Density and viscosity at phase transition in CO_2-dodecanol mixtures

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Supercritical fractionation is a popular alternative separation technique to traditional separation processes such as distillation and liquid-liquid extraction. Most often supercritical CO_2 is used as mass transfer agent, making the fractionation environmentally friendly and suitable for applications in food processing. Little information is currently available for the design of equipment for supercritical fractionation, leading to use of design correlations developed for sub-critical conditions. These correlations lead to costly over-design of equipment and excessive piloting of processes. A need therefore exists to describe the mass transfer that occurs in a supercritical fractionation column. The mass transfer that takes place during fractionation is influenced by physical properties of the mixture such as the density and viscosity, and little data of these properties have been published.

In this work the phase behaviour of two binary and one ternary mixtures of CO_2 and alcohols is presented. The binary mixtures are CO_2 + 1-dodecanol and CO_2 + 2-dodecanol, while the ternary mixture is CO_2 + (50% 1-dodecanol + 50% 2-dodecanol). The purpose of studying these systems is to provide the phase behaviour and physical property data required for a later mass transfer study. The phase transition pressures at various temperatures were measured, as well as the density and dynamic viscosity. Measurements were conducted up to 75°C and 29.0 MPa. The phase transition was detected visually using a variable volume static view cell. The density was determined from measurement of mass and a calibrated volume. The viscosity was calculated from the resonant frequency of a torsional quartz crystal immersed in the mixture during phase transition.

All three mixtures investigated display temperature inversion i.e. an increase in temperature leads to a decrease in phase transition pressure. The solubility of the alcohols in the CO_2 decreases in the order: 2-dodecanol > (50% 1-dodecanol + 50% 2-dodecanol) > 1-dodecanol. The decrease in the solubility is linked to the shielding effect on the hydroxyl group as it shifts away from the terminal carbon atom. Thus a mixture containing primary and secondary alcohols could be fractionated using supercritical CO_2. The measured density and viscosity of the mixtures tend to decrease with increasing temperature, which is typical liquid-like behaviour. The density of the three mixtures tend to have similar values at the same temperature and pressure, while the viscosity of the ternary mixture lies closer to the binary CO_2 + 2-dodecanol viscosity. Thus in a fractionation column, the composition of the liquid phase may have a stronger influence on its viscosity than on its density.

Low-alcohol concentration mixtures have densities and viscosities that are significantly higher than pure CO_2 properties at similar temperatures and pressures. Pure component physical properties are therefore not recommended for use to estimate the supercritical fluid phase properties during fractionation. The measurements presented in this work can be incorporated in a mass transfer model that better describes supercritical fluid fractionation. Future work will investigate developing a suitable model for this purpose.