High-Pressure Phase Behaviour, Modelling and Uncertainty Propagation of the 1-Nonanol, n -Hexadecane, and CO_2 System

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Aim and Objectives

Investigate and model the high-pressure phase behaviour of the 1-nonanol + n-hexadecane + CO_2 system and assess the impact of measurement uncertainty on model predictions.

- Measure high-pressure bubble- and dew point (HPBDP) data to identify cosolvency effects and temperature inversions
- Evaluate and optimise RK-Aspen's model prediction as a function of its model parameters
- Determine the effect of measurement uncertainties on the thermodynamic model correlations and predictions

Background

- C_8 – C_{20} alcohols produced from olefins via the Oxo process are valuable in the detergent and surfactant industries
- The Oxo process feed, often sourced from a Fischer-Tropsch plant, contains inert alkanes
- Supercritical Fluid Fractionation (SFF) with CO_2 as solvent is a promising method for separating alcohols from alkanes
- High-pressure conditions and solute-solute interactions in the representative 1-nonanol + n-hexadecane system complicate the thermodynamic modelling in Aspen Plus®

Methodology

Load the cell with the required solute(s) and CO_2 → Allow thermal equilibration and increase the cell pressure → Visually measure the phase transition point by decreasing the pressure → Correlate measured vapour pressure data and binary VLE data with RK-Aspen → Predict ternary HPBDP data using selected solute-solute parameters → Estimate pressure, temperature, and compositional uncertainties → Obtain perturbed HPBDP data sets with Monte Carlo Simulations (MCSs) → Refit the model parameters for each perturbed HPBDP data set

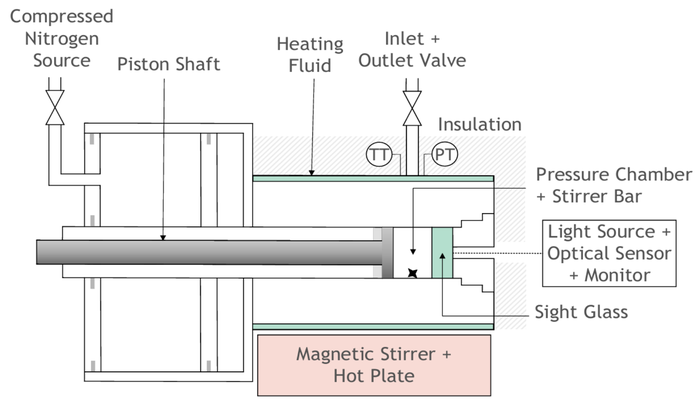

Figure 1: HPBDP Experimental Setup

Experimental Results

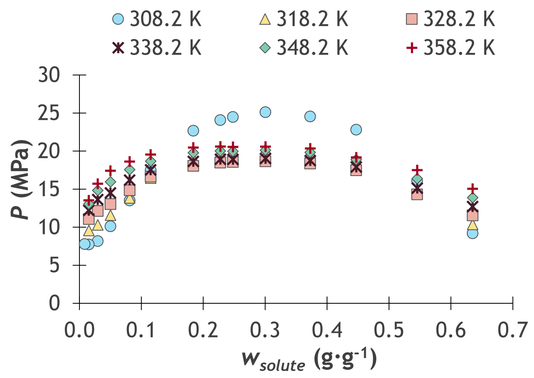

Figure 2: 1-Nonanol + CO_2 HPBDP Data

Temperature inversion: higher transition pressures at lower temperatures

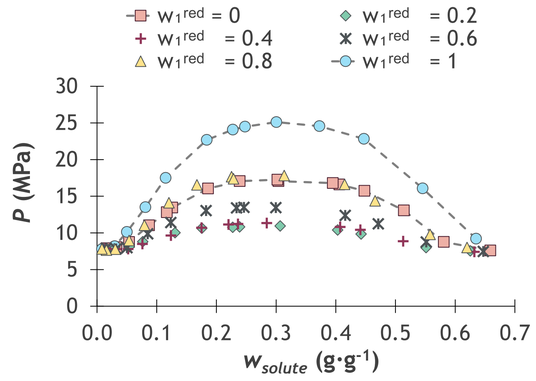

Figure 3: HPBDP Data at 308.2 K for Different Solvent-Free 1-Nonanol Fractions (w_1^{red})

Cosolvency: solubility of mixtures in CO_2 are greater than either pure components

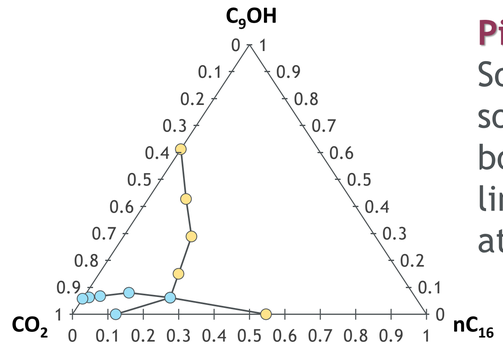

Figure 4: Phase boundaries at 308.2 K and 10.94 MPa

Pinch point: Solute and solvent rich boundary lines overlap at w_1^{red} = 0.2

RK-Aspen

- The regression function in Aspen Plus® struggles to predict the mixture critical region (between low and high solute concentrations)
- Polar parameters + binary solute-solvent + binary solute-solute interaction parameters can be adjusted to increase the accuracy of RK-Aspen
- The prediction is sensitive to its input parameters

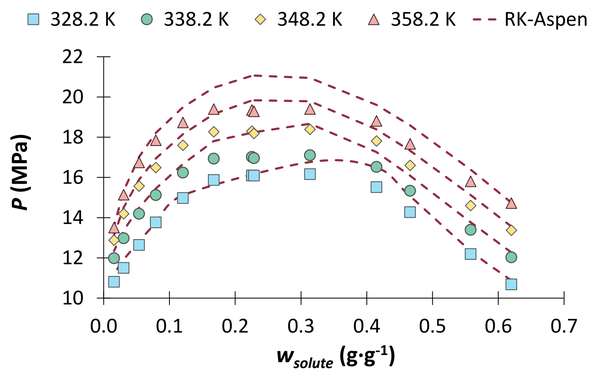

Figure 5: RK-Aspen Predictions Without Solute-Solute Parameters for w_1^{red} = 0.8

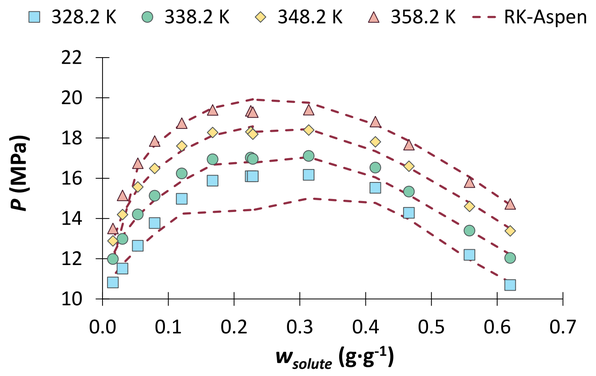

Figure 6: RK-Aspen Predictions with Solute-Solute Parameters for w_1^{red} = 0.8

Insights and Further Work

- **Significant cosolvency effects and temperature inversions occur** due to solute-solute interactions in the 1-nonanol + n-hexadecane + CO_2 system, which complicate thermodynamic modelling in Aspen Plus®
- The **RK-Aspen** model successfully predicts the phase behavior of the 1-nonanol + n-hexadecane + CO_2 system but **signifantly deviates from measurements at low temperatures and in critical regions**
- Future work will involve **propagating measurement uncertainties** and further **optimizing binary interaction parameters**