Isothermal Vapor−Liquid Equilibrium Data for the 1,1,2,3,3,3-Hexafluoroprop-1-ene +1,1,2,2,3,3,4,4-Octafluorocyclobutane Binary System: Measurement and Modeling from (292 to 352) K and Pressures up to 2.6 MPa

Francois J. Conradie,[†] Philippus L. Crouse,[†] Xavier Courtial,[‡] Wayne M. Nelson,*[,‡] Isaak J. van der Walt,[§] and Deresh Ramjugernath[‡]

[†]Fluoromaterials Science and Process Integration, Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa

[‡]Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Durban 4041, South Africa

[§]The South African Nuclear Energy Corporation Ltd, Pretoria, 0240, South Africa

ABSTRACT: Isothermal vapor−liquid equilibrium data are presented for the 1,1,2,3,3,3-hexafluoroprop-1-ene and 1,1,2,2,3,3,4,4-octafluorocyclobutane binary system at (292.89, 323.02 and 352.71) K, with pressures ranging from (0.3 to 2.6) MPa. The data were measured using an apparatus based on the "static-analytic" method, equipped with a single movable rapid online sampler-injector (ROLSI). The expanded uncertainties are estimated at 0.11 K, 4 kPa, 0.010 and 0.007 for the temperature, pressure, and the equilibrium liquid and vapor mole fractions, respectively. The experimental vapor−liquid equilibrium data were correlated using the Peng−Robinson equation of state with the Mathias−Copeman alpha function. The model provides a satisfactory description of the experimental data.
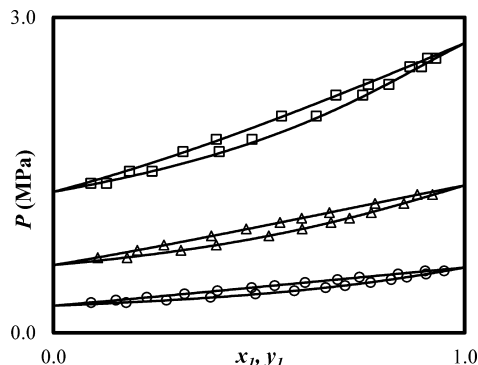
Introduction

Pyrolysis of polytetrafluoroethylene (PTFE) yields a multi-component gaseous mixture consisting of tetrafluoroethylene (TFE), hexafluoropropylene (R1216 or HFP), octafluorocyclobutane (RC318 or OFCB), and perfluoroisobutylene.[1] This depolymerization process can be run continuously, under specific conditions, to achieve high yields (>94%) of tetrafluoroethylene.[1] High grades of tetrafluoroethylene can thereafter be potentially obtained via conventional distillation. To understand the distillation process and design the distillation columns, accurate phase equilibrium data are a necessity. We have previously reported isothermal vapor−liquid equilibrium (VLE) data involving mixtures of tetrafluoroethylene with either hexafluoropropylene[2] or octafluorocyclobutane;[3] both systems were identified to be zeotropic and presented a minor deviation from Raoult's law over the temperature range studied. In this study, isothermal VLE data for the hexafluoropropylene + octafluorocyclobutane binary system have been measured at three temperatures from (292.89 to 352.71) K. The VLE data were measured with an apparatus based on the "static-analytic" method, using an equilibrium cell featuring a single movable rapid online sampler-injector (ROLSI).[4] To the best of our knowledge there is no VLE data which has previously been published in open literature for the R1216 + RC318 binary system. Thus, the VLE data presented herein constitutes new data. The new isothermal VLE data were well correlated by the

Peng−Robinson (PR)[5] equation of state (EoS) incorporating the Mathias−Copeman alpha function.[6]

Experimental Section

Materials. Both R1216 (C_3F_6) and RC318 (c-C_4F_8) were produced in-house at The South African Nuclear Energy Corporation (NECSA). The critical temperatures (T_c), critical pressures (P_c) and acentric factors, obtained from literature[7,8] as well as the Chemical Abstract Service (CAS) numbers, and purities as stated by the suppliers are listed in Table 1. All components were degassed via periodic vapor withdrawal. No significant impurities, beyond the manufacturer-stated chemical purities, were identified via gas chromatography.

Experimental Apparatus. The experimental isothermal VLE data were measured using an apparatus based on the "static-analytic" method. The principle of the apparatus is similar to that described by Laugier and Richon.[9] The apparatus has been described in our previous works.[2,3,10] In brief, the apparatus consists of a stainless steel equilibrium cell (approximately 40 cm^3) with two sapphire viewing windows and a movable ROLSI which was used to individually withdraw samples of the liquid and vapor phases at equilibrium. The mixture within the equilibrium cell was agitated via an internal magnetic stirrer bar. The temperature of the equilibrium cell was controlled by submerging the cell into a thermo-regulated solution. The pressure and temperature within the

Table 1. Critical Properties and Other Relevant Information for the Materials and the Mathias−Copeman Parameters for the Pure Components

component	CAS no.	purity[a]	critical properties			Mathias−Copeman coefficients[b]		
			T_c/K	P_c/MPa	ω	c_1	c_2	c_3
R1216[2,8]	116-15-4	0.999	358.9	3.136	0.3529	0.9188	−0.8018	3.8497
RC318[3,7]	115-25-3	0.997	388.4	2.777	0.3560	0.8542	0.4006	−0.2659

[a]Supplier purity (mole fraction) stated by the South African Nuclear Energy Corporation. [b]Mathias−Copeman coefficients regressed from the vapor pressure data available in literature.[2,3]

equilibrium cell were measured by a single (0 to 10) MPa gauge pressure transmitter (WIKA; model P-10) and two 100 Ω platinum resistance (Pt100) thermometer probes (WIKA; 1/10 DIN) respectively. Pressure and temperature outputs were transferred to an Agilent Data Acquisition Unit (34970A) which was connected to a desktop computer enabling the collection of real-time pressure and temperature data. Homogenous samples that were withdrawn from the equilibrium cell by the ROLSI were transferred directly to a Shimadzu G-17A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The GC was equipped with a Porapak Q column (length, 3 m; diameter, $^1/_8$ in., 80/100 mesh).

The (0 to 10) MPa pressure transmitter (WIKA; model P-10) was calibrated against a reference pressure transmitter connected to a digital calibrator multimeter (WIKA; model CPH 6000). The two Pt-100 probes were calibrated against a reference probe (WIKA; model CTH 6500). The response of the TCD was calibrated by injecting known amounts of each pure component into the GC using gastight syringes (SGE). The temperature and pressure of the injected gas were assumed to be equal to those measured at the outlet port of the gas cylinder. The accuracy of these assumptions is accounted for in the estimation of the expanded uncertainty for molar composition. The number of moles for the injected gas were estimated by the ideal gas equation ($n = PV/RT$).

Experimental Procedure. The equilibrium cell and associated loading lines were evacuated prior to the addition of the heavier component (RC318). This was undertaken to ensure the removal of residual components potentially retained in the sealing media of the equilibrium cell. RC318 was subsequently charged into the equilibrium cell and degassed in situ via periodic vapor withdrawal. The lighter component (R1216) was thereafter charged into the cell, corresponding to the desired pressure of the first equilibrium mixture. To ensure attainment of thermodynamic equilibrium the mixture was agitated at constant temperature for a period of at least 30 min, and thereafter it was ensured that the respective pressure and temperature profiles of the mixture were stable (within the reported experimental uncertainty) for at least 10 min. At equilibrium, samples of both the liquid and vapor phase were individually withdrawn via the ROLSI, and composition was analyzed using the GC. At least five samples of each phase were withdrawn to ensure measurement repeatability. Successive equilibrium mixtures were obtained by increasing the overall R1216 content within the equilibrium cell.

Experimental Uncertainty. The guidelines for the estimation of experimental uncertainty are available from the National Institute of Standards and Technology (NIST).[11] The combined uncertainty for either the pressure or temperature measurements

was evaluated by including the maximum error resulting from the calibration polynomial and the errors intrinsic to the reference instrument. The combined uncertainty for composition was evaluated by including errors from the calibration polynomial, potential errors in pressure, volume and temperature inherent to the direct injection technique following *the law of propagation of errors*,[11,12] and the repeatability of samples withdrawn from each phase at equilibrium.[2] The standard uncertainties for each of these aforementioned items are listed in Table 2. The combined

Table 2. Standard Uncertainties, u, of Pressure, P, Temperature, T, Volume, V, and Mole Numbers, n, Influencing the Measurands of this Work

source of uncertainty	estimated value	distribution	influenced parameter
standard pressure transmitter [kPa]	0.2	rectangular	P
standard temperature probe [K]	0.03	rectangular	T
correlation for P [kPa]	3.5	rectangular	P
correlation for T [K]	0.09	rectangular	T
correlation for n_i of RC318	2.5 %	rectangular	n_i, x_i, y_i
correlation for n_i of R1216	2.0 %	rectangular	n_i, x_i, y_i
correlation for n_i of RC318 (dilute region)	3.0 %	rectangular	n_i, x_i, y_i
correlation for n_i of R1216 (dilute region)	3.0 %	rectangular	n_i, x_i, y_i
V of injected gas from syringe[a]	2 %	rectangular	n_i, x_i, y_i
T of injected gas from syringe[a] [K]	2	rectangular	n_i, x_i, y_i
P of injected gas from syringe[a] [kPa]	1	rectangular	n_i, x_i, y_i
average repeatability of x_1	$\sigma = 0.002$	Gaussian	x_i, y_i
average repeatability of y_1	$\sigma = 0.002$	Gaussian	x_i, y_i

[a]Uncertainties inherent to the direct injection method, estimated from the ideal gas law.

uncertainty in the relative volatility was estimated using the combined standard uncertainties calculated for composition in both the liquid and vapor phases, following *the law of propagation of errors*. A coverage factor, $k = 2$, was applied to calculate the expanded uncertainties. The combined expanded uncertainty on average for temperature, pressure and both the liquid and vapor phase compositions are $U(T) = 0.11$ K, $U(P) = 0.004$ MPa, $U(x_1) = 0.010$, and $U(y_1) = 0.007$, respectively.

Correlations

The experimental data were correlated using the data regression tools available in Aspen Plus version 8.0 following the phi-phi method.[13] Vapor pressure data for R1216 and RC318 from our previous works and the isothermal VLE data were regressed using the Peng−Robinson equation of state with the Mathias−Copeman alpha function. The single binary interaction parameter (k_{12}) of the Peng−Robinson equation of state was fitted to the experimental $P−x−y$ data using the Britt-Luecke algorithm

(rigorous maximum likelihood method) to minimize an ordinary least-squares type objective function (minimizing the sum of the pressure and vapor phase composition residuals for isothermal data).[14] The quality of the data fit was statistically evaluated using the average absolute deviation (AAD), average absolute relative deviation (AARD), and the Bias. The AAD is defined as

$$\text{AAD}\ (\overline{\theta}) = \frac{1}{N_p} \sum_{N_p}^{1} |\overline{\theta}_{\text{exp}} - \overline{\theta}_{\text{calc}}| \tag{1}$$

where $\overline{\theta}_{\text{exp}}$ and $\overline{\theta}_{\text{calc}}$ are the experimental and calculated values of a measurand $\overline{\theta}$ (in this case P and y_1), and N_p is the total number of data points. The AARD and Bias are defined as

$$\text{AARD}\ (\overline{\theta}) = \frac{1}{N_p} \sum_{N_p}^{1} \frac{|\overline{\theta}_{\text{exp}} - \overline{\theta}_{\text{calc}}|}{\overline{\theta}_{\text{exp}}} \tag{2}$$

$$\text{Bias}\ (\overline{\theta}) = \frac{1}{N_p} \sum_{N_p}^{1} \frac{\overline{\theta}_{\text{exp}} - \overline{\theta}_{\text{calc}}}{\overline{\theta}_{\text{exp}}} \tag{3}$$

Table 3. Experimental Pressure, P, Liquid Phase Composition, x, and Vapor Phase Composition, y, Data for the Binary System R1216 (1) + RC318 (2) at Temperatures, T = (292.89, 323.02 and 352.71) K, Including the Expanded Uncertainties, U[a] (k = 2)

P/MPa	x_1	y_1	$U(x_1)$	$U(y_1)$
T/K = 292.89				
0.286	0.092	0.177	0.005	0.006
0.309	0.152	0.275	0.007	0.008
0.336	0.227	0.382	0.009	0.009
0.368	0.319	0.491	0.012	0.010
0.397	0.399	0.586	0.013	0.009
0.428	0.482	0.662	0.013	0.009
0.447	0.538	0.709	0.013	0.008
0.477	0.612	0.771	0.013	0.007
0.504	0.691	0.821	0.011	0.006
0.528	0.744	0.859	0.010	0.005
0.558	0.838	0.906	0.007	0.004
0.588	0.904	0.950	0.006	0.003
T/K = 323.02				
0.713	0.108	0.179	0.005	0.006
0.783	0.204	0.310	0.009	0.008
0.833	0.269	0.396	0.011	0.009
0.921	0.384	0.524	0.013	0.010
0.986	0.469	0.605	0.013	0.009
1.047	0.551	0.675	0.013	0.009
1.089	0.604	0.720	0.013	0.008
1.142	0.671	0.773	0.012	0.007
1.228	0.782	0.852	0.009	0.005
1.313	0.885	0.922	0.006	0.003
T/K = 352.71				
1.419	0.091	0.129	0.005	0.005
1.534	0.185	0.240	0.008	0.007
1.722	0.315	0.403	0.012	0.010
1.839	0.396	0.483	0.013	0.010
2.06	0.555	0.639	0.013	0.009
2.258	0.687	0.752	0.012	0.008
2.361	0.766	0.816	0.010	0.006
2.528	0.867	0.895	0.007	0.004
2.609	0.910	0.930	0.005	0.004

[a]$U(T) = 0.11$ K, $U(P) = 4$ kPa.

Results and Discussion

The experimental $P−x−y$ data for the R1216 + RC318 binary system, measured at three temperatures from (292.89 to 352.71) K, are presented in Table 3 and Figure 1.
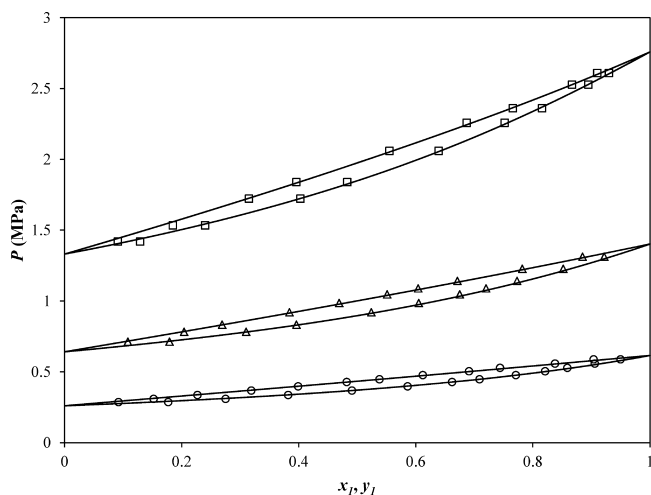

Figure 1. Plot of the $P−x−y$ data for the R1216 (1) + RC318 (2) binary system ($\bigcirc$, $T = 292.89$ K; $\triangle$, $T = 323.02$ K; $\square$, $T = 352.71$ K). The solid black line represents the modeled data using the Peng−Robinson equation of state.

This relatively close-boiling binary mixture presents quasi-ideal VLE behavior over the measured temperature range. Thus, the data should be accurately portrayed by a relatively simple model. The mixture presents a minor deviation from Raoult's law. Similar behavior were previously identified in the phase behavior for binary mixtures of tetrafluoroethylene with either hexafluoropropylene[2] or octafluorocyclobutane.[3] The VLE data were regressed using the PR EoS with the MC alpha function. A single binary interaction parameter, $k_{ij} = 0.002$, was regressed to all isotherms simultaneously. The model parameters as well as the statistical analysis of the data are listed in Table 4. On average, for all temperatures, an AAD

Table 4. Deviations between the Experimental and Model Data Using the Peng−Robinson Equation of State for the R1216 (1) + RC318 (2) Binary System at (292.89, 323.02 and 352.71) K

model parameters[a]		AAD[b]		AARD[c]		Bias[d]	
T/K	k_{12}	P/MPa	y_1	P %	y_1 %	P %	y_1 %
292.89	0.002	0.003	0.003	0.88	0.62	−0.24	−0.32
323.02	0.002	0.007	0.005	0.68	0.93	0.13	−0.93
352.71	0.002	0.013	0.004	0.75	1.36	−0.45	−1.09

[a]Data modeled using the Peng−Robinson equation of state (Mathias−Copeman alpha function). [b]Absolute average deviation (AAD) of a measurand $\overline{\theta}$: AAD $(\overline{\theta}) = 1/N_P \sum_1^{N_P} |\overline{\theta}_{\text{exp}} - \overline{\theta}_{\text{calc}}|$. [c]Absolute average relative deviation (AARD) of a measurand $\overline{\theta}$: AARD $(\overline{\theta}) = 1/N_P \sum_1^{N_P} (|\overline{\theta}_{\text{exp}} - \overline{\theta}_{\text{calc}}|)/\overline{\theta}_{\text{exp}}$. [d]Bias of a measurand $\overline{\theta}$: Bias $(\overline{\theta}) = 1/N_P \sum_1^{N_P} (\overline{\theta}_{\text{exp}} - \overline{\theta}_{\text{calc}})/\overline{\theta}_{\text{exp}}$.

of 0.008 MPa and 0.004 was observed for the pressure and vapor phase compositions, respectively. This equates to an AARD of 0.77% and 0.97% for the pressure and vapor phase compositions, respectively. The VLE data for the 352.71 K isotherm presents the highest deviations for both pressure and

vapor phase compositions. The single binary interaction parameter regressed over all isotherms simultaneously, provide a decent representation of the VLE data from (292.89 to 352.71) K; in the absence of isobaric VLE data, such parameters are highly useful for process design of equilibrium stage separation processes. The relative volatility is a critical parameter in assessing the feasibility of a separation process via distillation. A plot of the variance in the relative volatility with composition for each isotherm is shown in Figure 2. As expected the relative volatility decreases with an increase in temperature. Furthermore, it is observed that the relative volatility is slightly suppressed with an increase in the overall R1216 content.
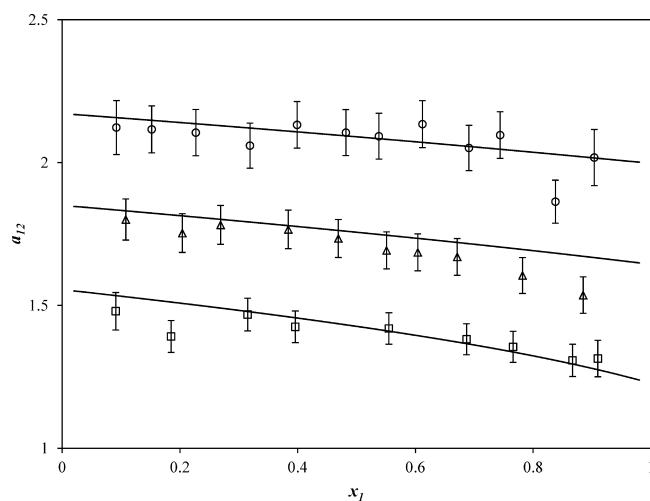

Figure 2. Plot of the composition dependence of the relative volatility for the R1216 (1) + RC318 (2) binary system (O, T = 292.89 K; $\triangle$, T = 323.02 K; $\square$, T = 352.71 K). The solid black line represents the modeled data (PR EoS). Error bars are presented for the relative volatility only.

Conclusions

New VLE data have been measured using a "static-analytic" method for the binary system 1,1,2,3,3,3-hexafluoroprop-1-ene and 1,1,2,2,3,3,4,4-octafluorocyclobutane at three different temperatures; (292.89, 323.02, and 352.71) K. The expanded uncertainties for temperature, pressure, and both the liquid and vapor phase compositions were estimated on average as $U(T)$ = 0.11 K, $U(P)$ = 0.004 MPa, $U(x)$ = 0.010, and $U(y)$ = 0.007, respectively. The experimental VLE data were observed to be zeotropic and were correlated using Peng−Robinson equation of state with the Mathias−Copeman alpha function.

Author information

Corresponding Author
*E-mail: nelsonw@ukzn.ac.za. Tel.: +27 31 2603121. Fax: +27 31 2601118.

Notes
The authors declare no competing financial interest.

References

(1) Walt, J. V. D.; Bruinsma, O. S. L. Depolymerization of clean unfilled PTFE waste in a continuous process. *J. Appl. Polym. Sci.* **2006**, *102* (3), 2752−2759.

(2) Conradie, F. J.; Crouse, P. L.; Courtial, X.; Nelson, W. M.; van der Walt, I. J.; Ramjugernath, D. Isothermal Vapor−Liquid Equilibrium Data for the 1,1,2,2-Tetrafluoroethene + 1,1,2,3,3,3-Hexafluoroprop-1-ene Binary System: Measurement and Modeling from (248 to 283) K. *J. Chem. Eng. Data* **2014**, *59*, 82−88.

(3) Conradie, F. J.; Crouse, P. L.; Courtial, X.; van der Walt, I. J.; Ramjugernath, D. Isothermal Vapor−Liquid Equilibrium Data for the 1,1,2,2-Tetrafluoroethene + 1,1,2,2,3,3,4,4-Octafluorocyclobutane Binary System: Measurement and Modeling from (248 to 283) K. *J. Chem. Eng. Data* **2012**, *57*, 1978−1983.

(4) Guilbot, P.; Valtz, A.; Legendre, H.; Richon, D. On Line Sampler-Injector, a Reliable Tool for HT-HP Sampling and on Line GC Analysis. *Analusis* **2000**, *28*, 426−431.

(5) Peng, D. Y.; Robinson, D. B. A New Two Parameter Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

(6) Mathias, P. M.; Copeman, T. W. Extension of the Peng−Robinson Equation of State to complex mixtures: Evaluation of various forms of the local composition concept. *Fluid Phase Equilib.* **1983**, *13*, 91−108.

(7) Daubert, T. E. *Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation*; Taylor & Francis: Washington, D.C, 1997.

(8) Coquelet, C.; Ramjugernath, D.; Madani, H.; Valtz, A.; Naidoo, P.; Meniai, A. H. Experimental Measurement of Vapor Pressures and Densities of Pure Hexafluoropropylene. *J. Chem. Eng. Data* **2010**, *55*, 2093−2099.

(9) Laugier, S.; Richon, D. New Apparatus to Perform Fast Determinations of Mixture Vapor−Liquid Equilibria up to 10 MPa and 423 K. *Rev. Sci. Instrum.* **1986**, *57*, 469−472.

(10) Subramoney, S. C.; Courtial, X.; Naidoo, P.; Coquelet, C.; Richon, D.; Ramjugernath, D. Isothermal Vapor−Liquid Equilibrium Data for the Ethylene + 1,1,2,3,3,3-Hexafluoro-1-propene Binary System between 258 and 308 K at Pressures up to 4.56 MPa. *Fluid Phase Equilib.* **2013**, *353*, 7−14.

(11) Taylor, B. N.; Kuyatt, C. E. *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. NIST Technical Note 1297*; National Institute of Standards and Technology: Gaithersburg, MD, 1994.

(12) Taylor, B. N.; Mohr, P. J.; Douma, M. *The NIST Reference on Constants, Units, And Uncertainty*; National Institute of Standards and Technology: Gaithersburg, MD, 2007; www.physics.nist.gov/cuu/index.html.

(13) *Aspen Plus*, version 8.0; Aspen Technology: Massachusetts, USA, 2010.

(14) Britt, H. I.; Luecke, R. H. The Estimation of Parameters in Nonlinear, Implicit Models. *Technometrics* **1973**, *15*, 233−238.