



Isothermal (vapour + liquid) equilibrium data for binary systems of (*n*-hexane + CO₂ or CHF₃)



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ABSTRACT

The (vapour + liquid) equilibrium (VLE) was measured for the (carbon dioxide + *n*-hexane) binary system at temperatures between $T = (303.1 \text{ and } 323.1) \text{ K}$. In addition, VLE and (vapour + liquid + liquid) equilibria (VLLE) were determined for the (trifluoromethane + *n*-hexane) binary system at temperatures between $T = (272.9 \text{ and } 313.3) \text{ K}$ and pressures in the range of $P = (1.0 \text{ to } 5.7) \text{ MPa}$. Measurements were undertaken in a static-analytic apparatus, with verification of experimental values undertaken using a static-synthetic equilibrium cell to measure bubble point pressures at several compositions.

The phase equilibrium results were modelled with the Peng–Robinson equation of state with the Mathias–Copeman alpha function, coupled with the Wong–Sandler mixing rules. Regression of the data was performed with the NRTL and the UNIQUAC activity coefficient models with the Wong–Sandler mixing rules, and the performance of the models was compared. Critical loci for both systems were estimated, using the calculation procedures of Ungerer *et al.* and Heidemann and Khalil.

For the (trifluoromethane + *n*-hexane) system, liquid–liquid immiscibility was experienced at the lowest temperature measured ($T = 272.9 \text{ K}$). At higher temperatures, no immiscibility was visible during the measurements; however, the models continued to predict a miscibility gap.

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1. Introduction

While conventional distillation may be the simpler and preferred method for most separation and purification problems, it is not always the best or most economical technique available [1]. At times, alternative separation techniques, such as liquid–liquid extraction or extractive distillation, can provide a better separation. Some of the main disadvantages of the current extraction techniques, however, include the high viscosities and the high toxicities of the solvents [2]. In liquid–liquid extraction and extractive distillation, the same characteristics that make the solvent useful (the solubilities and capacities), make the solute recovery difficult [3].

The nature of supercritical solvents means that their viscosities are substantially lower than those of liquids and the dispersion is greater, due to the reduced surface tension [2]. These phenomena lead to improved efficiency in the solute mass transfer into the solvent phase with supercritical fluid extraction. The separation of the supercritical solvent from the solutes can usually be achieved simply by employing a reduction in pressure.

Supercritical fluid (SCF) extraction can be performed at near ambient temperatures resulting in it being a more attractive option for the separation of heat sensitive systems [4,5]. The temperature of operation is, however, dependent upon the (solvent + solute) mixture critical temperature. It is therefore lucrative to utilise a solvent that has a critical temperature that is in close proximity to the ambient temperature.

Safety and economic considerations, are the two most important factors, amongst many, which must be considered when selecting a solvent for a SCF process [6]. For the safety requirements, the solvent must be non-toxic and non-flammable, and with regards to economics, it should be cheap and readily available. A vast amount of research has been conducted into supercritical fluid extraction processes, with the majority of these investigations using carbon dioxide (CO₂) as the solvent. This is due to good availability of CO₂, and because it fulfils safety requirements [6,7]. Short-chained *n*-alkanes have, on occasion, also been investigated as supercritical solvents, but not to the extent that CO₂ has been investigated and used [8–16]. There has not been a substantial amount of interest in replacements for carbon dioxide in supercritical fluid extraction processes, despite the recurrent requirement of polar co-solvent additions for assistance with the extractions [17,18].

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To avoid the need to use a co-solvent in the extraction process, the use of a polar solvent is proposed. This will simplify the downstream solvent recovery processes. Trifluoromethane (R-23, CHF₃) is a possible alternative supercritical solvent that fulfils all of the aforementioned criteria; including a low critical pressure and a critical temperature that is in close proximity to ambient temperature (see table 1).

The variety of components that are present in a 'real' petroleum stream are countless, rendering it impossible to individually measure and model the phase behaviour of each binary system present in the stream, in addition to the binary mixtures containing the solvent with each individual component. To approximate the behaviour of such a petroleum stream, the use of a 'model' petroleum stream has been proposed [19]. The binary phase equilibrium data measurements can then be conducted for the finite number of components in the model stream. This information provides an approximation and estimation as to the solvent performance with the 'real' stream. The design of a separation process would rely heavily on these measured binary equilibrium data [20].

Wirths and Schneider [21] conducted an investigation into the high pressure phase equilibria of several hydrocarbons with R-23, however, only *P-T-x* isopleths were reported due to the equipment being of the static-synthetic type. Poot and de Loos [22] measured the (vapour + liquid + liquid) equilibrium (VLLE) pressure for R-23 and hexane at temperatures between *T* = (253.76 and 281.78) K. They determined that the upper critical end point (UCE), at which the liquid immiscibility disappears, occurred at a temperature of *T* = 281.78 K. They did not, however, investigate the phase equilibria further than the VLLE pressures. The bubble point pressures at a number of temperatures and compositions for systems involving R23 and several phenyl-alkanes were measured by Bogatu et al. [23–25].

The phase equilibrium data for the systems containing R-23 with an *n*-alkane series were therefore measured with the intent of determining the performance of trifluoromethane as a solvent for the extraction of petroleum components by supercritical fluid extraction. The data for the binary system of (R-23 + *n*-hexane) are presented alongside the data for the (CO₂ + *n*-hexane) system.

2. Experimental

2.1. Materials

Carbon dioxide (CO₂, CAS Number 124-38-9) used in these measurements was purchased from Afrox South Africa. Trifluoromethane (CHF₃, R-23, CAS Number 75-46-7) was obtained from A-Gas (South Africa) (Pty) Ltd, and *n*-hexane (C₆H₁₄, CAS Number 110-54-3) was obtained from Sigma–Aldrich. Afrox South Africa also supplied the helium (Baseline 5.0), which was used for the gas chromatography analysis.

The stated purities, GC area percentages (mole basis), and the critical properties of the gases and *n*-hexane are listed in table 1. For *n*-hexane, the refractive index and density measured in this work, as well as values obtained from literature, are given in table 2. The refractive index was measured with an Atago RX7000 refractometer with an estimated uncertainty in the refractive index of $\pm 1 \cdot 10^{-4}$ and an estimated uncertainty in temperature of 0.01 K. The *n*-hexane density was measured with an Anton Paar DMA 5000 densimeter with uncertainties in the density and the temperature of 0.05 kg · m⁻³ and 0.05 K respectively.

Degassing of the *n*-hexane was performed *in-situ* in the equilibrium cell, by drawing a vacuum in the cell with a vacuum pump (0.2 kPa absolute for 10 min), after loading the liquid. Due to the large differences in volatilities of the components in the binary mixtures, degassing of the carbon dioxide or trifluoromethane could also be performed in the equilibrium cell. This was undertaken by repeatedly releasing some of the vapour phase that formed in the equilibrium cell, and thereafter allowing it to re-generate from the liquid. There were no 'heavier' components observed in the chemicals when analysing the purities with the gas chromatograph, and for this reason, no other purification techniques were employed.

2.2. Experimental apparatus

2.2.1. Static-analytic apparatus

A static-analytic type equilibrium cell, designed by Narasigadu et al. [26], was used to measure the (vapour + liquid) equilibrium and (vapour + liquid + liquid) equilibrium phase data. This apparatus has been used previously for a number of phase equilibrium data measurements, and is well documented [27,28].

TABLE 2

The refractive index, *R*^{*l*}, and density, ρ , of *n*-hexane at a temperature of *T* = 298.15 K.

<i>T</i> /K	<i>R</i> ^{<i>l</i>} (lit.)	<i>R</i> ^{<i>l</i>} (exp.) ^{<i>h</i>}	ρ (lit.)/kg · m ⁻³	ρ (exp.) ^{<i>i</i>} /kg · m ⁻³
298.15	1.3723 ^{<i>a</i>}	1.3724	655.1 ^{<i>a</i>}	655.241
	1.37242 ^{<i>b</i>}		655.3 ^{<i>b</i>}	
	1.37226 ^{<i>c</i>}		655.07 ^{<i>c</i>}	
	1.37236 ^{<i>d</i>}		655.28 ^{<i>d</i>}	
	1.3721 ^{<i>e</i>}			

^{*a*} [79].

^{*b*} [80].

^{*c*} [81].

^{*d*} [82].

^{*e*} [83].

^{*f*} [84].

^{*g*} [85].

^{*h*} *u*(*T*) = 0.01 K, *u*(*R*^{*l*}) = 1 · 10⁻⁴.

^{*i*} *u*(*T*) = 0.05 K, *u*(ρ) = 0.05 kg · m⁻³.

TABLE 1

The suppliers, stated purities, GC area fractions and critical properties (*T*_c, *P*_c) of the chemicals used in this study.

	Carbon dioxide	Trifluoromethane	<i>n</i> -Hexane
Supplier	Afrox South Africa	A-Gas (South Africa) (Pty) Ltd	Sigma–Aldrich
Stated purity	>0.999 ^{<i>a</i>}	>0.999 ^{<i>a</i>}	>0.99 ^{<i>b</i>}
GC peak area fraction (mole)	0.9959	0.9996	0.9904
<i>T</i> _c /K ^{<i>c</i>}	304.26	299.07	507.35
<i>P</i> _c /MPa ^{<i>c</i>}	7.377	4.836	3.03

^{*a*} Volumetric basis.

^{*b*} Mass basis.

^{*c*} [78].

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