The Hydration Number of Li$^+$ in Liquid Water*

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Abstract

A theoretical treatment based upon the quasi-chemical theory of solutions predicts the most probable number of water neighbors in the inner shell of a Li$^+$ ion in liquid water to be four. The instability of a six water molecule inner sphere complex relative to four-coordinated structures is confirmed by an 'ab initio' molecular dynamics calculation. A classical Monte Carlo simulation equilibrated 26 water molecules with a rigid six-coordinated Li(H$_2$O)$_6$$^+$ complex with periodic boundary conditions in aqueous solution. With that initial configuration for the molecular dynamics, the six-coordinated structure relaxed into four-coordinated arrangements within 112 fs and stabilized. This conclusion differs from prior interpretations of neutron and X-ray scattering results on aqueous solutions.

The hydration of ions in water is not only fundamental to physical chemistry but also relevant to the current issue of selectivity of biological ion channels. In the context of potassium channels [1,2,3], for example, the free energies for replacement of inner shell water ligands with peptide carbonyls donated by proteins of the channel structure seem decisive to the selectivity of the channel, specifically for preference of K^+ over Na^+. Studies to elucidate the thermodynamic features of such inner shell exchange reactions require prior knowledge of the ion hydration structures and energetics.

Unfortunately, our understanding of the inner hydration shell structure of ions in water is not as clear as it might be [4]. The simplest and most favorable case to pursue is the Li^+ solute. Neutron scattering measurements on LiCl solutions in liquid water have led to a firm conclusion that the Li^+ ion has six near-neighbor water molecule partners [4,5,6,7,8,9,10]. That result, however, has not been entirely uniform across studies of similar aqueous solutions [11,12] containing Li^+ ions. X-ray scattering results have been interpreted similarly [13] to indicate a hydration number of six, again with some nonuniformity [14]. In contrast, some spectroscopic studies have suggested tetrahedral coordination of the Li^+ ion in water [15] and an array of physical chemical inferences lend some support to that conclusion [16]. On the theoretical side, electronic structure calculations on the Li^+ ion with six water molecules predict a slightly, but distinctly, lower energy for a structure with four inner shell and two outer shell water molecules than for structures with six water molecules in the innermost shell [17,18]; results such as those seem to be universally supported by other electronic structure efforts [19,20]. Simulations have produced a range of results including both four and six inner shell water neighbors with considerable statistical dispersion [21,22,23,24,25,26,27,28,29,30,31,32]. It is well recognized, of course, that simulations are typically not designed to provide a sole determination of such properties, though they do shed light on the issues determining the hydration number of ions in water.

The theoretical scheme used here to address these problems for the Li^+(aq) ion is based upon the quasi-chemical organization of solution theory, which is naturally suited to these problems [33,34,35,36]. The first step is the study of the reactions

$$Li^+ + nH_2O \rightleftharpoons Li(H_2O)_n^+ \qquad (1)$$

that combine n water molecule ligands with the Li^+ ion in a geometrically defined inner sphere under ideal gas conditions. At a subsequent step an approximate, physical description of the aqueous environment surrounding these complexes is included [33,34,35,36]. The geometric definition of an inner sphere region enforces a physical balance in this method. The goal of this approach is to treat inner sphere ligands explicitly, in molecular detail, but at the same time to achieve a description of outer sphere hydration thermodynamics that is consistent from one complex to another. If minimum energy complex geometries were to shift different numbers of ligands to outer sphere regions, that would unbalance the thermodynamic description of the hydration of the inner sphere materials. For example, in the quantitative implementation of the quasi-chemical approach we specifically do not use the $Li[(H_2O)_4][(H_2O)_2]^+$ complex cited above, with two water molecules outside the inner sphere, even though this structure helpfully clarifies the physical issue.

Gas-phase thermochemical data required for the equilibria in Eq. (1) were obtained by electronic structure calculations using the Gaussian98 programs with the B3LYP hybrid density functional theory approximation [37]. All structures were fully optimized with a basis

including polarization functions on Li^+ (6-31G*) and both polarization and diffuse functions (6-31++G**) on the oxygen and hydrogen centers. At the optimum geometry and with the same basis set, harmonic vibrational frequencies of the clusters were calculated and atomic charges determined using the ChelpG capability in Gaussian98. Partition functions were then calculated, thus providing a determination of the free energy changes of the equilibria in Eq. (1) due to atomic motions internal to the clusters within the harmonic approximation.

Interactions of these complexes with the external aqueous environment [34] were treated with a dielectric model following the previous study of the hydrolysis of the ferric ion [35]. Classic electrostatic interactions based upon the ChelpG partial atomic charges were the only solution-complex interactions treated; in particular, repulsive force (overlap) interactions were neglected based on the expectation that they make a secondary contribution to the thermodynamic properties considered here. The external boundary of the volume enclosed by spheres centered on all atoms defined the solute molecular surface. The sphere radii were those determined empirically by Stefanovich and Truong [38], except R_{Li+}=2.0 Å for the lithium ion. Because the lithium ion is well buried by the inner shell waters, slight variations of the lithium radius were found to be unimportant. The value R_{Li+}=2.0 Å was identified as slightly larger than the nearest Li-O distances and significantly smaller than the Li-O distances (3.5 – 4.0 Å) for second shell pairs.

Results of the calculations are summarized in Fig. 1. Geometry optimization of each of the n-coordinated clusters confirms that the inner shell structures used in these calculations are not necessarily the lowest energy structures for a given number of water neighbors. Although a tetrahedral cluster of inner shell water molecules is the lowest energy structure for $Li(H_2O)_4^+$, a cluster with five inner shell water molecules is slightly higher in energy than a cluster with one outer shell and four inner shell water molecules. Similarly, the lowest energy cluster with six water molecules contains four inner shell water molecules arranged tetrahedrally and two outer shell water molecules.

Fig. 1 shows that the n=4 inner sphere cluster has the lowest free energy for a dilute (p=1 atm) ideal gas phase. Adjustment of the concentration of water molecules to the value $\rho_W = 1$ g/cm^3, to match the normal density of liquid water, changes the most favored cluster to the one with n=6 inner shell water molecules. Outer sphere interactions described by the dielectric model progressively destabilize the larger clusters, as they should since larger numbers of water molecules are being treated explicitly as members of the inner shell. As a consequence of including the outer sphere contributions, the final position of minimum free energy is returned to the n=4 structure, with the n=3 complex predicted to be next most populous in liquid water at T=298.15 K and p=1 atm. The mean hydration number predicted by this calculation is $\overline{n}$=4.0.

The current quasi-chemical prediction for the absolute hydration free energy of the Li^+ ion under these conditions is -128 kcal/mol, not including any repulsive force (packing) contributions. An extreme increase of R_{Li+} to 2.65 Å raises this value to about -126 kcal/mol, showing that the theoretical results are insensitive to the ion radius, as remarked above. Experimental values are -113 kcal/mol [39], -118 kcal/mol [40], and -125 kcal/mol [41], converted to this standard state. This dispersion of experimental values for the absolute hydration free energy of the Li^+ (aq) ion is accurately mirrored in the dispersion of reference values adopted for the absolute hydration free energy of the H^+ (aq) ion. Inclusion of repulsive force contributions would reduce the present calculated value slightly. Further-

more, Li^+(aq) is believed to have a strongly structured second hydration shell [23], which is treated only approximately in this calculation. Nevertheless, this level of agreement between calculation and experiment is satisfactory.

We additionally emphasize that the $Li(H_2O)_n^+$ complexes are treated in the harmonic approximation, although fully quantum mechanically. The low-n clusters might have more entropy than is being accounted for by the harmonic approximation. If this were the case, then low-n clusters would be more populous than currently represented. This would likely raise the theoretical value also.

To further test the $n=4$ prediction, 'ab initio' molecular dynamics calculations were carried out utilizing the VASP program [42]. Two checks established the consistency for these problems between the electronic structure calculations described above and the energetics involved in the molecular dynamics calculations. First, the electron density functional alternative implemented in VASP [43] was checked by comparing the electronic structure results obtained with the B3LYP hybrid electron density functional and the PW91 generalized gradient approximation exchange-correlation functional, using the Gaussian98 program and the same basis sets. As expected, satisfactory agreement was observed in the binding energies for sequential addition of a water molecule to the $Li(H_2O)_n^+$ clusters. Then the issues of pseudo-potentials and basis set were checked by optimizing cluster geometries with the VASP program and comparing to the results obtained for the same problems with Gaussian98. Again agreement was observed. For example, both procedures predicted the same lowest energy six-coordinated structure, the characteristic $Li[(H_2O)_4][(H_2O)_2]^+$ cluster, with nearly identical geometries.

To initiate the 'ab initio' molecular dynamics calculation, the optimum $n=6$ inner sphere structure, rigidly constrained, was first equilibrated with 26 water molecules under conventional Monte Carlo liquid simulation conditions for liquid water, including periodic boundary conditions. This system of one Li^+ ion and 32 water molecules was then used as an initial configuration for the molecular dynamics calculation. As shown in Fig. 2, the initial $n=6$ structure relaxed to stable $n=4$ alternatives within 112 fs. The results of longer molecular dynamics calculations will be reported later.

The 'ab initio' molecular dynamics and the quasi-chemical theory of liquids exploit different approximations and produce the same conclusion here. This *agreement* supports the prediction that Li^+(aq) has four inner shell water ligands at infinite dilution in liquid water under normal conditions. This prediction differs from interpretations of neutron and X-ray scattering data on aqueous solutions.

The conditions studied by these calculations and those targeted in the neutron scattering work do not match perfectly, particularly with regard to Li^+ concentration. Nevertheless, the theoretical methods are straightforward and physical, and, moreover, the distinct methods used here conform in their prediction of hydration number. Therefore, it will be of great importance for future work to fully resolve the differences between calculations and scattering experiments for these problems.

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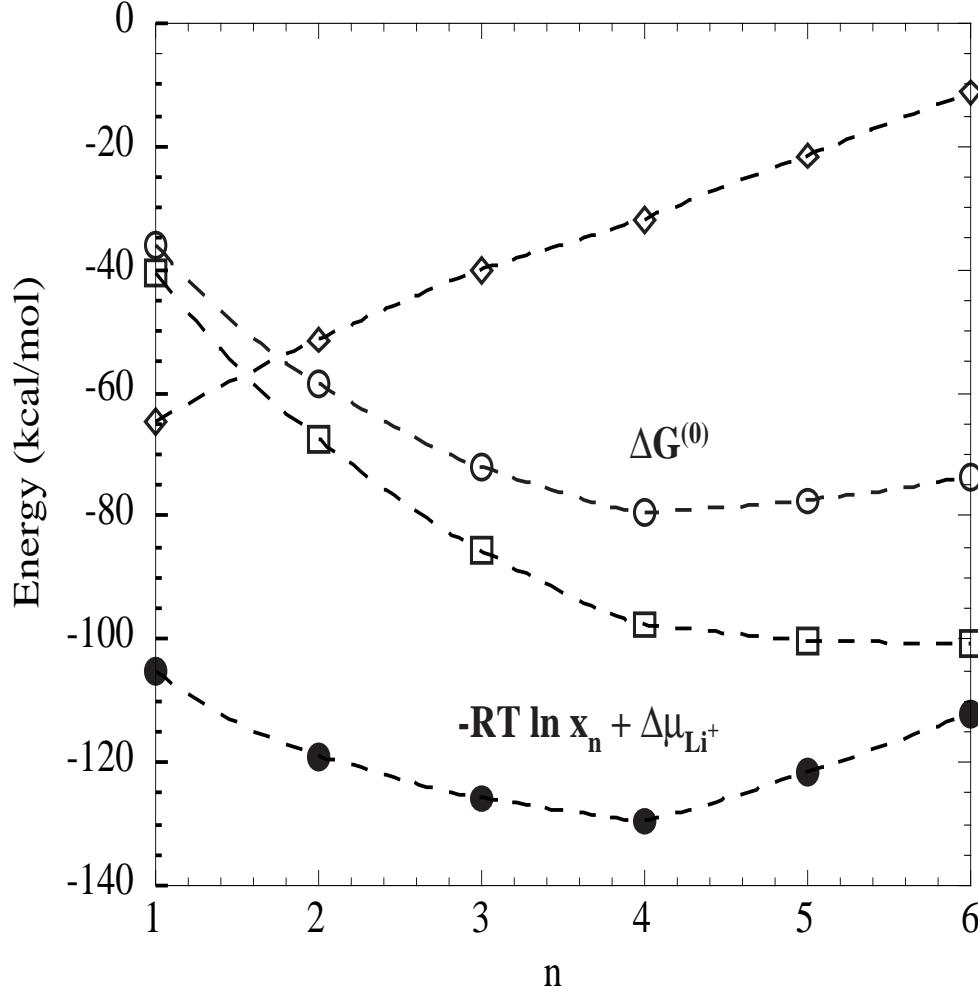[45] Sprik, M.; Hutter, J.; Parrinello, M. *J. Chem. Phys.* **1996**, 105, 1142.

Figure 1. Free energies for Li^+ ion hydration in liquid water as a function of the number of inner shell water neighbors at T=298.15 K. The results marked $\Delta G^{(0)}$ (open circles) are the free energies predicted for the reaction $Li^+ + nH_2O = Li(H_2O)_n^+$ under standard ideal conditions, including p = 1 atm. The minimum value is at n=4. The next lower curve (squares) incorporates the replacement free energy -nRT ln(RTρ_W/1 atm) that adjusts the concentration of water molecules to the normal concentration of liquid water, $\rho_W = 1$ g/cm^3 so that RTρ_W = 1354 atm [35]. The minimum value is at n=6. The topmost graph (diamonds) plots $\mu^*_{Li(H_2O)_n^+} - n\mu^*_{H_2O}$, the external-cluster contributions obtained from the standard dielectric model [34,35]. The bottommost results (solid circles) are the final, net values. The label provides the quasi-chemical expression of these net values [33,36] with x_n the fraction of lithium ions having n inner shell water neighbors and $\Delta\mu_{Li^+}$ the interaction part of the chemical potential of the lithium ions. This graph indicates that the n=4 inner sphere structure is most probable in liquid water under normal conditions.
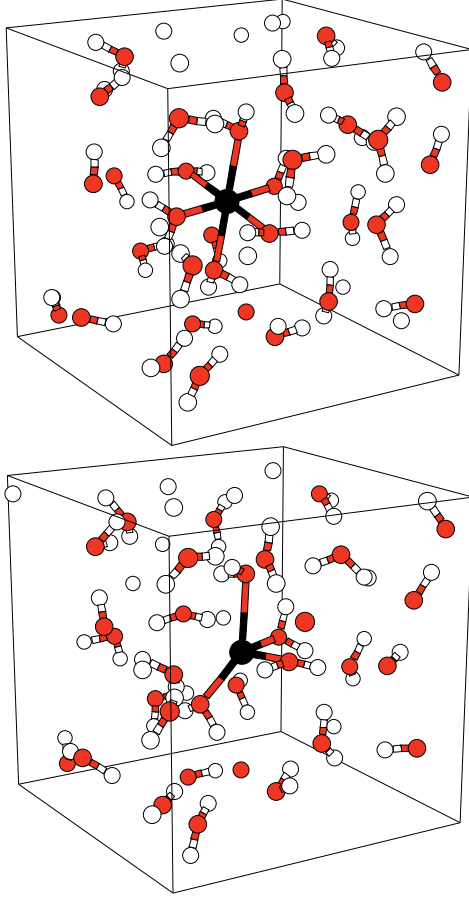
Figure 2. Structures from molecular dynamics calculations based upon a gradient-corrected electron density functional description of the interatomic forces. The ions were represented by ultrasoft pseudopotentials [44] and a kinetic energy cutoff of 396 eV, which was found satisfactory in related calculations [45], limited the plane wave expansions . The top panel is the configuration used as an initial condition. A hexa-coordinate inner sphere structure, rigidly constrained, was equilibrated with 26 additional water molecules by Monte Carlo calculations using classical model force fields and assuming a partial molar volume of zero. The bottom panel is the structure produced 112 fs later. The bonds identify water oxygen atoms within 2.65 Å of the Li^+ ion. The hydrogen, lithium, and oxygen atoms are shown as open, black, and gray circles, respectively.