Chemical Physics Letters 691 (2018) 437–443

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Combined distribution functions: A powerful tool to identify cation coordination geometries in liquid systems

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ARTICLE INFO

Article history:
Received 27 October 2017
In final form 27 November 2017
Available online 28 November 2017

Keywords:
Molecular dynamics simulations
Combined distribution functions
Ion solvation
Coordination geometries
Hydration complexes

ABSTRACT

In this work we have developed an analytical procedure to identify metal ion coordination geometries in liquid media based on the calculation of Combined Distribution Functions (CDFs) starting from Molecular Dynamics (MD) simulations. CDFs provide a fingerprint which can be easily and unambiguously assigned to a reference polyhedron. The CDF analysis has been tested on five systems and has proven to reliably identify the correct geometries of several ion coordination complexes. This tool is simple and general and can be efficiently applied to different MD simulations of liquid systems.

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1. Introduction

Identifying metal ion coordination geometries in liquid media is central in solution chemistry, because of its relevance in a large number of physicochemical processes in nature, industrial technologies and living organisms [1]. As concerns aqueous solutions, with the exception of some cases where very stable solvation complexes are formed [2,3], it is usually very difficult to single out the mean ion solution structure due to the strong disorder of the first hydration shell and because of the high mobility of solvent molecules surrounding the ion [4–10].

From a theoretical point of view, the most used and straightforward method is to calculate the angular distribution functions (ADFs) of the O-M-O′ angles derived from Molecular Dynamics (MD) simulations, and to compare them with the discrete distributions of the corresponding ideal polyhedra. However, in some cases the ideal symmetries for a given coordination number differ only slightly and the ADF analysis is not always adequate to definitely establish the first shell geometry.

Several efforts have been made in the literature to improve the information derivable from the ADFs, by comparing the functions calculated from the MD trajectories with continuous distribution functions corresponding to the geometry of a reference polyhedron pattern [11,12]. These continuous ADFs have been built by Kowall et al. by broadening the angle discrete lines using Gaussian functions with empirical widths [11], while recently Morales et al. have adopted Lorentzian functions defined starting from both quantum-mechanical and empirical information [12]. One of the most significant example in the literature of the difficulties encountered to identify ion solvation structures concerns lanthanoid (III) (Ln^{3+}) aqua ions [13–20]. For these ions, the possible coordination polyhedra are very similar to each other and rather complex procedures have been developed to identify these structures from MD simulations of lanthanoid aqueous solutions [11,16]. Kowall et al. for example calculated dot plots of the ion first shell after identification and superposition of the MD configurations with the underlying regular polyhedra [11]. On the other hand, Floris et al. introduced a method based on the diagonalization of the inertia tensor for a polyhedron formed by the oxygens of water molecules belonging to the lanthanoid first hydration shell [16]. For other ions, more straightforward procedures have been developed, as in the case of the Sc^{3+} ion, where the presence of a water molecule coordinated at very long distance from the ion allows the definition of an internal reference system in which the Sc^{3+} coordination polyhedron is easily singled out [21].

Here, we present a tool to identify ion coordination geometries in solution which is based on the calculation of Combined Distribution Functions (CDFs). The procedure is absolutely general and can be used to study the solvation properties of any ion in aqueous and non-aqueous solutions. We apply this tool to several example systems. In particular, we show its application to solutions where very stable and easily identifiable solvation complexes are found (i.e. Zn^{2+} in aqueous solution and Ce^{3+} in the ethyl ammonium nitrate (EAN) ionic liquid), and also to cases where the ions form more

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https://doi.org/10.1016/j.cplett.2017.11.056
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flexible or peculiar hydration structures (namely Ln^{3+} and Sc^{3+} ions in water).

2. Methods

The CDFs have been calculated from MD simulations of Zn^{2+} [2], La^{3+} [22], Lu^{3+} [22] and Sc^{3+} [21] in aqueous solution and of the Ce^{3+} ion in EAN [23]. The MD simulations of the Zn^{2+} and Sc^{3+} ions in water were performed using two-body effective potentials to describe the ion-water interactions, which have been obtained by fitting the parameters of suitable analytical functions on *ab initio* potential energy functions as described in detail in Ref. [24] for Zn^{2+} and Ref. [21] for Sc^{3+}. In order to include these ion-water effective pair potentials in the MD force field, a modified version of the GROMACS package has been employed to carry out the simulations, while using the SPC/E water model to describe water-water interactions [25]. The systems were composed of one ion and 819 water molecules placed in a cubic box, replicated using periodic boundary conditions. The simulations were carried out in the NVT ensemble (T = 300 K) using the Berendsen thermostat [26] (coupling constant of 0.1 ps). A cutoff of 9 Å was used to deal with non bonded interactions, with the Particle Mesh Ewald (PME) method to treat long range electrostatic effects [27]. A homogeneous background charge has been used to compensate for the presence of the ions. The simulations were carried out for 10 ns, after 5 ns and 3 ns of equilibration for Zn^{2+} and Sc^{3+}, respectively. The time step was 1 fs and a configuration every 25 time steps has been saved. MD simulations of the La^{3+} and Lu^{3+} aqueous solutions have been carried out using a similar simulation protocol with the following differences: the van der Waals interactions between the Ln^{3+} ion and the water molecules have been described by means of Lennard-Jones potentials with ad hoc developed parameter values [22]. The simulations were performed by means of the DL_POLY package [28] in the NVT ensemble at 300 K using the Nosé-Hoover thermostat [29,30]. Finally, the MD simulation of a 0.05 M solution of $Ce(NO_3)_3$ in EAN, corresponding to a molar ratio of 1:224, was performed using the DL_POLY package [28]. The force field parameters for EA and NO_3^- were taken from Lopes and Padua [31,32], while for the Lennard-Jones interactions involving Ce^{3+} we used the Lennard-Jones parameters developed by us in order to obtain accurate structural properties of Ce^{3+} in water [22]. On the other hand, the interaction between the Ce^{3+} ion and the oxygen atoms of the NO_3^- anions has been described using a Buckingham potential with ad hoc extrapolated parameter values [23]. The system was composed of 5 $Ce(NO_3)_3$ and 1120 EAN molecules placed in a cubic box, and periodic boundary conditions were used in order to mimic bulk conditions. After a series of equilibration runs, the final simulation production phase in the NVT ensemble (T = 300 K) was 10 ns long. The Nosé-Hoover thermostat was adopted to maintain the constant temperature condition [29,30], with a relaxation constant of 0.5 ps, and the SHAKE algorithm was employed to constrain the stretching interactions of the hydrogen atoms. Electrostatic long-range effects were computed with the EWALD method [27], while a cutoff distance of 12 Å was used for the nonbonded interactions.

It is important to stress that the reliability of the structural results obtained from the MD simulations of all the systems investigated in this work has been previously assessed by comparison with the Extended X-ray Absorption Fine Structure (EXAFS) experimental data, and an excellent agreement between theory and experiment has been obtained in all cases. An accurate description of the results obtained from the MD simulations can be found in Refs. [2,21–23].

The CDF analyses have been carried out by combining radial and angular distribution functions. In particular, CDFs between M-O distances and O-M-O′ angles, where O and O′ are atoms belonging to the first coordination shell of ion M, have been calculated by means of the following equation:

$$P(r,\theta) = \sum_t^{N_t}\sum_i^{N_M}\sum_j^{N_O}\sum_{k\neq j}^{N_O}\frac{1}{2}\frac{\delta(r_{ij}-r,\theta_{jik}-\theta)}{N_t N_M \rho_O V(r,\theta)} \tag{1}$$

where index t runs over the N_t frames of the MD simulation, index i runs over the N_M M ions in the simulation box, indexes j and k run over the N_O O atoms belonging to the first coordination shell of the i-th M ion, r_{ij} is the M-O distance, θ_{jik} is the O-M-O′ angle, and $V(r,\theta)$ is the volume unit at distance r and angle θ. ρ_O is the number density of O atoms in the MD simulation box. During the computation of the CDFs, for a given window delimited by the endpoints $r_a, r_b, \theta_a, \theta_b$ the volume unit $V(r,\theta)$ has been calculated as follows:

$$\begin{aligned} V(r,\theta) &= \int_{r_a}^{r_b}\int_{\theta_a}^{\theta_b} 2\pi r^2 \sin(\theta)\,dr\,d\theta \\ &= \frac{2}{3}\pi(r_b^3 - r_a^3)(\cos(\theta_a)-\cos(\theta_b)) \end{aligned} \tag{2}$$

It is important to stress that CDFs that combine radial and angular distribution functions have been previously used in the literature to highlight the local arrangement of molecules with respect to some internal axis of other molecules, which can correspond, for example, to a molecular bond or to the normal to a molecular plane [33–35]. In these calculations, only one vector of the CDF angle is intermolecular, while the other is fixed by the molecular geometry. The CDFs are computed by combining the angle distribution with the radial distribution of an intermolecular distance usually taken between two atoms of the two different molecules and the calculation does not require the use of a cutoff distance. However, with this kind of CDF analysis it is not possible to identify the overall geometrical arrangement of first shell solvent molecules around an ion. On the contrary, in our procedure both vectors in the angle definition are intermolecular, and this makes the use of a cutoff distance mandatory. Moreover, for each O-M-O′ angle two intermolecular distances are involved, namely M-O and M-O′, and our strategy to avoid the calculation of a high-dimensional function and to preserve the CDF two-dimensionality is to separate the contribution related to each computed angle into two parts: it contributes one half to the M-O distance and the other half to the M-O′ distance. This gives rise to the $\frac{1}{2}$ factor in Eq. (1).

Furthermore, we have calculated theoretical CDFs for the reference ideal polyhedra of the ion solvation complexes. In analogy with the CDFs calculated from the simulations, each O-M-O′ triplet of atoms in the polyhedron can be described as a triplet of geometrical parameters, namely the M-O and M-O′ distances (r_1, r_2) and the O-M-O′ angle (θ_i). Geometrical parameters of the ideal polyhedra considered in this work are listed in Table 1, together with the number of equivalent r_1-r_2-θ_i triplets (n_i) that recurs in each polyhedron. Starting from the geometrical parameters in Table 1 the CDF for a reference polyhedron is computed through the following equation:

$$P(r,\theta) = \sum_i^{N_\theta}\frac{1}{2}\frac{n_{r_1,\theta_i}(r,\theta) + n_{r_2,\theta_i}(r,\theta)}{\rho_O V(r,\theta)} \tag{3}$$

where index i runs over the N_θ different O-M-O′ inner θ_i angles of the polyhedron and $n_{r_1,\theta_i}(r,\theta)$ and $n_{r_2,\theta_i}(r,\theta)$ are Gaussian functions centered at (r_1,θ_i) and (r_2,θ_i), respectively. For a given θ_i angle of the polyhedron, $n_{r_1,\theta_i}(r,\theta)$ and $n_{r_2,\theta_i}(r,\theta)$ are chosen so that their integral is equal to the number of times the r_1-r_2-θ_i triplet recurs in the polyhedron. The widths σ_r and σ_θ of the Gaussian functions have been chosen in order to yield the best agreement with the CDFs computed from the MD simulations, in analogy with the

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