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Identification of hydrolysis of triply charged lanthanum in aqueous solutions by paper spray ionization and DFT.

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The chemical speciation of the rare earth elements (REE) in an aqueous medium is involved in all separation processes in which water is used. Although the hydrolysis constant is well determined, the structure of the chemical species in solution is still under debate. The electronic configuration of the M^{3+} REE is [Xe] 4fn, with $0 \leq n \leq 14$. The inner characteristic of the 4f orbitals makes the M^{3+} ions hard, and the electrostatic interaction must govern the hydrolysis process. It is desired to determine the predominant species in the solution to investigate the mechanisms at a molecular level of the separation processes. The present study aims to elucidate the La(III) species present in an aqueous acidic solution. We combine paper spray ionization mass spectrometry (PSI-MS) and Density Functional Theory (DFT) calculations. Hence, PSI-MS transfers ions from the condensed to the gas phase, whereas DFT calculations provide detailed information regarding their stability and structure. Mass spectra were acquired in positive with an Ion Trap analyzer. The aliquots were added to the chromatography papers in a triangular shape (10.0 mm wide × 14.0 mm high) and placed at a 5 mm. distance from the entrance of the mass spectrometer. The ionic spray voltage was 3 kV, the capillary voltage of 26 V, and the capillary temperature of 275°C. The spectra were recorded in the range of 70–1.000 Da., and the isotopic distribution patterns were calculated using the ISOPRO 3.1 software. The geometries were optimized using the PBE and M06 functional, employing the def2-TZVP basis sets. For lanthanum, the inner core electrons have been replaced by effective potentials (def2-ECP). The influence of the solvent environment, was considered, using (SMD)[1]. All calculations were performed using ORCA 5.0.4[2]. The $[La(H_2O)_{17}]^{3+}$ *m/z* 149, clusters decompose exclusively through sequential solvent evaporation. As desolvation progresses and charge density increases, the clusters reach the charge reduction competes with solvent loss. Both simple evaporation and the fragmentation of the $[La(H_2O)_{17}]^{3+}$ clusters into $[La(OH)(H_2O)_{22}]^{2+}$ *m/z* 276, $[La(OH)_2(H_2O)_{11}]^{+}$ *m/z* 371 and $[H(H_2O)_7]^{+}$ *m/z* 127 clusters are readily apparent in the mass spectrum. Selection of $[La(H_2O)_{17}]^{3+}$ ions in the quadrupole stripped off water molecules through multiple collisions to the point at which proton transfer occurred, and evaporation of a solvated proton as the Eigen cation most abundant, $[H(H_2O)_7]^{+}$ *m/z* 127. The division of each 3+ cluster into 2+ and 1+ clusters maintains more than their minimum solvation shells (8–9 waters). DFT calculations confirmed the thermodynamic stability of the formed species.

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