ABSTRACT

The investigation of the complexation of three distinct chelating oxygen-donor ligands, namely acetohydroxyamide (AHA), alizarin-oxalate (AR-Ox), bis-phosphine oxide (BPO) with lanthanides (Ln) provides valuable insights into their interactions. The study delves into the complexation of lanthanum with AHA using density functional theory (DFT) calculations. The research encompasses various analyses, optimized structure determination, thermochemical calculations, potential energy surface (PES) analysis, electron density profile determination, localized orbital locator (LOL), molecular orbitals (MOs), density of states (DOS) and vibrational spectral (Infra-Red (IR) spectra) analysis. The results show that the increase in the number of AHA ligands contribute to enhanced stability in lanthanum-AHA complexes. Structural and vibrational analysis indicates the presence of non-bonded interactions resembling hydrogen-like bonds between AHA and lanthanum. Orbital analysis provides crucial insights into the bond formation between lanthanum and oxygen atoms of the AHA ligand. The scope of the AHA complexation study has been extended to include lanthanide ions (La(III), Nd(III), Eu(III), Er(III), Lu(III)) in the presence of a mixture of nitrate and perchlorate ions as well as pure nitrate ions. Experimental characterization approaches such as spectroscopy (Ultraviolet-visible (UV-Vis), Nuclear magnetic resonance (NMR), and Timeresolved fluorescence (TRFS) spectroscopy) have been employed to validate the DFT calculations. Key factors have been assessed, viz. complex stability, ligand: lanthanide ratio, and optimal extraction conditions. The complexation of the alizarin-oxalate (AR-Ox) ligand with lanthanides has been investigated. DFT calculations have been conducted to explore the extraction capabilities of AR-Ox ligands under varying pH conditions, emphasizing the importance of designing new ligands for selective lanthanide separation. Furthermore, the interaction of BPO ligands and lanthanide ions has been studied using DFT calculations. Pyridine-bridged BPO complexes exhibit stronger and more stable interactions than methylene-bridged BPO complexes. The research highlights the significance of subtle differences in ligand design for selective lanthanide separation. Experimental and theoretical analyses have been combined to deepen the understanding of lanthanide complexation, providing a foundation for future advancements in this field.

Keywords: Density Functional Theory (DFT); Lanthanides (Ln); UV-visible (UV-Vis); Nuclear magnetic Resonance (NMR); Time-resolved fluorescence spectroscopy (TRFS); Infra-Red (IR) spectroscopy