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Ion hydration in high-density water

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Abstract. Structural modifications of the Zn^{2+} hydration properties under high pressure (up to 2.85 GPa) have been investigated by Molecular Dynamics (MD) simulations and the first shell structural results have been experimentally validated by X-ray Absorption spectroscopy. The first shell hydration complex of the Zn^{2+} ion retains an octahedral symmetry with a shortening of the Zn-O distance up to 0.04 Å and an increase of the thermal motion. The structural transformations occurring to water with increasing density are also investigated by MD simulations; the effect of pressure is to increase the number of interstitial water molecules, while the tetrahedral first shell cluster is only slightly distorted in the high-density conditions.

1. Introduction

The properties of aqueous solutions under pressure are fundamentally important for a wide range of scientific disciplines, such as geoscience, environmental sciences and planetary modeling. At high pressures (and temperatures) water exists in different liquid or solid phases whose properties are very different from those found at normal conditions. Supercritical water exists at temperatures above 600 K and pressures between 10 MPa and 1 GPa. It is characterized by a low dielectric constant (~ 6 in a typical supercritical regime) and weak hydrogen bonding formation which makes it an excellent solvent for non polar substances. Due to the broad range of applications, such as in the decomposition of organic wastes or in the hydrothermal synthesis, supercritical water has been extensively studied [1, 2, 3]. At pressures between 0.1 and 10 GPa and temperature between 300 and 500 K liquid water is in equilibrium with several forms of ice and its phase in this region is called compressed water. Due to the huge pressure, the phases existing in this zone are very different and much more dense than those found at normal conditions. Compressed water is a system that has recently gained much interest, and the effect of pressure on the structure and h-bond network of compressed water has been addressed by a variety of experimental and theoretical works [4, 5, 6, 7, 8, 9, 10]. Although different conclusions are drawn from these studies, they suggest the possible existence of a high-density state of water (HDW) which at a pressure of few kilobars gradually evolves at the expense of a low-density state of water (LDW) [7]. In HDW the second shell of neighbor molecules is thought to collapse onto the first one, as a consequence of the rupture of the h-bond network. However, the results of a Molecular Dynamics (MD) simulation [9] have shed light on the key role played by interstitial molecules in the second coordination shell, while in a recent neutron diffraction investigation the

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authors conclude that with increasing density water approaches a local structure common to a simple liquid [10]. Despite the plethora of studies on the properties of pure high-density water, to our knowledge there is only one work in the literature addressing the structural changes of ionic aqueous solutions under high pressure [11]. In this study the transformation of the Rb^+ and Br^- first hydration shells was investigated and dramatic effects in the anion hydration structure have been observed with increasing pressure.

Here we present an extensive study of the hydration properties of the Zn^{2+} ion in conditions of very high pressures (up to 2.85 GPa), combining Extended X-Ray Absorption Fine Structure (EXAFS) and MD simulations. The aim of this work is on the one hand to unveil the structural transformation occurring to water from the low- to the high-density conditions, on the other hand to investigate the pressure effects on the hydration structure of the Zn^{2+} ion, which is well known to be octahedral at ambient conditions [12, 13, 14].

2. Methods

Three MD simulations of Zn^{2+} in aqueous solution were carried out in order to reproduce the properties of the system in three different points of the phase diagram, i.e. 300 K and 0.1 MPa (d = 1006.8 g/l), 300 K and 1.0 GPa (d =1271.2 g/l), 360 K and P = 2.2 GPa (d = 1345.3 g/l). The system was composed by one Zn^{2+} ion and 819 water molecules in a cubic box. It was simulated for 15 ns (the first 5 ns were used for equilibration) in an NVT ensemble, using different box volumes in order to reproduce the chosen density, temperature and pressure conditions. The same two-body potential fitted on an ab-initio potential energy surface has been used to describe the ion-water interaction and all details can be found in Ref. [13]. A 0.1M Zn^{2+} aqueous solution was obtained by dissolving the appropriate amount of $Zn(NO_3)_2$ in water. The nitrate counter-ion has been chosen to prevent the formation of ionic pairs in the solution. Xray absorption spectra above the Zn K-edge have been measured using the high pressure setup based on the Paris-Edinburgh press developed at the BM29 beam line [15] of the European Synchrotron Radiation Facility. Four spectra have been recorded at different pressures and temperatures following the melting curve of the solution phase diagram. In particular spectra were recorded for pressure values of 0.10 MPa, 0.20 GPa, 1.97 GPa and 2.85 GPa. EXAFS data have been analyzed with the GNXAS software package [16].

3. Results

3.1. Zn^{2+} hydration properties

The upper panel of Figure 1 shows the comparison of the first peak of the Zn-O radial distribution functions $(g(\mathbf{r}))$ obtained from the three simulations. The change of thermodynamic conditions does not affect the first coordination shell hydration number, which is obtained by integration of g(r)'s up to the first minimum and is six in all cases. Conversely, the radial distribution functions show a shortening of the peak position (the first peak distances are 2.06, 2.05 and 2.04 A for the simulations at 0.1 MPa, 1.0 GPa and 2.2 GPa, respectively), and a broadening of the first peak as pressure increases, meaning that in compressed water the first coordination shell becomes more disordered. The effect of pressure changes is more evident on the structure of the second coordination shell, as shown in the lower panel of Figure 1. In this case the shift of the peak positions at shorter distances is about 0.11 Å (the second peak distances are 4.32, 4.26 and 4.21 Å for the simulations at 0.1 MPa, 1.0 GPa and 2.2 GPa, respectively), larger than what observed for the first hydration shell. Increasing coordination number values are obtained from the three simulations (they are 10.9, 12.7 and 29.0 for the simulations at 0.1 MPa, 1.0 GPa and 2.2 GPa, respectively). Moreover, the g(r) changes qualitatively increasing the pressure in the zone after 4.5 Å and at 2.2 GPa the second hydration shell is not only shifted towards the metal ion but expands outwards and is less separated from bulk water.



Figure 1. Comparison of the Zn-O g(r) first peak obtained from the three MD simulations (upper panel) and of the Zn-O g(r) second peak obtained from the three MD simulations (bottom panel).



Figure 2. a.d.f. of the ϕ , ζ and ψ angles obtained from the MD simulations at 0.1 MPa (black lines), 1.0 GPa (red lines) and 2.2 GPa (blue lines). (a) First hydration shell a.d.f of ϕ . (b) Second hydration shell a.d.f. of ϕ . (c) First hydration shell a.d.f. of ζ . (d) First hydration shell a.d.f. of ψ .

The angular distribution functions (a.d.f.) obtained from the three simulations of the ϕ , ζ and ψ angles (plotted as functions of $1 - \cos(\phi, \zeta, \psi)$) are depicted in Figure 2. Panel (a) shows the a.d.f. of ϕ angle formed by the water molecule dipole and the Zn-O vector. The distribution functions calculated from the three trajectories show very sharp peaks at $cos(\phi) = 1$, as the oxygen atoms point toward the ion and wagging movements are very limited. The curves related to the simulation at 0.1 MPa and 1.0 GPa go to zero at $\phi = 30^{\circ}$ while the a.d.f. obtained at 2.2 GPA drops to zero at $\phi = 38^{\circ}$ since the increase of pressure allows a small increase of rotational freedom of the first shell water molecules. Analysis of the second coordination shell a.d.f. gives quite different results: the simulations at 1.1 and 2.2 GPa show a change of slope and concavity as compared to the distribution obtained from the trajectory at 0.1 MPa, as the packing of the second hydration sphere forces the water molecules to deviate from the minimum potential energy alignment observed in the first simulation. Moreover, they are much broader, showing that in the compressed solutions wagging movements in the second hydration shell are much more important than at 0.1 MPa. Panel (c) shows the a.d.f. of ζ angle, formed by the Zn-O vector and the normal to the water plane. In all cases there is a well defined peak centered at $cos(\zeta) = 90^{\circ}$, showing that the Zn-O vector is located most of the time in the water molecular plane with a maximum deviations at 90° and 120°. The a.d.f.'s for the ψ angle (formed by two different Zn-O vectors) calculated at various pressures on first shell water molecules are shown in panel (d). All of the distribution functions have nearly coincident maxima at $1 - \cos(\psi) = 1$ and $1 - \cos(\psi) = 2$ (corresponding to ψ values of 90° and 180°), thus showing the existence of a stable octahedral coordination geometry, even at high pressures. Moreover, the a.d.f.'s go to zero at intermediate values, as water molecules are strongly constrained in their positions and large distortions of the octahedral symmetry are not expected.





Figure 3. Comparison between the experimental (blue dotted line) and theoretical (red solid line) EXAFS signals at different pressure values.

Figure 4. Pressure dependence of the Zn-O g(r) first peak obtained from the analysis of EXAFS spectra.

Table 1. Structural parameters of Zn-O g(r) first peak obtained from the EXAFS analysis. R is the mean Zn-O distance, σ is the Debye-Waller factor, and β is the asymmetry parameter.

Pressure	$R(\text{\AA})$	$\sigma^2({\rm \AA}^2)$	β
0.10 MPa	2.078	0.0087	0.2
$0.20 \ \mathrm{GPa}$	2.074	0.0088	0.2
$1.97 \mathrm{~GPa}$	2.053	0.010	0.2
$2.85~\mathrm{GPa}$	2.042	0.011	0.2

3.2. EXAFS Analysis

The analysis of EXAFS spectra reinforces the theoretical results obtained from MD simulations. Figure 3 shows the comparison between the experimental and theoretical EXAFS signals for pressure values of 0.2, 1.97, and 2.85 GPa. Note that both the quality of the experimental data and the agreement with the theoretical curve are excellent. The experimental Zn-O g(r) first peaks obtained from the EXAFS minimizations are shown in Figure 4 while the corresponding structural parameters are reported in Table 1. The experimental g(r)'s confirm that the Zn²⁺ ion first shell hydration number does not vary with pressure and the shift of the Zn-O g(r) peak position to shorter distances with increasing pressure is a clear evidence of the first hydration shell compression. The higher mobility of water molecules in the first coordination sphere is highlighted by the trend of the Debye-Waller factors. Moreover, the shift towards shorter distances of the Zn-O rising edge indicates that the oxygen atoms of the first shell water molecules in compressed water can reach regions of space not normally accessible at ambient conditions.



Figure 5. Comparison of the O-O g(r) obtained from the MD simulations carried out at P=0.1 MPa, 1.0 GPa and 2.2 GPa.



Figure 6. Distance distributions of groups of 1^{st} to 4^{th} , 5^{th} to 7^{th} , 8^{th} to 11^{th} , and 12^{th} to 15^{th} oxygen neighbors for P=0.1 MPa (black), 1.0 GPa (red) and 2.2 GPa (blue).

3.3. Water structure under pressure

In the second step of our analysis we have investigated the structural transformations occurring to water from the low- to the high-density conditions. To this end, we have carried out three MD simulations of pure water at the same thermodynamic conditions used in the simulations. Comparison between the water-water g(r)'s in pure water and in the second shell of the Zn^{2+} ion has shown that solvent molecules are not significantly influenced by the presence of the solute, and the impact of the ion on the structure of water does not extend in an appreciable way beyond the first hydration shell (data not shown). Conversely, remarkable differences among the oxygenoxygen g(r)'s were found with increasing pressure (see Figure 5). At 2.2 GPa a pronounced broadening of the O-O g(r) first peak, as compared to ambient conditions, is observed. This change is caused by a collapse of the second coordination shell, as a consequence of the rupture of the h-bond network. To get a deeper insight into the structural properties of water under high pressure we have calculated the g(r)'s of distance ranked groups of neighbors with respect to a given central water molecule (see Figure 6). The group of first neighbors (1-4) which form the tetrahedral first shell of the water molecule behaves rigidly with an almost density independent distance from the central molecule, in agreement with neutron diffraction results [10]. On the contrary, distances of all the other groups of neighbors decrease with increasing density, as more and more water molecules move towards the central one. Figure 7 shows the distribution of the oxygen-oxygen angle (labelled as ω) calculated on the four closest water molecules around a central oxygen atom. At ambient conditions the distribution is highly peaked at 109° , corresponding to a tethaedral arrangement. The intensity and the position of this peak is only slightly affected by increasing pressure, as the tetrahedral first shell cluster is minimally distorted in the high density conditions. Conversely, the intensity of the peak at 55° significantly increases at higher pressures and the position of the peak moves towards larger angles. This is the angle formed by the central oxygen, a tethraedral neighboring oxygen and the oxygen of an interstitial water molecule which is not h-bonded to any of the first shell molecules. The trend of ω distributions then suggests that the number of interstitial molecules increases under high pressure and that these molecules collapse into the first coordination shell. This result is reinforced by the analysis of the O_{1-4} -O- O_{5-8} angle (labelled as θ), i.e. the angle about an oxygen atom formed by its first four (1-4) and second four (5-8) neighbors (see Figure 8). At ambient conditions two peaks at 48° and 75° are found which merge into a single



Figure 7. a.d.f. of the O-O-O angle (ω) calculated on the four closest water molecules around a central oxygen atom obtained from the three MD simulations.



Figure 8. a.d.f. of the O_{1-4} -O- O_{5-8} angle (θ) calculated on the four closest water molecules around a central oxygen atom. O_{1-4} -O- O_{5-8} is the angle about an oxygen atom formed by its first four (1-4) and second four (5-8) neighbors.

peak centered at 60° at 2.2 GPa. As already pointed out in Ref [9], this peak is due to the presence of interstitial molecules. The growth of interstitial molecules with pressure has been also highlighted by computing the average number of h-bonds (\bar{n}) formed by the first four (1-4) and second four (5-8) neighbors of a central water molecule. A decrease of \bar{n} from 0.65 at ambient conditions to 0.43 at 2.2 GPa was found, in line with previous results.

4. Conclusions

In this paper we have presented a detailed structural study of the Zn^{2+} ion in aqueous solution under pressure. The octahedral structure of the Zn^{2+} first hydration shell is found to remain stable also under high pressure, while the Zn-O first shell distance is shortened and the hydrated complex becomes more disordered. These effects are in line with the substantial changes of the water structural properties, in which the number of interstitial second shell molecules, not hbonded to the first shell ones, increases significantly.

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