Phase equilibrium data for binary mixtures of carbon dioxide with {1,1,2,3,3,3-hexafluoro-1-propene or 2,2,3-trifluoro-3-(trifluoromethyl)oxirane} at temperatures between (233 and 273) K

Wayne Michael Nelson [*], Travis Pio Benecke, Deresh Ramjugernath

Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, 4041 Durban, South Africa

ABSTRACT

Isothermal vapour-liquid equilibrium data were measured for binary mixtures of carbon dioxide with either hexafluoropropylene or hexafluoropropylene oxide at five temperatures in the (233—273) K range. The experimental data presented in this manuscript supplement data which were previously measured at temperatures of 273 K and above. The data is required for the assessment of the operating conditions for a purification process for the production of high purity hexafluoropropylene oxide from a mixture of hexafluoropropylene and hexafluoropropylene oxide. The experimental *P-x-y* data were measured using an apparatus based on the "static-analytic" method. The experimental data were satisfactorily correlated using the Peng-Robinson Equation of State with the Mathias-Copeman alpha function.

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1. Introduction

Despite the negative perceptions of carbon dioxide (CO_2, or R744) as a greenhouse gas and its links with climate change, CO_2 is a versatile compound and has found many positive uses in industry; for example, as a chemical feedstock, solvent, and refrigerant [1]. 1,1,2,3,3,3-Hexafluoro-1-propene (hexafluoropropylene, HFP, or R1216) and 2,2,3-trifluoro-3-(trifluoromethyl)-oxirane (hexafluoropropylene oxide, or HFPO) are speciality fluorocarbons with important uses in the fluorochemical industry [2,3]. The interest in phase equilibria for the carbon dioxide + (HFP or HFPO) systems stems from the envisaged use of carbon dioxide as a stripping gas for the purification of HFPO from a mixture of HFP and HFPO [4]. We had previously undertaken measurements of isothermal vapour-liquid equilibrium (VLE) data for the binary systems of CO_2 + HFP and CO_2 + HFPO at (273 and 313) K [4]; no other VLE data on these studied systems are available in open literature. The data measured in this current study is to supplement the data measured in a previous study so as to obtain a better understanding of the phase behaviour at conditions below 273 K

[5]. The VLE data over a wide temperature range is required to assess the operating conditions for the purification unit. In open literature, phase equilibrium data involving mixtures of carbon dioxide with either perfluoroolefins or perfluoroepoxides are scarce. Phase behaviour of hydrocarbons and more specifically their perfluorinated counterparts with gases is interesting. For example, in regards to flue gas cleaning Gwinner et al. reported that per-fluorination of particular chemical families (i.e. esters, ethers, ketones, tertiary amines, and alkyl phosphates) leads to an increase in the solvent efficiency [6]. In this work, isothermal VLE data were measured for the binary systems of CO_2 + HFP and CO_2 + HFPO using an apparatus based on the 'static-analytic' method. The data were measured at five temperatures (273, 263, 253, 243, and 233) K. Accordingly, the data presented herein can be considered complementary to the abovementioned data, as the lower temperature range (273 K) is vastly extended (233 K). This is important, as currently, the Universal Quasi Chemical Functional-Group Activity Coefficients (UNIFAC) based predictive methods cannot be used to predict VLE, as the functional groups are not available for the description of HFP and HFPO [7]. The experimental VLE data were modelled using the Peng-Robinson (PR) Equation of State (EoS) incorporating the Mathias-Copeman (MC) alpha function [8,9].

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* Corresponding author.
  E-mail address: nelsonw@ukzn.ac.za (W.M. Nelson).

2. Experimental

2.1. Materials

Carbon dioxide (CO_2; CAS Number: 124-38-9) was supplied by Afrox (South Africa) with a certified purity of greater than 99.9%. Hexafluoropropylene (C_3F_6; CAS Number: 116-15-4) and hexafluoropropylene oxide (C_3F_6O; CAS Number: 428-59-1) were supplied by Pelchem with a specified purities of greater than 99%. The chemical characterization and properties are presented in Table 1. The components were not further purified, apart from degassing via periodic vapour withdrawal.

2.2. Apparatus

An apparatus based on the 'static-analytic' method was used to measure the isothermal VLE data. The apparatus has been previously discussed in detail [10,11]. A schematic of the apparatus is shown in Fig. 1. The core of the equilibrium cell consists of a sapphire tube compressed and sealed between two stainless steel (SS) 316 flanges, leading to an equilibrium chamber capacity of approximately 15 ml. The capillary tube of the rapid on-line sampler-injector (ROLSI) [12] enters the equilibrium cell via the top flange. To avoid disturbance in the fluid volume within the equilibrium chamber, a solid SS 316 rod (of same dimensions of the ROLSI capillary) enters through the bottom flange and follows the direction of travel of the ROLSI capillary tube. The solid rod is also used as a central axis for the rotation of the internal mixing device. 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 (Maxon; A-max). The temperature and pressure within the equilibrium cell were measured by two 100 Ω platinum resistance thermometer (Pt100) probes and a pressure transmitter (WIKA; 0–6 MPa gauge). The signals of these instruments were recorded using a computer linked to a data acquisition unit (Agilent; HP34970A). Homogenous samples of both the liquid and vapour phases were withdrawn via the ROLSI and were analysed using a gas chromatograph (GC) (Shimadzu; GC-2010) equipped with a thermal conductivity detector (TCD). The GC was equipped with a Porapak packed column (3 m in length; outer diameter of 3.14 mm, 50–80 mesh) and used helium as the carrier gas. The ROLSI and the sample lines were temperature-regulated to ensure that the analysed samples were representative of the equilibrium chamber contents.

Table 1
Pure-component parameters and properties for carbon dioxide (CO_2), hexafluoropropylene (HFP) and hexafluoropropylene oxide (HFPO).

	CO_2	HFP	HFPO
Component characterization			
Supplier/purity (%)[a]	Afrox/>99.9	Pelchem/>99	Pelchem/>99
GC peak area (%)[b]	>99.9	>99.8	>99.7
Critical properties and acentric factor[c]			
T_c (K)	304.13	358.9	359.3
P_c (MPa)	7.3773	3.136	2.931
ω	0.22394	0.3529	0.3338
Mathias-Copeman parameters (Peng-Robinson equation of state)			
$C_{1,i}$	0.7462	0.8302	0.8478
$C_{2,i}$	−0.9311	0.3709	0.0493
$C_{3,i}$	4.1279	−1.1024	0.1398

[a] Supplier purities on a volume basis.
[b] Area percentage of component identified by gas chromatography using a thermal conductivity detector and 3 m Porapak column.
[c] Properties for CO_2, HFP and HFPO from REFPROP V8.0 [16], Coquelet et al. [17]. and Dicko et al. [18]. respectively.

2.3. Calibrations

The Pt100 probes were calibrated against a reference temperature probe (WIKA Instruments; model CTH 6500). The pressure transmitter was calibrated against a standard pressure transmitter (WIKA Instruments; model CPT 6000; linearity $\leq$ 0.025% of the span). The response of the TCD of the GC was calibrated by injecting known volumes of each gas, using two gas-tight Hamilton syringes (250 and 50 μl) equipped with Chaney Adaptors. The number of moles of gas was calculated using the PR EoS. The TCD response for all components (TCD area vs. number of moles) was observed to be linear over the entire working range.

2.4. Experimental procedure

2.4.1. Vapour pressure
Prior to the equilibrium measurements, the cell was cleaned using a volatile solvent and was evacuated overnight. The evacuated equilibrium cell was pressurised with the respective pure component and the component degassed in situ. The pressure and temperature of the fluid were recorded in a stepwise manner by increasing the temperature monotonically from (233−273) K.

2.4.2. Vapour-liquid equilibrium
Either HFP or HFPO was loaded into the equilibrium cell as aforementioned. Carbon dioxide was subsequently charged into the cell at the desired pressure to create the first mixture. The mixture was agitated at constant temperature until the pressure had stabilised. At equilibrium, the liquid and vapour phases were individually sampled using the ROLSI and the composition determined by GC analysis. Multiple samples (at least seven) of each phase were analysed to ensure repeatability. During sampling of both phases, both the pressure and temperature values were recorded and averaged. To trace the entire phase envelope, the concentration of carbon dioxide in the mixture was increased (or at times decreased) in a stepwise manner, and similarly the pressure, temperature and composition data were recorded.

2.5. Experimental uncertainty

The expanded uncertainties (U) were expressed following the guidelines supplied by NIST [13]. Where necessary, the uncertainties were combined using the law of propagation of uncertainty. The standard uncertainties are listed in Table 2. The expanded uncertainties were estimated by applying a coverage factor of 2; defining a level of confidence of approximately 95%. The expanded uncertainties on average for temperature, pressure and both liquid and vapour phase compositions are $U(T) = 0.07$ K, $U(P) = 0.005$ MPa, $U(x_1) = 0.009$ and $U(y_1) = 0.003$ respectively.

2.6. Correlations

The experimental data were modelled following the phi-phi approach using the regression capabilities incorporated into Aspen Plus V8.0 [14]. The PR EoS was paired with the MC alpha function to improve the description of the pure-component vapour pressures. The PR EoS is:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \tag{1}$$

where V_m is the molar volume ($V_m = V/n$). The following mixing rules as utilized by Peng and Robinson [8] were used: