Phase Behaviour of Methanol + CO2 at Temperatures Between 230 and 423.15 K

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Methanol and carbon dioxide (CO_2) are found in various existing industrial processes and those on the path to net zero, especially in the context of carbon capture and utilisation. Methanol has a legacy of use as a solvent for capturing CO_2, and there is growing interest in methanol as a platform chemical for carbon utilisation, where it is produced from captured CO_2 and 'blue' or 'green' hydrogen and could form the core of a methanol economy. Knowledge of the thermophysical properties of this mixture is crucial, particularly with regards to separation processes. New experimental measurements of the phase behaviour of methanol + CO_2 have been made using an automated static-analytical apparatus. Previously designed to be calibrated with gaseous samples, adaptations have been made to allow for calibration with volumetrically-prepared liquid mixtures. Measurements were carried out along seven isotherms at temperatures of (230, 250, 273.15, 298.15, 330, 373.15, and 423.15) K with pressures from the lower limit of the sampling system (~0.5 MPa) to the mixture critical pressure. The results displayed good agreement with the numerous literature data sources available across these temperatures. These data have been used to optimise temperature dependant binary interaction parameters for two different mixing rules for the Peng-Robinson equation of state. These models perform well in comparison to relevant alternative models, including predictive cubic and SAFT-type equations of state.