Molecular Modeling of Amine-Based Deep Eutectic Solvents for CO2 Capture Employing COSMO-RS and Soft-SAFT Equation of State

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It has been recognized that carbon capture, utilization, and storage (CCUS) is one of the critical technologies for short- to medium-term economically feasible decarbonization. The widespread implementation of mature technology that utilizes aqueous amine solvents for post-combustion CO_2 capture (PCC) in large-scale CCUS operations faces obstacles due to the significant energy requirements for solvent regeneration, as well as, to a lesser extent, issues related to salt formation and equipment corrosion. Deep Eutectic Solvents (DESs) are an emerging family of green solvents exhibiting environmentally friendly properties such as non-volatility and biodegradability. Their high boiling point and low volatility promise reduced solvent losses and regeneration energy requirements, which is of interest for finding alternative solvents for CO_2 capture to replace conventional solvents. The formulation of an amine-based DES as one of its primary components can potentially lend these solvents the high uptake capacity of amine molecules, while maintaining the benign environmental properties of DESs. However, much work remains to be done for a full assessment of these novel solvents before they can be used in industrial applications, including the need for experimental data or accurate models for their full characterization.

In this study, a molecular based equation of state, soft-SAFT [1] is utilized to accurately model the thermophysical properties (*i.e.,* density, vapor pressure and viscosity), CO_2 solubility and heat of absorption for amine-based DESs formulated from a choline chloride (ChCl) hydrogen bond acceptor with several amines as hydrogen bond donors (HBDs) including (monoethanolamine) MEA, (diethanolamine) DEA and (Methyl diethanolamine) MDEA. These solvents are modeled using the pseudo-component approach with the HBA and HBD of the DES modeled as a single associating chainlike molecule [2]. Towards formulating the molecular models descriptive of the studied system, additional microscopic insight was obtained using the quantum chemistry-based technique COSMO-RS, utilizing the σ-profile and σ-potential to identify the different interactions in the resulting DESs. A three associating sites model was adopted for the amine-based DESs, with one negative (*i.e.,* Cl^-) and two positive sites (*i.e.,* -NH_2/-NH/-N and -OH), only allowing positive-negative interactions, with association parameters transferred from other molecules from our previous contributions [2,3]. Subsequently, experimental single-phase density and vapor pressure were used in optimizing the non-associating parameters (*i.e.,* chain length (m), segment diameter (σ) and dispersive energy (ε)).

The results of the proposed models were in excellent agreement with the experimental data at a specific DES molar ratio. In order to enhance the transferability of the parameters, it was determined that linearly correlating the chain length m as a function of DES molar ratio [4], while fixing σ and ε, was an effective approach to model the thermophysical properties of studied systems at other molar ratios, without degeneracy of modeling accuracy. The molecular models were then used to determine the CO_2 solubility and enthalpy of absorption for these solvents. The CO_2 chemisorption process was mimicked through the addition of specific reactive sites on the CO_2 molecule capable of forming highly localized hydrogen bonding with the nitrogen on the amine molecule in the DES. The specific associating parameters were fitted to available CO_2 solubility isotherms in these solvents, showing excellent agreement with experimental data.

The results of this work demonstrate the advantages of coupling of COSMO-RS and soft-SAFT for the concise developments of molecular models for alternative solvents. Additionally, these models are readily available for engineering simulators to determine the large-scale feasibility of these solvents as an alternative for CO_2 capture.

References

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