Abstract

The amplified awareness in reducing the volume of CO_2 in the Earth's environment inspired the thesis' focus on the phase behaviour of CO_2 and organic compounds related to various classes that could be used as physical solvents for CCS, or as substrates for clathrate hydrates, CO_2 enhanced oil recovery (EOR), and oil upstream treatment. Beyond acquiring a fundamental understanding of binary and ternary systems of carbon dioxide and different types of organic substances, the goals of the thesis were to accurately measure new experimental data, and to model those using equations of state based on a semi-predictive/predictive strategy. For these purposes, our study started with a thorough literature search regarding the experimental methods at high-pressures, modelling methods, and systems investigated.

In this thesis the first vapour-liquid equilibrium data and the critical curve are reported for the carbon dioxide + 2,4-dimethylpentane binary system (***publication I*** in the second part of this work). The liquid–vapour critical line was determined up to 121.4 bar and 422.35 K, as well as vapour–liquid equilibrium (VLE) data at different constant temperatures (323.15, 343.15, 363.15, and 383.15) K and pressures between (10.4 and 120.4) bar. Phase behaviour investigation was carried out in a high-pressures (HP) cell fitted with a pair of sapphire windows, one acting as a piston, hence volume up to 60 cm^3, utilizing a static-analytical approach with phases sampling by the so called ROLSI valves (rapid online sample injectors) connected to a gas chromatograph (GC) for composition determination. The isothermal and critical data points for the carbon dioxide + 2,4-dimethylpentane binary mixture were modelled with the cubic equations of state (EoSs), i.e., Soave–Redlich–Kwong (SRK), Peng–Robinson (PR), and General Equation of State (GEOS), and predictive model PPR78, in combination with van der Waals mixing rules (one- and two-parameter conventional mixing rules, 1PCMR and 2PCMR). The calculations demonstrated that the selected models are capable of correctly reproducing the phase behaviour of the mixture under study.

Publication II of this thesis presents a predictive approach to model the global phase behaviour of carbon dioxide and different classes of organic compounds at high-pressures. Thus, using binary interaction parameters tailored for the carbon dioxide + 2-butanol binary system, the phase behaviour was successfully predicted for carbon dioxide +*n*-Butane, + 1-Butanol, + 1,2-Dimethoxyethane, and + Ethyl acetate. The binary interaction set was determined for the carbon dioxide + 2-butanol binary mixture in a predictive way, being the intersection of the experimental temperature of the experimental upper critical endpoint (UCEP) and the experimental critical pressure maximum (CPM) traced by paths in k_{12}–l_{12} diagram. The calculations were performed with the Soave-Redlich-Kwong (SRK) cubic equation of state (EOS), coupled with classical van der Waals mixing rules (two-parameter conventional mixing rule, 2PCMR).

Publication III of this thesis reports for the first time the phase behaviour of a ternary system, namely carbon dioxide + cyclopentane + cyclohexane, at high-pressures. The isothermal vapour–liquid equilibrium measurements were performed at 353.15 K. The new measured data were modelled with the RK–PR equation of state coupled with classical van der Waals (2PCMR).

Keywords: carbon dioxide; 2,4-dimethylpentane; *n*-butane; 1-butanol; 2-butanol; ethyl acetate; 1,2- dimethoxyethane; cyclopentane; cyclohexane; phase equilibria; high-pressures; phase diagrams; EoSs (GEOS, SRK, PR, RK–PR, PPR78); mixing rules.