Vapor-Liquid Equilibria for Propane (R-290) + 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) at Various Temperatures

Jong Sung Lim,* Gimyeong Seong, and Hee-Kook Roh

Department of Chemical and Biomolecular Engineering, Sogang University, C.P.O. Box 1142, Seoul 100-611, South Korea

Byung Gwon Lee

Division of Environment and Process Technology, Korea Institute of Science and Technology (KIST), P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

Isothermal vapor-liquid equilibrium data for propane + 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) were measured at (273.15, 283.15, 293.15, 303.15, 313.15, and 323.15) K, respectively. The experiments were carried out using a circulation-type equilibrium apparatus to measure temperature, pressure, and the compositions of the liquid and vapor phases. The experimental data were well correlated with the Peng–Robinson equation of state (PR-EOS) using the Wong–Sandler mixing rules and the Carnahan–Starling–De Santis equation of state (CSD-EOS). This system shows strong positive azeotrope.

Introduction

In recent years, the utilization of light hydrocarbons such as propane, butane, and propylene is believed to be a good solution for developing CFC-alternative refrigerants in the future because these are inexpensive, plentiful, and environmentally benign chemicals. However, they are toxic, flammable, and explosive. Other CFC alternative refrigerants are HFCs which have good performance and are more environmentally benign, but HFCs' GWP (global warming potential) is a thousand higher than that of CFCs. One of the solutions to compensate their weakness is mixing two alternatives. Mixing light hydrocarbons and HFCs can provide a good solution, making up for the weaknesses.

Vapor—liquid equilibrium (VLE) data are the most important data requested to evaluate the performance of refrigeration cycles and to determine their optimal compositions. Azeotropic mixtures have merit because 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 VLE data for the binary mixture of propane + HFC-227ea at six equally spaced temperatures between (273.15 and 323.15) K were measured using a circulation-type equilibrium apparatus in which both phases were continuously recirculated. The experimental data were correlated with the Peng–Robinson equation of state (PR-EOS)⁴ using the Wong–Sandler mixing rule⁵ combined with the NRTL excess Gibbs free energy model and the Carnahan–Starling–De Santis equation of state (CSD-EOS).⁶ In the range of experimental temperatures, the average absolute deviations of pressure and vapor-phase compositions between experimental and calculated values were determined, and the relevant parameters were presented. Almost all the calculated values with this model give good agreement with the experimental data, and thus the system exhibits an azeotrope.

Experimental

Chemicals. High-quality chemicals of HFC-227ea and propane were used for VLE measurement. HFC-227ea was supplied

by DuPont (USA) with a guaranteed purity in mass fraction higher than 0.998, and R290 (propane) was supplied by MG Industry (UK) with a guaranteed purity in mass fraction higher than 0.995. Furthermore, we also analyzed these two pure components with a gas chromatograph. The resulted mass fraction purities of HFC-227ea and R290 were higher than 0.999 and 0.9985, respectively. So, they were used without any further purification.

Experimental Apparatus. A schematic diagram of the experimental apparatus for measuring the VLE is given in Figure 1. Because the vapor—liquid equilibrium apparatus used in this work was the same as that used in our previous work,^{7–13} only a brief description is given here. It was a circulation-type in which both liquid and vapor phases were recirculated continuously. The equilibrium cell was a type-316 stainless steel vessel with an inner volume of about 85 cm³. In its middle part, two Pyrex glass windows of 20 mm thickness were installed in the front and back so that the liquid level, mixing and circulating behaviors, and critical phenomena could be observed by a back light 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, 0.001 K, temperature resolution, 0.001 K, and measurement uncertainty, 0.001 K. The pressure was measured with a pressure transducer (model XPM60) and a digital 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,

* Corresponding author. E-mail: limjs@sogang.ac.kr.



Figure 1. Schematic diagram of the experimental apparatus: 1, equilibrium cell; 2, vapor circulation pump; 3, liquid circulation pump; 4, liquid sample valve; 5, vapor sample valve; 6, temperature indicator; 7, pressure indicator; 8, sample reservoir; 9, computer; 10, gas chromatograph; 11, circulator; 12, vacuum pump; 13, magnetic stirrer; 14, constant temperature water bath; 15, vapor phase heat exchanger; 16, liquid phase heat exchanger.

16.11.1995), and the calibrator uncertainty was 0.0005 MPa; the sensor uncertainty was 0.0001 MPa; and the measurement uncertainty was 0.0001 MPa. Therefore, the total uncertainty of the pressure measurement is 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 (Milton Roy Company) to reach the equilibrium state rapidly in the cell. The composition of the phases was determined by means of a gas chromatograph (Gow-Mac model 550P) connected online to the VLE cell. The response of the thermal conductivity detector (TCD) was carefully calibrated using the mixture prepared gravimetrically and the gas chromatographs (GC) with a Porapak Q column from Alltech Company. Data derived from gas chromatography were treated with a computer program (Autochro-WIN from Young-Lin Instrument Co., Ltd.). The uncertainty for the GC measurement and calibration is estimated to be within 0.001 in area fraction.

Experimental Procedures. Experiments to measure VLE data for the binary system of propane (1) + HFC-227ea (2) at various temperatures were performed by the following procedures. The system was first evacuated to remove all inert gases. A certain amount of HFC-227ea was supplied to 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 certain amount of propane was introduced into the cell from a sample reservoir. 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 was sufficient to obtain thermal equilibrium between the cell fluid and the thermostatic bath as well as the vapor and liquid phases. 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 the

Table 1. Characteristic Properties of the Chemicals (Critical Temperature T_{c} , Critical Pressure P_{c} , Acentric Factor w) from Database REFPROP 6.01¹⁸

| component | chemical formula | molecular weight | $T_{\rm c}/{ m K}$ | P _c /MPa | ω |
|---------------|-----------------------------------|---------------------|--------------------|---------------------|--------|
| propane (1) | C ₃ H ₈ | 44.10 | 369.85 | 4.248 | 0.1524 |
| HFC-227ea (2) | CF ₃ CHCF ₃ | 170.03 | 375.95 | 2.980 | 0.3632 |

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 values were considered to correspond to the equilibrium values. Considering the margin of error and the reproducibility of the GC, we generally estimated an overall uncertainty in the measurements of the composition of 0.002 in mole fraction for both the liquid and the vapor phases.

Correlation

In this work, the experimental VLE data were correlated with the Peng–Robinson equation of state (PR-EOS)⁴ and the Carnahan–Starling–De Santis equation of state (CSD-EOS).⁶ *PR-EOS*.

$$P = \frac{RT}{v_{\rm M} - b} - \frac{a(T)}{v_{\rm M}(v_{\rm M} + b) + b(v_{\rm M} - b)}$$
(1)

with

$$a(T) = \left(0.457235 \frac{R^2 T_c^2}{P_c}\right) \alpha(T)$$
(2)

$$b = 0.077796 \frac{RT_{\rm c}}{P_{\rm c}}$$
(3)

$$\alpha(T) = [1 + k(1 - \sqrt{T/T_c})]^2$$
(4)

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

Table 2. Coefficients (Temperature Dependent α and β) of Pure Components for the CSD-EOS¹⁷

| | α ₀ | $\alpha_1 \cdot 10^3$ | α ₂ •10 ⁶ | eta_0 | $\beta_1 \cdot 10^4$ | $\beta_{2} \cdot 10^{7}$ |
|----------------------|--|---|---|--------------------------------------|--|--|
| component | kJ•m ³ •kg ⁻¹ •mol ⁻² | $\overline{kJ \cdot m^3 \cdot kg^{-1} \cdot mol^{-2} \cdot K^{-1}}$ | $\overline{kJ \cdot m^3 \cdot kg^{-1} \cdot mol^{-2} \cdot K^{-2}}$ | $m^{3} \cdot kg^{-1} \cdot mol^{-1}$ | $\overline{\mathrm{m}^{3}\cdot\mathrm{kg}^{-1}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}}$ | m ³ ·kg ⁻¹ ·mol ⁻¹ ·K ⁻² |
| propane HFC-227ea | 2.988•10 ³ 5.988•10 ³ | -2.629 -3.438 | -1.097 -0.995 | 0.1430 0.2190 | -1.765 -2.940 | -0.5785 -0.5619 |

Table 3. Comparison of the Measured Pure Component Vapor Pressures P, with Reference Vapor Pressures P_{REF} From the Database REFPROP 6.01¹⁸

Table 4. Vapor-Liquid Equilibrium Measurements for the Propane (1) + HFC-227ea (2) System at (273.15 to 323.15) K

| T/K | P/MPa | P _{REF} /MPa | $\Delta P^{a}/MPa$ | $ \Delta P/P ^b$ |
|---------------|---------|-----------------------|--------------------|------------------|
| | | Propane | | |
| 273.15 | 0.476 | 0.474 | 0.002 | 0.004 |
| 283.15 | 0.632 | 0.636 | -0.004 | 0.006 |
| 293.15 | 0.833 | 0.836 | -0.003 | 0.004 |
| 303.15 | 1.079 | 1.079 | 0.000 | 0.000 |
| 313.15 | 1.366 | 1.369 | -0.003 | 0.002 |
| 323.15 | 1.709 | 1.713 | -0.004 | 0.002 |
| average value | | | | 0.003 |
| | | HFC-227ea | | |
| 273.15 | 0.195 | 0.193 | 0.002 | 0.010 |
| 283.15 | 0.280 | 0.278 | 0.002 | 0.007 |
| 293.15 | 0.389 | 0.389 | 0.000 | 0.000 |
| 303.15 | 0.527 | 0.530 | -0.003 | 0.006 |
| 313.15 | 0.704 | 0.706 | -0.002 | 0.003 |
| 323.15 | 0.920 | 0.922 | -0.002 | 0.002 |
| averag | e value | | | 0.005 |

$$^{\mu}\Delta P = P - P_{\text{REF}} \cdot ^{b} |\Delta P/P| = (|P - P_{\text{calcd}}|)/P$$

where the parameter *a* is a function of temperature; *b* is constant; *k* is a constant characteristic of each substance; ω is the acentric factor; *P* (MPa) is the pressure; *P*_c (MPa) is the critical pressure; *T* (K) is the absolute temperature; *T*_c (K) is the critical temperature; *T*_r is the reduced temperature; and *v*_M is the molar volume.

The Wong–Sandler mixing rules⁵ were used in this 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

$$b_{\rm m} = \frac{\sum_{i} \sum_{j} x_i x_j (b - a/RT)_{ij}}{(1 - A_{\infty}^{\rm E}/CRT - \sum_{i} x_i a_i/RTb_i)}$$
(6)

with

$$(b - a/RT)_{ij} = \frac{1}{2} [(b - a/RT)_i + (b - a/RT)_j](1 - k_{ij}) \quad (7)$$

and

$$\frac{a_{\rm m}}{b_{\rm m}} = \sum_{i} x_{i} \frac{a_{i}}{b_{i}} + \frac{A_{\infty}^{\rm E}}{C}$$

$$\tag{8}$$

where *C* is a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ 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 freeenergy model at infinite pressure that can be equated to a lowpressure excess Gibbs energy model.¹⁴ In this study, we used the nonrandom two-liquid (NRTL) model¹⁵ given by

$$\frac{A_{\infty}^{\rm E}}{RT} = \sum_{i} x_i \frac{\sum_{j} x_j G_{ji} \tau_{ji}}{\sum_{r} x_r G_{ri}}$$
(9)

| Experimental Data | | | | | |
|-------------------|-----------------------|------------|-------|-----------------------|------------|
| P/MPa | <i>x</i> ₁ | <i>y</i> 1 | P/MPa | <i>x</i> ₁ | <i>y</i> 1 |
| | T = 273.15 K | | | T = 283.15 K | |
| 0.195 | 0.000 | 0.000 | 0.280 | 0.000 | 0.000 |
| 0.320 | 0.115 | 0.406 | 0.396 | 0.081 | 0.315 |
| 0.384 | 0.205 | 0.523 | 0.504 | 0.199 | 0.460 |
| 0.428 | 0.306 | 0.599 | 0.572 | 0.305 | 0.552 |
| 0.459 | 0.406 | 0.644 | 0.622 | 0.423 | 0.611 |
| 0.479 | 0.498 | 0.698 | 0.648 | 0.512 | 0.662 |
| 0.496 | 0.598 | 0.731 | 0.664 | 0.608 | 0.703 |
| 0.505 | 0.664 | 0.752 | 0.673 | 0.662 | 0.727 |
| 0.511 | 0.731 | 0.779 | 0.684 | 0.733 | 0.766 |
| 0.514 | 0.813 | 0.820 | 0.687 | 0.763 | 0.782 |
| 0.510 | 0.866 | 0.846 | 0.689 | 0.805 | 0.806 |
| 0.509 | 0.907 | 0.877 | 0.688 | 0.851 | 0.836 |
| 0.496 | 0.966 | 0.943 | 0.673 | 0.942 | 0.916 |
| 0.476 | 1.000 | 1.000 | 0.632 | 1.000 | 1.000 |
| | T = 293.15 K | | | T = 303.15 K | |
| 0.389 | 0.000 | 0.000 | 0.527 | 0.000 | 0.000 |
| 0.564 | 0.109 | 0.332 | 0.696 | 0.081 | 0.244 |
| 0.689 | 0.225 | 0.488 | 0.855 | 0.195 | 0.423 |
| 0.776 | 0.344 | 0.579 | 0.983 | 0.327 | 0.541 |
| 0.835 | 0.469 | 0.646 | 1.074 | 0.479 | 0.631 |
| 0.862 | 0.562 | 0.688 | 1.117 | 0.591 | 0.687 |
| 0.885 | 0.665 | 0.731 | 1.145 | 0.725 | 0.754 |
| 0.892 | 0.752 | 0.775 | 1.150 | 0.797 | 0.791 |
| 0.895 | 0.776 | 0.789 | 1.151 | 0.841 | 0.828 |
| 0.893 | 0.815 | 0.812 | 1.136 | 0.900 | 0.877 |
| 0.892 | 0.858 | 0.841 | 1.079 | 1.000 | 1.000 |
| 0.875 | 0.929 | 0.904 | | | |
| 0.833 | 1.000 | 1.000 | | | |
| | T = 313.15 K | | | T = 323.15 K | |
| 0.704 | 0.000 | 0.000 | 0.920 | 0.000 | 0.000 |
| 0.823 | 0.046 | 0.140 | 1.197 | 0.109 | 0.249 |
| 0.908 | 0.086 | 0.231 | 1.351 | 0.187 | 0.366 |
| 1.004 | 0.142 | 0.324 | 1.495 | 0.276 | 0.440 |
| 1.105 | 0.202 | 0.399 | 1.607 | 0.368 | 0.504 |
| 1.240 | 0.315 | 0.501 | 1.68/ | 0.449 | 0.572 |
| 1.364 | 0.477 | 0.607 | 1.785 | 0.611 | 0.654 |
| 1.412 | 0.532 | 0.637 | 1.800 | 0.629 | 0.680 |
| 1.446 | 0.579 | 0.663 | 1.830 | 0.757 | 0.762 |
| 1.478 | 0.706 | 0.761 | 1.837 | 0.800 | 0.773 |
| 1.481 | 0.796 | 0.801 | 1.826 | 0.807 | 0.807 |
| 1.459 | 0.899 | 0.872 | 1.816 | 0.913 | 0.884 |
| 1.424 | 0.970 | 0.954 | 1.709 | 1.000 | 1.000 |
| 1.300 | 1.000 | 1.000 | | | |

with

$$G_{ii} = \exp(-\alpha_{ii}\tau_{ii}) \text{ and } \tau_{ii} = (g_{ii} - g_{ii})/(RT)$$
 (10)

where

$$A_{ii} = (g_{ii} - g_{ji}) \tag{11}$$

The critical temperature (T_c) , critical pressure (P_c) , and acentric factor (ω) for both HFC-227ea and propane that were used to calculate the parameters for the PR-EOS are provided in Table 1. We have set the nonrandomness parameter, α_{ij} , equal to a fixed value of 0.3 for all of the binary mixtures studied here.

CSD-EOS. The CSD-EOS is given by

$$\frac{Pv_{\rm M}}{RT} = \frac{1+y+y^2-y^3}{(1-y)^3} - \frac{a}{RT(v_{\rm M}+b)}$$
(12)



Figure 2. P-x-y diagram for the propane (1) + HFC-227ea (2) system. Experimental data at: \bigtriangledown , 273.15 K; \triangle , 283.15 K; \bigcirc , 293.15 K; \square , 303.15 K; \diamond , 313.15 K; and \bigcirc , 323.15 K. –, Calculated with the PR-EOS using W–S mixing; ---, calculated with the CSD-EOS.

Table 5. Optimal Values of the Binary Parameters k_{12} and f_{12} , Adjustable Parameters for the NRTL Model τ_{21} and τ_{12} , and Absolute Average Relative Deviations of P and Absolute Average Deviation of y

| | PR-EOS | | | | | CSD-EOS | | |
|--------|------------|----------------|----------------|---------------------|--------------------|------------|---------------------|--------------------|
| T/K | k_{12}^a | $t_{21}{}^{b}$ | $	au_{12}{}^b$ | AARD-P ^c | AAD-y ^d | f_{12}^a | AARD-P ^c | AAD-y ^d |
| 273.15 | -0.0349 | 2.4929 | 5.4426 | 0.003 | 0.008 | 0.131 | 0.023 | 0.013 |
| 283.15 | 0.0017 | 2.2917 | 5.0456 | 0.004 | 0.014 | 0.126 | 0.012 | 0.016 |
| 293.15 | 0.2258 | 1.5390 | 2.5811 | 0.003 | 0.007 | 0.111 | 0.015 | 0.005 |
| 303.15 | 0.1141 | 2.2813 | 3.0849 | 0.005 | 0.005 | 0.113 | 0.013 | 0.005 |
| 313.15 | -0.0160 | 2.5326 | 5.0622 | 0.005 | 0.008 | 0.141 | 0.009 | 0.006 |
| 323.15 | 0.2036 | 1.8516 | 2.1418 | 0.004 | 0.008 | 0.124 | 0.008 | 0.009 |
| averag | e values | | | 0.004 | 0.008 | | 0.013 | 0.009 |

^{*a*} k_{12} and f_{12} are interaction parameters. ^{*b*} $\tau_{ij} = A_{ij}/RT$. The unit of A_{ij} and A_{ji} is kJ·mol⁻¹. ^{*c*} AARD- $P = 1/N \sum |(P_{exptl} - P_{calcd})/P_{exptl}|$. ^{*d*} AAD- $y = 1/N \sum |y_{exptl} - y_{calcd}|$.

Where

$$y = \frac{b}{4v_{\rm M}} \tag{13}$$

and $v_{\rm M}$ is the molar volume. For a pure component, the temperature dependence of *a* and *b* is represented by the following forms

$$a = \alpha_0 \exp(\alpha_1 T + \alpha_2 T^2) \tag{14}$$

$$b = \beta_0 + \beta_1 T + \beta_2 T^2 \tag{15}$$

The CSD-EOS using the approach of Morrison and McLinden¹⁶ was adopted to correlate the VLE data. The coefficients of α_0 , α_1 , and α_2 in eq 14 and β_0 , β_1 , and β_2 in eq 15 were cited from REFPROP 5.0¹⁷ and listed in Table 2.

In the application of the CSD-EOS for a mixture, there exist the effective molecular parameters a_m and b_m (the subscript m refers to the mixture) defined by using the following mixing rules

$$a_{\rm m} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij} \tag{16}$$

$$b_{\rm m} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j b_{ij}$$
(17)

where n is the number of components in the mixture.

When i = j, the values of a_{ii} and b_{ii} are those of a and b for the pure components which are determined by eqs 14 and 15. The values of a_{ij} and b_{ij} can be obtained if nearly any experimental property of the mixture is known. For the binary systems, the values of a_{12} and b_{12} can be expressed in the following forms

$$a_{12} = (1 - f_{12})(a_1 a_2)^{1/2}$$
(18)

$$b_{12} = \frac{1}{8}(b_1^{1/3} + b_2^{1/3})^3 \tag{19}$$



Figure 3. Deviation of pressure for the system propane (1) + HFC-227ea (2) from the PR-EOS using the W–S mixing rule at: \bigtriangledown , 273.15 K; \triangle , 283.15 K; \bigcirc , 293.15 K; \bigcirc , 303.15 K; \Diamond , 313.15 K; and \bigcirc , 323.15 K.



Figure 4. Deviation of vapor composition for the system propane (1) + HFC-227ea (2) from the PR-EOS using the W–S mixing rule at: \bigtriangledown , 273.15 K; \triangle , 283.15 K; \bigcirc , 293.15 K; \bigcirc , 303.15 K; \diamondsuit , 313.15 K; and \bigcirc , 323.15 K.

where f_{12} is the interaction parameter and a_i and b_i are properties of the pure components.

The parameters of both PR-EOS and CSD-EOS were obtained by minimizing the following objective function

objective function
$$= \frac{1}{N} \sum_{j}^{N} \left[\left(\frac{P_{j,\text{exptl}} - P_{j,\text{calcd}}}{P_{j,\text{exptl}}} \right) \right]^2$$
 (20)

Results and Discussion

Table 3 shows the comparison of measured vapor pressures of pure propane and HFC-227ea with those calculated from the database REFPROP 6.01,¹⁸ which is considered to be reliable

Table 6. Azeotropic Pressure P_{az} and Azeotropic Liquid Mole Fraction x_{az} for Propane (1) + HFC-227ea (2) as a Function of Temperature

| T/K | azeotropic pressure P _{az} /MPa | azeotropic composition x_{az} (propane mole fraction) |
|--------|---|---|
| 273.15 | 0.514 | 0.841 |
| 283.15 | 0.689 | 0.806 |
| 293.15 | 0.895 | 0.802 |
| 303.15 | 1.150 | 0.784 |
| 313.15 | 1.488 | 0.798 |
| 323.15 | 1.838 | 0.770 |

for the pure compounds considered and consistent with other literature data. As can be seen in this table, the deviations of



Figure 5. Variation of the azeotropic pressure with temperature for propane (1) + HFC-227ea (2). The equation of the fitting line is $P_{az} = 2.506 \cdot 10^{-4} (T/K)^2 - 0.123(T/K) + 15.405$ (323.15 K $\ge T \ge 273.15$ K).



Figure 6. Variation of the azeotropic composition with temperature for propane (1) + HFC-227ea (2). The equation of the fitting line is $x_{az} = -1.114 \cdot 10^{-4}$ T/K + 1.140 (323.15 K $\ge T \ge 273.15$ K).

vapor pressure (ΔP) between measured and calculated values from REFPROP 6.01¹⁸ are within 0.005 MPa. The average values of absolute relative deviations of *P* ($|\Delta P/P|$) between measured and calculated values were 0.001 for propane and 0.003 for HFC-227ea. The experimental data of isothermal VLE for the binary system of propane (1) + HFC-227ea (2) are listed in Table 4. These tables list 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.

Figure 2 shows the comparison of measured and calculated values with the PR-EOS and CSD-EOS for the binary system of propane (1) + HFC-227ea (2) at various temperatures. The experimental VLE data at (273.15, 283.15, 293.15, 303.15, 313.15, and 323.15) K are shown as reverse triangles, triangles, circles, squares, diamonds, and hexagons, respectively. The black solid lines represent the calculated data by the PR-EOS,

and the black dashed lines represent the calculated data by the CSD-EOS.

The interaction parameters of the binary mixtures for each isotherm, the binary parameters of the NRTL model with the Wong–Sandler mixing rules, and the average absolute relative deviations of pressure (AARD-*P*) and average absolute deviations of vapor-phase composition (AAD-*y*) between measured and calculated values are reported in Table 5. The average values of AARD-*P* and AAD-*y* for all the six temperatures were 0.004 and 0.008 for the PR-EOS and 0.013 and 0.009 for the CSD-EOS, respectively. Both the average absolute deviations of pressure and vapor-phase compositions of PR-EOS are less than those of CSD-EOS. So, only the results of error estimations with the PR-EOS for *P* and *y* were shown in Figures 3 and 4, respectively. From these figures and the low average deviations of *P* and *y*, we conclude that both the PR-EOS and the CSD-EOS could be used for predicting VLE data for propane (1) +

HFC-227ea, and the PR-EOS is more or less better than the CSD-EOS for these systems.

This mixture exhibited an azeotrope. Azeotropic data of this mixture have been determined at the compositions between 0.77 and 0.85 in mole fraction and at pressures between (0.51 and 1.84) MPa in the temperature range from (273.15 to 323.15) K. Azeotropic compositions and pressures are shown in Table 6 and Figures 5 and 6. As can be seen in these figures, azeotropic compositions and pressures are dependent on the temperature. In the range of experimental temperatures, the azeotropic compositions were correlated by the empirical equation, $x_{az} = -1.139 \cdot 10^{-3} T/K + 1.140$, and the azeotropic pressure was correlated by the empirical equation, $P_{az} / MPa = 1.541 \cdot 10^{-0.123} T/K + 2.506 \cdot 10^{-4} T^2/K^2$. These equations were fitted within the temperature range $T \ge 273.15$ K.

Conclusions

VLE data for binary systems of propane (1) + HFC-227ea (2) were measured at five equally spaced temperatures between (273.15 and 323.15) 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 strong positive azeotropes for the full temperature range studied here. According to the results of this work, the PR-EOS gave better correlation results than the CSD-EOS for propane (1) + HFC-227ea (2).

Acknowledgment

We gratefully acknowledge the help of Miss Hyun Ah Kim in getting experimental vapor—liquid equilibrium data for the propane + HFC-227ea system.

Literature Cited

- Poolen, L. J. V.; Holcomb, C. D.; Rainwater, J. C. Isoplethic Method to Estimate Critical Lines for Binary Fluid Mixtures from Subcritical Vapor-Liquid Equilibrium: Application to the Azeotropic Mixtures R32 + C3H8 and R125 + C3H8. *Ind. Eng. Chem. Res.* 2001, 40, 4610–4614.
- (2) Kayukawa, Y.; Watanabe, K. P_ρT_x Measurements for Gas-Phase Pentafluoroethane + Propane Mixtures by the Burnett Method. J. Chem. Eng. Data 2001, 46 (5), 1025–1030.
- (3) Park, Y. M.; Jung, M. Y. Vapor-Liquid Equilibria for the Pentafluoroethane (HFC-125) + Propane (R-290) System. J. Chem. Eng. Data 2002, 47, 818-822.
- (4) Peng, D. Y.; Robinson, D. B. A New Two Constant Equation of State. Ind. Eng. Chem. Fundam. 1976, 15, 59–64.
- (5) Wong, D. S. H.; Sandler, S. I. A Theoretically Correct Mixing Rule for Cubic Equations of State. AIChE J. 1992, 38, 671–680.

- (6) DeSantis, R.; Gironi, F.; Marrelli, L. Vapor Liquid Equilibrium from a Hard-Sphere Equation of State. Ind. Eng. Chem. Fundam. 1973, 15, 183–189.
- (7) Lim, J. S.; Park, J. Y.; Lee, B. G.; Lee, Y. W. Phase Equilibria of 1,1,1-Trifluoroethane (HFC-143a) + 1,1,1,2-Tetrafluoroethane (HFC-134a), and + 1,1-Difluoroethane (HFC-152a) at 273.15, 293.15, 303.15, and 313.15 K. *Fluid Phase Equilib.* 2002, *193*, 29–39.
- (8) Park, J. Y.; Lim, J. S.; Lee, B. G. High-Pressure Vapor-Liquid Equilibria of Binary Mixtures Composed of HFC-32, 125, 134a, 152a, 227ea and R600a (Isobutane). *Fluid Phase Equilib.* **2002**, *194–197*, 981–993.
- (9) Lim, J. S.; Park, J. Y.; Lee, B. G. Phase Equilibria of CFC Alternative Refrigerant Mixtures: 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) + Difluoromethane (HFC-32), 1,1,1,2-Tetrafluoroethane (HFC-134a), and + 1,1-Difluoroethane (HFC-152a). *Int. J. Thermophys.* 2001, 21, 1339–1349.
- (10) Lim, J. S.; Park, K. H.; Lee, B. G.; Kim, J. D. Phase Equilibria of CFC Alternative Refrigerant Mixtures. Binary Systems of Trifluoromethane (HFC-23) + 1,1,1,2-Tetrafluoroethane (HFC-134a), and Trifluoromethane (HFC-23) + 1,1,1,2,3,3,3- Heptafluoropropane (HFC-227ea) at 283.15 and 293.15 K. J. Chem. Eng. Data 2001, 46, 1580–1583.
- (11) Park, J. Y.; Lim, J. S.; Lee, B. G.; Lee, Y. W. Phase Equilibria of CFC Alternative Refrigerant Mixtures: 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) + Difluoromethane (HFC-32), + 1,1,1,2-Tetrafluoroethane (HFC-134a), and + 1,1-Difluoroethane (HFC-152a). *Int. J. Thermophys.* 2001, 22, 901–917.
- (12) Lim, J. S.; Park, J. Y.; Lee, B. G. Vapor-Liquid Equilibria of CFC Alternative Refrigerant Mixtures: Trifluoromethane (HFC-23) + Difluoromethane (HFC-32), Trifluoromethane (HFC-23) + Pentafluoroethane (HFC-125), and Pentafluoroethane (HFC-125) + 1,1-Difluoroethane (HFC-152a). *Int. J. Thermophys.* **2000**, *21*, 1339–1349.
- (13) Lim, J. S.; Park, J. Y.; Lee, B. G.; Kim, J. D. Phases Equilibria of CFC Alternative Refrigerant Mixtures. Binary Systems of Trifluoromethane + Isobutane at 283.15 and 293.15 K and 1,1,1-Trifluoroethane + Isobutane at 323.15 and 333.15 K. J. Chem. Eng. Data 2000, 45, 734–737.
- (14) Wong, D. S. H.; Orbey, H.; Sandler, S. I. Equation of state mixing rule for nonideal mixtures using available activity coefficient model parameters and that allows extrapolation over large ranges of temperature and pressure. *Ind. Eng. Chem. Res.* **1992**, *31*, 2033–2039.
- (15) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.
- (16) Morrison, G.; McLinden, M. O. Application of a Hard Sphere Equation of State to Refrigerants and Refrigerant Mixtures. *National Bureau* of Standards and Technology Note. **1986**, 1226, 1–14.
- (17) Huber, M.; Gallagher, J.; McLinden, M. O.; Morrison, G. NIST Thermodynamic and Transport properties of Refrigerants and Refrigerant Mixtures Database, REFPROP V.5.0, NIST 1996.
- (18) McLinden, M. O.; Klein, S. A.; Lemmon, E. W.; Peskin, A. P. Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database, REFPROP V.6.01, NIST 1998.

Received for review May 16, 2007. Accepted August 6, 2007. We gratefully acknowledge financial support from the Korea Ministry of Commerce, Industry & Energy, and the Korea Energy Management Corporation and Sogang University Research Grant in 2007.

JE700271N