XII Congresso Brasileiro de Termodinâmica
VIII Escola de Termodinâmica

De 5 a 9 de Maio de 2024
Curitiba - Paraná - Brasil

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CURITIBA 2024

Validation of computational protocols for ions hydration free energy calculations based on efficient quantum chemical methods

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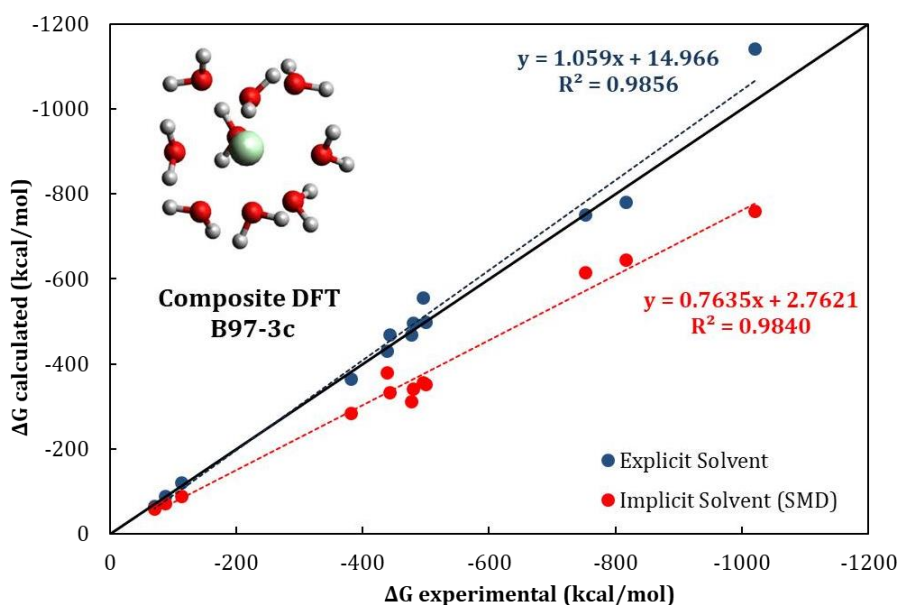[a]LABMOL, Centre for Mineral Technology (CETEM), Rio de Janeiro, RJ, Brazil
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GRAPHICAL ABSTRACT

ABSTRACT

The hydration of ions is a process in which water molecules surround and stabilize ions, forming a solvation layer around them. This stabilization occurs when an ion is submerged in water and is caused initially by electrostatic interactions between the dipoles of the water molecules and the ion charges and can evolve to chemical interactions through charge transfer and coordination bonds depending on the ion nature. Many natural and industrially important processes involve electrolyte solutions and chemical reactions in aqueous environments where these ions participate, such as in sea and ground waters, inorganic scaling, chemical synthesis, extractive metallurgy, and mineral processing. The study and thorough description of chemical systems involving ions are made possible by computational techniques such as quantum mechanics (QM) modeling and molecular mechanics (MM), which allow for simulations of atomic behavior. Each kind of modeling approach is suitable for different objectives. Solvation energies, association constants, dielectric constants, and the structure of the solvation layer around ions are among the often-studied topics. As such, a good description of the hydration thermodynamics of the relevant ions is an essential step in modeling complex reactive processes. The purpose of this work is to test recently developed

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QM methods for ion hydration free energy calculations, in order to validate their results towards experimental data and establish robust and computationally tractable protocols to further study chemical reactions involving metal ions, as in hydrometallurgical solvent extraction and battery materials recycling, for example. To do this, a range of metal cations was chosen, encompassing alkali, alkaline-earth, transition, and rare-earth metals, with charges from +1 to +6. Avogadro graphic program was used to prepare the structures of the metal aquo complexes. Two approaches were tested to determine the cations' hydration free energy (ΔG_{hyd}). A hydration reaction following the standard definition is considered in method (1) as $M^{m+}_{(g)} + n\ H_2O_{(aq)} \rightarrow [M(H_2O)_n]^{m+}_{(aq)}$, explicitly taking into account the water molecules, and computing the free energy using standard thermostatistical formulas. In method (2), the pure metal cation is subjected to the implicit continuum solvent model SMD (Solvation Model based on solute electron Density) and is expressed as $M^{m+}_{(g)} \rightarrow M^{m+}_{(aq)}$, that is a transfer process, not a reaction. Calculations for geometry optimization, frequency, and solvation were performed using the B97-3c composite DFT (Density Functional Theory) method and the Orca program. This is a modern, robust, and computationally balanced Density Functional approach, which drives its validation and testing for this particular problem, given its thorough testing for other kinds of properties calculations which have proven its quality in pair with more computationally demanding QM methods at a fraction of the cost. The results obtained by the explicit method (1) show lower errors compared to experimental data than the implicit method (2), as well as better correlation as indicated by the R^2 and angular coefficient values of the linear fits obtained. By further adjusting the data points with a single scaling parameter applied to the water molecule solvation free energy through least squares method, a linear model with angular coefficient close to 1 was reached. The favourability of ΔG absolute values increase with the cation charge in both techniques, as expected. Particularly, for the implicit solvent, the error magnitude is proportional to the charge magnitude. In contrast to the overall trend, the second approach is shown to have the lowest error when analyzing monovalent alkaline cations. Since the SMD-based approach does not require the inclusion of solvent molecules and computationally demanding frequency calculations, the usage of the implicit solvent is a viable choice in this instance, with minimum to no loss of accuracy. Based on the estimated error values, the explicit solvent method (1) is more accurate when comparing to the experimental data and seems to be mandatory for highly charged cations, especially because of the explicit interactions that occur between the water molecules as electron donors and not only as a dielectric medium. However, method (2) worked better for monovalent alkali cations since it had low errors and required less computing power, in line with the electronic structure of these cations. To expand the analysis to a wider variety of ions and further our comprehension of their thermodynamic behavior under various circumstances, new computations are currently being carried out.

Keywords: Solvation energies; Hydration of ions; Electrostatic interactions; Ion hydration free energy; Solvation,