DFT study of the interaction between lanthanum and the DEHPA and EHEHPA extractants

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Introduction: The rare earth elements (REE’s) are highly important due to its wide application in several areas, such as chemical engineering, metallurgy, catalysis and others.\textsuperscript{[1]} Due to the great demand and rare occurrence in concentrated and economically exploitable mineral deposits, the separation and purification of these elements have gained considerable relevance in the last decades.\textsuperscript{[2]} A very usual method of separation of REE’s is the solvent extraction or ion exchange.\textsuperscript{[1]} Organophosphorus cation exchangers (or acidic) extractants, such as DEHPA (di(2-ethylhexyl)phosphoric acid, Fig. 1a) and EHEHPA (2-ethylhexyl 2-ethylhexylphosphonic acid, Fig. 1b) are usually employed in organic phase to separate REE’s from aqueous phase (\[ \text{RE}_{\text{aq}} + 3\text{HX}_{\text{org}} \rightleftharpoons \text{RE(X)\textsubscript{3(org)}} + 3\text{H}^+\text{aq}\].)\textsuperscript{[2]} Experimental results point to superior extraction efficiency for DEHPA compared with EHEHPA.\textsuperscript{[1,3]} Since these ligands are conjugate basis of the acid extractants, the literature discuss the behavior of extraction by means of acid-base theories.\textsuperscript{[1]} By hardness and softness Pearson’s theory,\textsuperscript{[4]} DEHPA is a harder species with interacts better with the also hard trivalent RE cations. However, by Brönsted-Lowry’s theory,\textsuperscript{[5,6]} DEHPA is a acid stronger than EHEHPA (pKa 3.2 and 4.4 at 298K, respectively),\textsuperscript{[1]} consequently presenting a weaker conjugate base, which disfavors the interaction with RE\textsuperscript{3+}. Therefore, there is no consensus about the factors responsible to RE–extractant interaction. The understanding of these factors can contribute to the development of more efficient and selective extractants, since REE’s occur together in nature and due to their similar physical and chemical properties, the separation into the individual elements is very difficult.\textsuperscript{[1,2]} In this theoretical work, we propose a more detailed analysis for the structures of complexes of lanthanum (La) with DEHPA and EHEHPA extractants, by means of DFT calculations.

Key-words: lanthanum, rare earth, extractant, DFT

Methodology: The La(DEHPA)\textsubscript{3} and La(EHEHPA)\textsubscript{3} complexes (Fig. 1c,d) and the isolated ligands (Fig. 1f,g) were constructed and fully optimized using DFT/B3LYP methodology in Gaussian 03 program. The electrons of carbon, oxygen and hydrogen were described by D95V basis set and of phosphorus by 6-31G(d). The outer 18 electrons of La\textsuperscript{3+} were described by D95V basis set, whereas the core electrons by LANL2DZ pseudopotential. The complexation energy was calculated by Eq. 1 (\(E_{\text{complexation}} = E_{\text{complex}} - [E_{\text{La}^{3+}} + 3E_{\text{ligand}}]\)). Analysis of Mulliken population was realized to
obtain the fractional contribution of O=P=O portion to HOMO using the GaussSum 3.0 program. The Pearson’s hardness of the ligands was estimated according to Eq. 2 ($\eta = |E_\text{LUMO} - E_\text{HOMO}| / 2$). Natural Bond Orbital (NBO) calculations were performed to evaluate the La–O electron transfer processes in the complexes.

**Results and discussion:** The $\eta$ calculated hardness (Pearson’s theory) for DEHPA is slightly superior to EHEHPA (3.55 eV against 3.46 eV, Fig. 1e). Thus, as La$^{3+}$ is a hard cation, the La–DEHPA interaction is favored. Conform to Lewis$^7$ and frontier orbitals$^8$ theories, base is an electron donor and HOMO is responsible by the electron donation. After the optimization of both complexes, is verified that the O=P=O grouping coordinates directly with La$^{3+}$. The calculation of Mulliken population to isolated molecules shows that O=P=O presents higher contribution to HOMO in DEHPA than in EHEHPA (94% against 88%, Fig. 1f,g). The calculated NBO charges for La and O and the La–O distances present values very similar in both structures (Fig. 1h,i), indicating that the ionic contribution does not explain the strongest La–DEHPA interaction. NBO calculation shows that the total energy involved in O→La donation process for DEHPA is 40.6 kcal.mol$^{-1}$ higher than for EHEHPA. All performed analysis point to higher basicity of DEHPA, contributing for the higher La–DEHPA interaction comparing to La–EHEHPA, in agreement to experimental results.$^{[1,3]}$ Nevertheless, the calculated energy of complexation to the DEHPA and EHEHPA complexes, in gas phase, differs only by 1.0 kcal.mol$^{-1}$. Following the investigation, solvation models are being performed to evaluate the La–extractant interaction in aqueous phase.

**Conclusion:** All results point to higher basicity of the DEHPA conjugate base comparing to EHEHPA, in agreement to experimental results. However, the very small difference in the calculated complexion energy for La(DEHPA)$_3$ and La(EHEHPA)$_3$ complexes in gas phase, is an indicative that the hydration process should have an important role in the major ability of complexion for DEHPA compared to EHEHPA.

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**References:**