Phase Behavior and Physical Properties (Density and Viscosity) of Supercritical Carbon Dioxide + (1-Octanol and/or n-Alkanes)

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Supercritical fluid fractionation (SFF) has been proven to be a viable alternative to azeotropic distillation for the separation of *n*-alkanes from detergent-range alcohols (from C_8 to C_{20}). A good understanding of the phase behaviour, hydrodynamic phenomena and mass transfer performance is essential for the design of safe, cheap, and efficient SFF processes. The current gap in literature on density and viscosity data, used to determine mass transfer limitations and hydrodynamic properties, will increase inaccurate design of SFF processes.

This study presents experimentally measured density and viscosity of binary and ternary mixtures of supercritical CO_2 with (1-octanol and/or (*n*-dodecane or *n*-tetradecane)) at phase transition. A variable volume high-pressure cell equipped with a torsional quartz crystal viscometer was used to measure high-pressure bubble- and dew-point data (HPBDP) visually and non-visually, as well as density and viscosity data. Measurements were reported for solute mass fractions ranging from 0.015 to 0.65 g/g at temperatures from 308 to 348 K and pressures up to 28 MPa. The measured HPBDP and vapour density data were modelled using the RK-ASPEN model, the liquid density data using the COSTALD model and the viscosity data using the Chung-Lee-Starling and the TRAPP models; all these models are readily available in Aspen Plus® V11.

The binary HPBDP data were in agreement with previously published data and noted trends: The CO_2 + 1-octanol exhibited a temperature inversion at 308.2 K and the phase transition pressures of the CO_2 + 1-octanol are higher due to the hydroxyl group forming multimer structures. The ternary systems' HPBDP data revealed that introducing *n*-alkanes to the 1-octanol inhibits the formation of these multimers and negates the effect of temperature inversion. The RK-ASPEN model performed well in predicting the binary and the ternary HPBDP data. In addition, the nonvisual HPBDP data compared well with the visual measurements, with $\%AAD_P$ of less than 3 %.

This study also presented new density and viscosity data for all the relevant systems, but the chosen models performed poorly in predicting these physical properties. The density and viscosity data for the CO_2 + 1-octanol exhibited an inversion, introducing a non-ideal, non-linear relationship between the physical properties and the temperature. The addition of *n*-alkanes to 1-octanol for the CO_2 + 1-octanol + *n*-alkane systems removed the density and viscosity inversion effects identified in its CO_2 + 1-octanol binary subsystem.