



# Isothermal vapour-liquid equilibrium data for the binary systems of (CHF<sub>3</sub> or C<sub>2</sub>F<sub>6</sub>) and n-heptane



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## ARTICLE INFO

### Article history:

Received 7 March 2016

Received in revised form 12 June 2016

Accepted 27 June 2016

Available online 29 June 2016

### Keywords:

VLE

Static-analytic

Variable-volume

Trifluoromethane

Hexafluoroethane

n-Heptane

## ABSTRACT

Isothermal vapour-liquid equilibrium (VLE) values for two binary systems; trifluoromethane and n-heptane at temperatures between  $T = (272.9 \text{ and } 313.2) \text{ K}$ , and hexafluoroethane and n-heptane at temperatures between  $T = (293.0 \text{ and } 313.2) \text{ K}$  were measured with a static-analytic apparatus. Bubble pressures at temperatures between  $T = (293.0 \text{ and } 313.2) \text{ K}$ , at several compositions, were also measured with a variable-volume static-synthetic apparatus. Vapour-liquid-liquid equilibrium (VLLE) was found to occur for certain isotherms for both of the systems. The PR EOS, with the Mathias-Copeman (MC) alpha function, combined with either the classical mixing rule or the Wong-Sandler (WS) mixing rule was used to correlate the experimental results. Either the NRTL or the UNIQUAC activity coefficient model was used within the WS mixing rule.

The indirect extended scaling laws of Ungerer et al. were used to extrapolate critical loci from the experimental coexistence data, and the calculation procedure of Heidemann and Khalil was employed to calculate the mixture critical locus curves at temperatures close to the refrigerant critical temperatures. At lower temperatures on the mixture critical curve, gas-liquid critical points occurred, whereas, at higher temperatures, the critical points occurred along a liquid-liquid locus curve. The two systems were categorised according to the van Konynenburg and Scott classification.

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## 1. Introduction

Interest in the use of supercritical fluid extraction (SCFE) to provide a solution for difficult separation problems has drastically increased over the last couple of decades [1–3]. The most commonly used solvent for use in these SCFE processes is carbon dioxide, as it fulfils almost all of the requirements for a supercritical solvent [3–5]. However, the principal drawback in the use of supercritical carbon dioxide as the solvent in an extraction process is the low dielectric constant and low polarity of the CO<sub>2</sub> [3,5].

The simplest method to overcome the low polarity of the carbon dioxide is by the addition of co-solvents (modifiers), thereby increasing the solvating power of the solvent for the solutes of interest [3,6]. These co-solvents are most commonly liquids at ambient conditions. Their addition to the separation results in complications in the downstream product recovery processes, as a separation of two liquid streams must then be performed. It is therefore of interest to discover whether there are any alternative polar gases that could realistically replace the use of carbon dioxide and a co-solvent in extraction processes. A few refrigerants

(chlorofluorocarbons, hydrofluorocarbons and perfluorocarbons) exhibiting some of the characteristics essential for supercritical fluid solvents (suitable critical point, non-flammable, etc.) were therefore chosen [7].

The production and utilisation of chlorofluorocarbons has been banned by the Montreal Protocol [8] and therefore R-13 (monochlorotrifluoromethane), was not considered in this study. The remaining hydrofluorocarbons and perfluorocarbons that were likely candidates for supercritical solvents include trifluoromethane (R-23), hexafluoroethane (R-116), and difluoro-1,1-ethylene (R-1132a). R-1132a was not investigated, as it is a category 1 carcinogen [9]. Of the possible two remaining gases, the use of R-23 is likely to be advantageous, as the trifluoromethane molecules are highly polar.

A further reason behind this investigation into the performance of fluorinated hydrocarbons as supercritical solvents extends from a drive within South Africa to develop new technologies that make use of either fluorine in its pure form, or else chemicals that contain fluorine as a part of their molecules [10]. The field of fluorine chemistry is of interest in South Africa because of the large reserves of acid grade fluorspar available. Only 5 percent of the fluorspar that is mined in South Africa is processed locally, while the majority is exported as crude fluorspar. It is therefore desirable

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that novel uses for fluorinated compounds be developed, in order to expand the South African fluorine industry.

As a continuation of the study of high pressure phase equilibria for the evaluation of the performance of alternatives to carbon dioxide in supercritical fluid extraction processes, the isothermal phase equilibria for the systems of {trifluoromethane (1) + n-heptane (2)} and {hexafluoroethane (1) + n-heptane (2)} were measured. The measurements were conducted with a 'static-analytic type' phase equilibrium apparatus, and were verified by measuring bubble point data with a 'static-synthetic' variable volume apparatus. Five isotherms were measured for the trifluoromethane (1) and n-heptane (2) system at temperatures between  $T = (272.9 \text{ and } 313.2) \text{ K}$ , and three isotherms were measured for the hexafluoroethane (1) and n-heptane (2) system at temperatures between  $T = (293.0 \text{ and } 313.2) \text{ K}$ . A comprehensive search of the open literature indicates that there are no previous data reported for these systems.

## 2. Experimental

### 2.1. Materials

The trifluoromethane ( $\text{CHF}_3$ , CAS Number 75-46-7) and the hexafluoroethane ( $\text{C}_2\text{F}_6$ , CAS Number 76-16-4) were obtained from A-Gas (South Africa) (Pty) Ltd. The n-heptane ( $\text{C}_7\text{H}_{16}$ , CAS Number 142-82-5) was obtained from Merck KGaA. Helium (Baseline 5.0) which was used as a carrier gas for the gas chromatograph was purchased from Afrox South Africa.

The stated mass fraction purities, peak area fractions from GC analysis, as well as the literature pure component critical properties for the trifluoromethane [7], hexafluoroethane [11,12] and n-heptane [7] are listed in Table 1. The refractive indices and densities reported in literature [13–20], as well as those measured in this study, are provided in Table 2. The refractive indices were measured with an Atago RX7000 refractometer. This refractometer has uncertainties in refractive index and in temperature of  $1 \times 10^{-4}$  and 0.01 K respectively. The liquid densities were measured with an Anton Paar DMA 5000 density meter. The DMA 5000 has uncertainties in density and in temperature of  $0.005 \text{ kg}\cdot\text{m}^{-3}$  and 0.05 K respectively.

All of the components were degassed in situ after being loaded into the cell. The n-heptane was loaded first, and was degassed by drawing a vacuum within the cell for approximately 10 min. The vacuum pump used to pull this vacuum was capable of reducing the pressure to 0.2 kPa absolute. Thereafter, subsequent to the addition of the more volatile refrigerant, degassing was once again performed by releasing a small purge of the vapour phase from within the cell and then allowing this to regenerate. This purge procedure was repeated a number of times; usually until the pressure returned to the same value after the vapour phase was regen-

**Table 2**

The refractive indices,  $R^l$ , and densities,  $\rho$ , of n-heptane at temperatures of  $T = (293.15\text{--}300.40) \text{ K}$ . Values obtained by experimental measurement (exp.) are compared to data from the literature (lit.).

$T/\text{K}$	$R^l$ (lit.)	$R^l$ (exp.) <sup>i</sup>	$\rho$ (lit.)/( $\text{kg}\cdot\text{m}^{-3}$ )	$\rho$ (exp.)/( $\text{kg}\cdot\text{m}^{-3}$ )
293.15	1.38807 <sup>a</sup>	1.3878	683.66 <sup>f</sup> 683.82 <sup>g</sup>	683.8
295.15				681.6
297.15				679.9
298.15	1.38581 <sup>a</sup>	1.3852	679.3 <sup>b</sup>	679.1
	1.3857 <sup>b</sup>		679.4 <sup>c</sup>	
	1.3855 <sup>d</sup>		679.5 <sup>e</sup>	
	1.3851 <sup>f</sup>		679.4 <sup>h</sup>	
300.40				677.1

<sup>a</sup> Ref. [13].

<sup>b</sup> Ref. [16].

<sup>c</sup> Ref. [18].

<sup>d</sup> Ref. [14].

<sup>e</sup> Ref. [15].

<sup>f</sup> Ref. [17].

<sup>g</sup> Ref. [19].

<sup>h</sup> Ref. [20].

<sup>i</sup> Combined uncertainties,  $u(T) = 0.01 \text{ K}$ ,  $u(R^l) = 3 \times 10^{-4}$ .

<sup>j</sup> Combined uncertainties,  $u(T) = 0.05 \text{ K}$ ,  $u(\rho) = 0.45 \text{ kg}\cdot\text{m}^{-3}$ .

erated. No 'heavier' impurities were detected during the GC analysis of the pure components, and therefore these degassing procedures were deemed to provide sufficient purification of the chemicals for this study.

### 2.2. Experimental apparatus

A static analytic high pressure equilibrium apparatus, described in detail by Narasigadu et al. [21], was used to measure vapour-liquid equilibrium (VLE) and vapour-liquid-liquid equilibrium (VLLE) for the two refrigerant-hydrocarbon systems. A variable volume high pressure equilibrium apparatus, described in a previous paper [22], was used to measure the bubble pressures of these systems as a means of data verification.

Both equilibrium cells used in the apparatus of Narasigadu et al. and that described by Williams-Wynn et al. are constructed of sapphire crystal tubes, enclosed on both ends with stainless steel flanges. The temperatures of each of the cells are monitored by two Pt100 probes (model REB 1/10 DIN), supplied by WIKA Instruments, which are inserted into wells drilled into both the top and bottom flanges.

The static analytic cell is equipped with a moveable ROLSI™ which allows samples to be taken from any level within the cell. The composition of these samples is analysed with a Shimadzu GC-2010 gas chromatograph fitted with a thermal conductivity detector (TCD). A 3 m long SE30 column (10% dimethyl silicone elastomer liquid phase supported on Chromosorb W-HP 80/100) is used to separate the components. The pressure inside of the cell

**Table 1**

The suppliers, stated mass fraction purity, GC area fractions and critical temperature,  $T_c$ , and pressure,  $P_c$ , of the trifluoromethane, hexafluoroethane and n-heptane used in these measurements.

	Trifluoromethane $\text{CHF}_3$	Hexafluoroethane $\text{C}_2\text{F}_6$	n-Heptane $\text{C}_7\text{H}_{16}$
Supplier	A-Gas (South Africa) (Pty) Ltd	A-Gas (South Africa) (Pty) Ltd	Merck KGaA
Stated Purity/mass fraction	>0.999 <sup>d</sup>	>0.999 <sup>d</sup>	>0.995 <sup>e</sup>
GC Area Fraction	0.9996	0.9999	0.9974
$T_c/\text{K}$	299.07 <sup>a</sup>	293.03 <sup>b</sup>	540.3 <sup>a</sup>
$P_c/\text{MPa}$	4.836 <sup>a</sup>	3.013 <sup>c</sup>	2.756 <sup>a</sup>

<sup>a</sup> Ref. [7].

<sup>b</sup> Ref. [12].

<sup>c</sup> Ref. [11].

<sup>d</sup> Volumetric basis.

<sup>e</sup> Mass basis.

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