

Hydration Properties of Al³⁺ Ion using Empirical Ion-water Potential by Monte Carlo Simulation

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Neste trabalho, propriedades de hidratação do íon Al³⁺ são investigadas por simulações mecânico-estatísticas de Monte Carlo no *ensemble* NpT a 298,15 K e 1 atm usando um modelo de potencial efetivo de pares íon-água cujos parâmetros foram desenvolvidos por meio de busca empírica no espaço de fase configuracional durante o curso das simulações para reproduzir dados experimentais da estrutura da primeira camada de hidratação. Resultados estruturais obtidos a partir das simulações para números de coordenação e distâncias íon-oxigênio da água, correspondentes às camadas de hidratação primeira e segunda, estão em muito bom acordo com dados experimentais. A entalpia de hidratação predita a partir deste modelo também está em muito bom acordo com resultados experimentais e é bastante similar ao resultado obtido por Wasserman *et al.* a partir do modelo de íon hidratado. Contribuições de muitos corpos investigadas para um cluster [Al(H₂O)₆]³⁺ usando a teoria do funcional de densidade em cálculos mecânico-quânticos de primeiros princípios fornecem suporte à efetividade do potencial de pares íon-água desenvolvido quanto aos efeitos de muitos corpos incorporado nos parâmetros ajustados.

In this work, hydration properties of Al³⁺ ion are investigated by statistical mechanics Monte Carlo simulations in the NpT *ensemble* at 298.15 K and 1 atm using an effective ion-water potential model whose parameters were developed through empirical search in configurational energy space during the course of simulations to fitting structural experimental data of the first hydration shell. Computed structural results for coordination numbers and ion-water oxygen distances for both first and second coordination shells are obtained in very good agreement with experimental observations. The hydration enthalpy predicted from this simple model is also in very good agreement with experimental values and it is quite similar to the one obtained by Wasserman *et al.* from the hydrated ion model. Many-body contributions investigated for an [Al(H₂O)₆]³⁺ cluster using the density functional theory in *ab initio* quantum mechanical calculations provide support to the effectiveness of the ion-water pair potential developed concerning many-body effects of water molecules around the ion incorporated in the fitted parameters.

Keywords: aluminum ion hydration, ion-water interaction, aluminum aqueous solution, empirical potential, Monte Carlo simulation

Introduction

Trivalent aluminum ion in aqueous media has mainly been studied due for its effects on living systems and to for its technological applications. In the last decades,

many studies have demonstrated that Al³⁺ is toxic in plants, animals and humans, causing a negative impact on the environment.¹⁻³ Concerning technological interests, there are some indications that the competition between typical Al³⁺ ligands, such as acetyl acetonates, urea, carboxylic acids and water molecules, by the coordination of the Al³⁺ in the hydration shells could be

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related to the control of the [Al(H₂O)₆]³⁺ hydrolysis rate, which could have a decisive influence to the improvement of interesting properties of advanced materials.⁴⁻⁶ The knowledge on the nature of the interactions of hydrated metal ions is one of the most fundamental interests in physical chemistry of inorganic solutions.

Experimental data of aqueous ionic solutions^{7,8} produced in the last decades have improved our knowledge on aqueous chemistry of the Al³⁺. At theoretical level, molecular simulations are powerful tools which have contributed with insights on the properties of aqueous ionic solutions. This methodology is based on a microscopic description of the system in which potential energy surfaces play a central role. For highly charged ions in water, such as Al³⁺, pairwise additive potential functions have been employed as approximations to total potential energy functions, aiming low cost simulations. Within this scope, different potential models have been extracted either from *ab initio* quantum mechanics or empirical procedures with varying degrees of success.

Potential models have been investigated from *ab initio* quantum mechanical calculations using the hydrated ion concept in molecular dynamics studies by Sánchez Marcos and co-workers⁹⁻¹¹ for Cr³⁺, Be²⁺, Mg²⁺ and Al³⁺, by Bleuzen *et al.*¹² for Cr³⁺, and by Wasserman *et al.*¹³ for Al³⁺. The potential models proposed by these authors, in different ways, allow some flexibility to water molecules of the first coordination shell. In these models, however, water molecules of the first shell can not be exchanged with ones of the second shell. Ortega-Blake and Bernal-Uruchurtu,¹⁴ using pairwise additive potentials which permit water release from the first shell, as well as polarization of water molecules, have performed Monte Carlo simulations of the hydration of Ca²⁺ and Mg²⁺. All of these pair potentials, with varying degrees of accuracy and extent in accounting for many-body effects, have been produced improvement in the description of aqueous ionic solutions.

As many-body effects of molecules are not pairwise additive, their inclusion to construct pair potentials has also been done, but in an effective way, by using empirical procedures.¹⁵ Empirical ion-water potentials were successfully parameterized by Curtiss *et al.*¹⁶ for Fe²⁺ and Fe³⁺ in water using molecular dynamics, and by Åqvist¹⁷ in his studies using free energy simulations for Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ in water.

Empirical procedures take effectively into account the non additivity of many-body effects in pairwise potential functions, leading to most accurate results.¹⁸ This is achieved by considering solvent molecules of the solvation shells, as well as ones of the bulk, during the parameterization process. However, the main limitation of this approach is

that it fails in generality, which implies in unknown starting parameters at each new system.¹⁸ Nevertheless, parameters such as electronegativity, atomic radius and hardness of the ions can be used for giving insights into empirical parameterization process.

In this work, a statistical mechanics Monte Carlo study of the hydration of the Al³⁺ ion is presented using an ion-water potential empirically parameterized to effectively account many-body effects in the fitted parameters using a search procedure in configurational energy space through Monte Carlo simulations of one Al³⁺ ion in water. The effectiveness of the ion-water potential developed in this work is discussed by evaluating the magnitude of interaction energies of two-, three-, four- and higher-body for an [Al(H₂O)₆]³⁺ cluster by means of *ab initio* quantum mechanical calculations using density functional theory. Concerning many-body contributions, the literature reports *ab initio* self-consistent field studies for [Al(H₂O)₆]³⁺ clusters performed by Probst¹⁹ for Na⁺, Mg²⁺ and Al³⁺, by Curtiss and Jurgens²⁰ for Cu⁺ and Cu²⁺, and by Hermansson and co-workers²¹ which demonstrated that non-additive effects in hydrated clusters are much more important with increasing charge of the ion. Furthermore, it can be emphasized that there are many representative examples in which some dynamics aspects of interest between molecules of the coordination shells and ones of the bulk must be taken into account, such as in sol-gel process in materials research.⁴⁻⁶ Considering that an important feature of the present Al³⁺ ion-water interaction model is the flexibility which it allows to the water molecules of the first shell to exchange with the second shell, it is not of our knowledge that a simple Al³⁺ ion-water potential model including this feature has previously been studied.

Methodology

Ion-water and water-water potential functions

In an ionic hydration process within the pairwise additivity approximation at infinite dilution, the configurational energy can be partitioned into additive contributions of pairs of water-water and ion-water interactions. The functional form employed in this work for the ion-water interaction energy was applied in previous works for highly charged metal ions in aqueous solution,^{16,22,23} and it is composed by Coulomb plus short range terms,

$$E = \sum_j^w \left[A \exp(-Br_{Ij}) - \frac{D}{r_{Ij}^6} - \frac{E}{r_{Ij}^8} - \frac{F}{r_{Ij}^{12}} + \frac{q_I q_j}{4\pi\epsilon_0 r_{Ij}} \right] \quad (1)$$

In equation 1, summation is on sites j of a water molecule containing w sites, r_{ij} is the distance between the ion I and the site j , and q_j is the partial charge of the site j of the water molecule. For the present case, $q_j = +3|e|$. To represent the water-water interaction, the TIP4P model developed by Jorgensen *et al.*¹⁵ was employed. Then, in this work, the short range part of equation 1 only concerns the oxygen site of the water molecule, in agreement with the TIP4P water model statement. The experimental geometry of water was used.²⁴ The A , B , D , E and F parameters were fitted by empirical procedure as follows.

Parameter search through Monte Carlo simulation

To find an acceptable set of potential parameters to be used in simulation, a representative region of the configurational energy space for the particular system must be reached. To start the present optimization process, the input values used for the potential parameters were those empirically developed by Curtiss *et al.*¹⁶ for the Fe^{3+} in water. In order to perform preliminary investigations, these parameters were applied in equation 1 with distances in angstroms and partial charges in units of electron. The TIP4P water model¹⁵ and the experimental geometry for water²⁴ were considered in these calculations. The Fe^{3+} ion-water curve obtained for interaction between the Fe^{3+} and one TIP4P water molecule is shown in Figure 1. A minimum energy value of $-80.23 \text{ kcal mol}^{-1}$ at 1.90 \AA was found for the distance between the Fe^{3+} and the oxygen site of the water. Since the ionic radius²⁵ of the hexacoordinated Al^{3+} (0.675 \AA) is smaller than the one²⁵ of the Fe^{3+} (0.785 \AA), it is expected that the parameter B in equation 1 for the Al^{3+} be greater than the one for the Fe^{3+} ($B(\text{Fe}^{3+}) = 3.728 \text{ \AA}^{-1}$). Additional considerations on hardness also distinguish

these ions²⁶ (13.1 eV for the Fe^{3+} and 45.8 eV for the Al^{3+}). To start the parameterization process, these tendencies were considered as well as the potential parameters for Fe^{3+} and the minimum energy value obtained for Fe^{3+} ion-water curve (Figure 1). Fe^{2+} ion-water curve is also plotted in Figure 1 using parameters developed by Curtiss *et al.*¹⁶

Simulations were run in the NpT *ensemble* at 298.15 K and 1 atm , using the algorithm of Metropolis *et al.*,²⁷ in a modified version of the Diadorim program.²⁸ Periodic boundary conditions and spherical cut-off radius were used. From a previously equilibrated pure water box containing a small system of 390 TIP4P water molecules plus one ion in a cubic cell, initial configurations were obtained in which the ion was placed near to the center of the box. From the spatial positions, the Metropolis criterion was applied to accepting new positions, as well as new volume moves, with an acceptance/trial ratio about 0.45. A water molecule changed its position by randomly rotating and translating it as a whole along a randomly chosen Cartesian direction, according to increments in the range $\pm 15^\circ$ and $\pm 0.15 \text{ \AA}$, respectively. Attempts to move the volume were made at each 10^3 configurations. Increments of volume were allowed in the range $\pm 120 \text{ \AA}^3$. The ion was also allowed to move. Attempts to translate the ion were made at each 10^3 configurations and the allowed translation range was $\pm 0.05 \text{ \AA}$. In order to accelerate the convergence, the probability of attempting to move a water molecule around the ion was enhanced by the preferential sampling²⁹ $1/(r_{io}^2 + c)$, where r_{io} is the distance from the ion to the oxygen site of a water molecule, and c is an empirical constant chosen in this work as 40 \AA . The side length of the equilibrated simulation box containing the ion was 22.504 \AA , which corresponds to a volume containing a solution of $0.146 \text{ mol dm}^{-3}$.

To calculate the configurational energies, a full water-water interaction was considered whenever any site-to-site distance fell below spherical cut-off radius of 10 \AA . Correspondingly, the same value of spherical cut-off radius was used for the ion-water interaction specified by Equation 1, according to the procedure discussed above for any site-to-site distance r_{ij} . Beyond the cut-off radius, energy corrections for non Coulomb terms due to the long range forces were done using the formalism discussed by Allen and Tildesley.³⁰ For Coulomb terms, the same formalism was used to correct long range effects considering a scheme to calculate ion-water average energies beyond the spherical cut-off radius as a function of distance between ion and water. At every distance, 2×10^4 Monte Carlo steps were made considering movements for water molecule so that its orientation relative to the ion is changed by randomly rotating it as a whole along a randomly chosen Cartesian direction in the range -180° to $+180^\circ$, until convergence in energy is achieved.

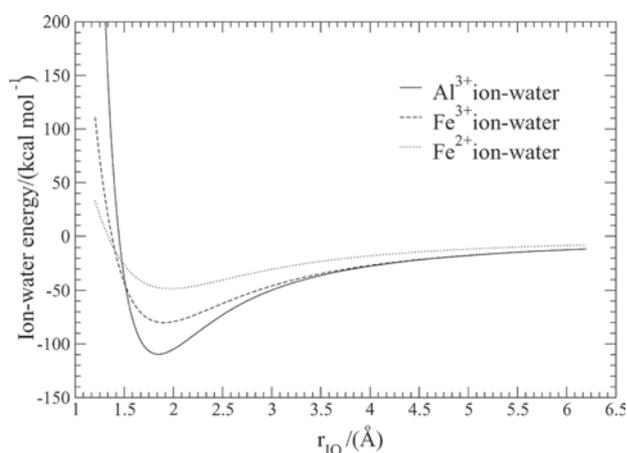


Figure 1. Potential energy curves for ion-water interactions using equation 1. The potential parameters for Al^{3+} are from this work; for both Fe^{3+} and Fe^{2+} , from Reference 16.

During the simulations, the A , B , D , E and F parameters were obtained by fitting experimental data for both hydration number and ion-water oxygen distance of the first hydration shell.^{7,8} The potential parameters obtained in the present process are listed in Table 1. Average properties were accomplished by generating 0.8×10^7 configurations. Periods of 0.4×10^7 configurations were discarded for equilibrium phase. Statistical uncertainties were calculated from separated averages over blocks of 0.4×10^6 configurations.

Many-body contributions to the total energy for an [Al(H₂O)₆]³⁺ cluster

The total energy of an aluminum trivalent ion I and n water molecules (w) can be expanded in a series of m -body energy terms,²⁰

$$\begin{aligned} E([\text{Al}(\text{H}_2\text{O})_n]^{3+}) &= E^{(1)}(I) + \sum_{i=1}^n E^{(1)}(w_i) + \\ &+ \sum_{i=1}^n E^{(2)}(Iw_i) + \sum_{j>i=1}^n E^{(2)}(w_iw_j) + \\ &+ \sum_{j>i=1}^n E^{(3)}(Iw_iw_j) + \sum_{k>j>i=1}^n E^{(3)}(w_iw_jw_k) + \\ &+ \dots + \sum_{n>\dots>l>k>j>i=1}^n E^{(m)}(Iw_iw_jw_kw_l\dots w_n) \end{aligned} \quad (2)$$

where Al³⁺ and water molecules are taken as particles of the interacting system composed by $m = n + 1$ particles, $E([\text{Al}(\text{H}_2\text{O})_n]^{3+})$ is the total energy of the system, $E^{(1)}$ are the energy terms of individual particles, $E^{(2)}$ are the two-body energy terms, $E^{(3)}$ are the three body energy terms, and so on. In equation 2, $E([\text{Al}(\text{H}_2\text{O})_n]^{3+}) - E^{(1)}(I) - \sum_{i=1}^n E^{(1)}(w_i)$ is the binding energy $BE([\text{Al}(\text{H}_2\text{O})_n]^{3+})$.

In this work, the many-body contributions to the total energy for a cluster with one aluminum trivalent ion and six water molecules, $([\text{Al}(\text{H}_2\text{O})_6]^{3+})$, were evaluated. To calculate each one of the terms of equation 2, the density functional theory (DFT) at the B3LYP/CC-pVTZ level^{31,32} was applied. All of the computational calculations were performed by using the GAUSSIAN 98 series of programs.³³ The total energy $E([\text{Al}(\text{H}_2\text{O})_6]^{3+})$ was obtained from geometry optimization and frequency analysis at the T_h symmetry. The frequency analysis shows the optimized geometry is a local minimum on the potential energy surface. Single point energy calculations were accomplished

to calculate $E^{(1)}$, $E^{(2)}$, $E^{(3)}$, ... , $E^{(7)}$ terms at the optimized geometry of the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ cluster.

To calculate energy terms in equation 2 for the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ cluster at the T_h symmetry, the summation $\sum_{i=1}^6 E^{(1)}(w_i)$ reduces to 6 equivalent energy terms for one water molecule at the geometry of the cluster. For the summation $\sum_{j>i=1}^6 E^{(2)}(w_iw_j)$, there are 15 two-body interaction terms due to combinations of two water molecules which can be arranged in six spatial positions ($C(6,2)$) at the geometry of the cluster. In this combination, it were found 12 two-body terms in which the angle between water molecules is 90°, and 3 two-body terms in which this angle is 180°. Then,

$$\begin{aligned} \sum_{j>i=1}^6 E^{(2)}(w_iw_j) &= 12E_{90^\circ}^{(2)}(ww) + 3E_{180^\circ}^{(2)}(ww) \\ &= 12[E_{90^\circ}(ww) - 2E^{(1)}(w)] + 3[E_{180^\circ}(ww) - 2E^{(1)}(w)] \end{aligned} \quad (3)$$

where $E_{90^\circ}(ww)$ and $E_{180^\circ}(ww)$ are total energies for water dimers at 90° and 180°, respectively, at the optimized geometry of the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ cluster. Subscripts for water molecules were omitted on the right-hand side of equation 3.

For the summation $\sum_{k>j>i=1}^6 E^{(3)}(w_iw_jw_k)$ in equation 2, there are 20 three-body interaction terms (as a result of a $C(6,3)$ combination) for the which 12 triplets correspond to water molecules at a same plane, $E_s^{(3)}(www)$, and 8 triplets for the which waters do not, $E_d^{(3)}(www)$. Then,

$$\begin{aligned} \sum_{k>j>i=1}^6 E^{(3)}(w_iw_jw_k) &= 12E_s^{(3)}(www) + 8E_d^{(3)}(www) \\ &= 12[E_s(www) - 3E^{(1)}(w) - 2E_{90^\circ}^{(2)}(ww) - E_{180^\circ}^{(2)}(ww)] + \\ &+ 8[E_d(www) - 3E^{(1)}(w) - 3E_{90^\circ}^{(2)}(ww)] \end{aligned} \quad (4)$$

where $E_s(www)$ are the total energies for water triplets in which the water molecules are at a same plane, and $E_d(www)$ are the total energies for water triplets in which the water molecules are not in a same plane. All of these calculations were performed at the optimized geometry of the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ cluster. Subscripts were omitted on the right-hand side of equation 4.

For the summation $\sum_{j>i=1}^6 E^{(3)}(Iw_iw_j)$ in equation 2, there are 15 energy terms (as a result of a $C(6,2)$ combination) for the which 12 terms correspond to dimers of water molecules whose angle between them is 90° and 3 dimers for the which the angle is 180°. Then,

Table 1. Potential parameters for Al³⁺ ion-water interaction in equation 1

Parameter	$A / (\text{kcal mol}^{-1})$	$B / (\text{Å}^{-1})$	$D / (\text{kcal mol}^{-1} \text{Å}^6)$	$E / (\text{kcal mol}^{-1} \text{Å}^8)$	$F / (\text{kcal mol}^{-1} \text{Å}^{12})$
Empirical value	279950	4.438	2985	350	-4980

$$\sum_{j>i=1}^6 E^{(3)}(Iw_iw_j) = 12E_{90^\circ}^{(3)}(Iw_iw_j) + 3E_{180^\circ}^{(3)}(Iw_iw_j)$$

$$= 12[E_{90^\circ}(Iww) - E^{(1)}(I) - 2E^{(1)}(w) - 2E^{(2)}(Iw) - E_{90^\circ}^{(2)}(ww)] +$$

$$+ 3[E_{180^\circ}(Iww) - E^{(1)}(I) - 2E^{(1)}(w) - 2E^{(2)}(Iw) - E_{180^\circ}^{(2)}(ww)] \quad (5)$$

where $E_{90^\circ}(Iww)$ and $E_{180^\circ}(Iww)$ are the total energies for clusters composed by the ion and two water molecules whose water-ion-water angle is 90° and 180° , respectively, at the optimized geometry of the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ cluster. In equation 5, $E^{(2)}(Iw) = E(Iw) - E^{(1)}(I) - E^{(1)}(w)$, where $E(Iw)$ is the total energy of the ion and one water molecule at the optimized geometry of the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ cluster.

For the summations in equation 2 including $E^{(4)}$, $E^{(5)}$, $E^{(6)}$ and $E^{(7)}$ terms, the calculations were performed following a similar procedure.

Results and Discussion

For a qualitative comparison, Figure 1 shows the Al^{3+} ion-water curve obtained for the interaction between the Al^{3+} and only one TIP4P water molecule when empirical parameters in Table 1 were applied in equation 1, as well as the ion water curves for the Fe^{3+} and Fe^{2+} ions using the corresponding parameters for these ions developed by Curtiss *et al.*¹⁶ It is clearly seen from this Figure that the expected behavior concerning size and hardness of the ions is reproduced, because (i) the ion-water minimum region is slightly shifted to smaller r_{IO} values for the Al^{3+} (1.85 Å) in comparison with the Fe^{3+} (1.90 Å) and Fe^{2+} (1.97 Å) ions, (ii) in going from the ion-water minimum region to shortest distances, the ion-water energy values increase more quickly for the Al^{3+} than for the Fe^{3+} and Fe^{2+} ions, and (iii) the ion-water minimum region is deeper for the Al^{3+} (-109.66 kcal mol⁻¹) than for the Fe^{3+} (-80.23 kcal mol⁻¹) and Fe^{2+} (-48.55 kcal mol⁻¹) ions. In what follows, results for structure and energetic refer to average properties from simulations.

The Al^{3+} -O and Al^{3+} -H radial distribution functions (rdf's) and the corresponding Al^{3+} -O and Al^{3+} -H coordination numbers are presented in Figures 2 and 3, respectively. In Figure 2, a well defined peak for the Al^{3+} -O rdf indicates strong interaction between the water molecules of the first coordination shell and the ion. The Al^{3+} -O rdf goes to zero for distances between about of 2.15 Å to 3.14 Å, and a similar pattern is found for the Al^{3+} -H rdf which goes to zero between 2.92 Å to 3.47 Å. Concerning the Al^{3+} -O rdf in Figure 2, the first maximum centered at 1.92 Å identifies the contact average distance between the ion and the oxygen site of a water molecule in the first coordination shell. This result, defined as $r_{IO(1)}$, is presented in Table 2 along

with the X-ray estimates of 1.87-1.90 Å for this distance.⁸ The running integration number calculated for the first peak of the Al^{3+} -O rdf up to the first minimum at 2.15 Å is 6, identifying the average number of water molecules in the first coordination shell (defined as $n_{IO(1)}$ in Table 2). The hexacoordination of the Al^{3+} in water has been determined by measurements of hydration numbers from NMR spectroscopy⁸ and it is predicted by $n_{IO(1)}$ in the present ion-water model. This result is also supported by the running integration number calculated for the first peak of the Al^{3+} -H rdf centered at 2.59 Å up to the first minimum at 2.92 Å, yielding an average number of 12 hydrogen sites in the first shell defined as $n_{IH(1)}$ in Table 2. These results can be seen by the Al^{3+} -O and Al^{3+} -H coordination numbers shown in Figure 3. Also, X-ray diffraction measurements have indicated a second hydration shell of 12-14 water molecules around the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ specie.^{7,8} In this work, the running integration number calculated for the second peak of the Al^{3+} -O rdf up to the second minimum at 4.35 Å yields an average number of about 12 water molecules in the second coordination shell (defined as $n_{IO(2)}$ in Table 2), in favor of the lower X-ray experimental value. An average result of 14 water molecules was found by Sánchez Marcos and co-workers¹¹ using the hydrated ion model.

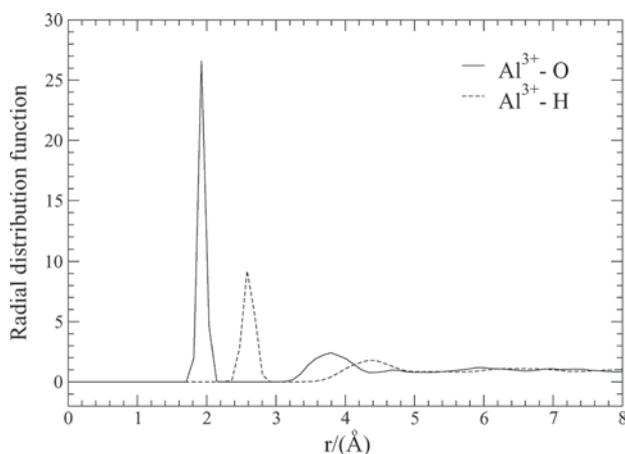


Figure 2. Al^{3+} ion-oxygen site and Al^{3+} ion-hydrogen site radial distribution functions.

Figure 4 refers to average configurational energies obtained from simulations considering the Al^{3+} ion-water and water-water interactions as a function of the distance of the ion to the oxygen site of the water molecules. It is clearly noted from this Figure that the average water-water interaction is repulsive in the first coordination shell, while the ion-water interaction is attractive until long distances due to major action of Coulomb forces. The ion-water minimum energy was calculated in -112.54 kcal mol⁻¹ at average distance of 1.92 Å. Since average water-water interaction is repulsive in the first hydration shell, it is

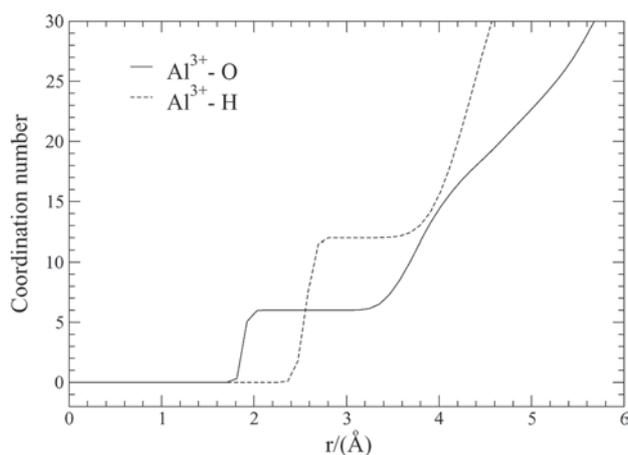


Figure 3. Al³⁺ ion-oxygen site and Al³⁺ ion-hydrogen site coordination numbers.

Table 2. Calculated average structural properties of Al³⁺ in water at 298.15 K and 1 atm. Subscripts O(*k*) and H(*k*) represent the O and H sites of the water molecule, respectively, in the *k*-th coordination shell. Experimental results are also listed. Average distances in angstroms

Property	This work	Experiment
1 st hydration shell		
$r_{\text{IO}(1)}$	1.92	1.87-1.90 ^a
$r_{\text{IH}(1)}$	2.59	
$n_{\text{IO}(1)}$	5.998	5.82-6.07 ^a , 6 ^b
$n_{\text{IH}(1)}$	11.998	
2 nd hydration shell		
$r_{\text{IO}(2)}$	3.80	3.99-4.15 ^a
$r_{\text{IH}(2)}$	4.35	
$n_{\text{IO}(2)}$	11.578	12-14 ^a

^aReference 8; ^bReference 7.

not surprising that this average distance is greater than the distance of 1.85 Å calculated for one ion and only one water molecule (Figure 1). The discontinuity in energy that appears for both Al³⁺ ion-water and water-water interactions from about 2.15 Å to 3 Å clearly distinguishes the first hydration shell from the second one, as indicated by the absence of water molecules in this region (Figure 2). After about 3 Å, a continuum in energy appears. It can be added that the ion and its first shell resemble an unity moving through the solution, in accord with hydrated ion concept. The repulsive water-water interaction energy in Figure 4 is less intense in the second coordination shell and operates until about 4 Å. A similar pattern is found for a divalent ion, such as Fe²⁺, as shown in this Figure (ion-water minimum energy of -48.546 kcal mol⁻¹ at 1.97 Å).

Dependence of system size on energy results was assessed performing simulations with increasing number of water molecules. Then, two additional pure water systems containing 780 and 1560 TIP4P water molecules were

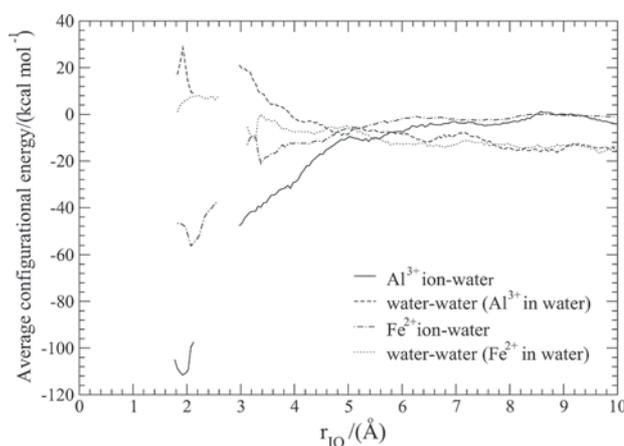


Figure 4. Average configurational energies for ion-water and water-water interactions as a function of the distance of the ion to the oxygen site of water molecules.

constructed using cubic boxes. Two other systems containing 780 and 1560 TIP4P water molecules plus one Al³⁺ ion each one, were also constructed using cubic boxes and the simulation protocol discussed above. The corresponding side lengths of 28.296 Å and 35.824 Å, or 0.073 mol dm⁻³ and 0.036 mol dm⁻³ Al³⁺ solutions, respectively, were reached in the average period. Cut-off radii of 14 Å and 17.5 Å were used for these systems, respectively, as well as for those composed by pure water, to calculate ion-water and water-water energies. Table 3 presents results for average water-water potential energies *per* water molecule for both pure water and Al³⁺ in water systems. In this Table is included the potential energy value of -9.92 kcal mol⁻¹ for liquid water estimated from experimental enthalpy of vaporization.³⁴ Concerning the computed results for pure water presented in Table 3, it is observed that when the number of water molecules increases, the average water-water potential energy shows most accordance with the corresponding experimental estimative. The same pattern is found for the average water-water potential energies in the Al³⁺ in water systems, close to the experimental estimative for pure liquid water (-9.92 kcal mol⁻¹) as the number of water molecules increases, which is expected for a solution approaching infinite dilution.

Table 3. Calculated average water-water potential energies *per* water molecule for both pure water and Al³⁺ in water systems for *N* water molecules at 298.15 K and 1 atm. Energies in kcal mol⁻¹

System	This work			Ref. 34
	<i>N</i> = 390	<i>N</i> = 780	<i>N</i> = 1560	
Pure water	-10.021	-9.912	-9.951	-9.92 ^a
Al ³⁺ in water	-8.944	-9.431	-9.713	

^aPotential energy of liquid water estimated from experimental enthalpy of vaporization.

The hydration energy was also estimated for the systems containing 390, 780 and 1560 TIP4P water molecules plus one Al^{3+} ion each one. In these studies, the hydration energy (defined as ΔE_{hyd} in Table 4) was calculated by $E_{\text{fw}} + E_{\text{ww}} - E_{\text{ww}}^p$, in which E_{fw} and E_{ww} are average configurational energies corresponding to ion-water and water-water contributions, respectively, and E_{ww}^p is the average configurational energy for pure water systems. Results obtained for these quantities are presented in Table 4. As showed in this Table, the calculated E_{ww} and E_{ww}^p energy terms are very large values. The solvation relaxation energy, calculated as the difference between these values, $E_{\text{ww}} - E_{\text{ww}}^p$, is shown in Figure 5 as function of Monte Carlo steps for $N = 390, 780$ and 1560 water molecules. This term shows large fluctuations depending on the Monte Carlo steps performed in the simulation until about 0.8×10^7 steps. After this quantity of steps, the convergence appears. The effect of the solvent relaxation term even far way from the ion can be observed inspecting the average results in Table 4 as a function of the system size. For the small system, $N = 390$, the calculated relaxation energy value ($420 \pm 4 \text{ kcal mol}^{-1}$) is larger than the ones for the other two systems ($375 \pm 8 \text{ kcal mol}^{-1}$ for $N=780$, and $372 \pm 11 \text{ kcal mol}^{-1}$ for $N = 1560$) indicating an

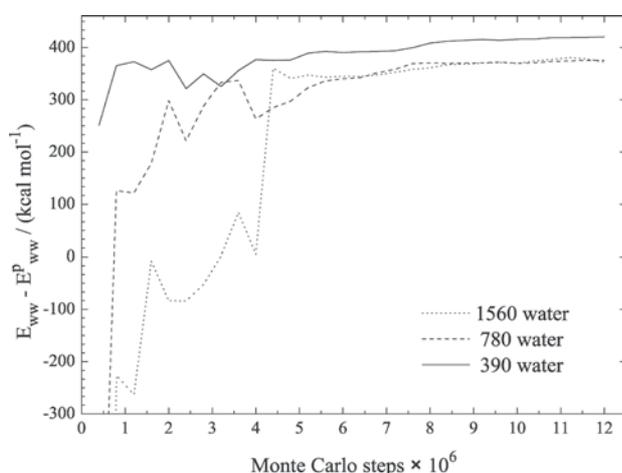


Figure 5. The solvent relaxation energy, $E_{\text{ww}} - E_{\text{ww}}^p$, as a function of Monte Carlo steps.

Table 4. Calculated average energies for Al^{3+} in water for N water molecules at 298.15 K and 1 atm. ΔE_{hyd} estimated by $E_{\text{fw}} + E_{\text{ww}} - E_{\text{ww}}^p$. The upper-script p refers to pure water. Energies in kcal mol^{-1}

Property	This work			Others
	$N = 390$	$N = 780$	$N = 1560$	
E_{fw}	-1419	-1474	-1479	
E_{ww}	-3488	-7356	-15152	
E_{ww}^p	-3908	-7731	-15524	
ΔE_{hyd}	-999	-1099	-1107	
ΔH_{hyd}	-999 ± 6	-1099 ± 9	-1107 ± 12	-1106 ± 6^c , -1115^b , -1120^a

^aFrom experiment, Reference 7, at 298 K and 1 atm; ^bFrom experiment, Reference 35; ^cFrom molecular dynamics, Reference 13.

insufficient number of water molecules in the small system to reproduce properly the hydration energy.

In Table 4, the E_{fw} values were corrected for Coulomb contributions beyond the cut-off radii of 10 Å, 14 Å and 17.5 Å by, respectively, $-18.45 \pm 0.02 \text{ kcal mol}^{-1}$, $-9.64 \pm 0.02 \text{ kcal mol}^{-1}$ and $-4.95 \pm 0.02 \text{ kcal mol}^{-1}$. Since the $p \Delta V$ terms were found negligible ($-0.012 \text{ kcal mol}^{-1}$ for 1560 water molecules), the hydration enthalpy (defined as ΔH_{hyd} in Table 4) estimated by $\Delta E_{\text{hyd}} + p \Delta V$ was calculated to be $-1107 \pm 12 \text{ kcal mol}^{-1}$ for the larger system. This result are in good agreement with experimental values of hydration enthalpy^{7,35} of $-1115 \text{ kcal mol}^{-1}$ and $-1120 \text{ kcal mol}^{-1}$. The hydration enthalpy calculated from the present ion-water model is also quite similar to the one obtained by the hydrated ion model, $-1106 \pm 6 \text{ kcal mol}^{-1}$, by Wasserman *et al.*¹³ in a molecular dynamics study.

The good agreement between all structural and energetic results obtained in this work and the experimental observation is not surprising. They were derived from an effective ion-water potential model whose parameterization was performed taking into account not only water molecules of the first and the second hydration shells of the ion but also by considering water molecules of the bulk in spite of using a pair potential analytical function to modeling the interaction between ion and water. One emphasizes at this point the role of the water molecules of the bulk to obtain good results for hydration enthalpy, as revealed by our results showed in Table 4.

Another point to stress is that the effective ion-water potential model empirically fitted in this work differs from the fitting procedure used by the Rustad and Hay³⁶ and the Bakker *et al.*²¹ Rustad and Hay have obtained potential parameters from an *ab initio* procedure considering potential energy surface of one Fe^{3+} ion with a single water molecule to construct an ion-water pair potential. Bakker *et al.*²¹ have developed an ion-water pair potential and an water-ion-water three body potential by fitting *ab initio* interaction energies extracted from potential energy surfaces of two- and three-body, respectively. As discussed above,

Table 5. Total energies (in a.u.) for the ion, water, ion and water clusters and water clusters at the optimized geometry of the [Al(H₂O)₆]³⁺ cluster. Al³⁺ = *I* and H₂O = *w*

$E([\text{Al}(\text{H}_2\text{O})_6]^{3+})$	-700.316687318	$E_d(www)$	-229.365725924
$E(I)$	-240.407869195	$E_s(Iwww)$	-470.547900951
$E(w)$	-76.4593183734	$E_d(Iwww)$	-470.523775860
$E(Iw)$	-317.185385091	$E_s(wwww)$	-305.817209065
$E_{90^\circ}(ww)$	-152.914245992	$E_d(wwww)$	-305.815893269
$E_{180^\circ}(ww)$	-152.916372653	$E_s(Iwwww)$	-547.170177832
$E_{90^\circ}(Iww)$	-393.879645529	$E_d(Iwwww)$	-547.152240433
$E_{180^\circ}(Iww)$	-393.912408791	$E(wwwww)$	-382.263381604
$E_s(wwww)$	-229.367490424	$E(Iwwwww)$	-623.74682179

a different approach was used in this work for which contributions beyond three-body was effectively incorporated in the fitted potential parameters.

To support the efficacy concerning many-body effects of the ion-water potential developed in this work, many-body contributions were calculated for the [Al(H₂O)₆]³⁺ cluster using the density functional theory at the B3LYP/CC-pVTZ level. The geometrical parameters for the optimized structure at *T_h* symmetry were found to be 1.935 Å for Al-O distance, 0.974 Å for the O-H distance, and 107.1 Å for the HOH angle. Table 6 shows the results for binding energy and many-body interaction energies for the [Al(H₂O)₆]³⁺ cluster calculated from the total energies for ion, water, water clusters, and ion and water clusters at the optimized geometry of the [Al(H₂O)₆]³⁺ cluster showed in Table 5. From Table 6, the interaction energies of tree-, four-, five-, six-, and seven-body for the cluster appear with alternating signs with the series converging very slowly, indicating that all these terms are important to reproduce the binding energy (*BE*) of the cluster. As an example, the summation over $E^{(6)}$ for water molecules resulting in -321.8 kcal mol⁻¹ shows a large attractive value which can not be neglected to estimate the *BE* of the cluster. The summation over tree-body interaction terms, $E^{(3)}$, for example, are repulsive. It can be explained by the large value of the ion charge which polarizes the H-O bond in water molecules, increasing repulsive forces between water molecules. Adding one water molecule to the tree-body terms, at the geometry of the cluster, one found an attractive value as a result of the summation over interaction terms $E^{(4)}$, indicating a cooperative effect between water molecules. The summation over all these interactions from $E^{(2)}$ up to $E^{(7)}$ give the binding energy of -723.5 kcal mol⁻¹ for the [Al(H₂O)₆]³⁺ cluster. Following an *ab initio* procedure in which the ion-water pair potential is extracted from a potential energy surface of one Al³⁺ ion with a single water molecule, it would expected an ion-water potential energy *per* water molecule of about -200 kcal mol⁻¹, or $1/6 \sum_{i=1}^6 E^{(2)}(Iw_i)$, as showed in Table 6,

which is a very different result from that obtained by our empirical result of about -110 kcal mol⁻¹ (Figure 4) for Al³⁺ ion-water interaction. In Figure 4, the average geometry of the Al³⁺-water pairs is not frozen with the minimum at r_{IO} distance of 1.92 Å. The *ab initio* optimized distance r_{IO} was found to be 1.935 Å at the structure of the [Al(H₂O)₆]³⁺ cluster with *T_h* symmetry group. As the two values are quite similar, one can compare the interaction energies shown in Table 6 with the average configurational energy from simulation in Figure 4. The *ab initio* two-body interaction energy for ion-water, $E^{(2)}(Iw_i)$ *per* water molecule of -200 kcal mol⁻¹ presents an artificial stabilization which, in part, is due to the neglect of the three-, four- and higher order interaction energy terms.

Conclusions

In this work, a Monte Carlo study of the Al³⁺ ion hydration was performed using an empirical ion-water potential. Calculated results for coordination numbers and ion-water oxygen distances for the first and the second coordination shells of the Al³⁺ in water were found in very good agreement with experimentally derived X-ray and NMR measurements, although only the experimental results of structure of the first shell (coordination number and the ion-water oxygen distance) were fitted during the empirical optimization process. Furthermore, by using a large enough number of water molecules in the simulation box, the calculated hydration enthalpy was found in good agreement compared to experimental and theoretical results, without any additional optimization upon the potential parameters. These findings can be attributed in part by considering the molecules of the coordination shells and the ones of the bulk in the empirical optimization process, in which the many-body effects of water molecules around the Al³⁺ could effectively be incorporated in the fitted parameters. These conclusions are supported by *ab initio* quantum mechanical results for the magnitude of two- and higher-body interac-

Table 6. Binding energy (*BE*) and many-body interaction energies (kcal mol⁻¹) of the [Al(H₂O)₆]³⁺ cluster. Al³⁺ = *I* and H₂O = *w*

$BE([Al(H_2O)_6]^{3+})$	-723.5
$\sum_{i=1}^6 E^{(2)}(Iw_i)$	-1198.0
$\sum_{j>i=1}^6 E^{(2)}(w_iw_j)$	37.3
$\sum_{j>i=1}^6 E^{(3)}(Iw_iw_j)$	684.6
$\sum_{k>j>i=1}^6 E^{(3)}(w_iw_jw_k)$	22.9
$\sum_{k>j>i=1}^6 E^{(4)}(Iw_iw_jw_k)$	-341.6
$\sum_{l>k>j>i=1}^6 E^{(4)}(w_iw_jw_kw_l)$	-93.9
$\sum_{l>k>j>i=1}^6 E^{(5)}(Iw_iw_jw_kw_l)$	274.3
$\sum_{r>l>k>j>i=1}^6 E^{(5)}(w_iw_jw_kw_lw_r)$	94.9
$\sum_{r>l>k>j>i=1}^6 E^{(6)}(Iw_iw_jw_kw_lw_r)$	-31.8
$\sum_{n>r>l>k>j>i=1}^6 E^{(6)}(w_iw_jw_kw_lw_rw_n)$	-321.8
$\sum_{n>r>l>k>j>i=1}^6 E^{(7)}(Iw_iw_jw_kw_lw_rw_n)$	149.6

1 a.u. = 627.5095 kcal mol⁻¹.

tion energy terms to the total energy for an [Al(H₂O)₆]³⁺ cluster which suggest that higher-body contributions are a significant part to be considered in constructing potentials for the Al³⁺ ion.

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