The onset of dissociation in the aqueous LiOH clusters: a solvation study with the effective fragment potential model and quantum mechanics methods

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Abstract

The first systematic study on the solvation of the LiOH(H₂O)ₙ (n = 1–6, 8) clusters is herein presented by using both the molecular-mechanics effective fragment potential (EFP) model and full quantum mechanics methods. Aqueous clusters are sequentially calculated first with the LiOH solute molecule described by a restricted Hartree–Fock (RHF) wavefunction and the H₂O solvent molecules by the EFP model (EFP/RHF), and then with the full quantum mechanics RHF and Möller–Plesset second-order perturbation (MP2) theories. Calculated properties include equilibrium geometries, Mulliken charges, bond lengths and orders, and relative energies inter alia. Present results indicate that at the least six H₂O molecules are necessary to be added to one LiOH molecule to cause its spontaneous dissociation into a Li⁺/OH⁻ separated ion pair. Another instance of dissociation is also observed in one of the LiOH(H₂O)₈ isomers. EFP/RHF reasonably reproduces RHF structural properties and dissociation patterns but discrepancies arise in the solute charge description. Comparisons of the present theoretical results with previous EFP studies and with a few experimental data are also discussed.

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1. Introduction

In recent years, there has been a renewed interest in studying dissolution mechanisms and solvation effects by both modern experimental techniques and accurate computational methods [1]. The importance of those investigations can be readily seen by simply recalling the essential role played by solvation in the vast majority of chemical processes. Although the main features of dissolution and solvation are routine topics in chemistry textbooks, many microscopy details of those phenomena still remain uncertain. Fortunately, the emergence of more precise experimental techniques and the incessant growth in computational power are making possible very meticulous studies on dissolution and solvation at the molecular level. For instance, it has been recently established experimentally that the first primary hydration shells of the OH⁻(H₂O)₃ and F⁻(H₂O)₄ clusters in the gas phase do consist of exactly three and four H₂O molecules (n = 3 and 4), respectively [2]; and the first genuine, primary-shell, hexa-coordinated Na⁺ cluster in the gas phase has been also recently synthesized and detected [3].

Although dissolution and solvation take place in bulk phase, the investigation of microscopic processes in a solution sample may become experimentally difficult and computationally costly. Therefore, a feasible approach to investigate solvation is to deal with individual clusters of one solute molecule coordinated with a few solvent molecules in the gas phase. This approach is so advantageous that even valid inferences about the solvation processes involving the Na⁺ and K⁺ ions in channel proteins have been drawn in that way [4]. The step-wise addition of solvent molecules to a bare solute in a cluster, via either experiments or computer simulations, can certainly reveal the minute details of dissolution and solvation and record the evolution of the system properties from a single and isolated molecule of solute to the bulk phase.

In the context of a theoretical investigation on solvation, an active field of research is the prediction of the minimum
number of H$_2$O molecules necessary to cause the dissociation of a single, isolated molecule of a strong acid [1], a strong hydroxide [5], or an ionic salt [6]. In a dilute aqueous solution of those species, one cation and one anion from the binary solute can form an ion pair that is coordinated by a few H$_2$O molecules. Two clearly distinct types of ion pairs can occur in a strong electrolyte solution: the separated ion pair and the contact ion pair, respectively. In a separated ion pair, the distance between the two ions is appreciably larger than their corresponding bond length in the isolated solute molecule in the gas phase. On the other hand, in a contact ion pair, the ions separation remains relatively close to that gas-phase bond length even when the pair is coordinated with a few H$_2$O molecules. The appearance of a genuine separated ion pair signals the onset of the solute dissociation in the solvent environment. Much of the theoretical analysis on aqueous solvation and ion-pair formation has been devoted to study strong electrolytes bearing Na$^+$ and Cl$^-$ ions such as NaCl [6–12], HCl [13–22] and NaOH [5] inter alia. For instance, in a recent study, Jungwirth [6] has theoretically predicted the formation of a Na$^+$/Cl$^-$ separated ion pair exhibiting a Na–Cl separation of 4.43 Å in the isolated NaCl(H$_2$O)$_6$ cluster by using Møller–Plesset second-order perturbation theory (MP2). This particular solvation environment for the formation of a Na$^+$/Cl$^-$ separated ion pair is not surprising because the NaCl(H$_2$O)$_6$ cluster with a prism shape presents a balanced, three-dimensional, cage structure. In an interesting series of studies, Yoshikawa and Gordon [5] have also recently investigated the appearance of both separated and contact ion pairs for single NaOH and NaCl molecules solvated with up to six H$_2$O molecules. These authors could theoretically predicted that genuine Na$^+$/OH$^-$ and Na$^+$/Cl$^-$ separated ion pairs are formed in the NaOH(H$_2$O)$_n$ and HCl(H$_2$O)$_n$ clusters, exhibiting large ion separations of 4.15 and 4.00 Å; 4.03 and 4.65 Å; and 4.36 and 4.38 Å, at the levels of the effective fragmented potential (EFP), restricted Hartree–Fock (RHF), and MP2 theories, respectively [5].

Although studies on the aqueous solvation of several Na$^+$ compounds [6–12] have been conducted at length, there are comparatively few experimental and computational studies on the solvation of Li$^+$ compounds [9,11,23,24]. The present investigation is therefore the first systematic theoretical study on the solvation of the strong LiOH base in the presence of up to eight H$_2$O molecules. The motivations for investigating such a particular system are diverse. First of all, any systematic study on solvation involving the alkali-metal ions should include the whole series of those ions in order to explain how the ions size and electronic configurations affect the solvation processes [4,5,24]. In that context, it will be of particular interest to compare the microscopic behavior of a LiOH molecule in an aqueous cluster with that of the most common NaOH in order to explain the different macroscopic properties of these two bases in bulk solution (e.g. the lower solubility of LiOH in H$_2$O). Another reason to investigate Li$^+$ compounds is that this ion has the smallest number of electrons in the series of alkali-metal ions, a circumstance that would make the simulation of large (LiOH)$_n$(H$_2$O)$_m$ clusters less computationally costly. It is also worth noticing that the current use of the moderately water-soluble Li$_2$CO$_3$ salt in the clinical treatment of bipolar disorder may trigger several theoretical investigations on the solvation and coordination of the Li$^+$ ion in order to reveal the still unknown mode of action of this ion in the brain system [25].

The ideal approach for a solvation study on a solute–solvent cluster would be a full ab initio calculation in which the entire system, solute and solvent, is treated as a supermolecule at a high-level theoretical method. However, such a type of calculation is computationally very expensive and can eventually become unfeasible. As long as the number of solvent molecules increases so does the size of the basis set used and so does the number of expected local minima on the potential energy surface. Therefore, a full ab initio approach is only practical in systems with a small number of solvent molecules. A way around this limitation is to employ a mixed quantum/classical (QC) method, where the solute molecule is described by an ab initio wavefunction, whereas the solvent molecules are treated by a less expensive molecular-mechanics (MM) type of model such as the effective fragment potential (EFP) model [5,7,22,24]. EFP has been successfully applied to study numerous solvation processes in aqueous solutions involving NaCl [5,7], NaOH [5], alkali metal and alkaline-earth metal cation–water clusters M$^+$X$_n$(H$_2$O)$_{1−6}$ (M$^+$ = Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$) [24], anion–water clusters A$^−$(H$_2$O)$_{1−6}$ (A$^−$ = OH$^−$, F$^−$, SH$^−$, Cl$^−$ and Br$^−$) [26], oxynanion–water clusters A$^−$(H$_2$O)$_{1−4}$ (A$^−$ = ClO$_4^−$, HSO$_4^−$, NO$_3^−$, HPO$_4^{2−}$, HCO$_3^−$, HCO$_2^−$, SO$_2^−$, SO$_3^{2−}$, PO$_4^{3−}$) [27], and the amino acid glycine [28,29], inter alia. In particular, the systematic EFP and ab initio investigations by Merrill, Webb and co-workers in Refs. [24,26] are highly relevant to the present study because they included the cases of the Li$^+$ cluster ions that are the products of the complete dissociation of LiOH in water, respectively. Comparisons of our present results on the LiOH(H$_2$O)$_n$ (n = 1–6,8) clusters with those on the Li$^+$ cluster ions by Merrill et al. [24,26] will be discussed in Section 3.2.

The present work reports the first systematic study of the effects of adding up to eight H$_2$O molecules to a single LiOH molecule by both a mixed QC, ab initio/EFP [22] model treatment of the solute/solvent system and also by full ab initio descriptions of the whole solute–solvent supermolecule, respectively. In the mixed QC, ab initio/EFP approach, the quantum solute will be described at the level of the RHF theory (EFP/RHF), whereas in the full quantum treatments, the solute–solvent supermolecule will be calculated at both the RHF and MP2 levels of theory. An important aspect of the present study will be to attest
the ability of the EFP/RHF method to correctly predict the structural properties of both contact and separated ion pairs in comparison with the full ab initio methods.

2. Method and computation details

The EFP method has been explained in full detail in several papers [22] so that it will be briefly described herein. The EFP model was specifically developed to describe weak intermolecular interactions between a quantum mechanical solute and a molecular-mechanics solvent, where the latter is represented by an effective fragment potential. The model also includes the proper interactions among the different fragments. In the case of solute–fragment interactions, a one-electron term is incorporated into the ab initio Hamiltonian of the solute containing the Coulombic, polarization and exchange-repulsion/charge-transfer interactions, respectively. For the oth fragment molecule, the effective fragment potential \( V_{el}(\alpha, s) \) is given by

\[
V_{el}(\alpha, s) = \sum_{k=1}^{K} V_{el}^{k}(\alpha, s) + \sum_{l=1}^{L} V_{pol}^{l}(\alpha, s) + \sum_{m=1}^{M} V_{m}^{\text{rep}}(\alpha, s)
\]  

where \( s \) denotes the electronic coordinates. The three terms on the right-hand side of Eq. (1) represent the aforesaid Coulombic, polarization, and exchange-repulsion/charge-transfer interactions. The Coulombic potential is expressed in terms of the distributed multipolar analysis (DMA) [30] of the charge distributions of the solvent. \( K \) in the first term of Eq. (1) is the total number of DMA expansion points. For instance, in the case of a \( H_2O \) molecule, those expansion points are the atom centers and the midpoints on the bonds. Each multipolar expansion is carried up to octupole terms at each expansion point. The entire expansion is multiplied by a distance-dependent cutoff function to account for overlapping charge densities. The polarization of the solvent induced by the electric field of the solute molecule is treated self-consistently [22,31]. In this procedure, the dipole polarizability tensor of the solvent molecules is expanded into its bond and lone-pair components of the localized orbital dipole polarizabilities that are placed at the centroids of the \( L \) localized valence molecular orbitals. The exchange-repulsion/charge-transfer interactions are modeled by simple Gaussian functions located at the fragment centers denoted by \( m \) in Eq. (1), where \( M \) is the total number of those centers. Again, in the case of a \( H_2O \) molecule, those expansion centers are each atom and the molecule center of mass. In the present EFP implementation, those Gaussian functions are fit to the residual energy in a series of water dimer conformations from which the electrostatic and polarization components have been subtracted [5,7,22,24]. Notwithstanding this fitting procedure, it is important to note that genuine charge transfers to or from the EFP region are not permitted in this method [5,7,22,24]. Finally, analogous terms are used to describe the fragment–fragment interactions. The EFP model as described herein is available in the electronic structure code GAMESS [32].

Geometry optimizations of the \( \text{LiOH}(H_2O)_n \) (\( n = 1–6, 8 \)) clusters were first calculated at the level of EFP/RHF theory with the quantum LiOH molecule described with the 6-311++G** basis set and the \( H_2O \) molecules by the EFP model (EFP/RHF/6-311++G**). To assess the accuracy of these EFP/RHF/6-311++G** calculations with respect to full ab initio methods, the EFP/RHF optimized geometries were used as the initial guesses for successive geometry optimizations at the RHF/6-311++G** and MP2/6-311++G** levels. The full RHF calculations will allow determining the degree of accuracy that might be lost by the Q/C procedure in the EFP/RHF method. It is important to bear in mind that the EFP method was designed to reproduce results at the Hartree–Fock level. MP2 calculations will allow determining the effect of electron correlation in this type of systems. Except for a few MP2 geometry optimizations involving analytical Hessian evaluations, all the present computational procedures were performed with the GAMESS program [32]. The MP2 analytical-Hessian calculations were performed with the GAUSSIAN 98 program [33].

3. Results and discussion

The calculated properties for the \( \text{LiOH}(H_2O)_n \) (\( n = 1–6, 8 \)) clusters are presented in Tables 1–8. Li–OH bond lengths, Li and O Mulliken charges, Li–OH bond orders and relative energies for each of the \( \text{LiOH}(H_2O)_n \) (\( n = 1–6, 8 \)) isomers at the EFP/RHF/6-311++G** level of theory are shown in Table 1. The same properties but at the RHF/6-311++G** and MP2/6-311++G** levels of theory are presented in Tables 2 and 3, respectively. Li–OH bond distances for the specific case of the \( \text{LiOH}(H_2O)_6 \) isomer 6za with several basis sets and at the EFP/RHF/6-311++G**, RHF/6-311++G** and MP2/6-311++G** levels of theory are listed in Table 4. Boltzmann-averaged values of the Li–OH bond lengths, Li and O Mulliken charges, and Li–OH bond orders for the \( \text{LiOH}(H_2O)_n \) (\( n = 1–6, 8 \)) clusters at the three levels of theory herein considered are listed in Tables 5–7. The differences in the Mulliken charges between the RHF/6-311++G** and the EFP/RHF/6-311++G** methods for each LiOH atom and for the whole \( H_2O \) molecule in the \( \text{LiOH}(H_2O)_n \) (\( n = 1–6, 8 \)) clusters are listed in Table 8. Finally, the structures of the \( \text{LiOH}(H_2O)_n \) (\( n = 1–6, 8 \)) clusters at the EFP/RHF/6-311++G** level are depicted in Figs. 1–6, except for the case of the \( \text{LiOH}(H_2O)_6 \) isomer 6za that is depicted at the RHF/6-311++G** level in Fig. 5. Some relevant bond lengths of the \( \text{LiOH}(H_2O)_n \) (\( n = 1–3 \)) clusters are also depicted in Figs. 1 and 2 along with their structures; however, the corresponding bond lengths of the remaining
Table 1

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<th>Structure</th>
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<th>(q(\text{Li}))</th>
<th>(q(\text{O}))</th>
<th>BO</th>
<th>(\Delta E)</th>
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Structure refers to the identification numbers in Figs. 1–6; R is the Li–OH bond length in Å, \(q(\text{Li})\) is the Mulliken charge on Li, \(q(\text{O})\) is the Mulliken charge on O, BO is the Li–OH bond order, and \(\Delta E\) is the energy relative to the isomer a in kcal/mol.

LiOH(H\(_2\)O)\(_n\) (\(n = 5, 6, 8\)) clusters are omitted in their figures for the sake of clarity.

### 3.1. Equilibrium geometries, relative energies and dissociation processes

The Li–OH bond distance in the gas phase is predicted to be 1.590 and 1.607 Å at the RHF/6-311++G** and MP2/6-311++G** levels of theory, respectively. These values will be taken as the theoretically exact Li–OH bond lengths of the LiOH molecule to scrutinize the onset of the LiOH dissociation. When for a given LiOH(H\(_2\)O)\(_n\) (\(n = 1–6, 8\)) isomer, the Li–OH bond length is equal to or longer than twice the value of those theoretical bond lengths (i.e. 3.180 and 3.214 Å, respectively), the LiOH molecule within the cluster will be considered as dissociated into a Li\(^+\)/OH\(^-\) separated ion pair. Otherwise, the LiOH molecule will be considered as non-dissociated and therefore classified as a contact ion pair. Except for one intermediate case in one of the LiOH(H\(_2\)O)\(_3\) isomers at the MP2/6-311++G** level, all the calculated LiOH molecules within the clusters can be categorized into either a dissociated Li\(^+\)/OH\(^-\) separated ion pair or a non-dissociated contact ion pair.

#### 3.1.1. LiOH(H\(_2\)O)

In the case of the LiOH(H\(_2\)O) clusters, two stable isomers, where found, whose structures at the EFP/RHF/6-311++G** level are depicted in Fig. 1. Examination of the calculated optimal geometries reveals
In the case of the LiOH(H₂O)₂ clusters, two stable isomers were found whose structures at the EFP/RHF/6-311+G** level are depicted in Fig. 1. Isomer 2a exhibits a ring structure involving the three molecules of the cluster: the LiOH and the two H₂O molecules. One of the H₂O molecules is directly bonded to the LiOH, whereas the second H₂O molecule is hydrogen-bonded to both the first H₂O molecule and the OH group of LiOH through its O and through one of its H atoms, respectively. Isomer 2b presents two strained rings, where the two O atoms of the H₂O molecules are directly bonded to the Li atom, whereas one H atom per each H₂O molecule is hydrogen-bonded to the OH group of LiOH. Both isomers 2a and 2b present bent LiOH molecules with Li–O–H bond angles measuring 152 and 159°, respectively, at the EFP/RHF/6-311+G** level of theory. The relative energy of isomer 2b is higher than that of 2a.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Structural and energetic properties for LiOH(H₂O)ₙ (n = 1–6,8) with MP2/6-311++G**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Structure</td>
</tr>
<tr>
<td>LiOH(H₂O)</td>
<td>1a</td>
</tr>
<tr>
<td>LiOH(H₂O)₂</td>
<td>1b</td>
</tr>
<tr>
<td>LiOH(H₂O)₃</td>
<td>1c</td>
</tr>
<tr>
<td>LiOH(H₂O)₄</td>
<td>1d</td>
</tr>
<tr>
<td>LiOH(H₂O)₅</td>
<td>1e</td>
</tr>
<tr>
<td>LiOH(H₂O)₆</td>
<td>1f</td>
</tr>
<tr>
<td>LiOH(H₂O)₇</td>
<td>1g</td>
</tr>
<tr>
<td>LiOH(H₂O)₈</td>
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</tr>
<tr>
<td>LiOH(H₂O)₉</td>
<td>1i</td>
</tr>
<tr>
<td>LiOH(H₂O)₁₀</td>
<td>1j</td>
</tr>
<tr>
<td>LiOH(H₂O)₁₁</td>
<td>1k</td>
</tr>
<tr>
<td>LiOH(H₂O)₁₂</td>
<td>1l</td>
</tr>
<tr>
<td>LiOH(H₂O)₁₃</td>
<td>1m</td>
</tr>
<tr>
<td>LiOH(H₂O)₁₄</td>
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<td>1o</td>
</tr>
<tr>
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<td>LiOH(H₂O)₂₁</td>
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</tr>
<tr>
<td>LiOH(H₂O)₂₂</td>
<td>1v</td>
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</tr>
<tr>
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<td>1x</td>
</tr>
<tr>
<td>LiOH(H₂O)₂₅</td>
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<td>2b</td>
</tr>
<tr>
<td>LiOH(H₂O)₂₉</td>
<td>2c</td>
</tr>
<tr>
<td>LiOH(H₂O)₃₀</td>
<td>2d</td>
</tr>
<tr>
<td>LiOH(H₂O)₃₁</td>
<td>2e</td>
</tr>
<tr>
<td>LiOH(H₂O)₃₂</td>
<td>2f</td>
</tr>
<tr>
<td>LiOH(H₂O)₃₃</td>
<td>2g</td>
</tr>
</tbody>
</table>

Structure refers to the identification numbers in Figs. 1–6; R is the Li–OH bond length in Å, q(Li) is the Mulliken charge on Li, q(O) is the Mulliken charge on O, BO is the Li–OH bond order and ∆E is the energy relative to the isomer a in kcal/mol.

that in isomer 1a, the O–Li–O bond angle is of 158° at the EFP/RHF/6-311++G** level, while it is of 180° at the RHF/6-311++G** and MP2/6-311++G** ones (C₂ symmetry). Contrastingly, in the case of the NaOH(H₂O) clusters, an isomer analogous to 1a presents a C₂ symmetry at the three levels of theory herein considered [5]. On the other hand, the geometries and shapes of the LiOH(H₂O) isomer 1b remain similar at the three levels of theory. In addition, the Li–O–H bond angle at the EFP/RHF/6-311++G** level measures 178 and 163° in isomers 1a and 1b, respectively, being the LiOH molecule almost linear in the first isomer. Isomer 1b turns out to be more stable than 1a at the RHF6-311++G** and the MP2/6-311++G** levels, but a reverse order of stability shows at the EFP/RHF/6-311++G** one. No dissociation of LiOH into a Li⁺/OH⁻ separated ion pair is observed in this series of clusters.
Table 6
Boltzmann-averaged values of relevant structural properties for LiOH(H2O)n (n = 1–6) with RHF/6-311++G**

<table>
<thead>
<tr>
<th>n</th>
<th>⟨R(Li–OH)⟩</th>
<th>⟨q(Li)⟩</th>
<th>⟨q(O)⟩</th>
<th>(BO)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>1.590</td>
<td>0.614</td>
<td>−0.928</td>
<td>0.734</td>
</tr>
<tr>
<td>1</td>
<td>1.658</td>
<td>0.583</td>
<td>−0.956</td>
<td>0.621</td>
</tr>
<tr>
<td>2</td>
<td>1.707</td>
<td>0.570</td>
<td>−0.974</td>
<td>0.516</td>
</tr>
<tr>
<td>3</td>
<td>1.790</td>
<td>0.520</td>
<td>−0.985</td>
<td>0.415</td>
</tr>
<tr>
<td>4</td>
<td>1.798</td>
<td>0.620</td>
<td>−0.967</td>
<td>0.392</td>
</tr>
<tr>
<td>5</td>
<td>1.815</td>
<td>0.512</td>
<td>−0.984</td>
<td>0.448</td>
</tr>
<tr>
<td>6</td>
<td>1.873</td>
<td>0.552</td>
<td>−1.015</td>
<td>0.392</td>
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</table>

Boltzmann-averaged values at T = 298 K calculated with the zero-point E0 energies within the harmonic approximation. R is the Li–OH bond length in Å, q(Li) is the Mulliken charge on Li, q(O) is the Mulliken charge on O, and BO is Li–OH bond order.

Table 8
Differences in the Mulliken charges between RHF/6-311++G** and EFP/RHF/6-311++G** for each LiOH atom and for the whole LiOH molecule in several LiOH(H2O)n (n = 1–6) clusters

<table>
<thead>
<tr>
<th>Formula</th>
<th>Structure</th>
<th>ΔqLi</th>
<th>ΔqO</th>
<th>ΔqH</th>
<th>ΔqL i–OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH(H2O)</td>
<td>1a</td>
<td>−0.131</td>
<td>0.065</td>
<td>−0.004</td>
<td>−0.070</td>
</tr>
<tr>
<td></td>
<td>1b</td>
<td>−0.112</td>
<td>0.030</td>
<td>0.010</td>
<td>−0.072</td>
</tr>
<tr>
<td>LiOH(H2O)2</td>
<td>2a</td>
<td>−0.134</td>
<td>0.052</td>
<td>0.021</td>
<td>−0.061</td>
</tr>
<tr>
<td></td>
<td>2b</td>
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<td>0.124</td>
<td>−0.007</td>
<td>0.231</td>
</tr>
<tr>
<td>LiOH(H2O)3</td>
<td>3a</td>
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<td>0.189</td>
<td>0.020</td>
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</tr>
<tr>
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<td>0.155</td>
</tr>
<tr>
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<td>0.017</td>
<td>0.070</td>
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<tr>
<td>LiOH(H2O)4</td>
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<td>0.102</td>
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<tr>
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<td>0.025</td>
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<tr>
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<td>4e</td>
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<td>0.180</td>
<td>−0.026</td>
<td>0.137</td>
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<tr>
<td>LiOH(H2O)5</td>
<td>5a</td>
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<td>0.032</td>
<td>−0.174</td>
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<tr>
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<td>5b</td>
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<td>0.000</td>
<td>−0.136</td>
</tr>
<tr>
<td></td>
<td>5c</td>
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<td>0.214</td>
<td>0.004</td>
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<tr>
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<td>5d</td>
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<td>0.009</td>
<td>0.138</td>
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<tr>
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<td>0.030</td>
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<tr>
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<tr>
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<tr>
<td></td>
<td>5h</td>
<td>−0.354</td>
<td>0.146</td>
<td>0.029</td>
<td>−0.179</td>
</tr>
<tr>
<td>LiOH(H2O)6</td>
<td>6a</td>
<td>−0.397</td>
<td>0.208</td>
<td>0.016</td>
<td>−0.173</td>
</tr>
<tr>
<td></td>
<td>6b</td>
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<td>0.227</td>
<td>−0.011</td>
<td>0.188</td>
</tr>
<tr>
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<td>6c</td>
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<tr>
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<td>0.194</td>
</tr>
<tr>
<td></td>
<td>6e</td>
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<td>0.171</td>
<td>−0.013</td>
<td>0.112</td>
</tr>
<tr>
<td></td>
<td>6f</td>
<td>−0.550</td>
<td>0.143</td>
<td>0.023</td>
<td>−0.384</td>
</tr>
<tr>
<td></td>
<td>6g</td>
<td>−0.415</td>
<td>0.191</td>
<td>0.027</td>
<td>−0.197</td>
</tr>
<tr>
<td></td>
<td>6h</td>
<td>−0.403</td>
<td>0.191</td>
<td>0.015</td>
<td>−0.197</td>
</tr>
<tr>
<td></td>
<td>6i</td>
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<td>6j</td>
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</tr>
<tr>
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<td>6l</td>
<td>−0.554</td>
<td>0.169</td>
<td>0.008</td>
<td>−0.377</td>
</tr>
</tbody>
</table>

Structure refers to the identification numbers in Figs. 1–6; each difference in the Mulliken charges Δq(X = Li, O, H, LiOH) is defined as ΔqX = qX(RHF) − qX(EFP), i.e. as the excess (+) or defect (−) of charge in RHF with respect to EFP. ΔqL i–OH expresses the total charge on the LiOH solute in RHF because qL i–OH = 0.

isomers 3b and 3c, large differences in the Li–OH bond lengths are not observed at 3b any of the three levels of theory herein considered. Unlike the C3-symmetry isomer 3a, isomers 3b and 3c do display ring structures where hydrogen bonding plays a prominent role. Isomer 3b exhibits two strained rings involving one and two H2O molecules, respectively, and has the LiOH molecule acting as the linkage between both rings. Isomer 3c exhibits a single less-strained ring involving the four molecules in the cluster. The LiOH molecule is linear in isomer 3a but bent in the other two isomers. The energy of the isomer 3b turns out to be the lowest of the three LiOH(H2O)n structures at the EFP/RHF6-311++G** and the RHF/6-311++G** levels, whereas both isomers 3a and 3b are much more stable than isomer 3c at the MP2/6-311++G** level.
In the case of the LiOH(H₂O)₄ clusters, six stable structures were found whose structures at the EFP/RHF/6-311++G** level are depicted in Fig. 3. Except for isomer 4f, all the calculated clusters display ring structures, where again hydrogen bonding plays a prominent role. Both isomers 4a and 4b exhibit pairs of similar rings, each ring having two H₂O molecules, and have the LiOH molecule acting as the linkage between both rings. Isomer 4d displays two different rings involving two and three H₂O molecules, respectively, and has the Li–H₂O acting as the linkage between the two rings. Both isomers 4c and 4e have one ring involving three of the four H₂O molecules. Isomer 4f has a C₄ symmetry, being therefore the only structure for the LiOH(H₂O)₄ clusters not exhibiting rings. In the previously considered C₃-symmetry LiOH(H₂O)₃ isomer 3a, the Li–OH bond distance turned out to be much longer at the MP2/6-311++G** level than at the two others.
However, this situation is not observed in the \( C_4 \)-symmetry \( \text{LiOH(H}_2\text{O)}_4 \) isomer 4f, where the Li–OH bond length is somewhat longer in a MP2/6-311++G** calculation but not longer enough to classify this structure as an intermediate case between contact and separated ion pairs. Overall, isomer 4f has the longest Li–OH bond distance in the \( \text{LiOH(H}_2\text{O)}_4 \) series of isomers at the three levels of theory herein considered. In addition, isomer 4a and 4b have the lowest energies under the three methods of calculation. No dissociation of LiOH into a \( \text{Li}^+/\text{OH}^- \) separated ion pair is observed in this series of clusters.

### 3.1.5. \( \text{LiOH(H}_2\text{O)}_3 \)

In the case of the \( \text{LiOH(H}_2\text{O)}_3 \) clusters, eight stable isomers were found whose structures at the EFP/RHF/6-311++G** level are depicted in Fig. 4. For the specific case of the MP2/6-311++G** method, previously shown calculation for the \( \text{LiOH(H}_2\text{O)}_n \) \((n = 1–4)\) clusters via numerical evaluation of the MP2 Hessian have always rendered stable structures with all their normal-mode frequencies real. However, this type of calculations for the \( \text{LiOH(H}_2\text{O)}_3 \) clusters rendered at times some unstable structures with a few imaginary frequencies as a result of the limited accuracy of the numerical MP2 Hessian algorithm. Therefore, more accurate MP2/6-311++G** calculations involving analytical MP2 Hessian evaluations were performed by which structures with all their normal-mode frequencies real were finally obtained. All the stable \( \text{LiOH(H}_2\text{O)}_3 \) isomers exhibit ring structures, where hydrogen bonding again plays a prominent role. Isomers 5a, 5b, 5d, 5e and 5g display three rings, whereas isomers 5c, 5f and 5h display only two. Isomer 5a is the most stable structure at the first two levels of theory herein considered and exhibits three rings: one involving three \( \text{H}_2\text{O} \) molecules and the other two involving two \( \text{H}_2\text{O} \) molecules each. Isomer 5b has a relatively flat structure and exhibits three rings: one involving three \( \text{H}_2\text{O} \) molecules and the other two involving two \( \text{H}_2\text{O} \) molecules each; the \( \text{LiOH} \) molecule acts as the linkage between two of the three rings. On the other hand, isomers 5c and 5f exhibit two rings involving varying numbers of \( \text{H}_2\text{O} \) molecules each and both isomers have an extra \( \text{H}_2\text{O} \) molecule, not involved in the rings, directly bonded to the Li atom through its O atom. Similar ring structures can be discerned in the remaining isomers as shown in Fig. 4. In the \( \text{LiOH(H}_2\text{O)}_3 \) series of isomers, the calculated relative energies and Li–OH bond lengths slightly vary at each of the three levels of theory, with a deviation of about 2 kcal/mol in the case of the relative energies. No dissociation of LiOH into a \( \text{Li}^+/\text{OH}^- \) separated ion pair is observed in this series of clusters.

### 3.1.6. \( \text{LiOH(H}_2\text{O)}_5 \)

In the case of the \( \text{LiOH(H}_2\text{O)}_6 \) clusters, eleven stable isomers were found whose structures are depicted in Fig. 5 at the EFP/RHF/6-311++G** level, except for isomer 6za whose EFP/RHF/6-311++G** calculation failed to converged and is therefore depicted at the RHF/6-311++G** level. Isomer 6za stands out amongst these structures because of its clear exhibition of LiOH dissociation and of its seemingly cubic symmetry. No LiOH dissociation is observed in any of the other ten \( \text{LiOH(H}_2\text{O)}_6 \) isomers. Isomer 6za has a net \( C_3 \) symmetry with its \( C_3 \) axis along

---

**Fig. 4.** Structures of the \( \text{LiOH(H}_2\text{O)}_5 \) isomers at the EFP/RHF/6-311++G** level.
the aligned Li–O–H atoms and with the coordinated H₂O molecules arranged in accordance with the overall symmetry. Moreover, the Li and the O atoms of the original LiOH molecule and the six O atoms of the six H₂O molecules are placed on the eight vertices of a distorted cube with the $C_3$ Li–O–H axis coinciding with one of the $C_3$ axis of the cube. The distorted shape of the cube and the H atoms additionally bonded to the O atoms on the cube vertices prevent isomer 6za from adopting a perfect $O_h$ symmetry. Inspection of the data in Tables 2 and 3 reveals that the Li–OH bond length in isomer 6za measures 3.689 and 3.721 Å at the RHF/6-311++G** and MP2/6-311++G** levels, respectively, thereby revealing the LiOH dissociation into a Li$^+/OH^−$ separated ion pair. In addition, that predicted separated ion pair turns out to be the most stable structure in the LiOH(H₂O)$_6$ series of isomers at the MP2/6-311++G** level of theory. Unfortunately, the corresponding EFP/RHF/6-311++G** calculation for isomer 6za failed to converge and the expected dissociation prediction by this method could not be made. Therefore, a complete series of calculations for the $C_3$-symmetry LiOH(H₂O)$_6$ isomer 6az were performed with several basis sets in order to confirm the LiOH dissociation at the three levels of theory. The Li–OH bond lengths from those calculations are listed in Table 4. The results from all those available calculations at the RHF and MP2 levels support without exception the predicted LiOH dissociation in isomer 6az. With several basis sets: 6-31G, 6-31++G,
6-311G, 6-311G**, 6-311++G, 6-311++G(3df, 3pd) and cc-pVTZ, the EFP/RHF calculations do converge with their resulting values for the Li–OH bond lengths consistent with a LiOH dissociation and in satisfactory agreement with the available quantum mechanics results. In contrast, the EFP/RHF calculations with the 6-311++G(2d, 2p) and 6-311++G(2df, 2pd) basis sets converge but do not predict LiOH dissociation and no convergence is achieved with the few remaining basis sets herein tested. The data listed in Table 4 suggest that diffusion functions slightly increases the Li–OH bond distances, whereas polarization functions shorten them. When dissociation is predicted by EFP/RHF calculations, the Mulliken charge on the Li atom always remains close to 1.0 (Li\(^{+}\)) whereas that on the O atom ranges from −1.4 to −1.2. On the contrary, in the non-dissociating EFP/RHF/6-311G(2df, 2pd) calculation, the Mulliken charges on the Li and the O atoms are 0.66 and −0.85, respectively. This indicates that the Mulliken charge on the Li atom in an EFP/RHF calculation is close to 1.0 at dissociation but becomes fractional and lower than 1.0 when dissociation is not predicted. The situation is not so sharply defined for the full quantum mechanics calculations, which always predict dissociation, because the Mulliken charge on the Li atom is 0.36 and 0.38 at the RHF/6-311++G** and MP2/6-311++G** levels but it is about 1.0 at both the RHF/6-311(3df, 3pd) and MP2/6-311++G** levels.

Isomers 6a–6n are rather asymmetrical structures in comparison with the previously discussed isomer 6za and display no instance of LiOH dissociation. Those structures exhibit an astonishing wealth of shapes that defies any detailed written description. The number of ring structures per isomer ranges from two to five, and some rings are interconnected. Isomer 6a exhibits three rings involving two H\(_2\)O molecules each and with the LiOH molecule acting as a linkage of the three rings. Isomers 6c and 6j are structurally the simplest in this series, having only two rings each. In isomer 6c, one ring involves two H\(_2\)O molecules, whereas the other involves three; an extra H\(_2\)O molecule, not involved in the rings, is directly bonded to the Li atom. The structures of other LiOH(H\(_2\)O)\(_6\) isomers can be discerned in Fig. 5. It is worth noticing that the geometry of isomer 6m is a distorted form of the C\(_3\)-symmetry 6za isomer structure. At each of the three levels of theory herein considered, the values of the Li–OH bond lengths slightly varies over the non-dissociating series of LiOH(H\(_2\)O)\(_6\) isomers. However, the relative energies exhibit a somewhat large deviation of about 8 kcal/mol over the complete series of LiOH(H\(_2\)O)\(_6\) isomers.

3.1.7. LiOH(H\(_2\)O)\(_8\)

In the case of the LiOH(H\(_2\)O)\(_8\) clusters, eleven stable isomers were found at the EFP/RHF/6-311++G** level but only three of them. Isomers 8a, 8f and 8za could be calculated at the RHF/6-311++G** and MP2/6-311++G** levels at the time of this report; the structures of these three isomers are depicted in Fig. 6 at the EFP/RHF/6-311++G** level. Isomer 8za stands out amongst these structures because of its clear exhibition of LiOH dissociation at the three levels of theory and of its highly symmetric structure. Isomer 8za has a net C\(_4\) symmetry with its C\(_4\) axis along the aligned Li–O–H atoms; this axis is encircled by two crowns of four H\(_2\)O molecules each whose O atoms are arranged in a D\(_{4d}\) symmetry. The internuclear lines along each pair of H atoms in the four H\(_2\)O molecules of the upper crown are directed toward the C\(_4\) axis in an approximately radial direction, whereas those internuclear lines in the lower crown are tangential. Contrastingly, isomers 8a and 8f do not exhibit LiOH dissociation, have no definite symmetry, and display several ring structures. In these three isomers, the stability decreases in the order: 8a, 8f and 8za at the three levels of theory herein considered.

3.2. Boltzmann averages and comparison with previous theoretical work

In order to determine on a quantitative basis the clusters dissociation trends and to acquire a picture of the solute situation in a bulk solution, Boltzmann distribution averages at the absolute temperature \(T = 298\) K for the Li–OH bond lengths, Li Mulliken charges, O Mulliken charges, and Li–OH bond orders were calculated at the three levels of theory herein considered for each of the LiOH(H\(_2\)O)\(_n\) \((n = 1–6, 8)\) series of isomers. These calculations were based on the zero-point, relative energies of the isomers within the harmonic approximation. The results of this averaging procedure are listed in Tables 5–7 at the EFP/RHF/6-311++G**, RHF/6-311++G** and MP2/6-311++G** levels of theory, respectively. In the first
two methods, the Boltzmann-averaged Li–OH bond length (bond order) monotonically increases (almost monotonically decreases) as the number of H₂O molecules increases from 0 to 8. In the case of the MP2/6-311++G** calculations, the same trend is observed but with a sudden peak (dip) in the averaged Li–OH bond length (bond order) at the LiOH(H₂O)₃ clusters as a result of the predominant contribution to the average by the most stable and partially dissociated LiOH(H₂O)₃ isomer 3a. The observed trends in the averaged Li–OH bond lengths and orders clearly indicate the propensity of the LiOH solute molecule to dissociate into a Li⁺OH⁻ separated ion pair as the number of solvent molecules increases.

An important aspect in the present investigation is to determine the correctness of the atomic charge description on the LiOH solute by EFP and the related effect of genuine charge transfer from or to the solvent on the accuracy of the EFP calculations. As mentioned before, genuine charge transfers to or from the EFP region are not permitted in this method. To account for charge-transfer effects, the EFP charge-transfer component of the energy was originally fitted to a series of H₂O dimers [22]. Since charge transfer does not play a prominent role in those pure H₂O systems, the accuracy of EFP when applied to ionic systems like the LiOH(H₂O)ₙ (n = 1–6, 8) clusters, where charge transfer is expected to be relevant, should be scrutinized. Merrill, Webb and co-workers have carefully investigated these charge-transfer issues in EFP during their detailed studies on aqueous alkali metal-, alkaline-earth metal- and (oxy)anion-water ions [24,26,27]. By comparing EFP, RHF and MP2 results, these authors could determine that at the ab initio level of description, charge transfers from or to the solvent were substantial in the smallest-size ions at the ab initio level of description, charge transfers from or to the solvent were substantial in the smallest-size ions at the RHF/6-311++G** level but mostly within the range of +0.4 to +0.6 at the other two levels. These divergent charge trends between the EFP and the ab initio methods also manifest in the Boltzmann-averaged Mulliken charges shown in Tables 5–7. Therefore, EFP predicts that LiOH will tend to form contact or separated ion pairs having net Li⁺ and OH⁻ ions with almost integer Mulliken charges +1 and −1, respectively, as the number of solvent molecules increases. This effect seems to be caused by the EFP field on LiOH by somehow favoring an internal redistribution of the solute charges into Li⁺ and OH⁻ ions as successive H₂O molecules are added. However, comparison with ab initio results shows that such EFP solute charge separation is not genuine because the Mulliken charges on the Li and O atoms do not vary appreciably with the number of H₂O molecules in RHF and MP2 and, roughly speaking, remain around the values +0.5 and −1.0, respectively. If one assumes that the Coulombic and polarization fields by the EFP and the ab initio methods do not differ much then the described EFP charge separation may be induced by the full quantum methods up to some degree but will be offset by the now permitted charge transfers on each LiOH atom and on the whole LiOH molecule with H₂O molecules, the differences in the Mulliken charges ΔQₐₓ = qₐₓ – qₑₓ between the RHF/6-311++G** and the EFP/RHF/6-311++G** methods for the species X = Li, O, H and LiOH in the LiOH(H₂O)ₙ (n = 1–6, 8) clusters are listed in Table 8. Since the solute total charge in EFP is zero by model construction, ΔQₐₓ measures directly the total charge interchanged between the whole LiOH molecule and the solvent at the RHF level that turns out to be always negative (net electrons gain). Data on Table 8 indicate that the dissociating isomers 6za and 8za display large LiOH electron transfers of 0.441 e⁻ and 0.377 e⁻ from the solvent, respectively, whereas most of the non-dissociating isomers exhibit LiOH electron transfers of 0.1 e⁻ to 0.2 e⁻; exceptionally, the non-dissociating isomer 6j shows a high LiOH electron transfer of 0.384 e⁻. Therefore, the extent of solute/solvent charge
transfers in the LiOH(H_2O)_n (n = 1–6,8) clusters are considerable and their values are close to those found in the Li^+(H_2O)_{1–6} ions by Merrill et al. [24]. The values of \( \Delta q_{Li}, \Delta q_{O} \) and \( \Delta q_{H} \) measures the errors in the EFP atomic charge predictions with respect to RHF and those turn out to be negligible in the case of the H atom but considerable in the cases of the O and the Li atoms, specially in the latter. It is not possible to separate in this analysis the contributions of the solute internal charge redistribution and the solute charge transfer with the solvent to the values of \( \Delta q_X \). However, it is reasonable to conclude that the individual Li and O atoms have significantly interchanged charge with the solvent, with Li taking electrons from and O giving electrons to the H_2O molecules. The total charge transfer on LiOH seems to be dominated by the large charge transfer on the Li atom. Although the LiOH solute at EFP/RHF/6-311++G** level has an incorrect charge distribution on its atoms and lacks the extra negative charge present in its full quantum counterparts, the agreement between this method and RHF/6-311++G** in structural properties such as Li–O bond lengths and LiOH–H_2O distances can be deemed satisfactory. For instance, in the non-dissociating cases, the EFP and RHF Li–OH bond lengths differ by about 0.02 Å on average. In the dissociating cases correctly predicted by EFP, the agreement between the EFP and RHF Li–OH bond lengths is less satisfactory but still quite fair for a breaking bond. In some cases, the highest departures of the EFP Li–OH bond lengths from the RHF ones are correlated to high values of \( \Delta q_{LiOH} \) (e.g. isomers 6m, 6n and 8a). Overall, the satisfactory agreement between EFP and RHF in the structural properties of the present study is in keeping with the findings by Merrill et al. [24], according to which EFP can still provide an accurate description of Li-bearing aqueous compounds in spite of extensive charge transfers. However, agreement in the relative energies \( \Delta E \) is less satisfactory because some instances of conflicting orders in the clusters relative stabilities are observed. The \( \Delta E \) values can be affected by charge-transfer processes. A more detailed analysis in terms of both the Morokuma–Kitaura [34] and the reduced variational space (RVS) [35] energy decompositions will single out the individual contribution of each energy component (Coulombic, polarization and exchange-charge transfer) to the overall accuracy of the present EFP calculations. Those analyses are postponed for future work.

At this point, it will be opportune to briefly compare the results of the present investigation on the LiOH base with the previous ones of its homologous NaOH base [5], especially in regard to some macroscopic properties of their bulk solutions. LiOH is noticeably less soluble in water (12.8 and 17.5 g per 100 cm^3 at 20 and 100 °C, respectively) than NaOH (42.0 and 347.0 g per 100 cm^3 at 0 and 100 °C, respectively) [36]. Although the basicity of LiOH and NaOH in aqueous solution at the same concentration are indistinguishable, gas-phase proton affinities experiments [37] show a lower basicity in the isolated LiOH molecule than in the NaOH one. Basic knowledge of inorganic chemistry indicates that the different chemical properties between the Li^+ and the Na^+ compounds are mostly a direct consequence of the differences between their ionic radii (0.90 and 1.16 Å, respectively [36]). In that regard, straightforward application of Fajans Rules [38] will predict a lesser ionic character in LiOH than in NaOH because of the smaller radius of Li^+. That decreased ionic character in LiOH should explain its lower aqueous solubility and lower gas-phase basicity. It was expected that a comparison of the main results of the present LiOH investigation with those of NaOH would perhaps provide a microscopic explanation for the macroscopic differences between the properties of LiOH and NaOH solutions. Although the solvation patterns of LiOH and NaOH show differences in detail, the present results for LiOH does not indicate that this base has a lesser propensity toward dissociation in aqueous clusters than NaOH. Particularly, an isolated LiOH molecule requires of six H_2O molecules to undergo its spontaneous dissociation as an isolated NaOH molecule does as well [5]. More drastic differences between the solvation behavior of LiOH and NaOH may probably be found if larger aqueous clusters are investigated.

Finally, it should be mentioned that there are not available experiential data for the LiOH(H_2O)_n (n = 1–6,8) clusters in the gas phase to compare the present results. However, an indirect comparison with some related experimental results will be discussed in Section 4.

4. Summary and conclusions

Solvation of the LiOH base in aqueous solutions at the microscopic level has not been studied theoretically until the present work. Geometry optimizations of the LiOH(H_2)O_n (n = 1–6, 8) clusters were first calculated at the level of the EFP/RHF theory with the quantum LiOH molecule described by a RHF/6-311++G** wavefunction and with the classical H_2O molecules by the EFP model (EFP/RHF/6-311++G**); those EFP/RHF optimized geometries were used as the initial guesses for successive geometry optimizations with the RHF/6-311++G** and MP2/6-311++G** methods. Inspection of the structural properties calculated with the full quantum mechanics RHF/6-311++G** and MP2/6-311++G** methods clearly indicates that as the number of H_2O molecules added to the bare LiOH solute increases so does its Li–OH bond length with a concomitant decrease in the Li–O–H bond order. This observed effect illustrates the progression of a single LiOH molecule toward its dissociation into a separated Li^+OH^- ion pair in bulk solution. With these two full quantum mechanic methods, most of the calculated LiOH(H_2O)_n (n = 1–6,8) clusters contain a non-dissociated LiOH molecule within. However, in two calculated structures, the C_3-symmetry LiOH(H_2O)_6 isomer 6za and the C_4-symmetry LiOH(H_2O)_8 isomer 8za, the formation of
a separated Li\(^+\)/OH\(^-\) ion pair is observed at both the RHF/6-311++G** and MP2/6-311++G** levels. More importantly, the LiOH(H\(_2\)O\(_8\)) isomer 6za turns out to be the most stable structure in the LiOH(H\(_2\)O\(_8\)) series of isomers at the MP2/6-311++G** level. This finding establishes that it is necessary to add at least six H\(_2\)O molecules to a single LiOH molecule to provoke its spontaneous dissociation into a separated Li\(^+\)/OH\(^-\) ion pair in an aqueous cluster. On the contrary, the dissociated LiOH(H\(_2\)O\(_6\)) isomer 8za is not the most stable structure in the LiOH(H\(_2\)O\(_8\)) series of isomers at both the RHF/6-311++G** and MP2/6-311++G** levels nor is the LiOH(H\(_2\)O\(_6\)) isomer 6za at the RHF/6-311++G** one in its corresponding series. An intermediate situation with a partially dissociated LiOH molecule is also observed in the LiOH(H\(_2\)O\(_3\)) isomer 3a at the MP2/6-311++G** level, which is the most stable structure in the LiOH(H\(_2\)O\(_3\)) series. No direct experimental results on the LiOH(H\(_2\)O\(_n\)) (n = 1–6,8) clusters are available but comparisons with measurements on related species are possible. For instance, in the dissociated isomer 6za, the dissociating OH\(^-\) group is coordinated with three H\(_2\)O molecules forming a nearly C\(_5\)-symmetry OH\(^-\)(H\(_2\)O\(_3\)) moiety that is somewhat similar to the recently observed, first-solvation-shell, C\(_5\)-symmetry OH\(^-\)(H\(_2\)O\(_3\)) cluster [2] in the gas phase. However, to make that dissociating moiety be exactly the same as the experimental OH\(^-\)(H\(_2\)O\(_3\)) cluster, it would be necessary to rotate the three H\(_2\)O molecules around their axes along the HOH–OH\(^-\) hydrogen bonds to place the three H atoms not involved in hydrogen bonding farther away from the OH\(^-\) group. Those conformational changes will spontaneously happen if the dissociating OH\(^-\)(H\(_2\)O\(_3\)) moiety is farther removed from the cluster. On the contrary, in the isomer 8za, the dissociating moiety is a nearly C\(_4\)-symmetry OH\(^-\)(H\(_2\)O\(_3\)) ion, which will rearrange into a first-solvation-shell OH\(^-\)(H\(_2\)O\(_3\)) cluster with an additional second-shell H\(_2\)O molecule [2] if farther removed from the cluster. Finally, in isomers 6za and 8za, the dissociating Li atom is not at the center of the cluster but in an apex position: the Li\(^+\) ion dissociates carrying a few H\(_2\)O molecules on one side.

Inspection of the EFP/RHF/6-311++G** results for the whole LiOH(H\(_2\)O\(_n\)) (n = 1–6,8) series of clusters show a reasonable agreement with those done with the full quantum mechanics methods. At a qualitative level, the geometries, shapes and structural details of the calculated clusters display very similar features at the three levels of theory herein considered. At a quantitative level, the agreement between the EFP/RHF/6-311++G** and the RHF/6-311++G** methods is satisfactory in terms of structural properties (e.g. Li–OH bond lengths). This is expected because the EFP method was designed to reproduce closely the RHF results. However, the agreement in the relative energies (\(\Delta E\)) at the EFP/RHF/6-311++G** and RHF/6-311++G** levels is less satisfactory because some instances of conflicting orders in the clusters relative stabilities are observed. It seems that the inclusion of electronic correlation in the MP2 method is crucial to predict some finer details of the dissociation process. For instance, both the EFP/RHF/6-311++G** and the RHF/6-311++G** calculations fail to reproduce the LiOH partial dissociation of the LiOH(H\(_2\)O\(_3\)) isomer 3a as the MP2/6-311++G** calculations do. More importantly, the RHF/6-311++G** method clearly predicts LiOH dissociation in the LiOH(H\(_2\)O\(_6\)) isomer 6az but that structure turned out not to be the most stable in the LiOH(H\(_2\)O\(_6\)) series. As discussed in detail in Section 3.1.6, the EFP/RHF method applied to the calculation of that LiOH(H\(_2\)O\(_6\)) isomer 6za converge and correctly predict LiOH dissociation with the 6-31G, 6-31++G, 6-311G**, 6-311++G, 6-311++G(3df, 3dp) and cc-pVTZ basis sets; converges but fails to predict dissociation with the 6-311++G(2d, 2p) and 6-311++G(2df, 2p) ones; and fail to converge with the 6-31G**, 6-31++G**, 6-311++G**, cc-pVQZ and STO-3G ones. Considering all the calculated LiOH(H\(_2\)O\(_6\)) isomer 6za structures in the present investigation, it can be seen that the instances of a converged EFP/RHF calculation with an accurate dissociation prediction in agreement with the full quantum mechanics results (seven cases) outnumber those converged calculations with an erroneous dissociation prediction (two cases). Currently, it is not possible to identify the reasons for that lack of convergence and/or for those converged but incorrect results. Most likely, the cause may lie in the delicate balance involving the intermolecular interactions between the EFP classical solvent and the quantum solute parts, including a basis set dependency from the latter. Only a careful numerical analysis of the implicated factors, including the Morokuma–Kitaura [34] and the reduced variational space (RVS) [35] energy decompositions, will reveal the origin of these two problems. However, it is very important to emphasize that those limitations encountered in a few EFP/RHF calculations are by no means insurmountable. Lack of convergence may be remedied by condition-
of the EFP/RHF method with the full ab initio calculations can be deemed satisfactory. Therefore, the present investigation gives further support to EFP as a reliable and feasible method to study solvation effects in relatively large aqueous clusters of ionic compounds.

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