QUANTUM CHEMICAL MODEL OF DYE EXTRACTION USING DEEP EUTECTIC SOLVENTS

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Deep eutectic solvents (DES) are a highly promising and environmentally friendly alternative to existing extraction methods; however, there is currently a significant deficit of fundamental thermodynamic data and theoretically grounded models capable of predicting extraction efficiency without the need for expensive and time-consuming experiments.

This work aims to perform quantum chemical modeling of the Sudan dyes extraction process using DES based on menthol/thymol and and carboxylic acids (C6-C10) to analyze the efficiency and accuracy of the chosen models in comparison with existing experimental data [1].

Molecular geometries were optimized using the ORCA 6.0.1 package at the B3LYP level of theory. Two distinct modeling variants were implemented. The first variant involved the evaluation of three competing complexation processes in the solution: the self-association of DES components (terpene-acid interaction) and the formation of complexes between the dye and individual DES components (dye-terpene and dye-acid), with their respective Gibbs free energies calculated. The second variant utilized the openCOSMO-RS package to calculate solvation free energies.

Both complex formation energies and solvation energies demonstrate high agreement with experimental extraction trends. For Sudan I, the calculated ΔG_{solv}values increased from -68,86 kcal/mol (C_6) to -66,61 kcal/mol (C_{10}), following the experimental drop in extraction efficiency. Analysis of the calculated Gibbs free energies of complex formation enabled a detailed evaluation of extraction feasibility and helped identify the specific DES component responsible for dye recovery.

The extraction process was successfully modeled using two complementary approaches, providing insights into both the molecular complexation mechanism and bulk phase behavior. The results confirm that evaluating Gibbs free energies of complex formation is a reliable method for determining the role of each DES component in the extraction process. This modeling framework allows for the efficient prediction of solvent performance and can be used to tailor DES compositions for specific analytical requirements in the future.

1. A. Shishov et al., "Deep eutectic solvents with low viscosity for automation of liquid-phase microextraction based on lab-in-syringe system: Separation of Sudan dyes," Talanta. – 2023. – Vol. 255., Apr. 2022, https://doi.org/10.1016/j.talanta.2022.124243