

Measurement of Vapor–Liquid Equilibria for the Binary Mixture of Pentafluoroethane (HFC-125) + Propane (R-290)

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Isothermal vapor–liquid equilibrium data for the binary mixture of pentafluoroethane (HFC-125) + propane (HC-290 or R-290) at six temperatures between (268.15 and 313.15) K were measured by using a circulation-type equilibrium apparatus. The experimental data were correlated with the Carnahan–Starling–De Santis equation of state (EOS) and the Peng–Robinson EOS using the Wong–Sandler mixing rules. It was confirmed that the data calculated by these EOSs have good agreement with experimental data. In this system, strong positive azeotropic behaviors were observed over the whole temperature range studied here.

Introduction

Hydrofluorocarbons (HFCs) and hydrocarbons (HCs) have been considered as promising alternative refrigerants in place of chlorofluorocarbons (CFCs) since HFCs and HCs ozone depletion potentials and global warming potentials are low. HFCs are stable but very expensive; on the other hand, hydrocarbons are flammable but are not expensive. The mixtures of the two compounds may have good potential for alternative refrigerants. Vapor–liquid equilibrium (VLE) data are required as one of the most important types of information to evaluate the performance of refrigeration cycles and to determine their optimal compositions. Azeotropic mixtures have merit since their behaviors are similar to pure compounds. However, very few experimental data have been reported previously in the literature.^{1–3} In this work, isothermal vapor–liquid equilibria data for the binary mixture pentafluoroethane (HFC-125) + propane (R-290) at six temperatures of (268.15, 273.15, 283.15, 293.15, 303.15, and 313.15) K were measured by using a circulation-type equilibrium apparatus. The experimental data were correlated with the Carnahan–Starling–De Santis equation of state (CSD EOS)⁴ and the Peng–Robinson equation of state (PR EOS)⁵ using the Wong–Sandler mixing rule.⁶ The interaction parameters and average deviations of pressures and vapor-phase compositions obtained by this EOS were presented.

Experimental Section

Chemicals. HFC-125 (supplied by Dupont (USA) with a declared purity of >99.8 mass %) and R-290 (provided by MG Industry (UK) with a declared purity of >99.5 mass %) were used for the measurements of VLE. The purities of the chemicals were guaranteed by the manufacturers, and they were used without any further purification.

Apparatus. The schematic diagram of the experimental apparatus for measuring the VLE is given in Figure 1. The

VLE data were measured in a circulation-type apparatus, in which both vapor and liquid phases were continuously recirculated. Since the experimental apparatus used in this work is the same as that used in previous work,^{7–13} it is briefly summarized here. The equilibrium cell is a type-316 stainless steel vessel with an inner volume of about 85 cm³. In its middle part, a pair of Pyrex glass windows of 20-mm thickness was installed so that the liquid level, mixing and circulating behaviors, and critical phenomena could be observed during operation. A stirrer, rotated at variable speeds by an external magnet, was used to accelerate the attainment of the equilibrium state and to reduce concentration gradients in both phases.

The temperature of the equilibrium cell in the water bath was maintained by a circulator from Jeio Tech, Korea. The temperature in the cell was measured with a platinum-resistance sensor and a digital temperature indicator model F250MkII precision thermometer from Automatic Systems Laboratories, Ltd., United Kingdom. They were calibrated by the National Measurement Accreditation Service accredited calibration laboratory. The total uncertainty in temperature measurements is estimated to be within ± 0.01 K, including sensor uncertainty, ± 0.01 K, temperature resolution, ± 0.001 K, and measurement uncertainty, ± 0.001 K. The pressure was measured with a pressure transducer, Model XPM60, and digital pressure calibrator, Model PC 106, from Beamax, Finland. Pressure calibrations are traceable to National Standards (Center for Metrology and Accreditation Cert. No. M-95P077, 14.11.1995, M-M 730, 16.11.1995, and M-95P078, 16.11.1995), and calibrator uncertainty was ± 0.0005 MPa, sensor uncertainty was ± 0.001 MPa, and measurement uncertainty was ± 0.001 MPa. Therefore, total uncertainties of the pressure are estimated to be within ± 0.001 MPa.

The vapor and liquid phases in the equilibrium cell were continuously recirculated by a dual-head circulation pump from the Milton Roy Company in order to reach the equilibrium state rapidly in the cell. The composition of the phases was determined by means of a gas chromatograph of Gow-Mac model 550P connected online to the VLE

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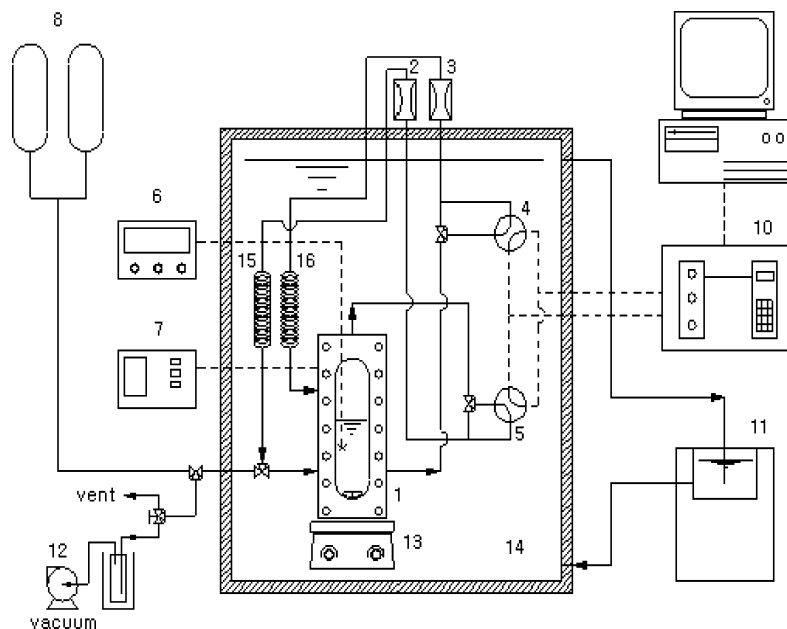


Figure 1. Schematic diagram of the experimental apparatus.

cell. The response of the thermal-conductivity detector (TCD) was carefully calibrated using the mixture prepared gravimetrically and the gas chromatographer (GC) with a Porapak Q column from Alltech company. Data derived from gas chromatography were treated with computer program (Autochro-WIN from Young-Lin Instrument Co., Ltd.).

Experimental Procedures. Experiments for a binary system were performed by the following procedures. The system was first evacuated to remove all inert gases. A certain amount of propane was introduced into the cell, and then the temperature of the entire system was held constant by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. A proper amount of HFC-125 was supplied to the cell from a charging cylinder. The mixture in the cell was stirred continuously with the magnetic stirrer for over 1 h. Both the vapor and liquid phases were recirculated by the dual-head circulation pump until an equilibrium state was established. It is believed that 1 h or more is sufficient to obtain thermal equilibrium between the cell fluid and the thermostatic bath. After equilibration, the pressure in the equilibrium cell was measured and then vapor and liquid samples were withdrawn from the recycling lines by the vapor and liquid sampling valves, respectively. The compositions of the samples were measured by immediately injecting them into the GC, which was connected online to vapor and liquid sampling valves. The GC was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. At least five analyses were performed for each phase, and the average value was considered to correspond to the equilibrium value. Considering the margin of error and the reproducibility of GC, we generally estimated an overall accuracy in the measurements of the composition of ± 0.002 in the mole fraction for both the liquid and the vapor phases.

Correlation

The experimental VLE data were correlated with the CSD and PR EOSs.

CSD EOS. The CSD EOS⁴ is given by

$$\frac{PV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(V + b)} \quad (1)$$

with

$$y = \frac{b}{4V} \quad (2)$$

$$a = \alpha_0 \exp(\alpha_1 T + \alpha_2 T^2) \quad (3)$$

$$b = \beta_0 + \beta_1 T + \beta_2 T^2 \quad (4)$$

where a is an attraction parameter and b is a molecular volume. The following mixing rules¹⁴ were used to obtain equation of state parameters for a mixture

$$a_{12} = (1 - f_{12})(a_1 a_2)^{1/2} \quad (5)$$

$$b_{12} = \frac{1}{8} (b_1^{1/3} + b_2^{1/3})^3 \quad (6)$$

where f_{12} is an interaction parameter and a_i and b_i are properties of a pure components. Coefficients α_i and β_i for pure components were cited from REFPROP 5.0.¹⁵

PR EOS.

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \quad (7)$$

with

$$a(T) = (0.457235 R^2 T_c^2 / P_c) \alpha(T) \quad (8)$$

$$b = 0.077796 RT_c / P_c \quad (9)$$

$$\alpha(T) = [1 + \kappa(1 - T_r^{0.5})]^2 \quad (10)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (11)$$

The parameter a is a function of temperature, b is constant, and κ is a constant characteristic of each substance. The Wong–Sandler mixing rules⁶ were used in this

Table 1. Coefficients of Pure Components for CSD Equation of State

| component | α_0 | $\alpha_1 \times 10^3$ | $\alpha_2 \times 10^6$ | β_0 | $\beta_1 \times 10^4$ | $\beta_2 \times 10^7$ | source |
|-----------|--|---|---|---|--|--|---------------------------|
| | $\text{kJ m}^3 \text{ kg}^{-1} \text{ mol}^{-2}$ | $\text{kJ m}^3 \text{ kg}^{-1} \text{ mol}^{-2} \text{ K}^{-1}$ | $\text{kJ m}^3 \text{ kg}^{-1} \text{ mol}^{-2} \text{ K}^{-2}$ | $\text{m}^3 \text{ kg}^{-1} \text{ mol}^{-1}$ | $\text{m}^3 \text{ kg}^{-1} \text{ mol}^{-1} \text{ K}^{-1}$ | $\text{m}^3 \text{ kg}^{-1} \text{ mol}^{-1} \text{ K}^{-2}$ | |
| HFC-125 | 3427.922 | -3.1746132 | -1.7572861 | 0.1493804 | -1.8085107 | -1.1881331 | REFPROP 5.0 ¹⁵ |
| propane | 2988.277 | -2.6290195 | -1.097062 | 0.1429625 | -1.7651912 | -0.5785137 | |

Table 2. Characteristic Properties of the Chemicals

| component | chemical formula | MW | T_c/K | P_c/MPa | ω | source |
|-----------|---------------------------|--------|----------------|------------------|----------|----------------------------|
| HFC-125 | CHF_2CF_3 | 120.02 | 339.33 | 3.629 | 0.3035 | REFPROP 6.01 ¹⁸ |
| propane | C_3H_8 | 44.10 | 369.85 | 4.248 | 0.1524 | |

Table 3. Comparison of the Measured Pure Component Vapor Pressures with the Database REFPROP 6.01¹⁸ and ASHRAE Handbook¹⁹

| T/K | P/MPa (measured) | P/MPa (REFPROP ¹⁸) | $\Delta P^a/\text{MPa}$ | $ \Delta P/P ^b(\%)$ | ASHRAE ¹⁹ | $\Delta P^a/\text{MPa}$ | $ \Delta P/P ^b(\%)$ |
|--------------|------------------------------|--|-------------------------|----------------------|----------------------|-------------------------|----------------------|
| HFC-125 | | | | | | | |
| 268.15 | 0.5737 | 0.5713 | 0.0024 | 0.4183 | 0.5722 | 0.0015 | 0.2615 |
| 273.15 | 0.6714 | 0.6710 | 0.0004 | 0.0596 | 0.6720 | -0.0006 | 0.0894 |
| 283.15 | 0.9076 | 0.9088 | -0.0012 | 0.1322 | 0.9104 | -0.0028 | 0.3085 |
| 293.15 | 1.2028 | 1.2045 | -0.0017 | 0.1413 | 1.2066 | -0.0038 | 0.3159 |
| 303.15 | 1.5660 | 1.5668 | -0.0008 | 0.0511 | 1.5694 | -0.0034 | 0.2171 |
| 313.15 | 2.0049 | 2.0056 | -0.0007 | 0.0349 | 2.0098 | -0.0049 | 0.2444 |
| Propane | | | | | | | |
| 268.15 | 0.4079 | 0.4059 | 0.0020 | 0.4903 | 0.4061 | 0.0018 | 0.4413 |
| 273.15 | 0.4769 | 0.4743 | 0.0026 | 0.5452 | 0.4743 | 0.0026 | 0.5452 |
| 283.15 | 0.6372 | 0.6364 | 0.0008 | 0.1255 | 0.6365 | 0.0007 | 0.1098 |
| 293.15 | 0.8392 | 0.8362 | 0.0030 | 0.3575 | 0.8363 | 0.0029 | 0.3456 |
| 303.15 | 1.0746 | 1.0787 | -0.0041 | 0.3815 | 1.0788 | -0.0042 | 0.3908 |
| 313.15 | 1.3643 | 1.3690 | -0.0047 | 0.3445 | 1.3692 | -0.0049 | 0.3592 |

$$^a \Delta P = P_{\text{exp}} - P_{\text{cal}}, \quad ^b |\Delta P/P(\%)| = |(P_{\text{exp}} - P_{\text{cal}})/P_{\text{exp}}| \times 100.$$

work to obtain EOS parameters for a mixture from those of the pure components. These mixing rules for a cubic equation of state can be written as

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{(1 - A_{\infty}^E/CRT - \sum_i x_i a_i/RTb)} \quad (12)$$

with

$$(b - a/RT)_{ij} = \frac{1}{2} [(b - a/RT)_i + (b - a/RT)_j] (1 - k_{ij}) \quad (13)$$

and

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_{\infty}^E}{C} \quad (14)$$

and where C is a numerical constant equal to $\ln(2^{1/2} - 1)/2^{1/2}$ for the PR EOS used in this work. The single adjustable parameter (k_{ij}) for each binary pair is referred to as the Wong–Sandler mixing rule parameter. Also, A_{∞}^E is an excess Helmholtz-free energy model at infinite pressure that can be equated to a low-pressure excess Gibbs energy model.¹⁶ In this study, we use the nonrandom two-liquid (NRTL) model¹⁷ given by

$$\frac{A_{\infty}^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \quad (15)$$

with

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

and

$$\tau_{ij} = A_{ij}/(RT) \quad (16)$$

where $A_{ij} = (g_{ij} - g_{ji})$. The critical temperature (T_c), critical pressure (P_c), and acentric factor (ω) for both HFC-125 and propane that were used to calculate the parameters for the PR EOS are provided in Table 2. We have set the non-randomness parameter, α_{ij} , to equal a fixed value of 0.3 for all the binary mixtures studied here. The parameters of these equations were obtained by minimizing the objective function

$$\text{objective function} = \frac{1}{N} \sum_j^n \left[\left(\frac{P_{j,\text{exp}} - P_{j,\text{cal}}}{P_{j,\text{exp}}} \right) 100 \right]^2 \quad (17)$$

Results and Discussion

Table 3 shows the comparison of measured vapor pressure of pure HFC-125 and propane with those calculated from the database REFPROP 6.01¹⁸ and the ASHRAE handbook,¹⁹ which are considered to be reliable for the pure compounds considered and consistent with other literature data. The average deviation ($|\Delta P/P|$) between measured and calculated values from the data of REFPROP 6.01 is 0.157% for HFC-125 and 0.366% for propane, and that of ASHRAE handbook is 0.270% for HFC-125 and 0.376% for propane. As can be seen in this table, the deviations (ΔP) between measured and calculated values from the data of REFPROP 6.01 and the ASHRAE handbook were within 5 kPa. The experimental data of isothermal VLE for the binary system of HFC-125 + propane are shown in Table

Table 4. Vapor–Liquid Equilibrium Measurements for the HFC-125 (1) + Propane (2) System

| experimental data | | | PR EOS | | | | CSD EOS | | | |
|-----------------------------|-------|--------------------|-----------------------------|--------------------|-------------------------|----------------|-----------------------------|--------------------|-------------------------|----------------|
| $P_{\text{exp}}/\text{MPa}$ | x_1 | $y_{1,\text{exp}}$ | $P_{\text{cal}}/\text{MPa}$ | $y_{1,\text{cal}}$ | $\Delta P^a/\text{MPa}$ | Δy_1^b | $P_{\text{cal}}/\text{MPa}$ | $y_{1,\text{cal}}$ | $\Delta P^a/\text{MPa}$ | Δy_1^b |
| $TK = 268.15$ | | | | | | | | | | |
| 0.4079 | 0.000 | 0.000 | 0.4052 | 0.000 | 0.0027 | 0.000 | 0.4063 | 0.000 | 0.0016 | 0.000 |
| 0.5943 | 0.157 | 0.367 | 0.5945 | 0.374 | 1.000 | -0.007 | 0.5963 | 0.374 | -0.0020 | -0.007 |
| 0.6686 | 0.320 | 0.488 | 0.6703 | 0.494 | -0.0002 | -0.006 | 0.6722 | 0.494 | -0.0036 | -0.006 |
| 0.7106 | 0.533 | 0.584 | 0.7063 | 0.585 | -0.0017 | -0.001 | 0.7060 | 0.582 | 0.0046 | 0.002 |
| 0.7052 | 0.710 | 0.655 | 0.7058 | 0.665 | 0.0043 | -0.010 | 0.7042 | 0.661 | 0.0010 | -0.006 |
| 0.6706 | 0.860 | 0.769 | 0.6722 | 0.771 | -0.0006 | -0.002 | 0.6687 | 0.773 | 0.0019 | -0.004 |
| 0.5737 | 1.000 | 1.000 | 0.5693 | -0.0044 | -0.0016 | 0.000 | 0.5715 | 1.000 | 0.0022 | 0.000 |
| $TK = 273.15$ | | | | | | | | | | |
| 0.4769 | 0.000 | 0.000 | 0.4735 | 0.000 | 0.0034 | 0.000 | 0.4749 | 0.000 | 0.0020 | 0.000 |
| 0.6920 | 0.166 | 0.376 | 0.6921 | 0.371 | -0.0001 | 0.005 | 0.6962 | 0.375 | -0.0042 | 0.001 |
| 0.7682 | 0.308 | 0.475 | 0.7701 | 0.478 | -0.0019 | -0.003 | 0.7741 | 0.482 | -0.0059 | -0.007 |
| 0.8208 | 0.506 | 0.572 | 0.8184 | 0.575 | 0.0024 | -0.003 | 0.8175 | 0.571 | 0.0033 | 0.001 |
| 0.8284 | 0.679 | 0.628 | 0.8258 | 0.656 | 0.0026 | -0.028 | 0.8219 | 0.649 | 0.0065 | -0.021 |
| 0.7864 | 0.854 | 0.763 | 0.7893 | 0.773 | -0.0029 | -0.010 | 0.7818 | 0.774 | 0.0046 | -0.011 |
| 0.6714 | 1.000 | 1.000 | 0.6692 | 1.000 | 0.0022 | 0.000 | 0.6715 | 1.000 | -0.0001 | 0.000 |
| $TK = 283.15$ | | | | | | | | | | |
| 0.6372 | 0.000 | 0.000 | 0.6357 | 0.000 | 0.0015 | 0.000 | 0.6377 | 0.000 | -0.0005 | 0.000 |
| 0.8904 | 0.138 | 0.328 | 0.8905 | 0.328 | -0.0001 | 0.000 | 0.8832 | 0.324 | 0.0072 | 0.004 |
| 1.0204 | 0.309 | 0.470 | 1.0214 | 0.466 | -0.0010 | 0.004 | 1.0211 | 0.470 | -0.0007 | 0.000 |
| 1.0886 | 0.542 | 0.583 | 1.0871 | 0.583 | 0.0015 | 0.000 | 1.0900 | 0.586 | -0.0014 | -0.003 |
| 1.0870 | 0.717 | 0.668 | 1.0850 | 0.679 | 0.0020 | -0.011 | 1.0891 | 0.680 | -0.0021 | -0.012 |
| 1.0486 | 0.830 | 0.767 | 1.0512 | 0.765 | -0.0026 | 0.002 | 1.0558 | 0.764 | -0.0072 | 0.003 |
| 0.9076 | 1.000 | 1.000 | 0.9081 | 1.000 | -0.0005 | 0.000 | 0.9102 | 1.000 | -0.0026 | 0.000 |
| $TK = 293.15$ | | | | | | | | | | |
| 0.8392 | 0.000 | 0.000 | 0.8360 | 0.000 | 0.0032 | 0.000 | 0.8385 | 0.000 | 0.0007 | 0.000 |
| 1.1202 | 0.145 | 0.310 | 1.1204 | 0.323 | -0.0002 | -0.013 | 1.1389 | 0.310 | -0.0187 | 0.000 |
| 1.3280 | 0.329 | 0.473 | 1.3303 | 0.508 | -0.0023 | -0.035 | 1.3202 | 0.468 | 0.0078 | 0.005 |
| 1.4080 | 0.511 | 0.566 | 1.4046 | 0.592 | 0.0034 | -0.026 | 1.3989 | 0.570 | 0.0091 | -0.004 |
| 1.4200 | 0.674 | 0.656 | 1.4178 | 0.659 | 0.0022 | -0.003 | 1.4152 | 0.662 | 0.0048 | -0.006 |
| 1.3700 | 0.831 | 0.774 | 1.3732 | 0.770 | -0.0032 | 0.004 | 1.3710 | 0.779 | -0.0010 | -0.005 |
| 1.2028 | 1.000 | 1.000 | 1.2065 | 1.000 | -0.0037 | 0.000 | 1.2065 | 1.000 | -0.0037 | 0.000 |
| $TK = 303.15$ | | | | | | | | | | |
| 1.0746 | 0.000 | 0.000 | 1.0798 | 0.000 | -0.0052 | 0.000 | 1.0820 | 0.000 | -0.0074 | 0.000 |
| 1.4320 | 0.140 | 0.291 | 1.4323 | 0.292 | -0.0003 | -0.001 | 1.4350 | 0.286 | -0.0030 | 0.005 |
| 1.6778 | 0.329 | 0.457 | 1.6813 | 0.466 | -0.0035 | -0.009 | 1.6784 | 0.455 | -0.0006 | 0.002 |
| 1.7970 | 0.518 | 0.570 | 1.7905 | 0.576 | 0.0065 | -0.006 | 1.7904 | 0.570 | 0.0066 | 0.000 |
| 1.8130 | 0.696 | 0.685 | 1.8115 | 0.681 | 0.0015 | 0.004 | 1.8121 | 0.682 | 0.0009 | 0.003 |
| 1.7566 | 0.832 | 0.786 | 1.7616 | 0.789 | -0.0050 | -0.003 | 1.7615 | 0.790 | -0.0049 | -0.004 |
| 1.5660 | 1.000 | 1.000 | 1.5732 | 1.000 | -0.0072 | 0.000 | 1.5683 | 1.000 | -0.0023 | 0.000 |
| $TK = 313.15$ | | | | | | | | | | |
| 1.3643 | 0.000 | 0.000 | 1.3725 | 0.000 | -0.0082 | 0.000 | 1.3732 | 0.000 | -0.0089 | 0.000 |
| 1.7894 | 0.144 | 0.280 | 1.7898 | 0.282 | -0.0004 | -0.002 | 1.8022 | 0.274 | -0.0128 | 0.006 |
| 2.1126 | 0.338 | 0.449 | 2.1174 | 0.470 | -0.0048 | -0.021 | 2.1117 | 0.448 | 0.0009 | 0.001 |
| 2.2668 | 0.522 | 0.570 | 2.2581 | 0.580 | 0.0087 | -0.010 | 2.2560 | 0.568 | 0.0108 | 0.002 |
| 2.2924 | 0.703 | 0.695 | 2.2895 | 0.691 | 0.0029 | 0.004 | 2.2878 | 0.692 | 0.0046 | 0.003 |
| 2.2396 | 0.813 | 0.782 | 2.2471 | 0.780 | -0.0075 | 0.002 | 2.2431 | 0.781 | -0.0035 | 0.001 |
| 2.0049 | 1.000 | 1.000 | 2.0178 | 1.000 | -0.0129 | 0.000 | 2.0034 | 1.000 | 0.0015 | 0.000 |

$$^a \Delta P = P_{\text{exp}} - P_{\text{cal}}, \quad ^b \Delta y_1 = y_{\text{exp}} - y_{\text{cal}}.$$

Table 5. Values of Binary Parameters and Average Deviations of P and y

| TK | PR EOS | | | | | CSD EOS | | |
|--------|------------|----------|----------|-------------------|--------------|------------|-------------------|--------------|
| | f_{12}^a | A_{12} | A_{21} | $\delta P^b/(\%)$ | δy^c | f_{12}^a | $\delta P^b/(\%)$ | δy^c |
| 268.15 | 0.9611 | 0.2410 | 0.2934 | 0.380 | 0.0064 | 0.1381 | 0.389 | 0.0039 |
| 273.15 | -0.2346 | 0.2648 | 0.3538 | 0.325 | 0.0071 | 0.1385 | 0.511 | 0.0060 |
| 283.15 | 0.1164 | 0.2834 | 2.1601 | 0.214 | 0.0026 | 0.1394 | 0.322 | 0.0030 |
| 293.15 | 0.4679 | -1.4004 | 0.2720 | 0.216 | 0.0115 | 0.1363 | 0.530 | 0.0030 |
| 303.15 | 0.2449 | -1.5276 | 1.5342 | 0.271 | 0.0033 | 0.1372 | 0.255 | 0.0020 |
| 313.15 | 0.3235 | 0.6241 | 1.3684 | 0.370 | 0.0056 | 0.1385 | 0.346 | 0.0017 |

$$^a \text{The unit of } A_{ij} \text{ and } A_{ji} \text{ is } \text{kJ}\cdot\text{mol}^{-1}. \quad ^b \delta P = 1/N \sum |(P_{\text{exp}} - P_{\text{cal}})/P_{\text{exp}}| \times 100. \quad ^c \delta y = 1/N \sum |y_{\text{exp}} - y_{\text{cal}}|.$$

4. This table lists the measured mole fraction of the liquid and vapor phases, pressures, and temperatures in equilibrium and the deviations between measured and calculated pressures (ΔP) and vapor compositions (Δy), point by point. The interaction parameters of binary mixtures for each isotherm, the binary parameters of the NRTL model with the Wong–Sandler mixing rules, and the average

absolute deviations of pressure (δP) and vapor-phase composition (δy) between measured and calculated values are reported in Table 5. Figure 2 shows the comparison of measured and calculated values with the PR and CSD EOSs for HFC-125 + propane at (268.15, 273.15, 283.15, 293.15, 303.15 and 313.15) K. The average values of AAD P (%) and AAD y were 0.232 and 0.0034 for the PR EOS

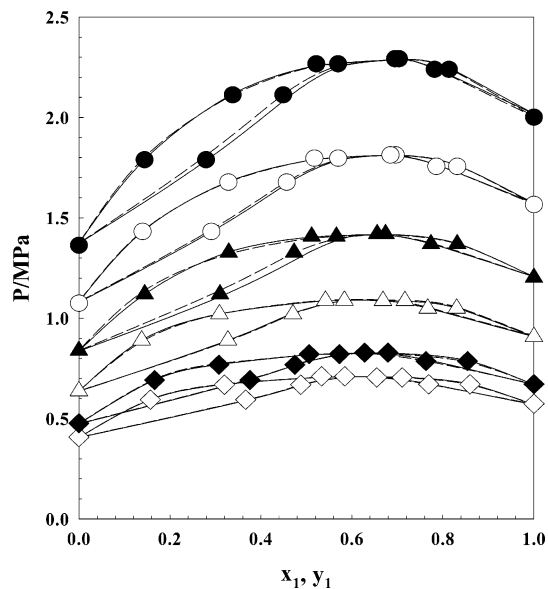


Figure 2. Pxy diagram for the HFC-125 (1) + propane (2) system: (\diamond), at 268.15 K; (\blacklozenge), at 273.15 K; (\triangle), at 283.15 K; (\blacktriangle), at 293.15 K; (\circ), at 303.15 K; (\bullet), at 313.15 K; (dashed line), calculated with PR EOS; (solid line), calculated with CSD EOS.

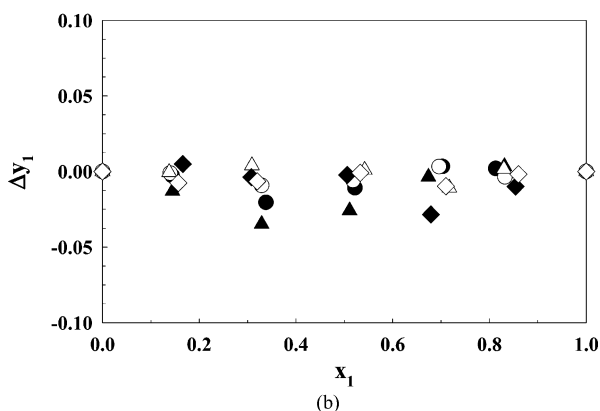
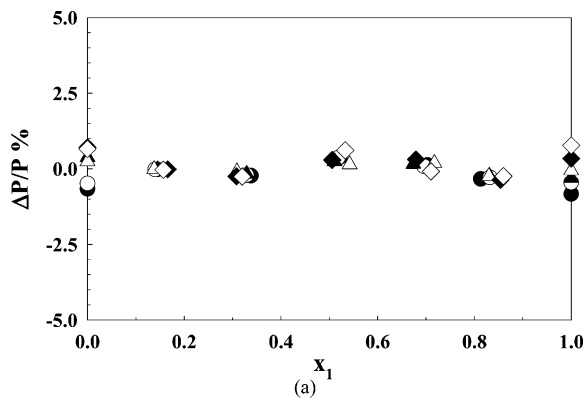


Figure 3. Deviation ($\Delta P/P = 100(P_{\text{exp}} - P_{\text{calc}})/P_{\text{calc}}$, $\Delta y_1 = y_{1,\text{exp}} - y_{1,\text{calc}}$) between experimental data and calculated values using PR EOS for the HFC-125 (1) + propane (2) system: (\diamond), at 268.15 K; (\blacklozenge), at 273.15 K; (\triangle), at 283.15 K; (\blacktriangle), at 293.15 K; (\circ), at 303.15 K; (\bullet), at 313.15 K; (a) $\Delta P/P$ vs x_1 , (b) Δy_1 vs x_1 .

and 0.421 and 0.0037 for the CSD EOS, respectively. This result is shown in Figure 3. From this figure and the low average deviations of P and y , we conclude that the calculated values using the PR and the CSD EOSs give good agreement with the experimental data. This mixture exhibited the azeotropes. Azeotropic data of this mixture

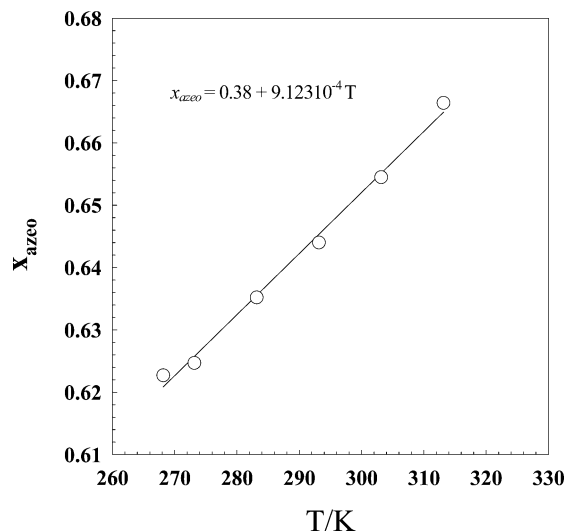


Figure 4. Variation of the azeotropic composition with temperature for the HFC-125 (1) + propane (2) system.

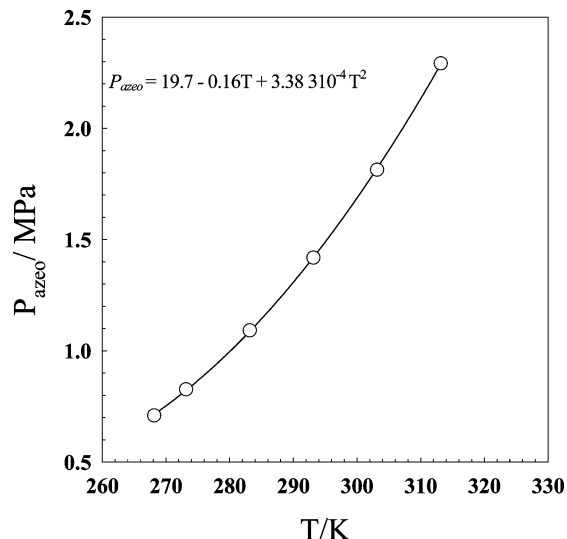


Figure 5. Variation of the azeotropic pressure with temperature for the HFC-125 (1) + propane (2) system.

Table 6. Azeotropic Data of the HFC-125 (1) + Propane (2) System

| T/K | azeotropic composition x_{azeo} /mole fraction | azeotropic pressure P_{azeo} /MPa |
|--------|--|---|
| 268.15 | 0.6227 | 0.7097 |
| 273.15 | 0.6352 | 0.8271 |
| 283.15 | 0.6247 | 1.0921 |
| 293.15 | 0.6440 | 1.4186 |
| 303.15 | 0.6545 | 1.8140 |
| 313.15 | 0.6664 | 2.2921 |

have been determined at the composition between 0.62 and 0.67 in mole fraction, and pressures between (0.70 and 2.30) MPa in the temperature range from (268.15 to 313.15) K. Azeotropic compositions and pressures are shown in Table 6 and Figures 4 and 5. As can be seen in these figures, azeotropic compositions and pressures are dependent on the temperature. In the range of experimental temperature, azeotropic compositions were correlated by the empirical equation, $x_{\text{azeo}} = 0.38 + 9.12 \times 10^{-4} T$, and azeotropic pressure was correlated by the empirical equation, $P_{\text{azeo}} = 19.7 - 0.16T + 3.38 \times 10^{-4} T^2$.

Conclusions

The VLE data for binary systems of HFC-125 + propane were measured at six temperatures between (268.15 and 313.15) K using a circulation-type equilibrium apparatus. The experimental data were correlated with the PR EOS using the Wong–Sandler mixing rules and the CSD EOS. Calculated results with these equations have given satisfactory results in comparison with the experimental data. This system shows a strong positive azeotrope for all the temperature range studied here.

List of Symbols

$a(T)$ = temperature-dependent constant of EOS

a = attraction parameter

A_{ij} = adjustable parameters

$\alpha_0, \alpha_1, \alpha_2$ = coefficients for the temperature dependence of a

b = molecular volume

$\beta_0, \beta_1, \beta_2$ = coefficients for the temperature dependence of b

g_{ji} = an energy parameter characteristic of the i – j interaction

f_{12} = CSD and PR EOSs parameter

P, P_c = pressure, critical pressure (MPa)

R = gas constant, 8.3144 (J mol⁻¹ K⁻¹)

T, T_c, T_r = absolute temperature, critical temperature, reduced temperature (K)

v = liquid molar volume

x = liquid mole fraction

y = vapor mole fraction

$y = b/4V$

Greek Letters

Δ = deviation

ω = acentric factor

Subscripts

c = critical property

cal = calculated

exp = experimental

i, j = i th and j th components of the mixture

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