}(H_2O)_3^+] [H^+]}{[\text{Be}(H_2O)_4^{2+}]}$$

(2)

corresponding to the reaction

$$\text{Be}(H_2O)_4^{2+} \rightleftharpoons \text{BeOH}(H_2O)_3^+ + H^+$$

(3)

under standard conditions (1 M ideal solution). The reaction as written re-
Table 2
Electronic energy (a.u.), thermal corrections (a.u.) to the free energy, and excess chemical potential (kcal/mole) using dielectric continuum approximation with charges obtained at B3LYP/6-311+G(2d,p).

| Species              | \(E\)  | \(G_{corr}\) | \(\mu^*\) |
|----------------------|--------|--------------|------------|
| Be\(^{2+}\)         | -13.65289 | -0.01303 | —          |
| Be\((\text{H}_2\text{O})_4\)\(^{2+}\) | -320.12296 | 0.07259 | -230.9 |
| BeOH\((\text{H}_2\text{O})_3\)\(^+\) | -319.92375 | 0.05970 | -73.9 |
| Be\(_2\text{OH}(\text{H}_2\text{O})_6\)\(^{3+}\) | -563.42051 | 0.13225 | -412.0 |
| Be\(_2\text{OH}^3\)\(^+\) | -103.83704 | -0.00627 | —         |
| H\(_2\text{O}\)       | -76.45951 | 0.00298 | -7.7      |
| HO\(^-\)             | -75.82779 | -0.00771 | —         |
| HO \cdot (\text{H}_2\text{O})\(_3\)\(^-\) | -305.32036 | 0.04705 | -72.3 |

quires us to know the hydration free energy of the proton, estimates of which have large uncertainties [14]. Alternatively, using a reference reaction such as the dissociation of water can obviate the need for knowing the proton hydration free energy. Thus consider

\[
\text{Be(}\text{H}_2\text{O})_4\text{)}^{2+} + \text{HO}^- \rightleftharpoons \text{BeOH(}\text{H}_2\text{O})_3\text{)}^+ + \text{H}_2\text{O} \tag{4}
\]

Knowing the energetics of eq. 4 permits calculation of the pK\(_a\) of the tetra-aquo cation, according to

\[
K_a = K \times \left(\frac{K_w}{[\text{H}_2\text{O}]}\right) \tag{5}
\]

Here \(K\) is the equilibrium ratio of eq. 4 with all concentration units the same, \(K_w = [\text{HO}^-][\text{H}^+]\) the standard ion product for water; here pK\(_w\) = 15.7 [30]. An added advantage of using a reference reaction as above is that some cancellation of errors can be encouraged.

The excess chemical potential of HO\(^-(\text{aq})\) in reaction 4 above is also obtained within the quasi-chemical approach and with the tri-hydrated quasi-component [15]. The computed value of -105 kcal/mole is in good agreement with recently reported values [31].

If all standard concentrations are 1 M, then using the values in table 2 the free energy change for reaction 4 is -18.5 kcal/mole. Eq. 5 then yields pK\(_a\) \(\approx\) 3.8.
By fitting experimental free energy changes for the case of low total Be$^{2+}$ concentration [1,4], it is found that Be(H$_2$O)$_4^{2+}$ exists in appreciable amounts only below a pH of 3.5. The present calculated pK$_a$ is in excellent agreement with these observations. This value of pK$_a$ has the standard interpretation that the deprotonated complex BeOH(H$_2$O)$_3^{+}$ is above a thousand times more probable than Be(H$_2$O)$_4^{2+}$ at neutral pH. That a spontaneous deprotonation is not observed in our simulations is reflective of the limited simulation time and the possibility of this process being activated. Nevertheless, when an OH$^-$ was introduced into the AIMD simulation by extraction of a proton distant from the beryllium ion, ligand exchange by proton shuffling was accomplished in less than a ps.

**Formation of** [Be · OH · Be]$^{3+}$: The [Be · OH · Be]$^{3+}$ cluster is one of the many clusters that beryllium forms [1], but it is the simplest. Other clusters could be constructed with this unit. Thus understanding the formation thermodynamics of this cluster is of first interest.

The solvation free energy of the complex [Be · OH · Be]$^{3+}$ is obtained from the following reaction.

\[
\text{Be} \cdot \text{OH} \cdot \text{Be}^{3+} + 6\text{H}_2\text{O} \rightleftharpoons \text{Be} \cdot \text{OH} \cdot \text{Be} \cdot (\text{H}_2\text{O})_6^{3+}
\]  

Here it is assumed that each of the originally tetra-hydrated Be$^{2+}$ loses one water and gains a HO$^-$ to form the complex (fig. 1). Using eq. 1 for the present case, the quasi-chemical estimate of the solvation free energy of [Be · OH · Be]$^{3+}$ is obtained as -834.5 kcal/mole.

With this solvation free energy estimate, we can enquire about the thermodynamics of the complexation reaction below.

\[
2\text{Be}^{2+} + \text{HO}^- \rightleftharpoons [\text{Be} \cdot \text{OH} \cdot \text{Be}]^{3+}
\]  

The change in the excess chemical potential for the reaction is 405.9 kcal/mole, whereas the ideal contribution *i.e.*, for an ideal gas at 1 atm pressure, is -424.2 kcal/mole for this change. This gives the net free energy change of -18.3 kcal/mole not accounting for standard concentration. Converting to the standard concentration of 1 M adjusts this by $-2 \cdot R T \ln 24.46$ to the calculated free energy change of -22.1 kcal/mole.

An experimental value for the complexation reaction is -14.4 kcal/mole[1,4]. The calculated energetics are in the right range, but the agreement is only fair. Note also that a small difference between large numbers is being computed; thus even minor errors will tend to get amplified. A physical conclusion is that the hydration contribution is more 20 times larger than the net standard free energy change for this reaction; neglecting hydration effects would lead to a
qualitatively incorrect result. Below we consider ways to improve upon these initial estimates.

4 Concluding Discussions

The quasi-chemical approach leads to free energies that are in reasonable agreement with available experimental estimates. But this agreement should not obscure the severe approximations that have been made in applying the theory to practical calculations. For divalent cations, it is unclear if purely an inner-shell complex would provide adequate accuracy of solvation free energy estimate. There are potentially two possible avenues for improvement which we indicate below.

First, the outer-sphere hydration contributions can be obtained using classical molecular mechanics approaches instead of the dielectric continuum model used above. Such an approach is now being undertaken for water clusters on monovalent cations (Asthagiri, et al. in preparation) and this can likely be used for Be(H₂O)₄²⁺ as well.

Second, it is possible to expand the chemical potential of the tetra-aqua cation in terms of its own inner-shell (i.e. the Be²⁺ cation’s 2nd shell). This seems particularly natural here because the inner shell structures are physically definite (fig. 2). The hydration contribution of those 2nd shell structures could be obtained using a dielectric continuum model. Also it is possible to apply a lower level of quantum chemical approximation to describe the coupling of the 1st and 2nd shells. Then with an improved estimate for the solvation free energy of the tetra-aqua cation, one could obtain a better estimate for the solvation free energy of Be²⁺. This approach is the iterated quasi-chemical scheme and a variant has been successfully applied to hard-sphere fluids [32]. In the present case, however, this approach would be daunting for many reasons. (A) Obtaining statistically representative 2nd-shell complexes in the gas-phase is difficult. (B) The rigid-rotor harmonic oscillator approximation is dubious for applications to such clusters. (C) Applying the quasi-chemical theory to such large clusters demands consideration of packing effects. This latter issue is actively under study at present (Ashbaugh and Pratt, in preparation).

The neglect of packing aspect is certainly one the reason underlying the merely fair agreement for the [Be·OH·Be]³⁺ thermochemistry. It is also likely that anharmonic effects are non-negligible for clusters such as Be₂OH³⁺ and Be₂OH(H₂O)₆³⁺. But despite these substantial limitations, it is heartening to obtain the qualitatively correct trends. In our pKₐ calculations, however, by arranging the equation to have similarly sized species on both sides of the equality we were able to mitigate these uncertainties.
5 Acknowledgements

The work at Los Alamos was supported by the US Department of Energy, contract W-7405-ENG-36, under the LDRD program at Los Alamos. LA-UR-03-0073.

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