Experimental and Thermodynamic Modelling of CO_2 Solubility in Methanol and Methanol–Water Mixtures for the Rectisol Process

Introduction

The Rectisol process is a physical solvent-based process that uses methanol at cryogenic temperatures as a solvent for acid gas removal, it was jointly developed by the German Lurgi and Linde in the 1950s [1, 2]. The process is cost-effective, well-established and widely recognized as one of the earliest methods for producing high-purity syngas and CO_2 streams. It requires operation at very low temperatures to achieve increased capacity for H_2S and CO_2 at an acceptable viscosity [3]. This process mitigates dehydration and the formation of ice and hydrates at low temperatures.
The study of phase equilibrium and thermodynamic models for binary and multicomponent CO_2-methanol mixtures at sub-zero temperatures is essential for the design and optimisation of acid gas removal systems using the Rectisol technology.
Although extensive research has been carried out on CO_2-methanol systems at elevated temperatures, data on multicomponent systems and temperatures below 273.15K are still scarce. Solubility of CO_2 in Methanol was studied by Lyu et al., [1] in the temperature range of 213.15 to 273.15K at pressures from vacuum to 3.3450 MPa. Chang and Rousseau [4] reported the solubility of CO_2 in methanol and methanol-water in the temperature range of 243 to 298K at pressures up to 5.47 MPa. Kobayashi and Hong [5] reported the Vapour-Liquid Equilibrium of CO_2 in Methanol at a temperature range of 230 to 330K and at pressures up to 10 MPa. Höhler et al., [6] investigated the solubility of CO_2 in methanol and other solvents at a temperature range of 253.15 to 453.15K at pressures up to 54bar. Weber et al [7] reported the solubility of CO_2 in Methanol at temperatures of 223 to 300K and pressures from 3 to 18.0 MPa.

Materials and Method

The chemicals used in this experiment were carbon dioxide (0.999 mole fraction), methanol (0.999 mole fraction) and deionised water. The experimental setup used in this work is based on the design described by Pezhman and Chapoy [8] and Wise and Chapoy [9], with minor modifications.
A 300 ml piston-less titanium cylindrical high-pressure vessel was used as the measurement cell. The cell is enclosed within an insulating jacket connected to a circulatory bath to maintain a constant temperature of the system. The temperature of the fluid inside the measurement cell was monitored using a calibrated Platinum Resistance Thermometer (PRT) probe, which was inserted into the insulating jacket. A high-precision pressure transducer is used to measure the system pressure of the measurement cell.
Firstly, CO_2 is loaded into a 600ml pressure cell, which has been cleaned and vacuumed. All the lines were subsequently purged with high-pressure CO_2 to prevent cross-contamination. The 300ml piston-less measurement cell was also cleaned and vacuumed to minimise the interference of air and ensure accurate solubility measurements. A 250ml Erlenmeyer flask containing about 200g of methanol was connected to the measurement cell, and the solvent was charged into the cell through differential pressure injection. After charging the methanol, a pneumatic rocking system was used to agitate the fluid in the measuring cell to accelerate mass transfer until equilibrium was reached.
Before sampling, the pneumatic rocking system was disabled, and the cell was locked in a vertical position. The 600ml pressure cell containing the CO_2 was connected to the experimental setup, the lines were purged with pure CO_2 and the fluid in the measuring cell was allowed to stabilise for several minutes before commencing sampling. A pre-weighed Erlenmeyer flask was connected to the bottom of the measurement cell and also connected to a gasometer. It was ensured that the drainage valve of the gasometer was closed before the sampling. The initial volume and pressure of the gasometer were recorded as well as the equilibrium temperature and pressure of the measurement cell. The bottom valve of the measurement cell was opened gradually to prevent a sudden drop in the pressure, which will disrupt the equilibrium conditions of the measurement cell. During sampling, CO_2 from the 600 mL storage cell was manually injected through the top valve to maintain constant pressure in the measurement cell.

The separated gas was transferred to the gasometer, while the liquid phase collected in the Erlenmeyer flask was continuously stirred using a magnetic stirrer to facilitate complete gas separation. Sampling was continued until approximately 400 cm^3 of gas had been collected to improve measurement accuracy. When enough gas was collected in the gasometer, the bottom valve was closed, and the liquid phase in the Erlenmeyer flask was allowed to stir for an additional 30 minutes at ambient conditions before it was disconnected and weighed. Using the rotary crank of the gasometer, the internal volume of the gasometer was adjusted until the pressure returned to the initial pressure observed at the beginning of the sampling. Lastly, the final volume of the gasometer was recorded for further calculations.

Results and Discussions

Vapour-liquid equilibrium data obtained in these experiments for CO_2-Methanol and CO_2 methanol-water mixtures at 50wt% and 95wt% are presented in the following figures:

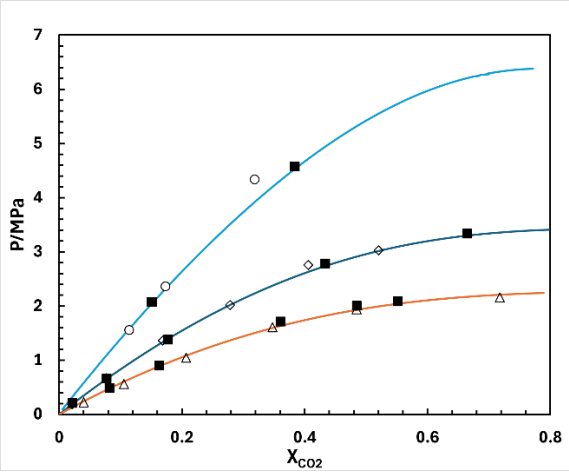

Fig 1: *Solubility of CO_2 in Methanol at different isotherms. (▪) this work, literature data: (◦) Gui et al [10], (◊) Lyu et al [1], (Δ) Chang and Rousseau [4]. T= 298.15K, 273.15K, 258.15K.*

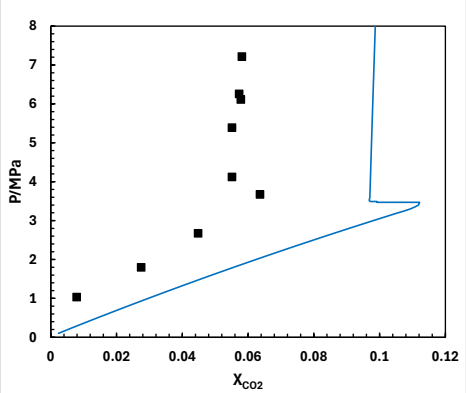

Fig 2: *Solubility of CO_2 in 50 wt% methanol at 273.15K. (▪), this work*

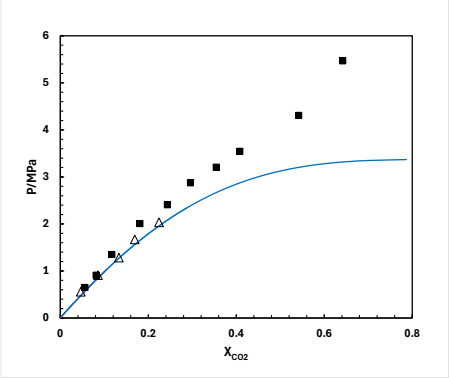

Fig 3: *Solubility data of CO_2 in 95 wt% methanol at 273.15K. (▪) this work, (Δ) Höhler et al [6]*

The thermodynamic model used for the phase equilibria of CO_2 with methanol and methanol solutions was fully described by [8, 9]. In summary, the thermodynamic model is based on the uniformity of fugacity of each component throughout all the phases. The CPA-SRK (Cubic Plus Association – Soave-Redlich-Kwong) Equation of State (EoS) was used throughout this work to model the vapour–liquid equilibrium behaviour of the system.

In this study, the solubility of CO_2 in methanol and methanol-water mixtures was measured at 258.15K, 273.15K and 298.15K. The experimental data obtained in this work for the for the CO_2–methanol system together with the CPA-SRK model correlations demonstrate good agreement with literature

datasets across the investigated composition range, confirming the reliability of the experimental methodology and the model as shown in Figure 1.
In figure 2, higher deviations were observed between the experimental measurements and the model predictions at higher pressures. This suggest that the that the model may not adequately account for the non-ideal interactions occurring in the methanol-water-CO_2 system, especially at high pressure conditions. Figure 3 compares the measured CO_2 solubility in 95 wt% methanol at 273.15K with literature data reported by Höhler et al [6]. Good agreement was observed between the present measurements and the literature values, confirming the reliability of the experimental data and the model. However, while the thermodynamic model reproduced the general trend at low CO_2 concentrations, increasing deviations were observed at higher loadings, which also suggests limitations in the model.
Comparisons of figures 2 and 3 show that the solubility of CO_2 in 95 wt% is higher compared to the solubility of CO_2 in 50 wt% water. At constant temperature, the methanol-rich mixture (95 wt% methanol) exhibits higher CO_2 solubility than the more aqueous mixture (50 wt% methanol), as shown by the wider attainable CO_2 liquid-phase composition range.

Conclusions

In this work, the isothermal solubility data of Carbon dioxide in methanol and methanol mixtures were measured at temperatures from 298.15K to 258.15K and at pressures from 0.21 MPa to 8 MPa. Comparison with literature data showed good agreement for the pure methanol validating the reliability of the experimental data and the model used in this work. The observed trends were consistent with previously reported phase equilibrium behaviour for CO_2-methanol system. However, larger deviations were observed for the methanol-water mixtures, particularly at higher pressures which suggests that urther refinement of model parameters and binary interaction coefficients may be required to accurately represent the non-ideal behaviour of mixed-solvent systems.

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