



Computational Insights into Co^{2+} , Ni^{2+} , and Fe^{3+} Partitioning Mechanisms in PEO/SCN Salt Aqueous Two-Phase Systems

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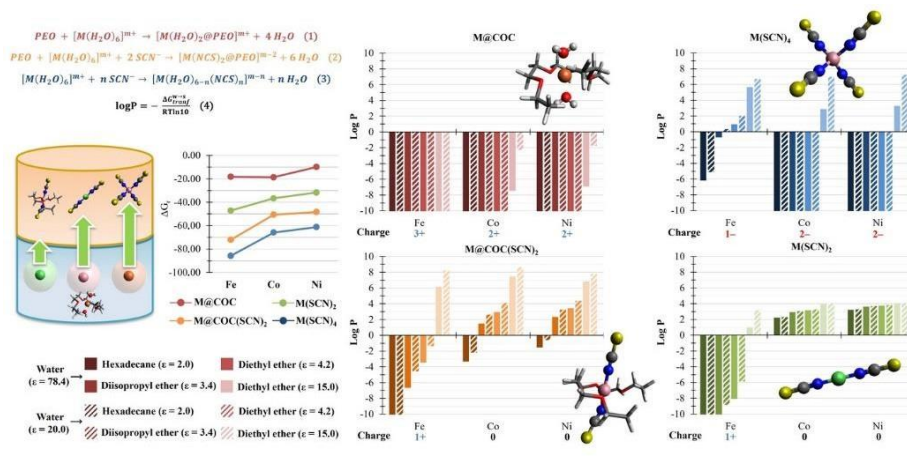
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GRAPHICAL ABSTRACT



ABSTRACT

The growing demand for cobalt and nickel in electronic devices and green energy sources has prompted research into more efficient and environmentally friendly extraction methods. The interference of iron as a major contaminant complicates the separation and recovery of Co and Ni. Aqueous two-phase systems (ATPS) have emerged as a sustainable alternative to solvent extraction, but understanding metal partitioning in these systems is challenging due to the intricate thermodynamics of phase separation. This study focuses on an ATPS formed by poly(ethylene oxide) (PEO) and thiocyanate (SCN^-) salt for Co^{2+} , Ni^{2+} , and Fe^{3+} extraction without auxiliary complexing agents. Density Functional Theory calculations in the presence of implicit solvents were conducted, in the Orca package, to explore two possible mechanisms: coordination bonding between metal and PEO and hydrophobic solvation. Metal complexation reactions involving PEO fragments, water molecules, and SCN^- ligands were evaluated. Free energy calculations (ΔG_r) and partition coefficients ($\log P$) were computed to



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assess metal cation solvation in various solvents, simulating ATPS phases. Results indicate that in water solvent, the favorability order for species formation is $M@COC < M(SCN)_2 < M@COC(SCN)_2 < M(SCN)_4$, with $Ni^{2+} < Co^{2+} < Fe^{3+}$, agreeing with experimental results. Solvation profiles indicate better solvation of charged species in water and a preference for ether-type solvents for anionic complexes, while neutral species exhibit the least favorable solvation in water. In summary, specific interactions between PEO and TM cations alone are unlikely to drive separation, as $M@PEO$ partitioning is much unfavored. However, it can synergize with the formation of $M@PEO(SCN)_2$ complexes. Hydrophobic solvation affects both neutral and anionic complexes, influencing their transfer to the polymer-rich phase. While not responsible for Co/Ni selectivity, it acts as a general driving force in the separation process.

Keywords: Aqueous Two-Phase Systems, Extractive Metallurgy, Separation Mechanism, Density Functional Theory