# INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
## SHORT ABSTRACT OF THESIS

| | | |
|---|---|---|
| Name of the Student | : | **Nikhil Kumar** |
| Roll Number | : | **176107105** |
| Programme of Study | : | **Ph.D.** |

Thesis Title: **Solvation and Extraction Mechanism of Aromatic Solutes and Asphaltene utilizing Deep Eutectic Solvents: Experimental and Atomistic Simulation Studies**

| | | |
|---|---|---|
| Name of Thesis Supervisor(s) | : | **Prof. Tamal Banerjee** |
| Thesis Submitted to the Department/ Center | : | **Chemical Engineering** |
| Date of completion of Thesis Viva-Voce Exam | : | **10th April 2023** |
| Key words for description of Thesis Work | : | **Aromatic, Extraction, Molecular dynamics Simulation, DFT, Non-covalent interaction, Asphaltene** |

---

### Short Abstract

Deep eutectic solvents (DES) have emerged over the last two decades as a novel class of ionic liquids (ILs). In their broadest sense, DESs are usually formed by mixing a quaternary ammonium salt (typically choline chloride and derivatives) with hydrogen bond donor molecules such as amines, amides, alcohols, carboxylic acids, sugars, or polyols. The mixing of these two components upon gentle heating and in a specific molar ratio leads to a depression of the melting point, resulting in most of the cases in a liquid at room temperature, where no waste is produced, and no further purification steps are needed. Furthermore, DES's components are often biodegradable and non-toxic.

The first part of this Ph.D. thesis focusses on the study of the liquid structure of DESs so as to understand the application of these solvents in solvation and extraction. Here, the atomistic Molecular Dynamics (MD) simulations provide the structural properties of these solvents by combining them with aromatic and aliphatic solutes. The aromatic components such as benzene and thiophene were found to be hydrogen-bonded to the DES entity. Here, the precursor of the

DES, namely monoethanolamine (MEA), had a higher hydrogen bond affinity than its counterpart HBA (choline chloride). According to the present study results, the aliphatic portion in DES components is less encouraged, as their solubility for aliphatic compounds rises with an increase in the chain length of alkyl groups. We chose methyltriphenylphosphonium bromide (MTPB)-based solvents for the separation of the aromatic portion as they had minimal solubility for the aliphatic fraction. The selected DESs are considered the most promising solvents due to their higher extraction efficiency and distribution coefficient for the hydrocarbon stream.

After understanding DES liquid structure and specific solute-solvent interaction, the DES, comprising of hydrogen bond acceptor (HBA), namely methyltriphenylphosphonium bromide (MTPB), along with ethylene glycol (EG) as a hydrogen bond donor (HBD), was formulated with a molar ratio of 1:4. The DES was then used to extract benzene and benzothiophene from representative diesel fuel components, namely a mixture of *n*-decane, *n*-dodecane, and *n*-hexadecane. The extraction efficiency achieved for benzene and benzothiophene using the (MTPB+EG) was in the range of 80–83% for a single stage and more than 98% for three stages or more. The cluster chemistry study studied through DFT calculations revealed that the aromatic compound interacts favourably with the MTP cation and EG of the DES through multiple non-covalent interactions (e.g., $C{-}H\cdots\pi$, $Br^{-}\cdots O{-}H$, $Br^{-}\cdots C{-}H$ and $O{-}H\cdots\pi$) but does not interact directly with the bromide ($Br^{-}$) ion. In addition, the atomistic molecular dynamics (MD) simulation technique was then employed to investigate the equilibrium interphase behaviour of the DES + benzene + *n*-hexane ternary system with respect to its DES-rich and hydrocarbon-rich phases. In summary, HBA and HBD both play a predominant role in benzene extraction from hydrocarbon streams. Consequently, this study offers new findings for the computational MD simulation of benzene extraction from hexane, which becomes helpful in the absence of experimental data.

The second part of this Ph.D. thesis focuses on the dispersion of asphaltene in DESs. It aims to investigate the inhibition of petroleum asphaltene aggregation using a novel combination of deep eutectic solvents. Further, the COSMO-RS (Conductor-like Screening Model for Real Solvents) model was performed to screen possible combinations of DESs for asphaltene. Among the studied DES, the DES with thymol and diphenyl ether gave a higher solubility of asphaltene. An excellent agreement was obtained between the experimental and COSMO-RS predicted

excess enthalpies and activity coefficients. It gives the best performance for asphaltene solubility, reaching a value of 42.10 ± 0.58 mg/ml at 298.15 K and atmospheric pressure compared to the other conventional solvents. The Density Functional Theory (DFT), Baders theory of QTAIM (Quantum Theory of Atom in Molecule), and NCI (Non-Covalent Interaction) analysis suggest the formation of the DES-asphaltene complex via a combined effect of hydrogen bonding linkage with van der Waals and dispersion interaction, as supported by the electron density at BCP ($\rho_{BCP}$) and the positive sign of the Laplacian of electron density ($\nabla\rho_{BCP}^2$). The present study has paved the way forward to rationally design and understand the impact of structural variation of DESs for their interaction with asphaltene.