



A molecular picture of di(2-ethylhexyl)phosphoric acid dimerization through free energy calculations

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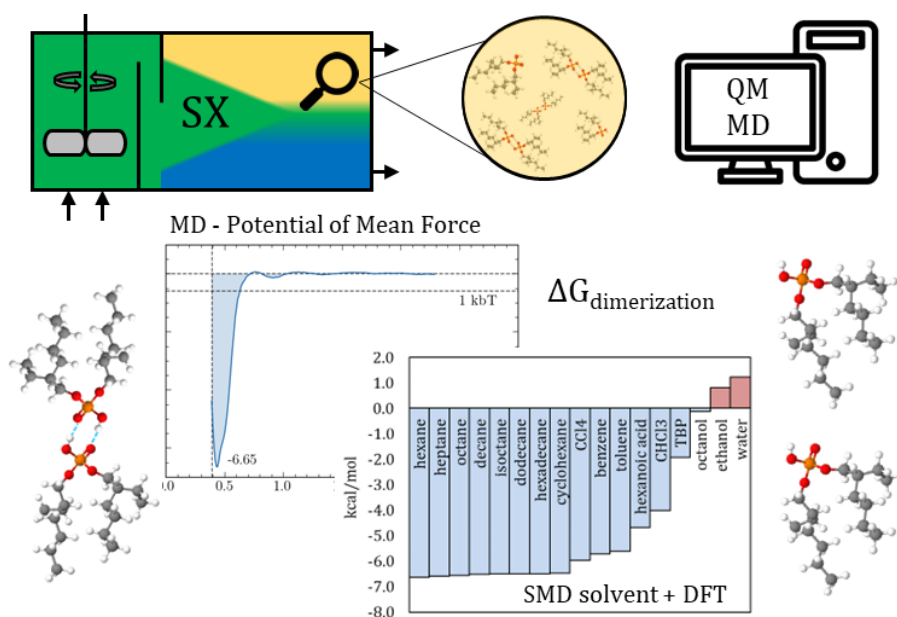
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GRAPHICAL ABSTRACT



ABSTRACT

Solvent extraction, widely applied in chemical and metallurgical sectors, serves as a pivotal technique for separation and purification. In hydrometallurgy, it concentrates, and purifies metals extracted from minerals or secondary sources to yield high-quality electrolytes for obtaining final solid products. Typically, an organic, water-immiscible diluent is blended with extractants, like organophosphorus acids. Among them, di(2-ethylhexyl)phosphoric acid (D2EHPA) is widely used, particularly in the processing of metals such as zinc, nickel, and rare earths. D2EHPA typically forms dimers stabilized by a double hydrogen bond in apolar solvents, leading to a cyclic structure. However, the distribution of aggregates can vary as the solution concentration increases or solvent changes. Computational chemistry methods were



XII CBTERMO

VIII ESCOLA DE TERMODINÂMICA
CURITIBA 2024

XII Congresso Brasileiro de Termodinâmica VIII Escola de Termodinâmica

De 5 a 9 de Maio de 2024

Curitiba - Paraná - Brasil

employed to understand the dimerization of D2EHPA in different solvents. Classical force fields were assessed for modeling D2EHPA and hydrocarbon diluents. Steered Molecular Dynamics Simulations and Umbrella Sampling techniques were used to explore the dimerization free energy profile, considering the explicit effect of the solvent. Electronic structure calculations, incorporating quantum chemically accurate free energies under implicit SMD solvents of various natures, were performed using different methods. The MD results closely aligned with quantum mechanical results, showcasing the approximation capabilities of the tested methods. Implicit solvent calculations indicated a tendency to break the D2EHPA dimer in polar, hydrogen bonding solvents, while values in apolar solvents remained similar. The calculated ΔG values demonstrated good agreement with reference equilibrium data from the literature, validating the approaches. Ongoing efforts include further simulations and model refinement to make these methods suitable for studying complex solvent extraction systems involving metals, their speciation, and the physical properties of such phases.

Keywords: solvent extraction, dimerization, organophosphorus compound, molecular dynamics simulation, quantum chemical calculations.