# Separation of Detergent Range Alkanes and Alcohols with Supercritical Fluids: Ternary and Multicomponent Phase Behaviour

C.E. Schwarz[a,*], J.H. Knoetze[a], C. Latsky[a], M. Ferreira[a] and F.C.v.N. Fourie[a]

[a] Department of Process Engineering, Stellenbosch University, Banhoekweg, Stellenbosch, 7600, South Africa

[*] cschwarz@sun.ac.za

## ABSTRACT

Detergent range alcohols (10 to 20 carbon atoms) used in the production of surfactants are usually produced via oxidation of alkanes or hydrogenation of alkenes. Both production processes result in a product stream containing alkanes and alcohol, which subsequently need to be fractionated. Additionally, a distribution of carbon numbers is also present due to the origin of the alkane or alkene stream. Therefore a process is required to separate alkanes and alcohols. Traditional separation processes are either not technically viable due to cross-over melting and boiling points or pose difficulties in remove organic solvents. Previous binary phase equilibria and pilot plant scale measurements have shown that supercritical $CO_2$ is able to separate the alkanes and the alcohols. However, some trends observed in the pilot plant data can not easily be explained based on the binary phase behaviour data. It is postulated that the differences arise from the assumption of no solute-solute interaction. There therefore exists a need to investigate the solute-solute interactions in the $CO_2$ + alkane + alcohol system.

The objective of this paper is to present results on the solute-solute interactions present in $CO_2$ + alkane + alcohol systems. In particular systems with similar boiling were studied:
- $CO_2$ + n-tetradecane + 1-dodecanol
- $CO_2$ + n-tetradecane + 1-decanol
- $CO_2$ + n-dodecane + 1-decanol
- $CO_2$ + n-dodecane + 3,7-dimethyl-1-octanol
- $CO_2$ + 1-decanol + 3,7-dimethyl-1-octanol
- $CO_2$ + n-dodecane + 1-decanol + 3,7-dimethyl-1-octanol

All systems containing linear alcohols showed a temperature inversion at high 1-decanol concentrations. Additionally, all systems showed a degree of co-solvency in the region of the highest concentration of the most soluble component. This co-solvency was noted throughout the temperature range studied (308 to 358 K) and was more prominent for systems where the constituent components have similar solubilities in $CO_2$. As a result of the co-solvency, at certain temperature and pressure combinations a region exists where two regions of immiscibility are present, with a region of total miscibility in-between. Operation at these conditions may therefore produce results other than predicted if the prediction does not take solute-solute interactions into account.

To date, limited success has been achieved in modelling these systems. Equations of state struggle to capture the complex molecular interactions. However, with the use if binary interaction parameters (BIPs) fair predictions can be attained that capture some of the phase behaviour complexities. Future work includes incorporating equations of state together with fitted BIPs into process models to improve prediction of the separation process.