



CO₂ + *n*-dodecane + 3,7-dimethyl-1-octanol: High pressure experimental phase equilibria data and thermodynamic modelling



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ABSTRACT

New high pressure VLE data for the ternary mixture CO₂ + *n*-dodecane (*n*C₁₂) + 3,7-dimethyl-1-octanol (37DM1O) are presented. A static apparatus with online analysis was used to measure phase compositions at 35, 55 and 75 °C, and pressures between 68 and 157 bar. In the high-*n*C₁₂ region the mixture displayed enhanced solubility, presenting as a pinched two phase band and s-shaped liquid phase curves. Relative solubility, an indicator of fractionation sharpness, increased with 37DM1O content and the 75:25 *n*C₁₂:37DM1O mixture cannot be separated using CO₂. RK-ASPEN, SR-POLAR, PR-BM and PC-SAFT models were evaluated for their ability to correlate these data. RK-ASPEN and PC-SAFT models provided the best and worst correlation of equilibrium pressures with respective percentage average absolute deviations of 3.1% and 8.5%. RK-ASPEN model was impressive in its ability to capture the co-solubility pinch seen for the 75:25 *n*C₁₂:37DM1O mixture and the resultant s-shaped liquid phase complexity.

1. Introduction

Continued research on the use of supercritical solvents has enabled the development of a separations technology niche. Initial industrial applications focused mainly on the extraction of high value organic products from natural matrices but nowadays the tuneable properties of supercritical solvents are utilised in, amongst other, pharmaceuticals and novel materials development [1], enhanced oil recovery [2] and liquefied natural gas transport [3].

Detergent alcohols in the range C₈–C₂₀ are often used as precursors in the production of alcohol ethoxylate surfactants [4]. Two popular catalytic detergent alcohol production pathways involve the hydroformylation of an alkene and subsequent hydrogenation of the aldehyde [4,5] or direct oxidation of an alkane [6,7]. The hydroformylation/hydrogenation approach is often applied to a distillation cut containing both alkenes and inert alkanes, whilst the alkane oxygenation approach is often incomplete. To drive economies of scale the feed stream may also contain a variety of carbon backbone lengths [5]. As a result, detergent alcohol product streams may exhibit a range of carbon backbone lengths, and contain significant residual alkanes, linear and branched alcohol isomers. These species' boiling points are often narrowly distributed or overlap, and supercritical fluid extraction (SFE) is considered as an alternative means of product fractionation.

Sizing of and control logic development for a SFE process requires a

sound understanding of the mixture phase behaviour [8] and, in this regard, accurate and robust predictive models are valuable [9]. However, predictive models often fail for such systems because complex phase behaviour exists in high pressure mixtures containing one supercritical species [10]. In addition, systems containing both polar and non-polar species often exhibit strong deviations from ideality [11,12]. Experimental phase equilibria data remains a key contributor toward bridging this gap. Binary solvent-solute data, though useful, do not capture the solute-solute interactions that exist in ternary and higher mixtures. Ternary VLE data is better suited toward quantifying such solute-solute interactions but, unfortunately, remain scarce because the experiments are costly, time-consuming, and often reliant on successive, representative yet non-disruptive sampling from a small volume, high pressure equilibrium state [13].

This background has, to some extent, driven high pressure phase equilibria research at Stellenbosch University and the work presented forms part of a larger project which investigates the phase behaviour of the solutes *n*C₁₂, 37DM1O and C₁₀OH in two different solvents, CO₂ and ethane. These solute species are representative of the aforementioned detergent alcohol product stream, and the solvents CO₂ and ethane have shown promise in their ability to fractionate similar mixtures [14]. The three key objectives of this study are to i) generate high pressure phase equilibria data for the ternary mixture CO₂ + *n*C₁₂ + 37DM1O at 35, 55 and 75 °C; ii) assess the ability of CO₂ to separate the solute

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Nomenclature

2E1H	2-Ethyl-1-hexanol
37DM1O	3,7-Dimethyl-1-octanol
AAD	Average absolute deviation
BIP	Binary interaction parameter
C ₁₀ OH	1-Decanol
CSSRL	Constant solute–solute ratio lines
k_{ij}	Binary interaction parameter
l_{ij}	Binary interaction parameter
m	Segment number in PC-SAFT
M	Number of data points
nC_{12}	<i>n</i> -Dodecane
$p_{1/2/3}$	SR-POLAR polar parameter
P	Pressure
P_c	Critical pressure
P_r	Reduced pressure (P/P_c)
P^{sat}	Saturated vapour pressure
ROLSI™	Rapid on-line sampler injector
SFE	Supercritical fluid extraction
SP_{ij}	Separation potential between species <i>i</i> and <i>j</i>
Solute	nC_{12} or 37DM1O or C ₁₀ OH
Solvent	CO ₂ or ethane
T	Temperature
T_c	Critical temperature
T_r	Reduced temperature (T/T_c)

TSP	Total solubility pressure
u	Absolute uncertainty
x_i	Mole fraction of species <i>i</i>
X_i	Liquid phase mass fraction of species <i>i</i>
Y_i	Vapour phase mass fraction of species <i>i</i>
Z_i	Bulk solvent-free mass fraction of species <i>i</i>

Greek letters

α_{ij}	Relative solubility between species <i>i</i> and <i>j</i>
η_i	RK-ASPEN polar parameter
ε/k	Dispersion energy parameter in PC-SAFT
ε^{AB}/k	Association energy parameter in PC-SAFT
κ^{AB}	Effective association volume parameter in PC-SAFT
σ	Segment diameter in PC-SAFT
ρ^{sat}	Saturated liquid density
ω	Acentric factor

Superscripts and subscripts

<i>exp</i>	Experimental
<i>i, j</i>	Component identifications
<i>sat</i>	Saturated
TSP	Total solubility pressure
\$	Extrapolation to 35 °C
*	VLE data via simultaneous sampling with two samplers

species nC_{12} and 37DM1O; and iii) use the new VLE data to evaluate the ability of four thermodynamic models, available within in a commercial process simulator, to correlate the measured equilibrium pressures and compositions.

2. Materials and methods**2.1. Project outline**

Experimental data for CO₂ + nC_{12} + 37DM1O were measured at 35, 55 and 75 °C and pressures between 68 and 157 bar. The larger project, which is also concerned with C₁₀OH and ethane, governed the target pressures, and three factors were considered when defining these: i) overlapping reduced pressures; ii) overlapping absolute pressures; and iii) binary total solubility pressures (TSP):

- The solvents CO₂ and ethane possess different critical pressures: $P_{c,CO_2} = 73.82$ bar and $P_{c,ethane} = 48.84$ bar. Thus, experimental pressures for CO₂-containing systems will necessarily be higher than for ethane-containing systems. Comparisons between these studies will be more informative if reduced pressures are similar.
- For comparative purposes, overlapping absolute pressures, both inter- and intra-solvent, are beneficial.
- The temperature-specific total solubility pressure (TSP), defined as the highest binary mixture bubble or dew point pressure, was identified for each of the six binaries and is listed in Table 1. For each ternary mixture, the TSP of the more soluble species (i.e., the lower TSP) was used as guideline. Preliminary experiments [15] and former pilot plant studies [14,16] have shown, at least qualitatively, that interesting phase behaviour might exist in the ternary system at pressures marginally higher than the lower of the two binary TSP's. As such, one target pressure was selected close to yet above the lower TSP.

An overall reduced pressure minimum of 0.9, which equates to 68 and 45 bar for CO₂ and ethane respectively, was chosen. The resulting target experimental pressures and system-specific TSP's are listed in

Fig. 1. The temperature-specific minimum experimental pressure was stepped up by one pressure-increment for each temperature-increment (i.e., 68 bar at 35 °C, 83 bar at 55 °C and 104 bar at 75 °C, with CO₂ as solvent).

Three CO₂ + nC_{12} + 37DM1O mixtures, which differ in solute-to-solute ratio, were studied experimentally. The three bulk nC_{12} :37DM1O mass fraction ratios, calculated on a solvent free basis, were 75:25, 50:50 and 25:75. In all subsequent references to solute ratios the first value applies to nC_{12} and the second to 37DM1O. The mixture-specific maximum experimental pressure was governed by the phase transition pressure thereof. No binary data were measured in this study. Binary data used for regressions or phase diagrams were obtained from literature and are referenced accordingly.

2.2. Experimental method

Experiments were conducted on a variable-volume (75–125 ml) static analytic apparatus. The setup enables visual observation of the cell contents with a medical endoscope, and operation upper limits of 150 °C and 300 bar. Jacketed liquid circulation in combination with a forced convection oven is used to heat the cell, and the content is magnetically stirred. ROLSITM samplers (Armines, France) coupled with online gas chromatography were used for sample extraction and analysis respectively. Refer to Fourie et al. [21] for a comprehensive

Table 1
Binary mixture total solubility pressures [bar].

Solvent	Solute	Temperature [°C]			Reference
		35	55	75	
CO ₂	nC_{12}	75	114	152	[17]
	37DM1O	125	152	180	[18]
	C ₁₀ OH	328 [§]	211	211	[18]
Ethane	nC_{12}	51 [§]	68	87	[19]
	37DM1O	69	102	128	[20]
	C ₁₀ OH	95	126	148	[20]

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