Phase behaviour of CO_2 + solute + solute ternary mixtures including 1-alcohols, *n*-alkanes, carboxylic acids and methyl esters

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Introduction

Supercritical (SC) fluids are an attractive alternative to traditional organic solvents. SC CO_2 is a popular solvent due to its availability, cost, non-toxicity and it is generally regarded as safe. Knowledge of the phase behaviour of CO_2 containing systems is thus necessary.

Carbon Dioxide + 1-Alcohols + *n*-Alkanes → Thoroughly investigated

Complex phase behaviour & significant solute + solute interactions → **What about other CO_2 + solute + solute systems?**

Experimental methodology

- High-pressure bubble- and dew-point (HPBDP) data measured using a variable volume static synthetic view-cell (Figure 1) with a maximum pressure of 300 bar
- Solute mass fractions ranged from 0.015 - 0.65
- Six temperatures considered between 308K–358K at 10K intervals

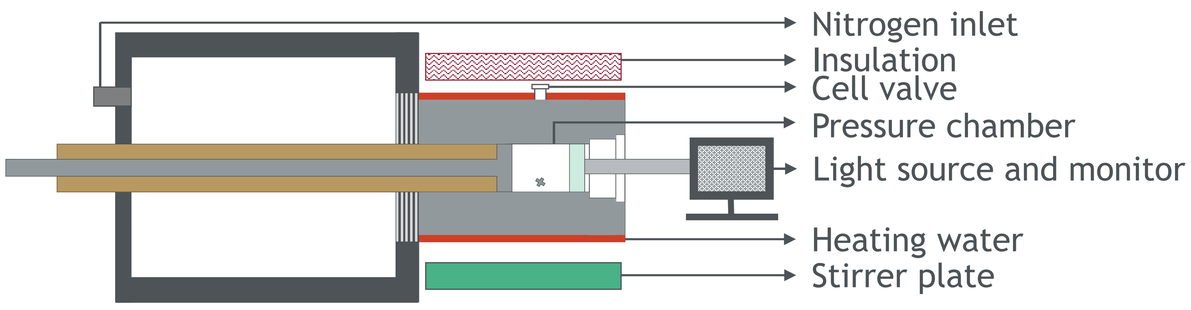
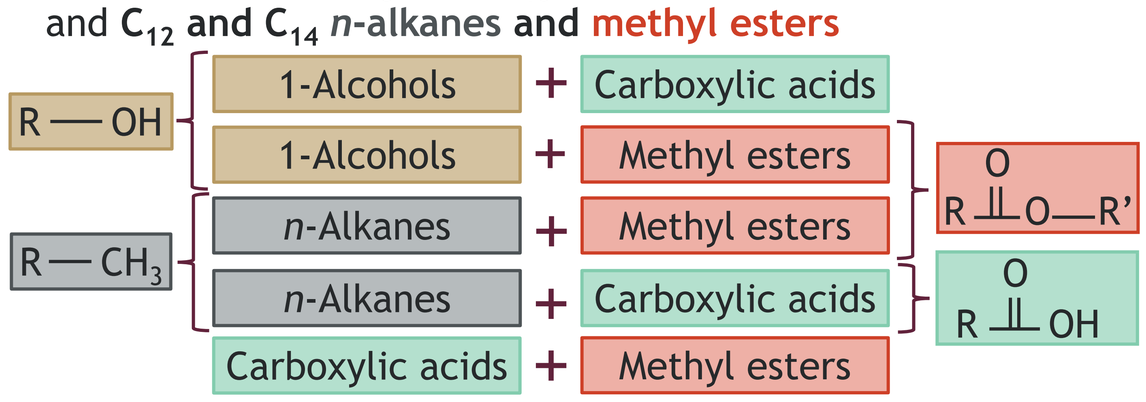


Figure 1: Static synthetic view-cell experimental set-up redrawn from Schwarz[1]

Experimental design

- Five groups of solute + solute mixtures in CO_2 considered
- Solutes included **C_8 and C_{10} 1-alcohols and carboxylic acids and C_{12} and C_{14} *n*-alkanes and methyl esters**



- Only 50:50wt% mixtures considered to identify which groups of systems presented complex phase behaviour

Results and major findings

- CO_2 + 1-octanol and CO_2 + 1-decanol binaries exhibit temperature inversions, but only CO_2 + 1-decanol + n-decanoic acid ternary showed a temperature inversion (Figure 2)

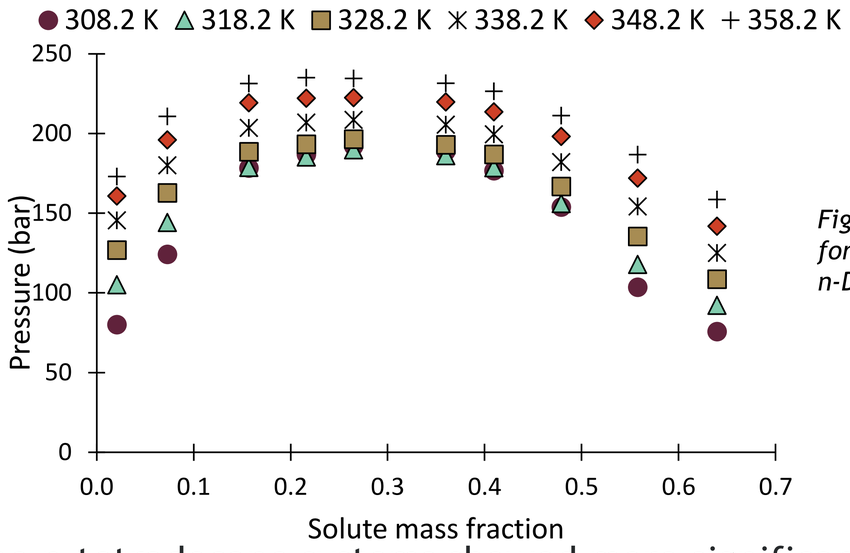


Figure 2: HPBDP data for CO_2 + 1-Decanol + n-Decanoic acid

- The n-tetradecane systems showed more significant co-solvency effects than the n-dodecane containing systems (Figure 4)

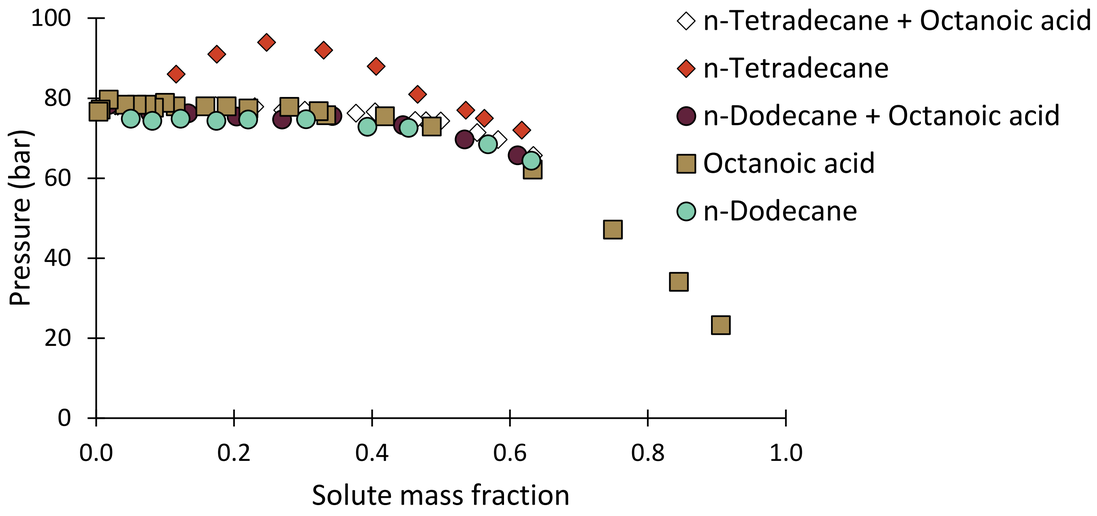


Figure 4: HPBDP data for CO_2 + n-Dodecane + Octanoic acid and CO_2 + n-Tetradecane + Octanoic acid and the constituent binaries at 308.2 K[4,5].

- The phase behaviour of the 1-alcohol + methyl ester groups is almost identical to the methyl ester binary data (Figure 3), indicating significant solute-solute interactions

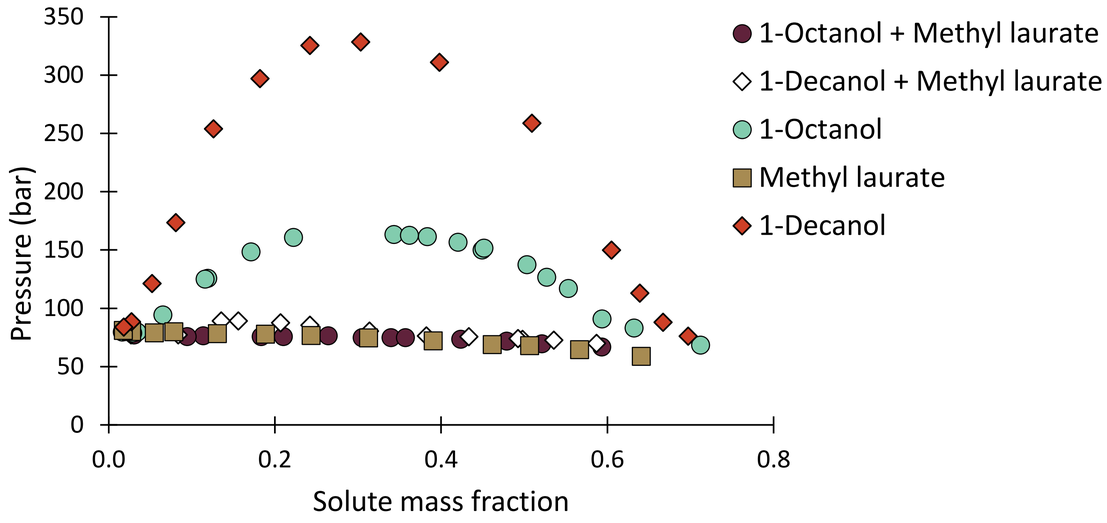


Figure 3: HPBDP data for CO_2 + 1-octanol + methyl laurate, CO_2 + 1-decanol + methyl laurate and the constituent binaries at 308.2 K[2,3].

- Co-solvency effects observed in each group except for the methyl ester + carboxylic acid systems (Figure 5)

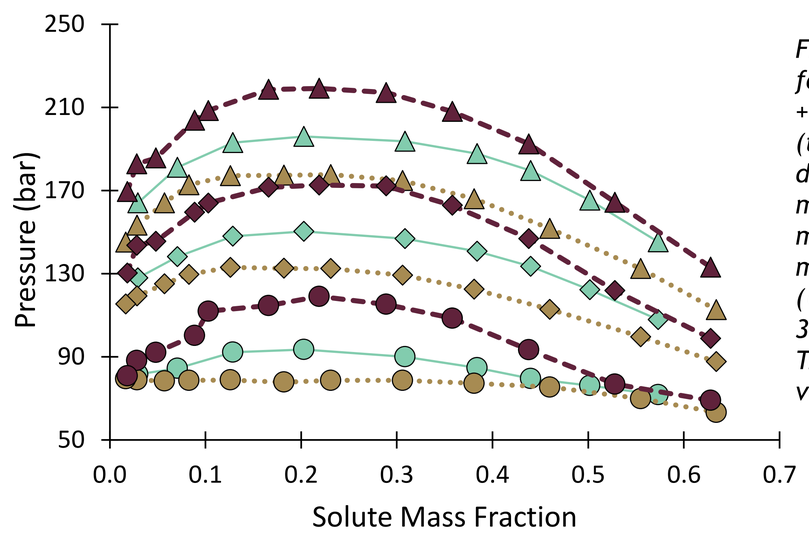


Figure 5: HPBDP data for CO_2 + decanoic acid + methyl myristate (teal markers), CO_2 + decanoic acid[6] (maroon markers) and CO_2 + methyl myristate (gold markers) at 308.2 K (●), 328.2 K (◆) and 348.2 K (▲). Trendlines added as a visual aid only.

Conclusions

- Complex phase behaviour observed in the CO_2 + 1-alcohol + carboxylic acid/methyl ester and CO_2 + *n*-alkane + carboxylic acid/methyl ester groups, but not in the CO_2 + carboxylic acid + methyl ester group
- Co-solvency effects most significant for *n*-tetradecane systems and the 1-alcohol + methyl ester group

References: [1] Schwarz, C.E. (2001) "Phase equilibrium of alkanes and supercritical fluids", Masters Thesis in Chemical Engineering [2] Fourie, F.C. v. N., Schwarz, C.E. and Knoetze, J.H. (2008), Journal of Supercritical Fluids, 47(2), pp. 161-167. [3] Zamudio, M., Schwarz, C.E. and Knoetze, J.H. (2011a), Journal of Supercritical Fluids, 59, pp. 14-26. [4] Zamudio, M., Schwarz, C.E. and Knoetze, J.H. (2013), Journal of Supercritical Fluids, 84, pp. 132-145. [5] Byun, H.S., Kim, K. and McHugh, M.A. (2000), Industrial and Engineering Chemistry Research, 39(12), pp. 4580-4587. [6] Schwarz, C.E. and Knoetze J.H. (2012), Journal of Supercritical Fluids, 66, pp. 36- 48

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