Extended Abstract

(For Ph.D. Open Seminar)

Synthesis and Thermodynamic Integrated Machine Learning Modelling of Deep Eutectic Solvents for CO_2 Capture and Azeotrope Separation

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SCOPE OF THESIS:

The scope of this thesis is to establish an integrated framework for the design, thermodynamic modelling and predictive statistical analysis of deep eutectic solvents (DESs) for carbon dioxide capture and azeotrope separation. The solvent systems from conventional amines to ionic liquids to deep eutectic solvents are explored and key limitations are identified. Data-driven frameworks are developed to estimate key physical and thermodynamic properties of DESs, and multivariate statistical analysis reveals underlying structure-property relationships. Eight novel DES formulations are synthesized and their CO_2 uptake is experimentally evaluated, while quantitative structure-property correlations (QSPR) models correlate molecular descriptors with CO_2 capture capability. Extractive-distillation experiments demonstrate the efficacy of DESs in separating the isopropanol-water azeotrope. The integrated experimental and computational approach establishes predictive capabilities for green-solvent design.

Chapter 1 Introduction

This chapter deals with the overview of CO_2 capture technologies, and operational limitations of first-generation amines and physical solvents. Second-generation ionic liquids were assessed for their tunable chemistry, alongside challenges of viscosity and high cost. Third-generation DESs were introduced, with emphasis on their facile preparation, negligible vapor pressure, and biodegradability. Key studies on CO_2 solubility in various DES systems-including ammonium and phosphonium-based mixtures, halogen-free DESs, and DES membranes-were summarized. Emerging predictive approaches, such as machine-learning models for CO_2 solubility, were discussed.

Chapter 2 Physical and Thermodynamic Property Estimation of DESs

A computational analysis of 102 prospective DESs from the literature is presented in Chapter 2. Each DES's thermodynamic and physical parameters were calculated using group-contribution methods and empirical correlations. The critical temperature, pressure, volume, and acentric factor were predicted by a modified Lydersen-Joback-Reid technique, while density and refractive index were determined by the group contributions method developed by Haghbakhsh. The molar and

free volumes of the DESs were computed using the Lorentz-Lorenz relation. The effect of the HBA-HBD combination on the physical properties of DESs was analyzed.

Chapter 3 Thermodynamic and Machine Learning Modelling of CO_2 Dissolution in DESs

In this chapter, Henry's law constants were determined from the pressure vs CO_2 mol fraction plot. Thermodynamic properties such as enthalpy, entropy, and Gibbs free energy were computed through Clausius-Clapeyron relations. The effect of calculated thermodynamic properties were assessed for CO_2 dissolution in DESs. The analysis yielded clear trends: DESs based on acidic hydrogen bond donors (such as organic acids) generally exhibited lower densities and lower Henry's constants (indicating higher CO_2 solubility) compared to those with alcoholic or amine-based donors. Furthermore, statistical analysis was performed to identify significant relationships between thermodynamic properties of DESs and CO_2 dissolution. A Random Forest (RF) and Gradient Boosting (GB) regression model were developed to predict CO_2 solubility from the calculated properties. This data-driven analysis provided additional validation that structural and volumetric characteristics of DESs are pivotal for CO_2 capture and it offers a predictive tool for screening efficient solvent.

Chapter 4 Synthesis and QSPR Modelling of Novel DESs for CO_2 Solubility

This chapter details the synthesis and evaluation of eight novel deep eutectic solvents for CO_2 solubility and establishes quantitative structure-property correlations (QSPR). CO_2 solubility studies were conducted utilising a high-pressure sorption analyser at 303K, with pressures up to 20 bar. Chapter 4 also explores the development of a QSPR model for the analysis of the impact of different properties on CO_2 solubility. The free molar volume exhibits significant negative correlations with H_x, indicating that larger microcavities facilitate the physisorption of CO_2 in DES. Critical pressure correlates positively, suggesting that stronger cohesive forces hinder uptake.

Chapter 5 Application of DESs for the separation IPA-Water Azeotrope

This chapter explores the application of deep eutectic solvents for the separation of the azeotropic mixture of isopropyl alcohol (IPA) and water using Glyceline and Ethaline. Conventional dimethyl sulfoxide (DMSO) solvent was used to compare the results for IPA dehydration. Process modelling and simulation were carried out in the Aspen Plus simulator (v.12.1). The process parameters such

as entrainer flow rate, binary feed stage, entrainer feed stage, column stages, reflux ratio, reboiler and condenser duties were evaluated using sensitivity analysis and design spec tools of the simulator. The results show that more than 99.9 mol % IPA purity can be achieved using DESs. The alternate process for DESs systems was proposed and compared with conventional process. Although high energy consumption was associated with DESs, their low raw material and equipment costs render them favourable for IPA–water separation compared to the DMSO solvent.

Chapter 6 Conclusions and Future Scope

This chapter summarises the key findings of this work and outlines future research directions. The conclusions drawn from this multi-faceted study confirm that deep eutectic solvents are promising, tunable media for CO_2 capture, capable of combining high absorption capacity with favourable regeneration characteristics. DESs can be leveraged to improve the efficiency of difficult separations like azeotrope separation. Reactive DESs formulations that combine physical and chemical absorption can be explored to further enhance CO_2 capacity. Machine-learning models can be utilized to predict new DES performance prior to synthesis, thereby accelerating the discovery of optimal solvents. Operational issues for scaling up experimental studies to pilot-scale CO_2 capture units may be evaluated for DESs.

List of Publications:

Gomey, A.K.; Tripathi, M.M.; Haider, M.B.; Kumar, R. "Comparative analysis of isopropyl alcohol dehydration using ionic liquids and deep eutectic solvent." *Journal of Ionic Liquids* 3 (2023) 100069.

Gomey, A.K.; Haider, M.B.; Kumar, R. "Designing of energy-efficient deep eutectic solvents for CO_2 capture: Insights from physical and thermodynamic property evaluation." *Journal of Molecular Liquids*, in press.

Gomey, A.K.; Singh, S.K.; Kumar, R. "Experiments and ML-QSPR modelling of physical CO_2 absorption in highly efficient deep eutectic solvents and performance index development." Submitted in *Journal of Chemical Information and Modelling*.

Gomey, A.K.; Medara, S.; Gangal, P.; Singh, S.K.; Haider, M.B.; Kumar, R. "Generational evaluation of CO_2 capture: From amines to ionic liquids and deep eutectic solvents." Submitted in *Journal of Cleaner Production*.

List of Conferences and Achievements

1. International Conference on "Technological Interventions for Promoting Sustainability" (CHEMCONFLUX22) - Motilal Nehru National Institute of Technology, Allahabad & Universiti Sains Malaysia, Pinang; April 14-16, 2022, **(2nd Prize Winner).**

2. International Conference on "Sustainability in Chemical Processes through Digitalization, Artificial Intelligence and Green Chemistry" (CHEMCON22) - Indian Institute of Chemical Engineers; December 27-30, 2022.

3. International Conference on "Trends in Energy and Environmental Research for Sustainable Development" (TEERSD-2023) - Guru Ghasidas Vishwavidyalaya, Bilaspur; November 2-3, 2023.

4. International Conference on "Energy Transition: Challenges & Opportunities" (CHEMCON23) - Indian Institute of Chemical Engineers; December 27-30, 2023.

5. International Conference on "Catalyzing Sustainable Future with Affordable Energy and Chemicals" (SEFCO-2025) - CSIR-IIP Dehradun; April 23-25, 2025.