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Optimum solvent concentration to lower energy demands for CO2 capture in refinery cases

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Abstract

The refinery sector is categorized as third biggest stationary CO_2 producers after the power sector and the cement industry. It contributes about 4% of the total anthropogenic CO_2 emissions and shares about 1 billion metric tons per year. Since the 1990s, a significant reduction in energy usage has been achieved in this sector, but it was not followed by a low CO_2 production. Direct CO_2 emission of up to 200 kg CO_2/ton crude oil remains to be reduced[1]. Carbon capture, utilization, and storage (CCUS) are one viable option technology to reduce these emissions. The absorption process with a chemical reactive absorbent is a mature and viable capture technology, but it still suffers from its high energy usage. Therefore, the solvent selection remains a vital tool to lessen the energy demand. An open-access novel low-energy solvent HS-3 has been proposed and verified in the lab scale[2] for post-combustion CO_2 capture. The HS-3 solvent consists of a tertiary amine that has a strong bicarbonate former[3] and a primary amine that has high reactivity. Blends of these two solvents were reported to be a promising solvent candidate, however, limited equilibrium data and thermodynamic property[4-5] were persisted and need to fully develop.

Energy requirement and environmental aspect are fundamental properties of the absorbent system and the design, operation, and performance of the absorption process[6]. The energy required is expressed in Eq. 1 and classified as three major sources, i.e., heat for reversion of the heat of reaction (Q_{Des}), sensible heats (Q_{Sens}), i.e., to obtain lean amine loading condition and stripping heat (Q_{Strip}), i.e. steam needed to maintain the pressure in the stripper.

$$Q_{Req.}\left(\frac{kJ}{mol\ CO2}\right) = Q_{Sens} + Q_{Des} + Q_{Strip} \quad (1)$$

Where the individual contribution is expressed as:

$$Q_{Sens} = \frac{\rho \cdot Cp \cdot \Delta T}{(\alpha_{rich} - \alpha_{lean}) \cdot C_{Am}}$$

$$Q_{Des} = -\Delta H_{abs\ CO_2}$$

$$Q_{Strip} = \frac{P^{Sat}_{H_2O}(T_{Top,Des.}) \cdot x_{H_2O,freebasis}}{P^{*}_{CO_2}(T_{Top,Des.})} \cdot \Delta H^{vap}_{H_2O}$$

Any developed empirical correlations[7-8] or rigorous thermodynamic models[9-10] for the equilibrium properties as a function pressure, temperature, amine, and CO_2 concentrations, could be used to estimate the reboiler duties. However, only rigorous thermodynamic models could be used to optimize solvent concentrations. .

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In this work, we will present a thermodynamic model for the HSE-3 solvent using available reported data and experiment results for each amine component and the blend. The final quaternary model will be used in a simulation to find an optimum concentration of each compound for the lowest energy demand. In the presentation, the effect of the equilibrium curves on driving forces will also be shortly discussed as low driving forces for CO2 can lead to a unreasonable high absorber.

Preliminary results for the developed thermodynamic model are presented in Figure 1 for each solvent component. The slope between the y-axis to x-axis reflects the heat of absorption. It is expected that the heat of absorption of the tertiary amine is lower than that of the primary amine (the slope is steeper for the primary amine). At the same loading and temperature, the partial pressure of CO_2 of the tertiary system is much higher in the primary amine system, or at the same CO_2 partial pressure, tertiary amine holds more CO_2 than that of primary at the same temperature as expected. Figure 2 shows two different blends of the two amines. It is clear that by changing the compoisition of the blend the VLE can be heavily influenced, indicating the rigorous models can provide a good starting point in optimizing the solvent concentration. And using rigorous thermodynamic models to optimize the composition of a amine blend could be used to optimize cyclic capacity, reasonable driving force in the absorber and the heat of absorption.

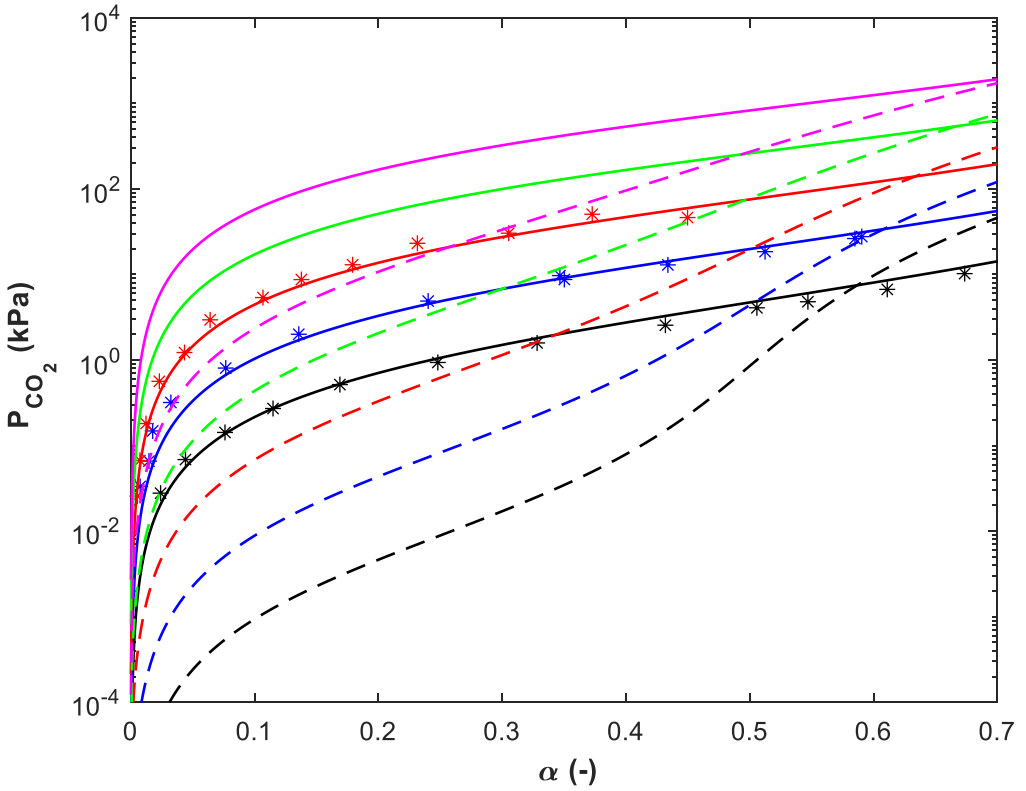

Figure 1 Representation of a thermodynamic model at different temperatures (40, 60, 80, 100 and 120°C) for 40 mass % of tertiary amine (points[4]) and 15 mass % of promoter amine (Dashed lines)

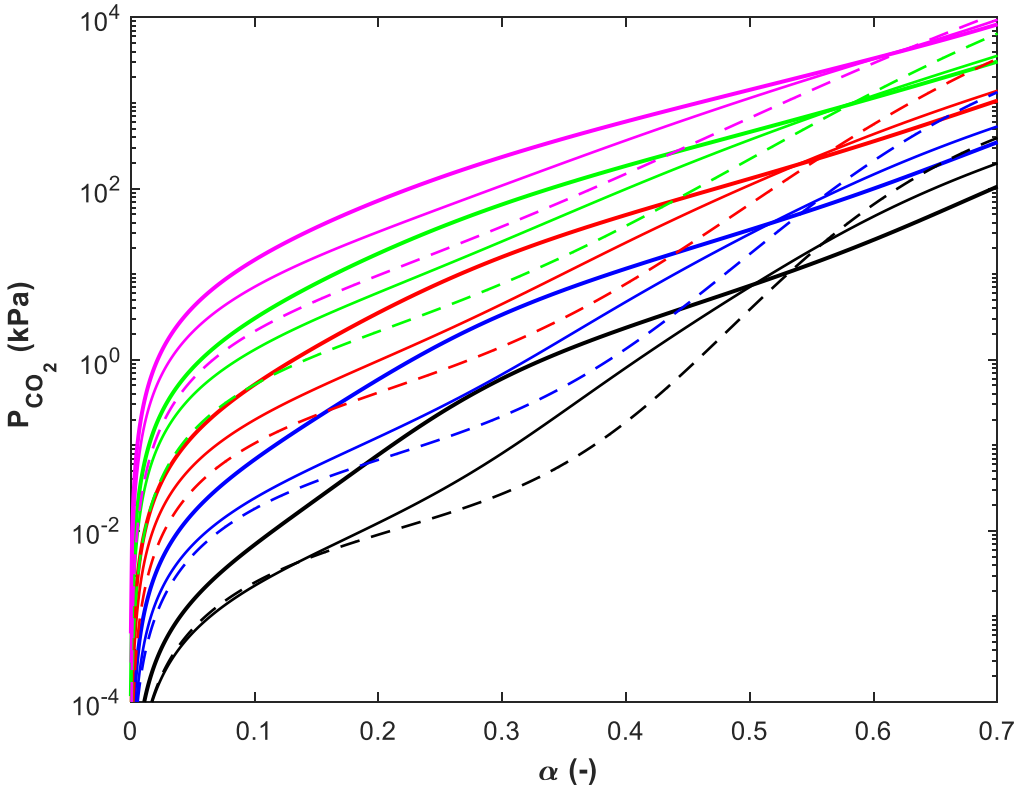

Figure 2 Representation of a thermodynamic model at different temperatures (40, 60, 80, 100 and 120°C) for the blend of two amines (Thicker solid lines, model for blend of 40 mass % of tertiary and 15 mass % of primary amines; Solid lines, model for blend of 25 mass % tertiary and 25 mass % primary amines) and 30 mass % of MEA (dashed lines)

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Keywords: HS-3; Refinery, CCUS; Thermodynamic;Simulation.

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