



# High-pressure phase equilibria data for mixtures involving ethene and perfluoro-*n*-octane from 293 to 353 K



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## ABSTRACT

Isothermal vapour–liquid equilibrium data were measured for ethene + perfluoro-*n*-octane mixtures at five temperatures in the 293–353 K range, and pressures up to 8 MPa. Experimental  $P$ – $x$ – $y$  data were measured using an apparatus based on the “static–analytic” method. The experimental data were correlated with a model comprising the Peng–Robinson equation of state with either the classical mixing rule or the Wong–Sandler mixing rule coupled with the Non-Random Two-Liquid activity coefficient model. The model gave good representation of the experimental data.

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## 1. Introduction

Perfluorocarbons have been shown to display a remarkable capacity to dissolve light gases [1]. In fact, perfluorocarbons have been noted to exhibit a three-fold increase in the solubility of light gases in comparison to their hydrocarbon counterparts [2]. Perfluorocarbons are both non-polar and non-associating, thus the mechanism for the dissolution of light gases has been linked primarily to the shape of the perfluorocarbon molecules [3]. Notably, the arrangements of the perfluorocarbon molecules form cavities which can accommodate small solute molecules within the solvent. Valtz et al. remarked that perfluorocarbons display a tremendous potential as physical solvents in petrochemical refinery gas absorption processes [4]. In light of the remarkable properties exhibited by perfluorocarbons, the Thermodynamics Research Unit has embarked on an experimental programme to better understand the phase behaviour and absorption capabilities of these compounds with regard to gases. To date, studies have been undertaken for perfluoropropane [5], perfluoro-*n*-butane [6–9], and perfluoro-*n*-octane [10]. It is well established that reliable

measurement and prediction of mixture properties are required for the design of chemical processes. Regarding vapour–liquid equilibrium (VLE), accurate and reliable data provide the benchmark criteria necessary for testing and developing thermodynamic models and fluid theories. In open literature, phase equilibrium data involving mixtures of perfluoroalkanes and olefins are scarce. Köster et al. published isothermal VLE data for the binary mixture of ethene (commonly referred to as ethylene) and perfluoro-*n*-butane (C<sub>4</sub>F<sub>10</sub>) in the temperature range 268–298 K [7]. In this work, we present VLE data for the binary mixture of ethene and perfluoro-*n*-octane (C<sub>8</sub>F<sub>18</sub>) from 293 to 353 K. The binary VLE data were measured using an apparatus based on the ‘static–analytic’ method. The experimental VLE data were modelled using the Peng–Robinson (PR) Equation of State (EoS) with either the classical [11] or the Wong–Sandler (WS) mixing rules [12]. The Wong–Sandler mixing rule was coupled with the Non-Random Two-Liquid (NRTL) activity coefficient model [13].

## 2. Experimental

### 2.1. Materials

Ethene (C<sub>2</sub>H<sub>4</sub>; CAS Number: 74-85-1) was supplied by Afrox (South Africa) with a certified purity of greater than 99.9% on a

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volume basis. Perfluoro-*n*-octane (C<sub>8</sub>F<sub>18</sub>; CAS Number: 307-34-6) was supplied by Apollo Scientific (England) with a certified purity of at least 99% by mass. The perfluoro-*n*-octane sample was characterized using density, refractive index, and vapour pressure measurements, and the purity checked using gas chromatography analysis. This was important to confirm that the perfluoro-*n*-octane was not comprised of a mixture of branched isomers. The density and refractive index were measured with a densimeter (Anton Paar; DMA 5000) and a refractometer (Bellingham & Stanley; Abbe 60LR) respectively. A Shimadzu GC-2010 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a Rtx-1 capillary column was used for the GC analysis. The chemical characterization and properties are presented in Table 1. Apart from degassing, the components were not further purified.

## 2.2. Apparatus

An apparatus based on the ‘static–analytic’ method was used to measure the isothermal VLE data. A schematic of the apparatus is shown in Fig. 1. The equilibrium cell is a second generation version of the low-volume equilibrium cell developed by Narasigadu et al. [14]. This updated design of the equilibrium cell follows the principles developed by Narasigadu et al. [14] but has improved mixing capabilities, and superior hermetic sealing for operation at high pressures. The shell of the equilibrium cell consists of a sapphire tube compressed and sealed with o-rings (nitrile for this work) between two stainless steel 316 flanges. The resultant capacity of the equilibrium chamber is approximately 15 ml. The capillary tube (having an outer diameter of 3 mm) of a single movable rapid on-line sampler-injector (ROLSI) [15] enters the equilibrium cell centrally through a threaded port in the top flange. Due to the low capacity of the equilibrium cell there is the potential for disturbance in the fluid volume (and hence equilibrium) with movement of the ROSLI capillary. This is compensated for by a 3 mm solid stainless steel 316 rod that enters through the bottom flange. The direction of travel of this solid rod follows that of the ROSLI capillary; this negates volume disturbances of the fluid within the equilibrium cell. Furthermore, the solid rod is also used as a central axis on which the internal mixing device rotates. The cell agitator consists of a polytetrafluoroethylene (PTFE) impellor that encloses a Neodymium ring magnet. This internal mixer rotates in unison with an external rotating Neodymium magnet driven by an overhead stirring device (Heidolph; model RZR 2020). The temperature and pressure within the equilibrium cell were measured by two 100 Ω platinum resistance thermometer (Pt100) probes and two

pressure transmitters (WIKA; 0–100 kPa; 0–25 MPa g) respectively. The signals of these instruments were recorded by a computer linked to a data acquisition unit (Agilent; HP34970A). Homogenous samples of both the liquid and vapour phases were withdrawn via the ROSLI and were analysed using a GC (Shimadzu; GC-2010) equipped with a TCD and a Rtx-1 capillary column using helium as the carrier gas. The ROSLI and the sample lines were temperature-regulated to ensure that the analysed samples were representative of the equilibrium chamber contents.

## 2.3. Calibrations

The Pt100 probes were calibrated against a reference temperature probe (WIKA Instruments; model CTH 6500). The pressure transmitters were calibrated against a standard pressure transmitter (WIKA Instruments; model CPT 6000; linearity ≤0.025% of the span). The response of the TCD of the GC was calibrated by injecting known volumes at known conditions (*T* and/or *P*) for both the liquid and gaseous components. A 0.5 μl liquid syringe (SGE) attached to a repeating adaptor was used for perfluoro-*n*-octane. The number of moles of perfluoro-*n*-octane were calculated from density data obtained from the National Institute of Standard and Technology (NIST) ThermoData Engine (TDE) [16]. Two gas-tight Hamilton syringes (250 and 50 μl), with the aid of a Chaney Adaptor, was used for ethene. The number of moles of ethene was calculated using the PR EoS. The TCD response for both components (Area vs. *n<sub>i</sub>*) was observed to be linear over the entire working range.

## 2.4. Experimental procedure

Before the equilibrium measurements were undertaken, the cell was cleaned with a solvent and was subjected to vacuum overnight at elevated temperatures; to ensure the removal of residual components potentially residing in the sealing media.

### 2.4.1. Vapour pressure

Perfluorooctane was charged into the evacuated equilibrium cell and degassed in situ. The temperature was increased monotonically, and the pressure and temperature of the fluid were recorded.

### 2.4.2. Vapour–liquid equilibrium

Perfluoro-*n*-octane was loaded into the equilibrium cell as described above, ethene was subsequently charged into the cell at the desired pressure to create the first mixture. The liquid phase was agitated at constant temperature until the pressure was stable. At equilibrium, the liquid and vapour phases were individually sampled using the ROSLI and the composition determined from the GC data. Multiple samples were analysed for each phase to check for repeatability. During sampling of both phases, an average for both the pressure and temperature values was recorded. To complete the entire phase envelope, the concentration of ethene in the mixture was increased, and similarly the pressure, temperature and composition data were recorded as abovementioned.

## 2.5. Experimental uncertainty

The expanded uncertainties (*U*) were expressed following the guidelines supplied by NIST [12]. The standard uncertainties, classified as either Type A or Type B, are displayed in Table 2. Where necessary, the uncertainties were combined using the law of propagation of uncertainty [17]. The expanded uncertainties were estimated by applying a coverage factor of 2; defining a level of confidence of approximately 95%. The expanded uncertainty on

**Table 1**  
Pure-component parameters and properties for ethene and perfluoro-*n*-octane.

	Ethene	Perfluoro- <i>n</i> -octane
Component characterization		
Supplier/purity (%)	Afrox/99.9 <sup>a</sup>	Apollo Scientific/99 <sup>b</sup>
GC peak area (%)	>99.9 <sup>c</sup>	>99 <sup>c</sup>
Liquid density @ 298 K	NA	$\rho_{\text{exp}} = 1.756$ ; $\rho_{\text{lit}} = 1.757^{\text{d}}$
Refractive index @ 293 K	NA	$\eta_{\text{exp}} = 1.268$ ; $\eta_{\text{lit}} = 1.270^{\text{e}}$
Critical properties and acentric factor <sup>f,g</sup>		
<i>T<sub>c</sub></i> (K)	282.3	502.2
<i>P<sub>c</sub></i> (MPa)	5.0418	1.478
$\Omega$	0.0866	0.5083

<sup>a</sup> On a volume basis.

<sup>b</sup> On a mass basis.

<sup>c</sup> Area percentage of component identified by gas chromatography using a thermal conductivity detector and a 30 m Rtx-1 RESTEK capillary column.

<sup>d</sup> Literature data for the liquid density of perfluoro-*n*-octane from NIST TDE [16].

<sup>e</sup> Literature data for the refractive index of perfluoro-*n*-octane from [23].

<sup>f</sup> Critical properties for ethene from REFPROP [24].

<sup>g</sup> Critical properties for perfluoro-*n*-octane from Aspen Plus V8.0 [18].

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