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Vapour-Liquid Equilibrium Data Measurement and Modelling for the Methane + Perfluorohexane System from 293.39 to 333.38 K

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ABSTRACT

This study presents vapour-liquid equilibrium (VLE) data for the methane + perfluorohexane system across five isotherms (293.39 to 333.38) K with pressures up to 6.669 MPa. The experimental data were obtained via a “static-analytical” based setup incorporating a Rapid Online Sampler Injector (ROLSI) for sampling of equilibrium phases and a gas chromatograph (GC) for analysing phase composition. Expanded uncertainties for temperature (T), pressure (P) and phase compositions (x , y) are estimated within 0.07 K, 0.011 MPa, and (0.020, 0.030), respectively. The experimental VLE data were regressed via the direct method using both the Peng–Robinson (PR) and the Soave–Redlich–Kwong (SRK) equations of state. In each case, the Mathias–Copeman alpha function was employed, and the calculations were performed using either the Wong–Sandler or the predictive SRK (PSRK) mixing rule in combination with the NRTL activity coefficient model. The model parameters were refined using a simplex algorithm optimized through the flash calculation objective function. The calculated average absolute deviation (AAD_{xy}) and bias ($Bias_{xy}$) values between the measured data and the models were both below 4%, indicating satisfactory data regression. Comparative analysis of the $CO_2 + C_6F_{14}$, $C_2H_6 + C_6F_{14}$ and $CH_4 + C_6F_{14}$ systems highlights C_6F_{14} 's strong selectivity as a physical solvent for C_2H_6 and CO_2 over CH_4 .

INTRODUCTION

Phase equilibrium studies are crucial for designing efficient separation processes. For gas absorption systems aimed at combating climate change by capturing solutes in solvents, it is essential to investigate phase equilibrium for systems involving potential solvents and individual components of flue gas. This study contributes to a broader investigation into the use of perfluorocarbons, ranging from C_4 to C_{16} , as physical solvents for flue gas cleaning applications.

Perfluorocarbons (PFCs) exhibit unique properties stemming from the strength of their carbon–fluorine bonds, which confer atypical chemical and thermal stability. The high gas absorption capability of PFCs, combined with their physicochemical properties, highlights their potential as physical solvents for industrial processes. Beyond their potential solvent capability, perfluorocarbons have diverse applications across multiple sectors, i.e., in medicine, they serve as gas carriers, blood substitutes, ultrasound contrast agents, surfactants, and anaesthetics; in refrigeration, they are used as environmentally safer alternatives to ozone-depleting substances like chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs); and in the semiconductor industry, they function as etching agents and dielectric fluids^{1–3}.

Previous work has successfully measured and thermodynamically modelled the VLE data of binary systems composed of C_4F_{10} + (CO_2 , C_2H_6 , NO , CO , CH_4 , H_2S , N_2 or O_2) and C_6F_{14} + (CO_2 , H_2S , C_2H_6 or CO) with findings reported in the open literature^{4–11}.

This study focuses on the VLE data for the CH_4 (1) + C_6F_{14} (2) system. The measured VLE data were obtained at five isotherms (293.39, 303.40, 313.39, 323.41 and 333.38) K via a static-analytical apparatus with phase sampling and composition analysis via a ROLSI and a GC, respectively. These data were modelled using the phi-phi approach. In which both the PR¹² and the SRK¹³ equations of state were used with the MC alpha function¹⁴, together with either the Wong-Sandler¹⁵ or the predictive SRK¹⁶ mixing rule and the NRTL activity coefficient model¹⁷, yielding successful results. The resulting parameters were adjusted via the flash calculation objective function. A comprehensive literature review confirms that the VLE data measurements and modelling for the CH_4 (1) + C_6F_{14} (2) system within the investigated conditions, have not been previously reported.

Experimental and /or Computational Methods

Chemical components

The primary chemical components investigated in this study are methane and perfluorohexane, both supplied at sufficient purity levels, requiring no additional purification other than in-situ degassing. Table 1 provides the supplier details, critical properties, and acentric factors of these components.

Table 1. Supplier details, critical properties and acentric of methane^a and perfluorohexane^a

component	CAS number	supplier	volume fraction	T _c /K	P _c /MPa	ω
Methane	74-82-8	Afrox	0.9950	190.60	4.600	0.008
Perfluorohexane	355-42-0	Across Organic	0.9800	451.70	1.905	0.494

^aProperty values taken from ref. 18

Experimental Apparatus

The setup used for VLE data measurements employs the static-analytical method and has been thoroughly detailed in previous works by Narasigadu¹⁹ and Tshibangu et al.²⁰. Its reliability was validated through prior measurements of vapour pressure data for C₂ H₆ and VLE data for the ethane + perfluorobutane system of El Ahmar et al.⁵ reported by Tshibangu et al.¹¹. In summary, the setup features a 17.4 cm³ cylindrical sapphire equilibrium cell, equipped with a charge/discharge valve and a stirring mechanism to ensure thorough mixing and rapid equilibrium of the components. The cell is submerged in a temperature-controlled liquid bath to maintain isothermal conditions.

Measurement of temperature inside the cell was achieved via two class A ceramic bulb WIKA temperature sensors (RER Pt-100 Ω), strategically positioned in the flanges at locations of the liquid and vapour phases. These sensors were regularly calibrated against a WIKA standard probe (Pt-100 Ω). The expanded temperature uncertainties were estimated to be within 0.07 K.

Measurement of pressure inside the cell was achieved via a WIKA P-10 pressure transducer ranging from 0 – 25 MPa. Periodic calibration of the transducer was performed using a

WIKA CPT 6000 standard pressure transducer. The expanded pressure uncertainties were estimated at 11 kPa.

Real-time logging of temperature and pressure data was facilitated by a computer connected to an Agilent 3497A data acquisition system.

Phase equilibrium sampling was carried out using a ROLSI sampler and compositional analysis was conducted using a Shimadzu GC-2014 GC equipped with a thermal conductivity detector (TCD). Separation of components in the GC was accomplished via a packed column (Porapak Q). The TCD calibration was intermittently achieved via direct injection of known amounts of each component of the binary system using gastight syringes (SGE-type). Expanded uncertainties in the computed phase composition were estimated within 0.02 mole fraction for the liquid phase and 0.03 mole fraction for the vapour phase.

Experimental Procedure

Measurement of VLE data was conducted following the procedure detailed by Narasigadu¹⁹ and Tshibangu et al.²⁰. The reliability of this procedure was previously validated through the successful reproduction of the vapour pressure data of ethane and the VLE data for the ethane + perfluorobutane system of El Ahmar et al.⁵, as reported by Tshibangu et al.¹¹. A summary of the procedure is as follows:

Before initiating measurement, the cell with its auxiliary lines was thoroughly flushed with ethanol to remove any trace impurities. Perfluorohexane, the component with lower volatility, was charged into the cell using a gastight syringe (SGE-type). The equilibrium cell was thereafter submerged in a temperature-controlled liquid bath, maintained at 293.39 K, value corresponding to the first isotherm, using a mechanical jack.

In-situ degassing of the perfluorohexane was conducted to eliminate any volatile impurities before proceeding with VLE data measurements. Methane, component with higher volatility, was incrementally charged into the cell until the desired pressure for each VLE data point was achieved. The cell contents were left to reach thermodynamic equilibrium under vigorous stirring, as indicated by unchanged internal temperature and pressure readings for at least 10 minutes. At equilibrium, the stirring speed was reduced to prevent entrainment of the components into the ROLSI capillary used for sampling. The ROLSI capillary was positioned either in the liquid or vapour phase for sampling reasons. The capillary was initially purged multiple times to ensure it was clear of any residual material before sampling. Five samples

were withdrawn from each phase, ensuring a repeatability margin of no more than 1%, and these samples were analyzed using a gas chromatography.

The same procedure was applied to each data point along the isotherm. Due to pressure limitations of the methane cylinder, VLE measurements could not be conducted at pressures exceeding 7 MPa. Prior to measuring the subsequent isotherm, the experimental cell was evacuated, and the full experimental procedure was restarted.

DATA REDUCTION

Regression of experimental VLE data was carried out with Thermopack, a software developed in-house at MINES, PSL University. The regression was performed using the homogeneous phi - phi approach, in which both the PR and the SRK EoS were used to compute both the liquid and vapour phase fugacities. In this approach, each equation of state was used in conjunction with the MC alpha function and the Wong-Sandler or the PSRK mixing rule, which incorporates the NRTL activity coefficient model. These combinations (PR-MC-WS-NRTL and SRK-MC-PSRK-NRTL), generate four adjustable parameters: three NRTL parameters (g_{12} - g_{22} , g_{21} - g_{11} , α_{ij}) and one binary interaction parameter (k_{ij}). The NRTL nonrandomness parameter (α_{ij}) was fixed at 0.3, which is consistent with the recommendation of Renon and Prausnitz²¹, to simplify parameter optimization while maintaining accurate phase equilibrium modelling.

The model parameters were adjusted through a simplex algorithm using the flash calculation objective function expressed as:

$$FC = \frac{100}{N} \left[\sum_1^N \left(\frac{x_{exp} - x_{cal}}{x_{exp}} \right)^2 + \sum_1^N \left(\frac{y_{exp} - y_{cal}}{y_{exp}} \right)^2 \right] \quad (1)$$

where FC denotes the objective function minimized during data regression; N is the total number of measurements; x_{exp} and x_{cal} are the experimental and computed liquid mole fractions, while y_{exp} and y_{cal} correspond to the experimental and computed vapour mole fractions, respectively.

Each measured isotherm was individually regressed and then all measured isotherms were collectively regressed to determine temperature-dependent parameters. These parameters are

essential for predicting isotherms that were not measured, which are useful in the conceptual design of unit operations.

To assess how well the selected models (the PR-MC-WS-NRTL or the SRK-MC-PSRK-NRTL) fit the experimental VLE data, the bias and average absolute deviation (AAD) were computed for both the liquid and vapour phase mole fractions. These metrics are defined below.

$$\text{Bias (\%)} = (100/N) \sum \left((U_{\text{exp}} - U_{\text{cal}}) / U_{\text{exp}} \right) \quad (2)$$

$$\text{AAD(\%)} = (100/N) \sum |U_{\text{cal}} - U_{\text{exp}}| \quad (3)$$

where N represents the total measurements, and U denotes the mole fraction of component, taken either in the liquid phase (x_1) or in the vapour phase (y_1).

The relative volatility (α_{ij}) between methane and perfluorohexane was determined using the expression shown below.

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i / x_i}{y_j / x_j} = \frac{y_i / x_i}{(1 - y_i) / (1 - x_i)} \quad (4)$$

where K refers to the equilibrium constant. y_i and y_j represent the vapour-phase mole fractions of component i and j , while x_i and x_j are their corresponding mole fractions in the liquid phase.

RESULTS AND DISCUSSION

Vapour pressure measurements for methane and perfluorohexane have been previously undertaken. The MC alpha function parameters associated with the PR and the SRK EoS for perfluorohexane were obtained from Tshibangu et al.¹⁰, while those for methane were sourced from Coquelet et al.²². All MC parameter values are summarized in Table 2.

Table 2. Mathias-Copeman parameters for the CH₄ and C₆F₁₄

component	PR EoS			SRK EoS		
	C_1	C_2	C_3	C_1	C_2	C_3
methane ^a	0.416	-0.173	0.348	0.549	-0.409	0.603
perfluorohexane ^b	1.108	-0.408	1.258	1.262	-0.351	0.389

^aObtained from Ref.22 . ^bObtained from Ref.10

VLE data for the CH₄ (1) + C₆F₁₄ (2) binary system were measured at five isotherms, as presented in Table 3. These data were subsequently regressed using the PR-MC-WS-NRTL and the SRK-MC-PSRK-NRTL models. Figure 1- 6 compare the regressed and the measured data.

Table 3. Measured VLE data for CH₄ (1) + C₆F₁₄ (2) system at five isotherms

P / MPa	x_1	y_1
T / K = 293.39		
0.403	0.018	0.921
0.704	0.039	0.959
1.000	0.059	0.970
1.378	0.080	0.978
1.889	0.109	0.982
2.500	0.143	0.984
3.163	0.178	0.986
3.766	0.209	0.987
4.322	0.236	0.988
4.864	0.261	0.988
5.529	0.291	0.987
6.292	0.321	0.987
T / K = 303.40		
0.416	0.015	0.87
0.723	0.034	0.918
1.031	0.053	0.956
1.417	0.074	0.964
1.937	0.101	0.974
2.556	0.134	0.978
3.263	0.172	0.979
3.853	0.201	0.982
4.424	0.228	0.982
4.97	0.255	0.982
5.634	0.284	0.981

6.409

0.321

0.982

T / K = 313.39

0.434	0.015	0.815
0.752	0.032	0.895
1.057	0.048	0.935
1.459	0.074	0.948
1.985	0.103	0.957
2.622	0.135	0.974
3.335	0.171	0.973
3.943	0.201	0.975
4.520	0.228	0.976
5.072	0.252	0.975
5.742	0.282	0.975
6.463	0.314	0.975

T / K = 323.41

0.457	0.015	0.735
0.785	0.030	0.871
1.089	0.050	0.908
1.503	0.072	0.934
2.088	0.105	0.949
2.689	0.135	0.957
3.423	0.171	0.959
4.032	0.201	0.966
4.616	0.228	0.966
5.171	0.252	0.967
5.845	0.282	0.967
6.561	0.311	0.966

$T / \text{K} = 333.38$

1.134	0.050	0.674
2.096	0.103	0.925
2.770	0.136	0.940
3.512	0.172	0.949
4.114	0.201	0.954
4.701	0.227	0.955
5.278	0.253	0.956
5.964	0.283	0.956

x_i, y_i : liquid and vapour mole fraction; Expanded uncertainty: $U(T) = 0.07 \text{ K}$ ($k = 2$); $U(P) = 0.011 \text{ MPa}$ ($k = 2$); $U(x_i) = 0.02$ ($k = 2$) and $U(y_i) = 0.03$ ($k = 2$).

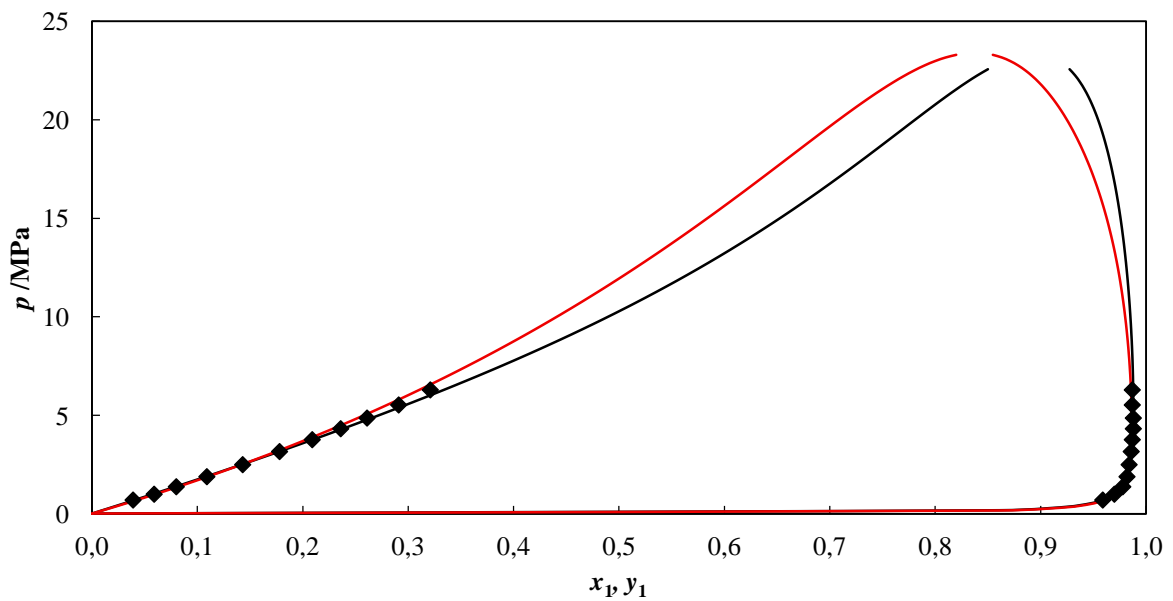


Figure 1. VLE data (P - x - y phase diagram) for the binary system: CH_4 (1) + C_6F_{14} (2). Measured VLE data: \blacklozenge , 293.39 K; Model: —, PR-MC-WS-NRTL; —, SRK-MC-PSRK-NRTL.

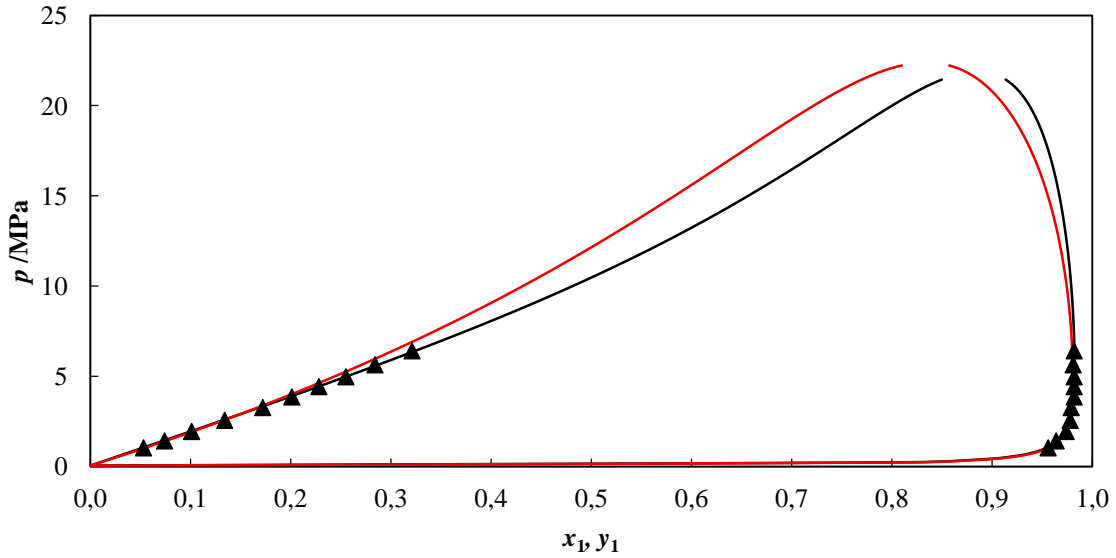


Figure 2. VLE data (P - x - y phase diagram) for the binary system: CH_4 (1) + C_6F_{14} (2). Measured VLE data: \blacktriangle , 303.40 K; Model: —, PR-MC-WS-NRTL; —, SRK-MC-PSRK-NRTL.

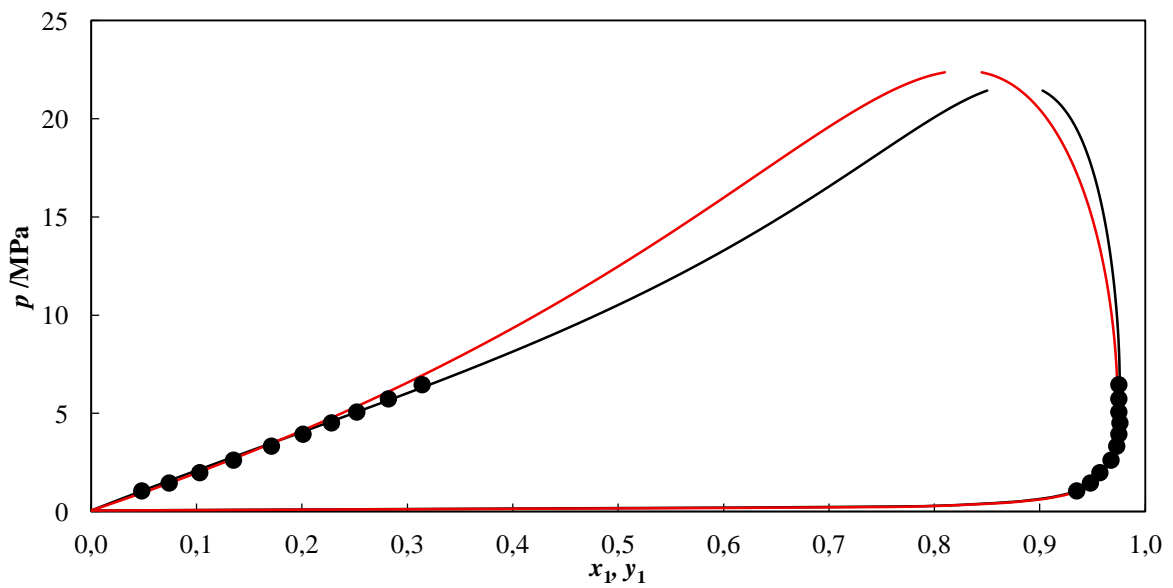


Figure 3. VLE data (P - x - y phase diagram) for the binary system: CH_4 (1) + C_6F_{14} (2). Measured VLE data: \bullet , 313.39 K; Model: —, PR-MC-WS-NRTL; —, SRK-MC-PSRK-NRTL.

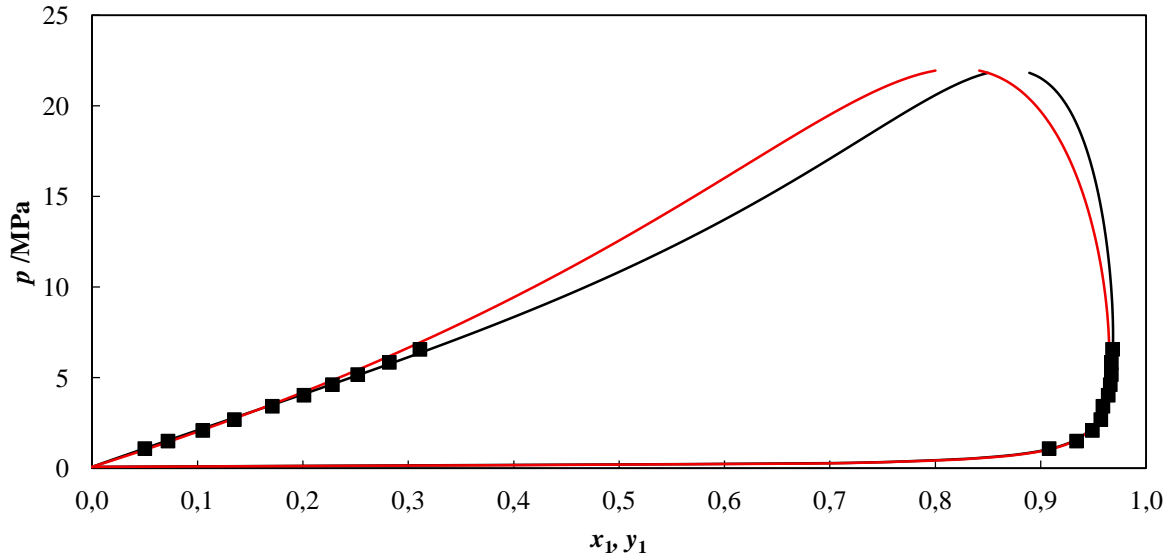


Figure 4. VLE data (P - x - y phase diagram) for the binary system: CH_4 (1) + C_6F_{14} (2). Measured VLE data: ■, 323.41 K; Model: —, PR-MC-WS-NRTL; —, SRK-MC-PSRK-NRTL.

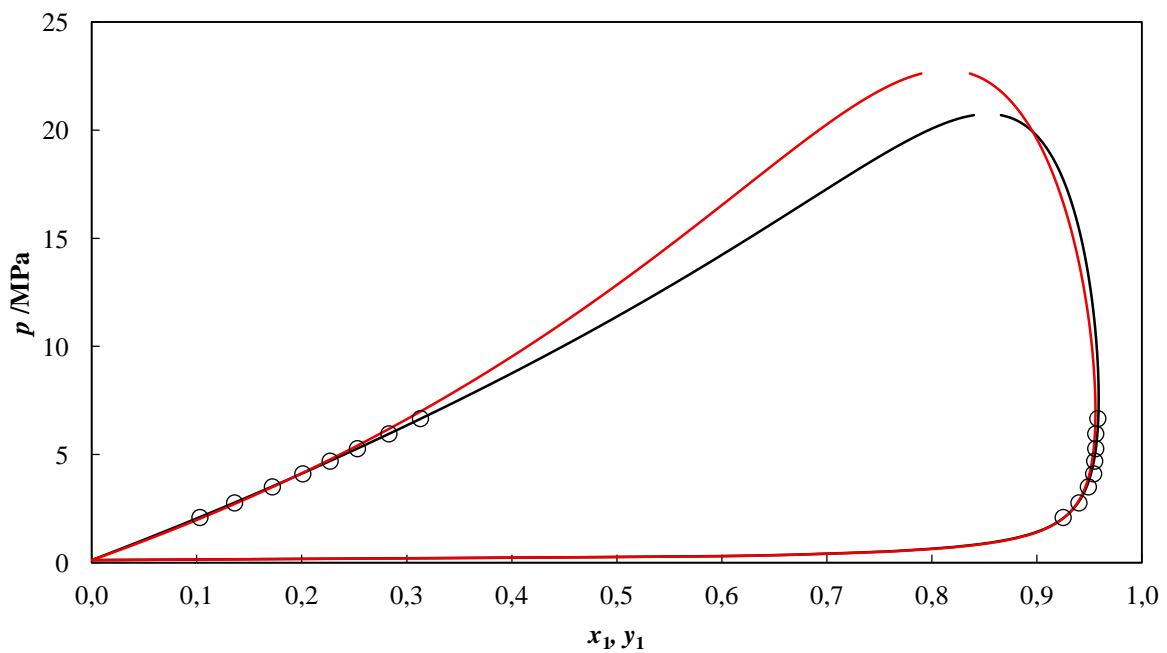


Figure 5. VLE data (P - x - y phase diagram) for the binary system: CH_4 (1) + C_6F_{14} (2). Measured VLE data: ○, 333.38 K; Model: —, PR-MC-WS-NRTL; —, SRK-MC-PSRK-NRTL.

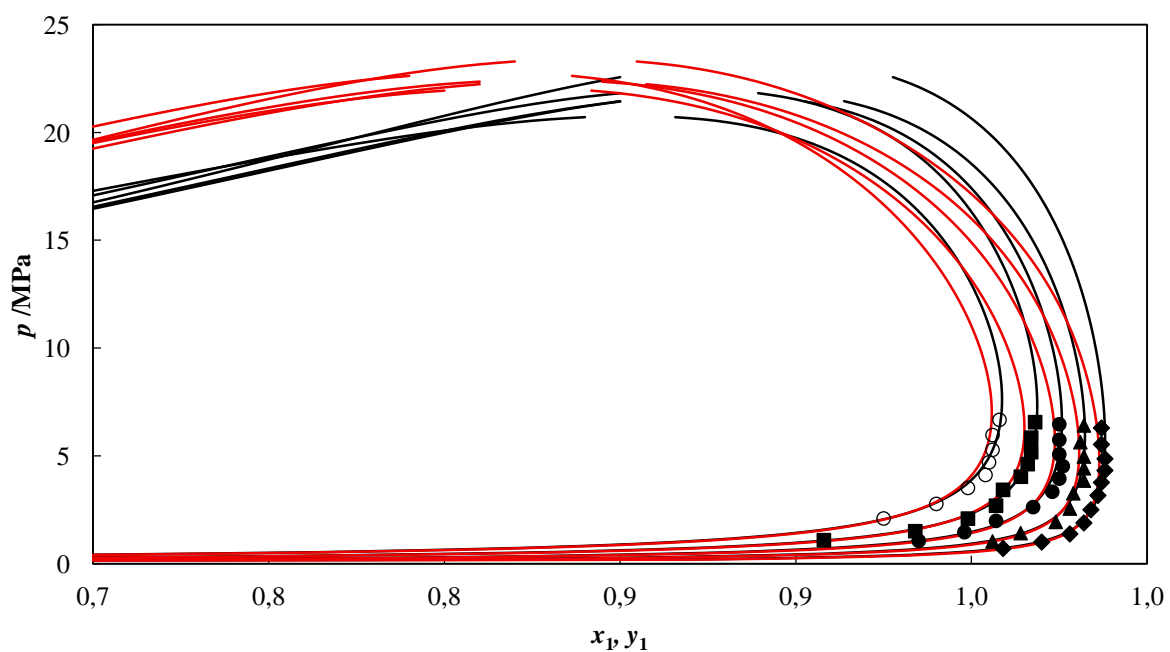
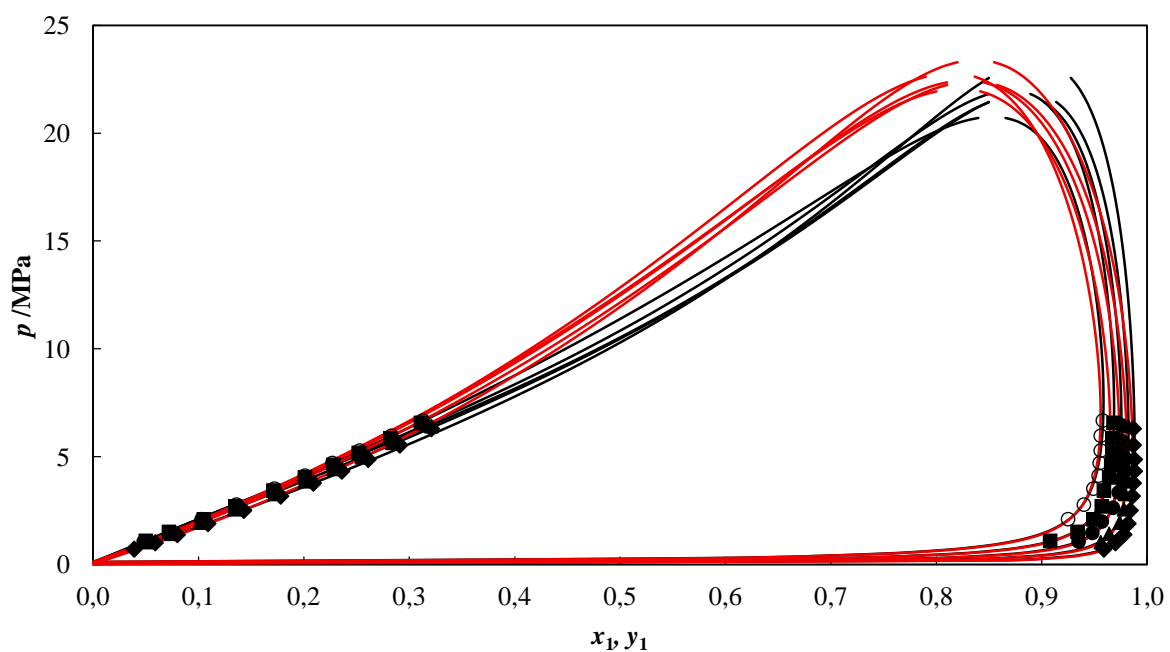


Figure 6. VLE data (P - x - y phase diagram) for the binary system: CH_4 (1) + C_6F_{14} (2).
 Measured VLE data: \blacklozenge , 293.39 K; \blacktriangle , 303.40 K; \bullet , 313.39 K; \blacksquare , 323.41 K; \circ , 333.38 K;
 Model: —, PR-MC-WS-NRTL; —, SRK-MC-PSRK-NRTL.

Figures 1 – 6 illustrate that both the PR-MC-WS-NRTL and the SRK-MC-PSRK-NRTL models provide satisfactory representations of the measured VLE data over the investigated temperature range. Nonetheless, the PR-MC-WS-NRTL model provides a much closer fit to the measured data. This qualitative assessment is supported quantitatively by the calculated statistical indicators, including, bias and AAD. The model parameters, derived from regression are presented in Table 4.

Table 4. PR-MC-WS-NRTL and SRK-MC-PSRK-NRTL model parameters for the CH₄ (1) + C₆F₁₄ (2) system

Isotherm /K	$(g_{12} - g_{22})/\text{J}\cdot\text{mol}^{-1}$	$(g_{21} - g_{11})/\text{J}\cdot\text{mol}^{-1}$	k_{ij}
PR-MC-WS-NRTL			
293.39	11721	-561.34	0.79
303.40	860.65	351.94	0.79
313.39	-798.81	2320.6	0.80
323.41	-918.14	2268.2	0.81
333.38	2980.3	-1367.6	0.81
SRK-MC-PSRK-NRTL			
293.39	153	-1677	—
303.40	1582	-2696	—
313.39	1622.5	-2785.8	—
323.41	1781.5	-2987.6	—
338.38	297.27	-2124.2	—

The NRTL parameters presented in Table 3 show that those derived from the PR-MC-WS-NRTL combination do not exhibit a consistent trend across the investigated temperature range. In contrast the binary interaction parameter k_{ij} displays only minimal variation with temperature. On the other hand, NRTL parameters obtained via the SRK-MC-PSRK-NRTL combination display a more systematic trend over the first four isotherms. The $(g_{12} - g_{22})$ values increase with temperature, while the $(g_{21} - g_{11})$ values decrease. A clearly and more consistent trend is expected to emerge once full sets of VLE data are available.

The PR-MC-WS-NRTL combination was further evaluated against the measured VLE data by comparing their corresponding relative volatility values, as depicted in Figure 7. The results demonstrate that the model provides a good fit to the measured VLE data.

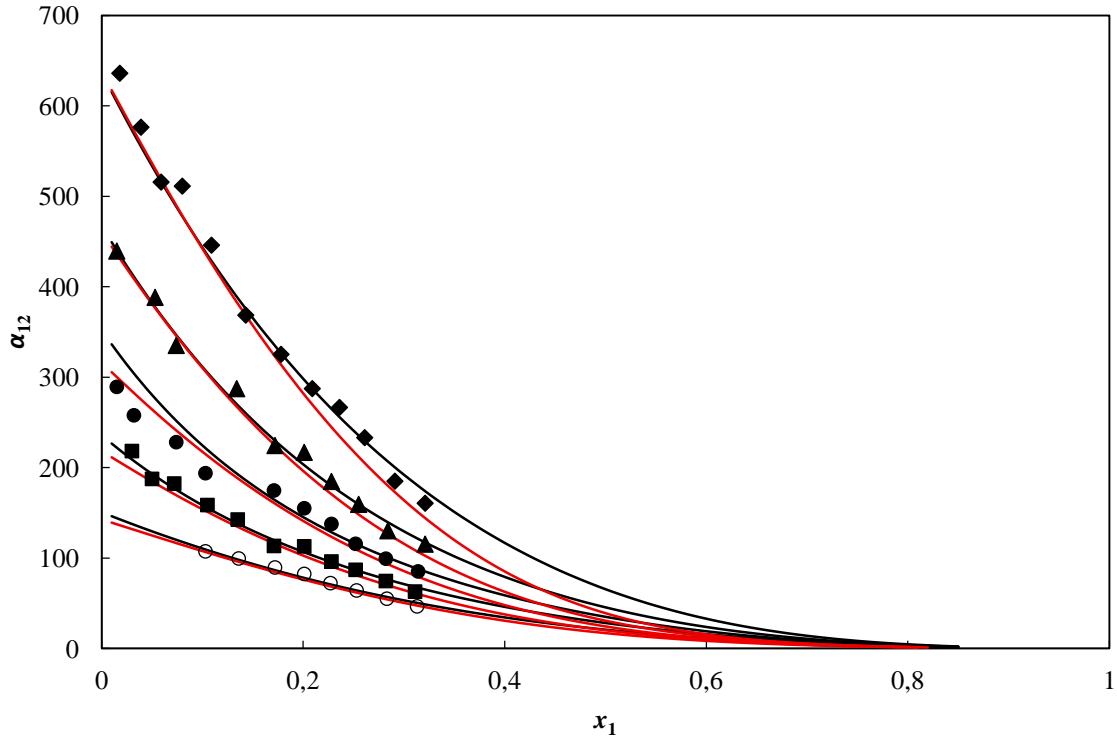


Figure 7. Plot of relative volatilities (α_{ij}) for the binary system: CH₄ (1) + C₆F₁₄ (2). Measured data: \blacklozenge , 293.39 K; \blacktriangle , 303.40 K; \bullet , 313.39 K; \blacksquare , 323.41 K; \circ , 333.38 K. Model: —, PR-MC-WS-NRTL; —, SRK-MC-PSRK-NRTL.

The statistical indicators, bias and AAD, computed from the comparison between modelled and experimental data and presented in Table 5, indicate that both models exhibit bias and AAD values below 4%. However, the PR-MC-WS-NRTL combination shows lower deviations across the first four isotherms. For the fifth isotherm, it yields the highest deviations, with a bias x of 3.75% and an AAD y of 2.67%. In contrast, the SRK-MC-PSRK-NRTL model generally shows higher bias x across all isotherms. Like the PR-based model, it also exhibits its highest AAD y for the fifth isotherm, reaching 2.77%. Overall, both models provide a satisfactory representation of the experimental data. Nevertheless, further measurements would be needed to conclusively determine which model offers a better overall fit.

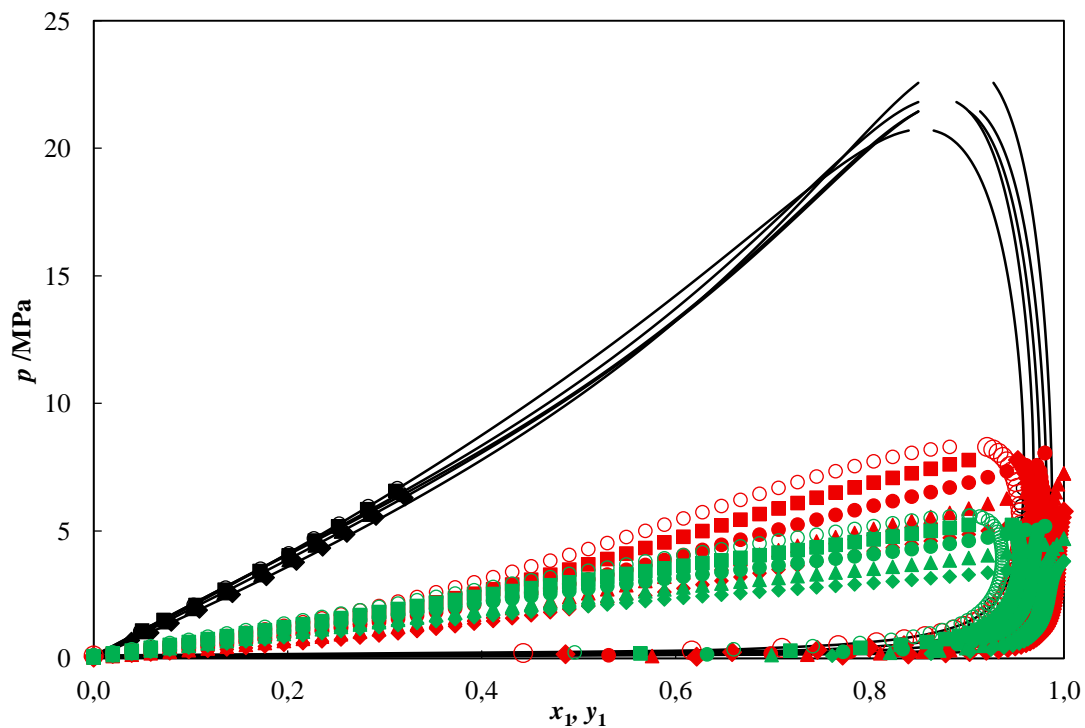
Table 5. Deviations, Bias and the AAD values derived from regressing the CH₄ (1) + C₆F₁₄ (2) VLE data using the PR-MC-WS-NRTL and SRK-MC-PSRK-NRTL models.

Isotherm / K	bias x %	AAD x %	bias y %	AAD y %
PR-MC-WS-NRTL				
293.39	-2.20	0.31	-0.07	0.14
303.40	0.03	1.03	-0.41	0.48
313.39	0.39	0.47	-0.51	0.65
323.41	-2.00	0.38	-0.82	0.79
333.38	-0.74	0.08	-3.75	2.67
SRK-MC-PSRK-NRTL				
293.39	-2.04	0.51	-0.07	0.21
303.40	-3.15	0.67	-0.45	0.57
313.39	-3.03	0.78	-0.57	0.80
323.41	-3.65	0.71	-0.82	0.92
333.38	-1.63	0.40	-1.64	2.77

The VLE data for the methane + perfluorohexane system were further compared with the corresponding data for the ethane + perfluorohexane and carbon dioxide + perfluorohexane systems, as reported by Tshibangu et al.¹¹ and Tochigi et al.⁹. However, the data from Tshibangu et al.¹¹ and Tochigi et al.⁹ were obtained at temperatures different from those used in the present CH₄ + C₆F₁₄ measurements. To enable a meaningful comparison, the phase equilibrium data for all three systems were collectively regressed to obtain temperature-dependent model parameters. These parameters were then used to predict VLE data at the specific temperatures studied for the CH₄ + C₆F₁₄ system. The resulting data for all three systems were graphically compared in Figure 8 to evaluate the selectivity of perfluorohexane for carbon dioxide relative to methane and ethane.

As shown in Figure 8, perfluorohexane exhibits selective absorption of carbon dioxide and ethane over methane. This behaviour can be attributed to the stronger intermolecular

interactions between perfluorohexane and the more polarizable carbon dioxide and ethane, in contrast to the relatively nonpolar and less interactive methane. At pressures ranging between 0 and 5 MPa, co-absorption of carbon dioxide and ethane is likely to occur in perfluorohexane at the investigated temperature range. However, at higher pressures, above 5 MPa, perfluorohexane appears to exhibit enhanced selectivity for ethane over carbon dioxide. This shift in selectivity can be attributed to pressure-induced changes in the perfluorohexane structure, which could enhance the van der Waals interactions with ethane while limiting the uptake of carbon dioxide.



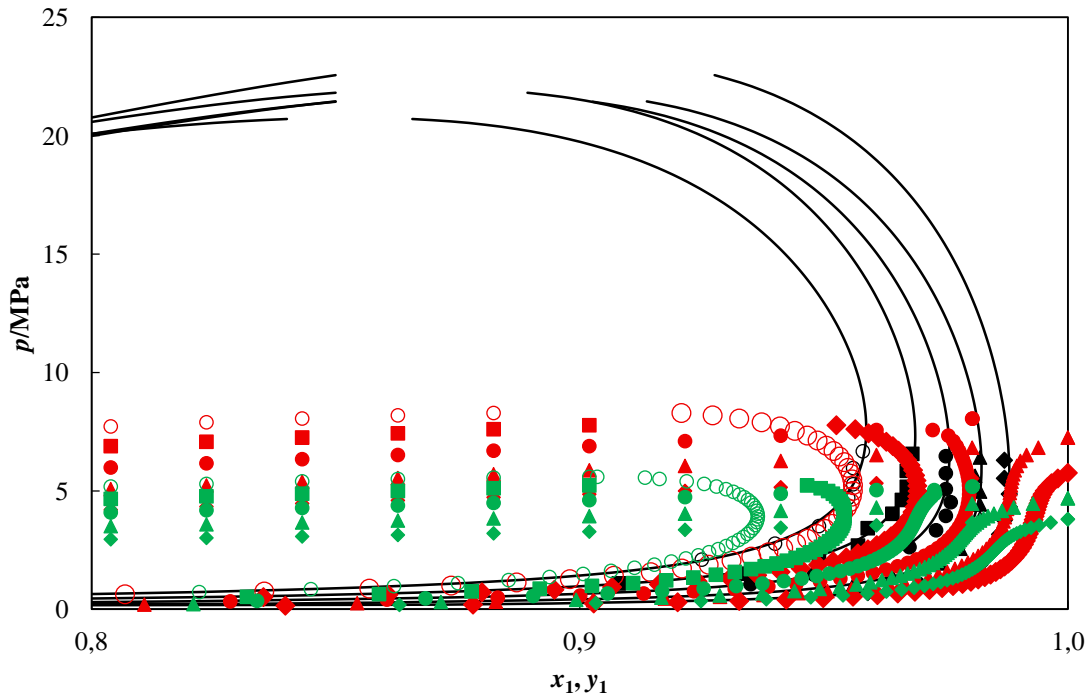


Figure 8. Selectivity of perfluorohexane for carbon dioxide relative to methane and ethane. VLE data for the binary system: CH_4 (1) + C_6F_{14} (2). Measured VLE data: \blacklozenge , 293.39 K; \blacktriangle , 303.40 K; \bullet , 313.39 K; \blacksquare , 323.41 K; \circ , 333.38 K; Model: —, PR-MC-WS-NRTL. VLE data for CO_2 + C_6F_{14} of Tochigi et al.⁹ predicted at \blacklozenge , 293.39 K; \blacktriangle , 303.40 K; \bullet , 313.39 K; \blacksquare , 323.41 K; \circ , 333.38 K. VLE data for C_2H_6 + C_6F_{14} of Tshibangu et al.¹¹ predicted at \blacklozenge , 293.39 K; \blacktriangle , 303.40 K; \bullet , 313.39 K; \blacksquare , 323.41 K; \circ , 333.38 K.

CONCLUSIONS

VLE data for the methane and perfluorohexane binary system were measured at temperatures ranging from (293.39 to 333.38) K using a static-analytical setup, as outlined in the article. The expanded uncertainties were estimated to be within 0.07 K for temperature, 0.011 MPa for pressure, and (0.02, 0.030) for phase compositions. The measured VLE data were successfully regressed using both the PR and the SRK EoS combined separately with the MC alpha function and either the Wong–Sandler or the predictive SRK mixing rule, which incorporates the NRTL activity coefficient model. A comparison of the CH_4 + C_6F_{14} VLE data with corresponding data for the CO_2 + C_6F_{14} and C_2H_6 + C_6F_{14} systems indicates that, up to approximately 5 MPa, C_6F_{14} shows strong affinity for CO_2 and C_2H_6 over CH_4 . Beyond this pressure, its selectivity shifts in favour of C_2H_6 over CO_2 .

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The manuscript was written through contributions of all authors.

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Notes

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