Solubility of N-Methyldiethanolamine (MDEA) in Carbon Dioxide (CO_2): Measurements and Modelling

1.0 Introduction

Amine-based absorption remains one of the most established and effective technologies for the removal of acid gases from industrial gas streams [1], with widespread application in natural gas processing, refining, and emerging carbon capture, utilisation, and storage (CCUS) systems. Among commercially deployed solvents, *N*-methyldiethanolamine (MDEA) is particularly attractive due to its high selectivity for acid gases, chemical stability, and relatively low regeneration energy demand [2–4]. As CCUS technologies expand into more extreme operating environments, including low-temperature and high-pressure conditions, a detailed understanding of the thermophysical behaviour of amine–CO_2 systems becomes increasingly important.

While the solubility of CO_2 in aqueous amine solutions has been extensively studied under conventional operating conditions [3,5–7], experimental data for MDEA in CO_2, where CO_2 is the continuous phase, remain limited. This lack of data introduces uncertainty in process modelling, particularly for applications involving cryogenic conditions, high-pressure transport, or integrated capture and storage schemes.

In parallel, accurate thermodynamic models are required to predict phase behaviour and solubility over wide ranges of temperature and pressure. Equations of state that incorporate both physical and associative interactions are especially relevant for amine–CO_2 systems, where hydrogen bonding and strong temperature dependence play a critical role [6,8]. Experimental validation across extended operating envelopes is therefore essential to assess the robustness and predictive capability of such models.

This study addresses these gaps by presenting new experimental solubility data for MDEA in CO_2 over a broad temperature and pressure range, including low-temperature, subcooled, and supercritical conditions. The results provide valuable insight into the pressure and temperature dependence of the CO_2–MDEA system and enable a critical evaluation of thermodynamic model performance. The findings contribute to improved confidence in process design and optimisation for amine-based gas treatment and CO_2 management strategies relevant to CCUS applications

2.0 Method and/or Theory

The solubility of N-methyldiethanolamine (MDEA) in carbon dioxide (CO_2) was determined using a high-pressure solubility apparatus, as illustrated in Figure 1.The experimental system consists of a CO_2 supply unit, a circulation and mixing section, a temperature-controlled rocking cell, and a pressure measurement and regulation system. High-purity CO_2 (≥99.99%) from a gas cylinder was introduced into the system through a series of valves and a pressure gauge for monitoring. A high-pressure pump was employed to compress the CO_2 to the desired operating pressure. The MDEA sample was loaded into the high-pressure equilibrium cell before CO_2 introduction. The system was designed to withstand pressures up to 700 bar and included tubing and fittings to prevent leakage and contamination.

A rocking mechanism, powered by an air source, was employed to periodically tilt the cell during the equilibration process, thereby enhancing mass transfer and accelerating the attainment of equilibrium. The cell temperature was precisely controlled using a thermal circulator bath, which circulated fluid through the jacket surrounding the equilibrium cell. The temperature was measured with a calibrated Platinum Resistance Thermometer (PRT), while system pressure was monitored using a high-accuracy pressure transducer (denoted as *P* in the schematic).

During each run, the system was first evacuated to remove air, and then the MDEA sample was charged into the equilibrium cell. CO_2 was introduced gradually until the target pressure was achieved. The mixture was then allowed to equilibrate under constant temperature and rocking conditions for a sufficient period (typically 24 hours) to ensure phase equilibrium. After equilibration, the solubility of the MDEA in the CO_2 phase was determined by sampling and subsequent analytical quantification. The number of moles of CO_2 was determined using its density at each sampling condition as obtained from the National Institute of Standards and Technology (NIST) thermophysical data.

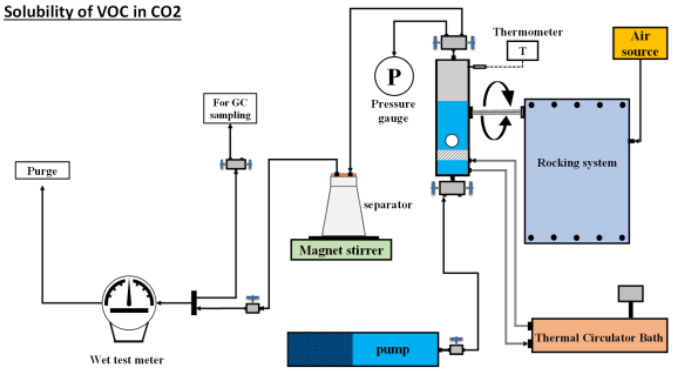

Figure 1. Schematic illustration of the solubility measurements set up

3.0 Modelling

The simplified cubic plus association (sCPA) equation of state (EoS) has been employed for modelling in this study. Details of the original approach to model the CO_2 – MDEA phase behaviour are explicitly explained in previous publications [6,8–10]. The CPA combines the widely known Soave-Redlich-Kwong (SRK) cubic equation of state with Wertheim's perturbation theory to account for the association terms of the association fluids. Its predictions are based on the uniformity of the participating components' fugacities [11] in all phases.

In terms of pressure P, the CPA-EoS can be described as:

$$P = P_{SRK} + P_{assoc.} \quad (1)$$

Where P_{SRK} is the pressure contribution from the SRK EoS, and $P_{assoc.}$ is the pressure contribution from the association term derived from Wertheim's theory. The SRK EoS is a widely used cubic equation of state, particularly effective for hydrocarbon systems. The SRK – EoS could be written in the form:

$$P_{SRK} = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (2)$$

To improve the accuracy of phase equilibrium predictions, the Huron-Vidal mixing rules, which combine an equation of state with an excess Gibbs free energy model has been employed in the modelling [12]. Also, to represent the non-ideal behaviour of mixtures, a modified Non-Random Two-Liquid (NRTL) local composition model has been added [12]. Thus, the co-volume (b) and the energy parameter (a) from (2)
are expressed as follows:

$$b = \sum_i x_i b_i \quad (3)$$

$$a = b\left[\sum_{i=1}^{n}\left(x_i \frac{a_i}{b_i}\right) - \frac{G_\infty^E}{\ln(2)}\right] \quad (4)$$

where G_∞^E is the excess Gibbs free energy taken from the modified NRTL model and is given as:

$$G_\infty^E = \sum_{i=1}^{n} Z_i \frac{\sum_{j=1}^{n} \tau_{ji} b_j z_j \exp(-\alpha_{ji}\tau_{ji})}{\sum_{k=1}^{n} b_k z_k \exp(-\alpha_{ki}\tau_{ki})} \quad (5)$$

and

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT} \quad (6)$$

The detailed formulation and application of the CPA-EoS are given by Kontogeorgis *et al.* [9,13]. Expression of the CPA – EoS, including the contribution association term, presented by [14], is written as:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+c(v-b)} - \frac{1}{2}\frac{RT}{v}\left(1 + \rho\frac{\partial \ln(g)}{\partial p}\right)\sum_i x_i \sum_{A_i}(1 - X^{A_i}) \quad (7)$$

4.0 Results and discussion

Figure 2 presents the experimental and CPA-SRK72-predicted mole fractions of MDEA in CO_2 at supercritical and sub-cooled conditions. At all investigated isotherms, the solubility of MDEA in CO_2 increases strongly with pressure, and it is temperature dependent. At a given pressure, MDEA solubility decreases slightly with increasing temperature, consistent with the reduced volatility of CO_2 at lower temperatures.
Figure 3 shows the experimental and CPA-SRK72-predicted mole fractions of MDEA in CO_2 at low temperature conditions (-20 ºC and -30 ºC). The solubility of MDEA in CO_2 is higher in this region, due to the temperature dependence as stated earlier. With -20 ºC, MDEA mole fractions are higher than with -30 ºC between 50 bar and 120 bar; beyond that, there is a slight contrast as the mole fractions become lower with -20 ºC compared to -30 ºC. Since solubility is pressure dependent, we can deduce that MDEA is more soluble in CO_2 at higher pressure and lower temperatures. Data comparison with the CPA-SRK72 model provides a generally good quantitative description of MDEA in CO_2 solubility, illustrating the reliability of the CPA-SRK72 model for accurate predictions.

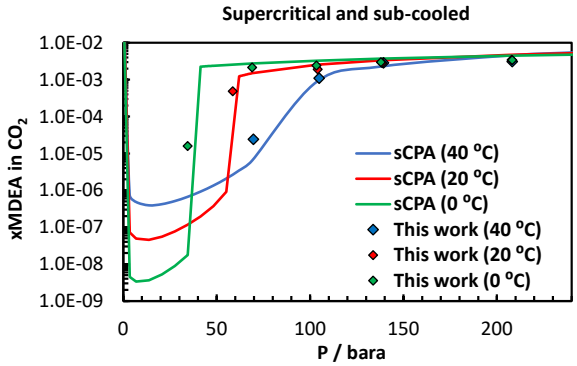

Figure 2. Solubility data for MDEA in CO_2 at three different isotherms (supercritical and sub-cooled conditions): model (thick lines); experimental data (diamonds).

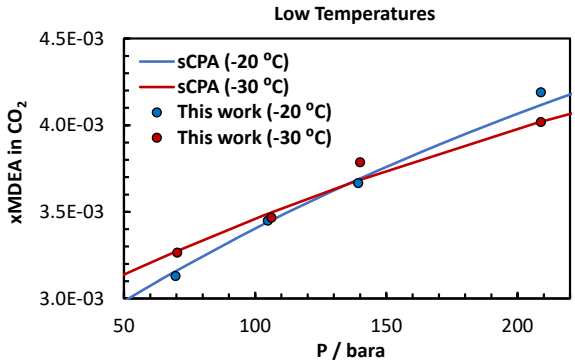

Figure 3. Solubility data for MDEA in CO_2 at two different isotherms (low temperature conditions): model (thick lines); experimental data (circles)

Conclusions

New experimental solubility data for MDEA in CO_2 have been presented over a wide temperature range from -30 ºC to 40 ºC and up to 277.14 bara. The CPA-SRK72 equation of state captures the qualitative pressure dependence of MDEA and exhibits relatively accurate predictive behaviour at all conditions. In all cases, the deviations between experimental and predicted values conform to the combined experimental uncertainty, indicating good agreement. The results highlight the strong temperature dependence of CO_2–MDEA interactions and demonstrate that improved representation of association effects and temperature-dependent interaction parameters can enhance the optimisation of MDEA–CO_2 systems for CO_2 capture.

Acknowledgements

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