

A Dynamic Model to Explain Hydration Behaviour along the Lanthanide Series

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An understanding of the hydration structure of heavy atoms, such as transition metals, lanthanides and actinides, in aqueous solution is of fundamental importance in order to address their solvation properties and chemical reactivity. A large number of studies have been performed on this topic from both experimental and theoretical points of view.^[1–5] In particular, molecular dynamics (MD) is often used in combination with extended X-ray absorption fine structure (EXAFS) experiments, and many details concerning structural and dynamical aspects are known, especially for transition metals.^[6–10] The lanthanides easily form highly charged (+3) hard cations, Ln^{3+} . However, even though different studies on the hydration of Ln^{3+} ^[11–22] have been reported recently, a clear and definitive picture bringing together experimental macroscopic data (like absolute partial molar volumes) with microscopic structural details (obtained from EXAFS experiments or theoretical calculations) is still lacking. Literature agrees on the evidence that the number of water molecules in the first coordination shell decreases along the series, passing from a coordination number (CN) of nine for La^{3+} to eight for Lu^{3+} (the last atom in the series).^[1] For some time, the standard explanation of CN 9–8 passage was the so-called gadolinium break.^[17–20] According to this model, the CN has a discontinuous variation from nine to eight at Gd^{3+} , due to the sudden change in the thermodynamic properties of the series at Gd^{3+} . Recently, Helm, Merbach and co-workers have studied water self-exchange reactions along the series by both theory and experiment. However, due to theoretical and experimental limitations, they could not establish a global picture that takes all the atoms in the series into account. Nonetheless, they provide several insights from both structural and dynamical points of view.^[1,13,21–26] They point out a more progressive modification of CN across the series, but the relationship between the macroscopic and microscopic properties is still an open question. A systematic theoretical study of lanthanide hydration can provide an important answer. Recently, a molecular dynamics study by Floris and Tani, investigating hydration of Nd^{3+} , Gd^{3+} and Yb^{3+} , respectively at the beginning, the middle and the end of the

series, did not show any change in coordination number across the series.^[27]

Herein, based on MD simulations with a new reliable classical pair interaction potential plus explicit polarization,^[28,29] we study hydration properties of the whole Ln^{3+} series. To the best of our knowledge, a systematic theoretical study in liquid water as reported here has not been done before. Our microscopic data, in agreement with recent experimental results, suggest the following picture: upon moving across the series from lighter to heavier lanthanides, the statistical predominance of one first hydration shell structure containing nine water molecules changes in favour of one containing eight water molecules. This statistical picture can explain the hydration behaviour along the series.

An analysis of the Ln^{3+} –water radial distribution function (RDF) (provided in the Supporting Information) along the series, gives the first shell Ln –O distances ($r_{\text{Ln-O}}$) and CNs. The resulting data are compared with the available experimental data in Figure 1. The distances between Ln^{3+} and the oxygen

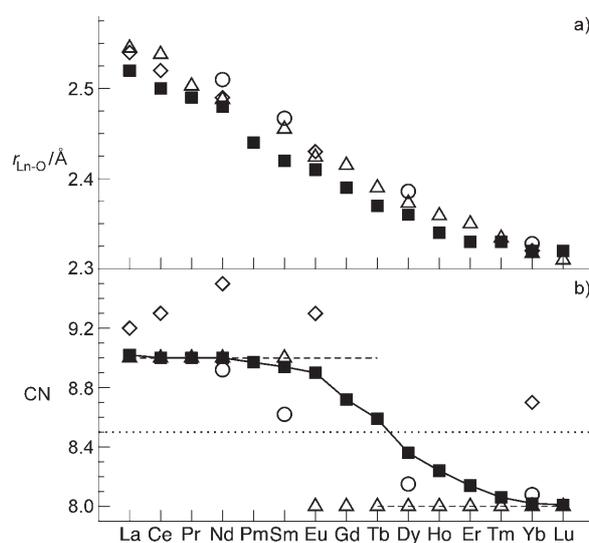


Figure 1. Structural properties obtained from MD simulations (■). Experimental data are also reported for comparison: (○),^[25] (◇)^[30] and (△).^[31] a) Ln – OH_2 distances, b) Coordination Numbers.

atoms of the water molecules in the first hydration shell (Figure 1a) have an almost linear dependence on the atomic number. The differences in $r_{\text{Ln-O}}$ values between our data and experimental data^[25,30,31] are no larger than 0.05 Å, and most of them lie within experimental uncertainty. On the other hand, the average coordination numbers (Figure 1 b), obtained as the

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integral of the RDF's first peak, display sigmoidal behaviour and we did not observe a sudden change at any point in the series. This is in agreement with the experiments reported by Helm and Merbach,^[1,25] even though our curve is shifted toward heavier atoms in the series. If we trace an horizontal line corresponding to a coordination number of 8.5, our CN curve crosses this line between Tb and Dy, while Gd has CN=8.7—in agreement with simulations done by Clavaguera et al.^[11] Recently, a DFT-based MD study^[12] reports CN=8 for hydrated Gd³⁺, but the time of only a few ps reported in this study is not enough to allow any exchange events. The structural meaning of a non-integer CN is that a fraction of the structures have CN=8 and a fraction have CN=9 during the simulation time. For La³⁺ to Pr³⁺ only, some structures with CN=10 are found as well, but we do not consider them here, since we are only interested in the path from CN=9 to CN=8. In Figure 2 we report the probability of having CN=9 or CN=8 as obtained across the lanthanide series. For Gd the CN=9

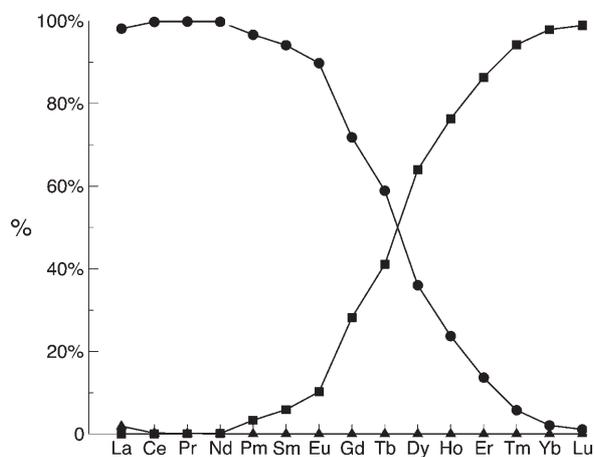


Figure 2. Percentage of CN=8 (■), CN=9 (●) and CN=10 (▲) first hydration shell configurations.

structure is still predominant (~70%) while the CN=8 structure is dominant starting from Dy. The latter has a specular CN=9/CN=8 ratio with respect to Tb. Thus, for Tb a CN=9 is obtained for 60% of configurations while for Dy a CN=8 is obtained for about 60% of configurations. These statistics are only meaningful when the MD runs are long enough. To understand what happens in this critical region of the series, the number of water molecule exchanges per nanosecond is shown in Figure 3. The exchange frequency (EF) is the number of exchanges for all nine or eight water molecules from the first sphere. The Gd–Ho central region is characterized by a high EF which corresponds to the lability of a particular kind of first solvation shell molecules, with a maximum located between Tb and Dy. The nine-fold coordination geometry is composed of six water molecules forming a prism and three equatorial ones, such that the tricapped trigonal prism (TTP) structure^[28] presented in Figure 4a is obtained. Visual observations of the trajectories confirm that this structure is stable for the lighter lanthanides. The 9–8–9 self-exchanges,

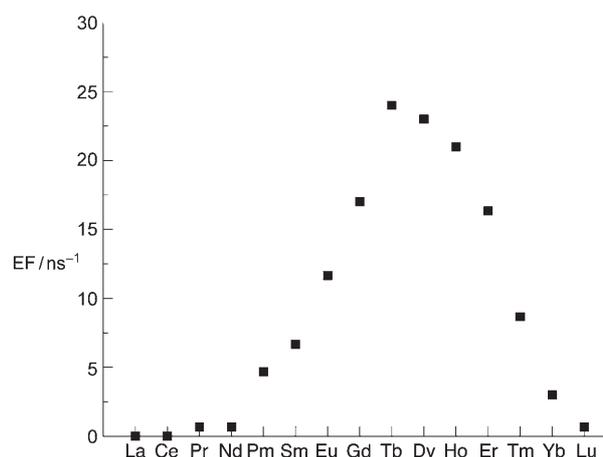


Figure 3. Number of exchanges per nanosecond (EF) in the first hydration shell as obtained from MD simulations.

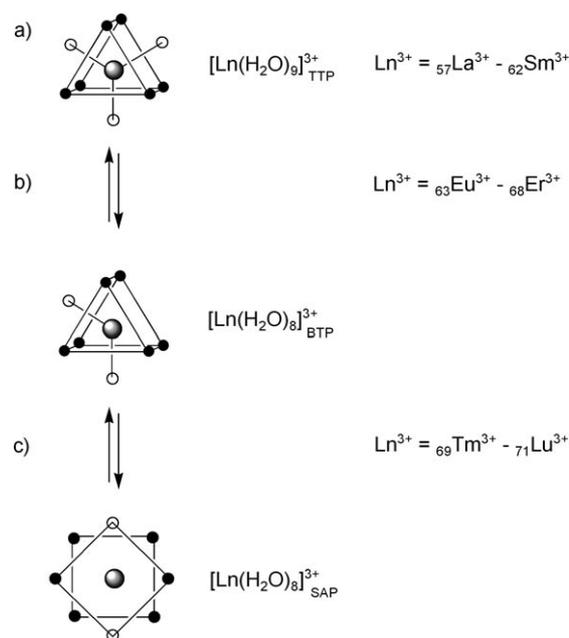


Figure 4. Hydration structure around Ln³⁺ showing the dynamic model which explains the decrease in CN across the series: a) light, b) middle-series and c) heavy lanthanides.

which start at Nd³⁺, involve the molecules in the centre triangle: the outgoing H₂O molecule leaves the centre triangle of the initial TTP structure and the incoming H₂O molecule finally stays in the centre triangle of the rearranged final TTP structure. Upon increasing the atomic number, an increase in the exchange frequency of the three centre triangle molecules is observed. In the middle of the series, these three molecules are more labile (Figure 4b). A progressive and continuous decrease in the CN is also observed. This is due to the statistical coexistence of two stoichiometries (CN=9 and CN=8) with many interchanges. The EFs are qualitative data and the most important point is that the dynamic behaviour across the series is qualitatively in agreement with experiments.^[1] This

qualitative result allows us to assess the dynamic model proposed herein.

Finally, for heavy lanthanides an eight-fold structure is observed. It fluctuates between a bicapped trigonal prism (BTP) and a square antiprism (SAP) (Figure 4c) as can be seen after the exchanges. The BTP structure is an intermediate of both the 9–8 and 8–9 reactions, whereas the CN=8 structure rearranges itself to the SAP structure upon reaching a stable state.

In summary, we found different exchange mechanisms, depending on the lanthanide: for light Ln^{3+} (La^{3+} – Pr^{3+}) we found only CN=9 structures and a few with CN=10. The exchange mechanism is a concerted associative one, as previously described by us.^[28] The EFs in Figure 3 are zero for La^{3+} and Ce^{3+} as only the CN=9 and CN=8 structures and dynamics are pertinent here. The exchange dynamics which takes CN=10 into account as well, was already presented for La^{3+} .^[28] From Nd^{3+} onwards, CN=8 structures are also present. Up to Eu^{3+} , we found that the CN=8 structure has a short lifetime (from 1 to 7 ps) while the CN=9 one has a longer lifetime (hundreds of ps). The mechanism of exchange is concerted dissociative (or limiting dissociative, following the definition of ref. [1]). In the critical middle region of the series, we found that CN=9 and CN=8 both become stable, with a CN=9 predominance up to Tb^{3+} and a CN=8 predominance from Dy^{3+} . Thus, the lifetimes of all the CNs are similar (17–40 ps). The mechanism for the 9–8–9 self-exchange is dissociative and it is associative for the 8–9–8 exchange. When CN=8 exists for longer times, there are two distinct reactions: one for the dissociation of a water molecule and one for the association of one. Thus, it is certainly difficult to decide unambiguously where the border lies between an exchange reaction and a dynamic equilibrium. Finally, for lanthanides having a clear predominance of CN=8, a concerted associative mechanism is observed (the CN=9 now has a short lifetime). Thus, disregarding the light lanthanides, where no CN=8 structures were found, our simulations show a changeover from a dissociative to an associative mechanism upon proceeding along the series—confirming the postulation of Helm and Merbach.^[1]

Without any supporting theoretical model, the coordination number is very difficult to obtain from EXAFS experiments. In the case of available EXAFS experiments on Ln^{3+} , no MD simulations were used to help determine the CN.^[31] Even if a minimal model is sufficient for the very beginning and the very end of the series, in the middle, the most interesting region, a dynamic picture is fundamental to a full understanding of hydration properties.

Concluding, herein we present a systematic molecular dynamics study of Ln^{3+} hydration in bulk water that can be used as reference for experimental and theoretical research in this and related fields. Our study of hydration structure and dynamics along the entire Ln^{3+} series provides a dynamic picture of the CN behavioural change from light (CN=9 predominating) to heavy (CN=8 predominating) lanthanides consistent with the exchange mechanism proposed by Helm, Merbach and co-workers.^[1,13] This scenario is summarized in Figure 4. The hydrated light lanthanides are stable TTP structures containing two kinds of water molecules: six molecules forming

the trigonal prism and three in the centre triangle. Towards the middle of the series both ionic radii and polarizabilities decrease, such that first-shell water–water repulsion increases and water–cation attraction decreases. This mainly applies for molecules of the centre triangle of the nine-fold structure. Thus, one of these molecules stay in the second hydration sphere of the lanthanide for longer average times, as one progresses along the lanthanide series. The interchange between predominantly CN=9 and CN=8 is found between Tb and Dy.

Therefore, we propose a model that determines the properties governing the change in the first-shell coordination number across the series, confirming the basic hypothesis proposed by Helm and Merbach.^[1] We show that it is not a sudden change in behaviour, but rather that it results from a statistical predominance of one first hydration shell structure containing nine water molecules over one containing eight. This is observed progressively across the series.

Computational Details

We have performed classical MD of all the Ln^{3+} cations by using the same Hamiltonian with a polarizable force field previously developed by us for La^{3+} in water.^[28,29] The original parameters for La^{3+} in water were extended to all the atoms in the series and modified, taking into account available data on polarizability,^[32] and ionic radii^[33] along the series.

Molecular dynamics simulations were performed by using the following interaction potentials [Eq. (1)]:

$$V_{\text{tot}} = V_{\text{elec}} + V_{\text{O-O}}^{\text{LJ}} + V_{\text{La-O}}^{\text{Buck6}} \quad (1)$$

where electrostatic interactions (V_{elec}) are composed by a typical charge–charge and a polarization term. In the first step the dipoles on each atomic site are calculated by a self-consistent procedure and then propagated through the dynamics using a Car–Parrinello-like scheme.^[34]

The non-electrostatic part was modelled with a typical Lennard-Jones potential for water (where only oxygen atoms are explicitly considered) while we used the following analytic expression for Ln–H₂O interactions [Eq. (2)]:

$$V_{ij}^{\text{Buck6}} = A_{ij}^{\text{Buck6}} \exp(-B_{ij}^{\text{Buck6}} r_{ij}) - \frac{C_{6,ij}^{\text{Buck6}}}{r_{ij}^6} \quad (2)$$

Here parameters obtained from La^{3+} were adapted to all the atoms in the series by considering ionic radii and polarization. We also calculated parameters for the non-naturally occurring element Pm, by linearly fitting the polarizability and the ionic radius. Parameters B and C and atomic Ln^{3+} polarizations are shown in the Table 1. Parameter A is the same for all atoms, $1.004 \times 10^6 \text{ kJ mol}^{-1}$.

MD simulations were done in the NVE ensemble equilibrated at 298 K using code developed by us. Each Ln^{3+} ion was immersed in a box containing 216 water molecules, where periodic boundary conditions and the smooth particle-mesh Ewald summations for long-range interactions were applied to mimic bulk conditions. A MD simulation of 3 ns was performed for each $\text{Ln}(\text{H}_2\text{O})_{216}^{3+}$ system, with a resulting average temperature of 298 K. More technical details are presented in our previous work on hydrated La^{3+} .^[28,29]

Table 1. Parameters of the non-electrostatic term and atomic polarization for all lanthanide atoms used in MD simulations.

Atom	B [\AA^{-1}]	C [$\text{kJ mol}^{-1} \text{\AA}^6$]	α [\AA^3]
La	3.480	$3.766 \times 10^{+4}$	1.41
Ce	3.500	$3.628 \times 10^{+4}$	1.35
Pr	3.517	$3.535 \times 10^{+4}$	1.29
Nd	3.533	$3.435 \times 10^{+4}$	1.23
Pm	3.603	$3.054 \times 10^{+4}$	1.21
Sm	3.617	$2.975 \times 10^{+4}$	1.17
Eu	3.630	$2.912 \times 10^{+4}$	1.11
Gd	3.643	$2.815 \times 10^{+4}$	1.06
Tb	3.656	$2.791 \times 10^{+4}$	1.01
Dy	3.667	$2.732 \times 10^{+4}$	0.97
Ho	3.681	$2.686 \times 10^{+4}$	0.94
Er	3.692	$2.649 \times 10^{+4}$	0.90
Tm	3.702	$2.589 \times 10^{+4}$	0.86
Yb	3.711	$2.565 \times 10^{+4}$	0.80
Lu	3.719	$2.527 \times 10^{+4}$	0.77

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