The hydration state of HO\(^{-}\)(aq)

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Abstract

The HO\(^{-}\)(aq) ion participates in myriad aqueous phase chemical processes of biological and chemical interest. A molecularly valid description of its hydration state, currently poorly understood, is a natural prerequisite to modeling chemical transformations involving HO\(^{-}\)(aq). Here it is shown that the statistical mechanical quasi-chemical theory of solutions predicts that HO\(\cdot\)[H\(_2\)O\(_3\)]\(^-\) is the dominant inner shell coordination structure for HO\(^{-}\)(aq) under standard conditions. Experimental observations and other theoretical calculations are adduced to support this conclusion. Hydration free energies of neutral combinations of simple cations with HO\(^{-}\)(aq) are evaluated and agree well with experimental values.

Key words: hydroxide ion, aqueous solution, quasi-chemical theory, coordination number, hydration free energy

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1 Introduction

In this Letter, we consider the hydration state of HO\(^{-}\)(aq) from the perspective of the quasi-chemical theory[1,2,3,4,5,6,7,8,9]. Then we draw upon earlier calculations on H\(^+\)(aq) [10], Li\(^+\)(aq) [4,11], and Na\(^+\)(aq) [12] and demonstrate that the predicted hydration state provides a satisfactory description of the pair hydration free energies for HOH, LiOH, and NaOH. The involvement of HO\(^{-}\)(aq) in the speciation of Be\(^{2+}\)(aq) has been studied recently by the same methods [13].

The H\(^+\)(aq) and HO\(^{-}\)(aq) ions are undoubtedly the most important ions in aqueous phase chemistry, and particularly biological chemistry. This is due
largely to the fact that they are intrinsic to the aqueous media and common extrinsic occupants of those phases encounter these species.

The Be\(^{2+}\)(aq) example noted above provides a specific motivation for the present work. Beryllium is an technologically important metal, but inhaled beryllium dust is toxic and causes chronic beryllium disease in a subset of exposed individuals. This disease eventually leads to lung failure and is presently incurable. It is well-established that the HO\(^-\) ions can cross-link Be\(^{2+}\) ions [14]. These colloidal beryllium-hydroxide clusters might ultimately trigger chronic beryllium disease.

Understanding the hydration state of HO\(^-\)(aq) is also a key to understanding its anomalously high diffusivity [15,16,17]. Indeed both H\(^+\) and HO\(^-\) are thought to diffuse by a proton/hole-hopping mechanism, and this has implications that extend from biological transport of these ions to the transport mechanisms in the polyelectrolyte membranes [18] involved in some fuel cell designs.

2 Quasi-chemical Theory

In the quasi-chemical approach [8], the region around the solute of interest is partitioned into inner and outer shell domains. For the case of HO\(^-\), the inner shell comprises the water molecules directly coordinated with the ion. This domain can be treated quantum mechanically, while the outer shell contributions can be assessed using classical force-fields or dielectric continuum models. The theory permits a variational check of the inner-outer partition [12], but this aspect has not been pursued here. In the present study outer shell contributions have been evaluated with a dielectric continuum model and the trends confirmed by molecular dynamics calculations using classical interatomic potentials.

The inner shell reactions are:

\[
\text{HO}^- + n\text{H}_2\text{O} \rightleftharpoons \text{HO[H}_2\text{O}]_n^- \tag{1}
\]

The free energy change for these reactions were calculated using the Gaussian programs [19]. The HO \cdot [H\(_2\)O\(_n\)]\(^-\) (n = 0 . . . 4) clusters were geometry optimized in the gas phase using the B3LYP hybrid density functional[20] 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 with the 6-311+G(2d,p) and the aug-cc-pVTZ basis sets, although most of our results pertain to the former basis.
For estimating the outer shell contribution, the ChelpG method [21] was used to obtain partial atomic charges. Then with the radii set developed by Stefanovich et al. [22], surface tessera were generated [23], and the hydration free energies of the clusters were calculated using a dielectric continuum model [24]. With this information and the binding free energies for the chemical reactions, a primitive quasi-chemical approximation to the excess chemical potential of \( \text{HO}^- (\text{aq}) \) in water is:

\[
\beta \mu_{\text{OH}^- (\text{aq})}^{ex} \approx -\ln \left[ \sum_{n \geq 0} \tilde{K}_n \rho_{\text{H}_2\text{O}}^n \right] 
\]

where \( \tilde{K}_n = K_n^{(0)} \exp \left[ -\beta \left( \mu_{\text{HO} (\text{H}_2\text{O})}^{ex} n^- - n \mu_{\text{H}_2\text{O}}^{ex} \right) \right] \). \( K_n^{(0)} \) is the equilibrium constant for the reaction Eq. 1 in an ideal gas state, \( n \) is the hydration number of the most probable inner shell cluster, and \( \beta = 1/k_B T \). The density factor \( \rho_{\text{H}_2\text{O}} \) appearing in EQ. 2 reflects the actual density of liquid water and its effect is included by a replacement contribution of \( -nk_B T \ln(\rho_{\text{H}_2\text{O}}/\rho_0) = -nk_B T \ln(1354) \), where \( \rho_{\text{H}_2\text{O}} = 1 \text{ gm/cm}^3 \) and \( \rho_0 = 1 \text{ atm}/RT \). (A detailed discussion on standard states and this replacement contribution can be found in Grabowski et al. [10].) Note EQ. 2 is a simplification of the broader theory, and approximations enter at that stage. But all these approximations are available for scrutiny and improvement [10].

In Table 1 the relevant energies are collected, and Fig. 1 gives the hydration free energy of the hydroxide anion for various hydration states. In order of decreasing stability \( \text{HO} \cdot [\text{H}_2\text{O}]_3^- > \text{HO} \cdot [\text{H}_2\text{O}]_2^- \sim \text{HO} \cdot [\text{H}_2\text{O}]_1^- > \text{HO} \cdot [\text{H}_2\text{O}]_4^- \) is found. The greater stability of \( \text{HO} \cdot [\text{H}_2\text{O}]_3^- \) is independent of the level of theory; calculations with the much larger aug-cc-pVTZ basis give the same trends. Clearly (Fig. 1) including the \( \text{HO} \cdot [\text{H}_2\text{O}]_4^- \) contribution to the sum does not appreciably alter the final excess chemical potential of \( \text{HO}^- (\text{aq}) \): the whole effect is due accurately to the \( \text{HO} \cdot [\text{H}_2\text{O}]_3^- \) quasi-component.

A comparative rationalization of the electronic structure results on \( \text{HO} \cdot [\text{H}_2\text{O}]_3^- \) and \( \text{HO} \cdot [\text{H}_2\text{O}]_4^- \) is the following: The nominal hydroxide hydrogen atom in these negative ions is less positively charged than is typical of water hydrogens. As a result, opportunities for hydrogen bond donation to that nominal hydroxide hydrogen have diminished profitability. The fourth water ligand then prefers to crowd among the other three on the oxygen side of the hydroxide anion.

To assess the influence of the level of theory used, we have calculated the free energy change for the reaction:

\[
\text{HO} \cdot [\text{H}_2\text{O}]_3^- + \text{H}_2\text{O} \leftrightarrow \text{HO} \cdot [\text{H}_2\text{O}]_4^- 
\]
Table 1
Electronic energy (a.u.), corrections (a.u.) to the free energy for zero-point and thermal motions, and excess chemical potential (kcal/mole) using dielectric continuum approximation with charges obtained at B3LYP/6-311+G(2d,p).

|       | E       | G corr | µ*     |
|-------|---------|--------|--------|
| H2O   | -76.45951 | 0.00298 | -7.7   |
| HO^-  | -75.82779 | -0.00771 | —      |
| HO[H2O]^- | -152.33413 | 0.00634 | -84.2   |
| HO[H2O]_2^- | -228.83014 | 0.02655 | -76.8   |
| HO[H2O]_3^- | -305.32036 | 0.04705 | -72.7   |
| HO[H2O]_4^- | -381.80433 | 0.07149 | -67.6   |
| HO[H2O]_3[H2O]^- | -381.80104 | 0.06450 | —      |

Fig. 1. Quasi-chemical contributions to the hydration free energy of HO^- (aq) as a function of the inner-shell coordination number n. •: contribution of individual terms -k_B T ln \( K_n \rho_{H_2O}^n \) to \( \mu^{ex} \); see Ref. [11]. ●: -k_B T ln \( \sum_{m=0}^{m=n} K_m \rho_{H_2O}^m \). △: \(-RT \ln K_n^{(0)} - nRT \ln [1354]; \times: \mu^{ex}_{HO(H_2O)_n} - n\mu_{H_2O}\). An observation volume of radius 1.7 Å centered on the anionic oxygen defined the inner shell. Change of that radius, say to 2.0 Å, would change the \( n = 0 \) contribution roughly by factor of (1.7/2.0). But that wouldn’t change the net result substantially since the \( n = 3 \) contribution dominates and the ion is nearly buried by the ligands in that case. This is an example of the variational character of the quasi-chemical theory noted above.
Table 2
Contributions to the free energy change of reaction 3. $\Delta G^\circ$ is the free energy change in the standard 1 atm pressure ideal gas state. $\Delta G$ accounts for the concentration of water (55.5 M), and the concentration of the quasi-components (1 M ideally diluted). $\Delta \mu^e$ is the change in the excess chemical potential. $\Delta G(aq)$ is the net free energy change.

| Theory     | $\Delta G^\circ$ | $\Delta G$ | $\Delta \mu^e$ | $\Delta G(aq)$ |
|------------|------------------|-------------|----------------|---------------|
| B3LYP      | -1.9             | -6.2        | 12.8           | 6.6           |
| BLYP       | -2.0             | -6.3        | 10.3           | 4.0           |
| PW91       | -1.6             | -5.9        | 13.5           | 7.6           |
| PBE        | -1.1             | -5.4        | 13.4           | 8.0           |
| MP2        | -4.6             | -8.9        | 13.6           | 4.7           |

using the BLYP, PW91, and PBE density functionals, with geometry optimizations at those levels. MP2 single point calculations have been performed on the B3LYP derived geometries as well. An important feature that emerges from Fig. 1 and Table 2 is that outer shell contribution favors HO $\cdot$ [H$_2$O]$_3^-$, at all levels of theory, principally by providing an assessment of the hydration of the separated ligands.

To check limitations of the dielectric continuum model for outer shell contributions, the charging free energies of HO $\cdot$ [H$_2$O]$_3^-$ and HO $\cdot$ [H$_2$O]$_4^-$ were obtained using classical molecular dynamics with TIP3P potential for water and the TIP3P van der Waals parameters for the oxygen and hydrogen atoms of the quasi-component. We find that $\mu^e_{\text{HO}[\text{H}_2\text{O}]_3^-} - \mu^e_{\text{HO}[\text{H}_2\text{O}]_4^-} = -6.9$ kcal/mol in reasonable agreement with the $-6$ kcal/mol found using a dielectric model. Importantly, the trend is unaltered. (See [25] for details on the classical simulation procedure.) Positive outer shell packing contributions are not addressed here, but these are expected to be slightly larger for HO $\cdot$ [H$_2$O]$_4^-$ than for HO $\cdot$ [H$_2$O]$_3^-$ and hence should enhance the calculated difference.

3 Discussions

Fig. 1 and Table 2 show that contributions for inner shell water additions to HO $\cdot$ [H$_2$O]$_3^-$ are in fact favorable; this is routinely observed [11] and implies that ligand hydration typically plays a significant role in establishing the probable coordination numbers.

Another common observation in applying a quasi-chemical approach to ion hydration problems is that aggregates beyond the most probable size begin to
find favorable outer shell placements for the later additions. This seems to be the case in the present problem too. Alternative arrangements of four water molecules, such as HO$\cdot$[H$_2$O]$_3$·[H$_2$O]$^-$, are more favorable than HO$\cdot$[H$_2$O]$_4$$^-$ by about 2 kcal/mole (Table 3). Numerous such arrangements are possible [26]. In the specific case we have considered, the fourth water molecule hydrogen-bonds with the inner shell water molecules, similar to structure OHW4III in Fig. 2 of [26].

Table 3 shows that the present inner shell computations are in reasonable agreement with experimental results. They are also in reasonable agreement with theoretical calculations reported in [26] with the differences attributable to differences in the basis sets for minimization and energy evaluations. Note that within the primitive quasi-chemical approach, outer-shell structures of the fourth water are excluded here because they are accounted for in outer shell contributions. Those arrangements are in fact part of the outer-sphere arrangements of the HO$\cdot$[H$_2$O]$_3$$^-$ quasi-component. For the n=4 case, one expects many isomers to be present, but thermochemical measurements obviously cannot specify the structure. The trends (Table 3) strongly suggest that in the gas-phase the n=4 cluster in fact must involve an outer-sphere arrangement of the fourth water. This shell-closure at n=3 was inferred by Moet-Ner and Speller [27] based on their thermochemical analysis of the step-wise attachment of water to HO$^-$. These authors also noted possible artifacts in a much earlier work [28] that did not show the shell effect.

Table 3
Standard free energy ($\Delta G^\circ$) for adding n water molecules to HO$^-$. The experimental results (with an error bar of about $\pm$ 1.5 kcal/mole) are from [27]. A: This work at B3LYP/6-311+G(2d,p). B: This work at B3LYP/aug-cc-pVTZ. The case 3+1 refers to the outer-sphere arrangement of the fourth water discussed in the text. Theoretical calculations for comparable structures from [26] at the B3LYP/aug-cc-pVDZ level are also shown.

| n   | Expt  | A     | B     | [26] |
|-----|-------|-------|-------|------|
| 1   | -20.0 | -22.5 | -20.5 | -20.5 |
| 2   | -31.2 | -34.5 | -31.1 | -32.2 |
| 3   | -40.2 | -42.8 | -38.0 | -40.1 |
| 3+1 | -47.0 | -41.4 | -43.2 |
| 4   | (-46.0) | -44.7 | -38.3 | -39.0 |

The lower energy of the outer shell arrangement of the fourth water was recently confirmed spectroscopically by Johnson and coworkers [29]. Those experiments showed that shell closure by the ligating water molecules occurs when three water molecules are hydrogen bonded to the HO$^-$ ion. New spec-
Table 4
Solvation free energy of neutral ion pairs (kcal/mole). The solutes are transferred from 1 M (ideal gas) to 1 M (ideally diluted solute). TIP3 and SPC/E refer to the potentials used for the water model. The pair hydration free energy for HOH was obtained based on the experimental gas phase free energy of dissociation (383.7 kcal/mole) [32], the known pK of water (15.7) [33] and the hydration free energy of water (-6.3 kcal/mole) obtained from phase-equilibria information. The values for LiOH and NaOH are from [34].

|       | TIP3P | SPC/E | Expt  |
|-------|-------|-------|-------|
| HOH   | -366.4| -367.8| -368.1|
| LiOH  | -236.2| -236.5| -233.3|
| NaOH  | -211.1| -212.5| -208.1|

Central features appeared with the addition of a fourth water molecule. These new features were a result of hydrogen bonding of the fourth water molecule to first solvation shell waters instead of direct coordination with HO⁻.

The conclusion that HO·[H₂O]₃⁻ is the predominant inner shell hydration number in liquid water under standard conditions has been supported by ab initio molecular dynamics (AIMD) simulations [17,30,31]. But thermodynamic tests can be considered too. Earlier quasi-chemical studies have confirmed the dominant coordination structure of H⁺, Li⁺ and Na⁺ [25,10]. The dominant coordination structure of Li⁺ and Na⁺ were also cross-checked against Born-Oppenheimer AIMD [11,12]. Thus we can compute the hydration free energy for the neutral ion combinations HOH, LiOH, and NaOH. These pair hydration free energies, obtained using classical molecular dynamics simulations for the outer shell contributions, are given in Table 4 (after Table III in [25]). The dominant HO·[H₂O]₃⁻ structure was also found to be the best descriptor for the ionization of water [25] and of Be[H₂O]₄²⁺ [13].

The agreement shown in Table 4 is excellent. The minor discrepancies are attributable to neglect of a variety of secondary effects: anharmonicity of the quasi-component structures, packing effects, and dispersion interactions. An assumption that HO·[H₂O]₄⁻ was the dominant form would have predicted these hydration free energies to be significantly more positive than the experimental results.

4 Conclusions

The present quasi-chemical theory applied to HO⁻(aq) leads to the conclusion that HO·[H₂O]₃⁻ is the dominant inner shell coordination struc-
ture for the $\text{HO}^-(\text{aq})$ ion in liquid water under standard conditions. The $\text{HO} \cdot [\text{H}_2\text{O}]_4^-$ is less favorable by nearly 7 kcal/mole ($\approx 12 \text{k}_B\text{T}$). The prediction of $\text{HO} \cdot [\text{H}_2\text{O}]_3^-$ as the dominant form has been successfully used in predicting the hydration free energies of neutral ion combinations $\text{HOH}$, $\text{LiOH}$, and $\text{NaOH}$. Thus based on different lines of investigation, we conclude that $\text{HO}^-$ is predominantly $\text{HO} \cdot [\text{H}_2\text{O}]_3^-$ in liquid water.

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