Vapor−Liquid Equilibria for the Pentafluoroethane (HFC-125) + Propane (R-290) System

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Isothermal vapor−liquid equilibrium data of the binary system pentafluoroethane (HFC-125) + propane (R-290) were measured in the temperature range from 273.15 K to 313.15 K at 10 K intervals and in the composition range from 0.1 to 0.8 mole fraction HFC-125. Temperature, pressure, and compositions of the liquid and vapor phases were measured with a circulation-type apparatus. The experimental data were correlated with the Carnahan−Starling−De Santis, Peng−Robinson, and Redlich−Kwong−Soave equations of state. Azeotropic behavior was revealed near 0.77 mole fraction HFC-125. The vapor pressure of the azeotropic system is between those of chlorodifluoromethane (HCFC-22) and the zeotropic mixture of difluoroethane (HFC-32) + HFC-125 (50−50). This azeotropic system hasu good potential to replace the use of HCFC-22 as a refrigerant.

Introduction

The regulation of CFCs and HCFCs has led to investigation of pure HFCs and HCs and mixtures of these fluids as alternative refrigerants. Particularly, hydrocarbons have been considered as alternative refrigerants because of their zero ozone-depletion potential, low toxicity, and chemical stability, although most hydrocarbons are flammable. The flammability of hydrocarbons can be reduced by mixing them with nonflammable alternative refrigerants. Accurate and reliable data on the thermophysical properties of these mixtures are essential for investigating the possibility of using these mixtures as alternative refrigerants. Vapor−liquid equilibrium data are one of the most important basic properties in evaluating the thermophysical properties of these mixtures and for determining their optimal composition. In this study, isothermal vapor−liquid equilibrium data of the binary system HFC-125 + propane were measured in the temperature range from 273.15 K to 313.15 K and correlated with the Carnahan−Starling−DeSantis (CSD),[1] Peng−Robinson (PR),[2] and Redlich−Kwong−Soave (RKS)[3] equations of state. On the basis of the measured vapor−liquid equilibrium data, azeotropic behavior of the binary system and the possibility of replacing HCFC-22 with the azeotropic system will be discussed

Experimental Section

Chemicals. The samples of pure HFC-125 were obtained from Du Pont Co. and propane was obtained from Air Products and Chemicals, Inc. The manufacturers stated that the purity of the chemicals was 99.9 mass %. The chemicals were used without further purification.

Apparatus and Procedures. The measurement of the vapor−liquid equilibrium was conducted in a circulation-type apparatus. This apparatus is shown schematically in Figure 1. It is described only briefly here because the apparatus and procedures have already been presented in more detail.[4,5] The apparatus consisted of an equilibrium unit, a sampling and analysis unit, and a supply unit. The core of the apparatus was the equilibrium unit, which consisted of an equilibrium cell, a magnetic pump, and a constant temperature-controlled bath. The equilibrium cell was made of Type-316 stainless steel with an inner volume of about 128 cm^3. Both the equilibrium cell and the magnetic pump were immersed in an isothermal bath that was filled with silicon oil. The temperature of the isothermal bath and equilibrium cell was maintained at a set point by a circulator. It took 5 or 6 h for the temperature of the bath and cell to stabilize at a set point. After confirming that the bath and cell temperature were maintained at a set point within ±0.02K, the magnetic pump was started. It pumped the vapor phase into the liquid phase to ensure proper mixing, thus enabling equilibrium to be quickly reached. It took about 30 min for the vapor and liquid phases to reach equilibrium. The bath and cell temperatures were measured with a 100 Ω platinum resistance sensor immersed in the cell and a precision thermometer (Yokogawa, 7563) with a precision of 0.01 K. The sensor and thermometer were calibrated on the ITS-90. The uncertainty in the temperature measurements was estimated to be ±0.02 K. The pressure was measured with a pressure transducer (Druck, PDCR 922) with a precision of 0.1 kPa. The pressure was read when the cell pressure was constant within 1 kPa to 2 kPa. The pressure transducer was calibrated against a quartz crystal pressure transducer after each series of experiments. The uncertainty of the pressure measurement was estimated to be 0.4%. After equilibrium was reached, the vapor and liquid samples for analyzing compositions were trapped in a space between two valves and introduced into evacuated sample cylinders. The space between the two valves for the liquid sample was about 0.1 cm^3. The volume of the sample cylinder was sufficient for the liquid sample to completely evaporate. The compositions of the vapor and liquid samples were determined using a gas chromatograph (HP 5890II) equipped with a Porapak-Q column (1.83-m long; 3.18-mm diameter; mesh range, 80/100) and a thermal conductivity detector. The compositions at one condition were measured at least three times to ensure accuracy and

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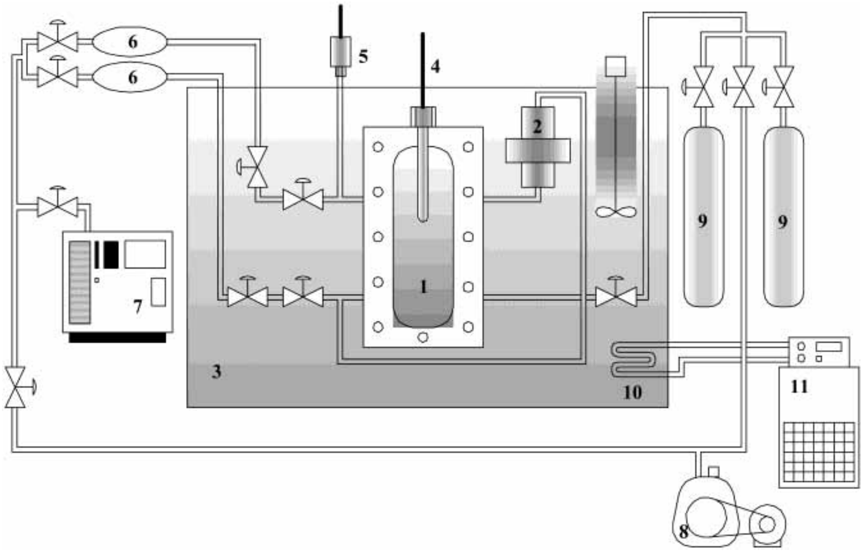

Figure 1. Schematic diagram of the vapor−liquid equilibrium apparatus: 1, equilibrium cell; 2, magnetic pump; 3, isothermal bath; 4, platinum resistance thermometer; 5, pressure transducer; 6, sample cylinder; 7, gas chromatograph; 8, vacuum pump; 9, refrigerant vessel; 10, heat exchanger; 11, cooler.

Table 1. Vapor−Liquid Equilibrium Data for the HFC-125 + Propane System

	mole fraction of HFC-125			mole fraction of HFC-125	
P (kPa)	liquid	vapor	P (kPa)	liquid	vapor
		T = 273.15 K			
474.6	0.0000	0.0000	810.3	0.5840	0.6838
595.6	0.0979	0.2731	834.1	0.8005	0.8014
696.4	0.2180	0.4446	670.1	1.0000	1.0000
		T = 283.15 K			
636.1	0.0000	0.0000	1074.2	0.5760	0.6677
783.5	0.0992	0.2811	1101.5	0.8286	0.8027
930.8	0.2293	0.4398	908.8	1.0000	1.0000
		T = 293.15 K			
836.5	0.0000	0.0000	1396.3	0.5800	0.6653
1010.5	0.0993	0.1923	1432.0	0.8312	0.8089
1187.2	0.2567	0.4243	1205.3	1.0000	1.0000
		T = 303.15 K			
1079.6	0.0000	0.0000	1779.7	0.5769	0.6541
1261.7	0.0974	0.2147	1825.8	0.8328	0.8134
1471.6	0.2069	0.3795	1565.6	1.0000	1.0000
		T = 313.15 K			
1368.4	0.0000	0.0000	2236.8	0.5671	0.6439
1568.5	0.0901	0.1899	2305.8	0.8287	0.8141
1841.9	0.2140	0.3536	2003.9	1.0000	1.0000

repeatability. The maximum variance of mole fraction among three measurements was <0.1%. The gas chromatograph was calibrated with the pure components of known purity and with mixtures of known composition that had been prepared gravimetrically. The uncertainty of the composition measurements was estimated to be ±0.3 mol %.

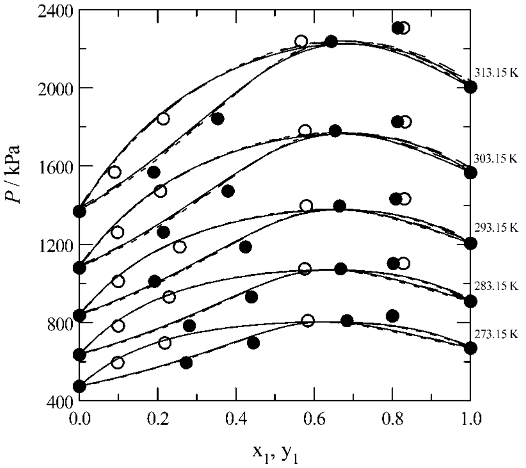

Figure 2. Vapor−liquid equilibrium data for the HFC-125 (1) + propane (2) system: (○,●) experimental data; (—) Carnahan−Starling−De Santis (CSD) equation of state; (- - -) Peng−Robinson (PR) equation of state; (— — —) Redlich−Kwong−Soave (RKS) equation of state.

Table 2. Summary of Experimental Data for the HFC-125 + Propane System

system/authors	no. points	pressure range (kPa)	temperature range (K)	composition range/mole fraction HFC-125
$P-V-x-y$/this work	30	474−2240	273−313	0.00−1.00
$P-\rho-T-x$/Kayukawa and Watanabe[6]	187	159−4917	305−380	0.00−0.75

Results and Discussion

Vapor−liquid equilibrium data for the binary system of HFC-125 + propane were measured in a temperature range from 273.15 K to 313.15 K at 10 K intervals. These data are presented in Table 1 and in Figure 2. Experimental data for the pressure−density−temperature−liquid composition ($P\rho Tx$) for HFC-125 + propane have been reported by Kayukawa and Watanabe.[6] A summary of the data of this work and that of ref 6 is presented in Table 2. A quantitative comparison between the two works was not possible because the data of this work are $PTxy$ data and those of ref 6 are $P\rho Tx$ data measured by the Burnett method, and the temperature ranges of the two works did not overlap.

The experimental results were correlated with the Carnahan−Starling−DeSantis (CSD),[1] Peng−Robinson,[2] and Redlich−Kwong−Soave[3] equations of state using the van der Waals mixing rules. The CSD equation of state is given as

$$\frac{Pv}{RT} = \frac{1+y+y^2-y^3}{(1-y)^3} - \frac{a}{RT(v+b)} \tag{1}$$

where

Table 3. Critical Properties and Acentric Factors of Pure Components (REFPROP)[7]

	propane	HFC-125
critical temperature, T_c (K)	369.85	339.33
critical pressure, P_c (kPa)	4248	3629.0
acentric factor	0.1524	0.3035

Table 4. Coefficients of the CSD EOS Used for Data Correlation (REFPROP)[7]

	propane	HFC-125
a_0 (kPa·L^2·mol^{-2})	2988.277	3427.9219
a_1 (K^{-1})	-2.629019×10^{-3}	$-3.1746132 \times 10^{-3}$
a_2 (K^{-2})	-1.097062×10^{-6}	$-1.7572861 \times 10^{-6}$
b_0 (L·mol^{-1})	0.1429625	0.14938043
b_1 (L·mol^{-1}·K^{-1})	$-1.7651912 \times 10^{-4}$	$-1.8085107 \times 10^{-4}$
b_2 (L·mol^{-1}·K^{-2})	-5.785137×10^{-8}	$-1.1881331 \times 10^{-7}$

Table 5. Binary Interaction Parameters for HFC-125(1) + Propane(2) System and Deviation of Pressure and Vapor Mole Fraction of HFC-125(y_1) from Equations of State

T (K)	k_{12}	$\delta(\Delta P/P)^a$ (%)	$\delta y_1{}^b$
	Canahan−Starling−De Santis		
273.15	0.1282	2.06	0.0451
283.15	0.1284	2.01	0.0412
293.15	0.1227	2.40	0.0323
303.15	0.1225	2.53	0.0285
313.15	0.1225	2.20	0.0181
	average	2.24	0.0330
	Peng−Robinson		
273.15	0.1384	2.23	0.0448
283.15	0.1388	2.20	0.0342
293.15	0.1324	2.33	0.0340
303.15	0.1319	2.53	0.0172
313.15	0.1312	1.96	0.0172
	average	2.25	0.0295
	Redlich−Kwong−Soave		
273.15	0.1404	2.27	0.0431
283.15	0.1402	2.23	0.0369
293.15	0.1333	2.62	0.0319
303.15	0.1330	2.44	0.0218
313.15	0.1333	2.37	0.0170
	average	2.38	0.0301

[a] $\delta(\Delta P/P) = (100/N)\Sigma(|P_{\mathrm{exp},i} - P_{\mathrm{cal},i}|/P_{\mathrm{exp},i})_i$. [b] $\delta y_1 = (1/N)\Sigma(|y_{1,\mathrm{exp},i} - y_{1,\mathrm{cal},i}|)_i$.

$$y = \frac{b}{4v} \tag{2}$$

with the following temperature-dependent parameters a and b:

$$a = a_0 \exp(a_1 T + a_2 T^2) \tag{3}$$

$$b = b_0 + b_1 T + b_2 T^2 \tag{4}$$

The same mixing rules were used for three equations of state,

$$a = \sum\sum \xi_i \xi_j a_{ij} \tag{5}$$

$$b = \sum\sum \xi_i \xi_j b_{ij} \tag{6}$$

where ξ_i is the mole fraction of the ith component and

$$a_{12} = (1 - k_{12})(a_{11}a_{22})^{1/2} \tag{7}$$

$$b_{12} = \frac{(b_{11}^{1/3} + b_{22}^{1/3})^3}{8} \tag{8}$$

where k_{12} is the binary interaction parameter. The critical properties and acentric factors of HFC-125 and propane are listed in Table 3. The coefficients of a and b of the CSD equation of state are cited from REFPROP[7] and are listed in Table 4.

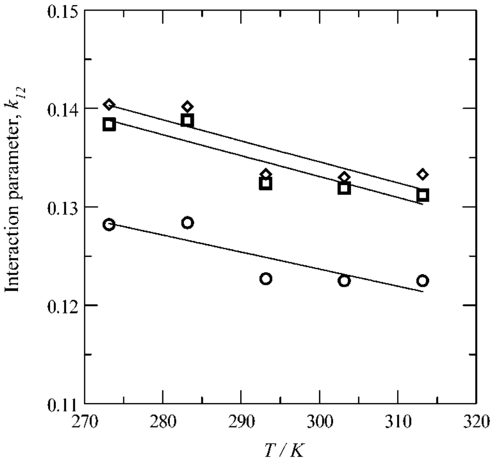

Figure 3. Binary interaction parameters in Carnahan−Starling−De Santis, Peng−Robinsion, and Redlich−Kwong−Soave equations of state for the HFC-125 + propane system at five temperature conditions: (○) CSD; (◇) RKS; (□) PR.

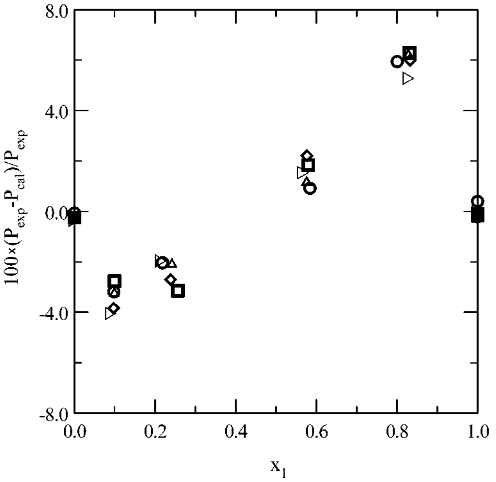

Figure 4. Deviation of the bubble point pressure for the HFC-125 (1) + propane (2) system between the measured data and the calculated results from the Carnahan−Starling−De Santis equation of state: percent deviation = 100 × ($P_{\mathrm{exp}} - P_{\mathrm{cal}}$)/$P_{\mathrm{exp}}$: (○) 273.15 K; (△) 283.15 K; (□) 293.15 K; (◇) 303.15 K; (tilted triangle) 313.15 K.

The binary interaction parameter k_{12} was determined by minimizing the objective function,

$$\mathrm{obj} = \sum_{i=1}^{N}\left(\frac{P_{\mathrm{cal},i} - P_{\mathrm{exp},i}}{P_{\mathrm{exp},i}}\right) \tag{9}$$

where N is the number of experimental points, "obj" is the objective function, and the subscripts "cal" and "exp" denote calculated and experimental results, respectively.

The binary interaction parameters were determined for five temperature conditions, that is, 273.15, 283.15, 293.15, 303.15, and 313.15 K and are presented in Table 5 and in Figure 3. It is evident that the binary interaction parameter for the three equations of state decreases slightly as the temperature increases.

The relative deviations between the experimentally measured data for the pressure and vapor-phase mole

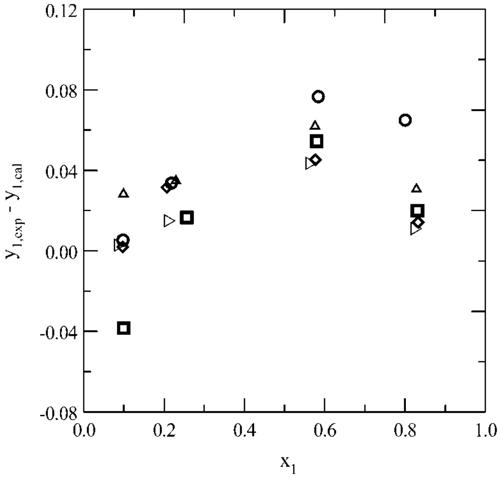

Figure 5. Deviation of the vapor-phase mole fraction of HFC-125 for the HFC-125 (1) + propane (2) system between the measured data and the calculated results from the Carnahan–Starling–De Santis equation of state; deviation = $y_{exp} - y_{cal}$: (○) 273.15 K; (△) 283.15 K; (□) 293.15 K; (◇) 303.15 K; (tilted triangle) 313.15 K.

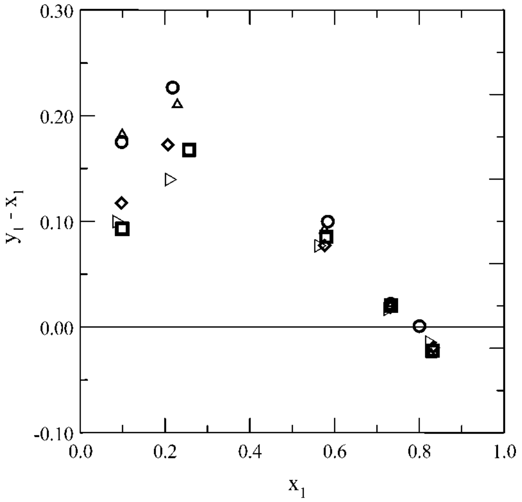

Figure 6. The difference between vapor composition and liquid composition ($y_1 - x_1$) against liquid composition x_1 for the HFC-125 (1) + propane (2) system: (○) 273.15 K; (△) 283.15 K; (□) 293.15 K; (◇) 303.15 K; (tilted triangle) 313.15 K.

fraction of HFC-125 and the calculated results from equations of state are given in Table 5. The average deviation between the measured pressures and calculated results from the CSD equation of state is about 2.24% and that from the PR equation of state is 2.25%. And that from the RKS equation of state is about 2.38%. It can be concluded that, on the basis of these results, the CSD equation of state correlated the experimental data only slightly better than the PR and RKS equations of state. Figures 4 and 5 show comparisons of the relative pressure and vapor-phase mole fraction of HFC-125 between the measured data and the calculated results from the CSD equation of state.

Azeotropic compositions are determined to meet either the condition

$$\left(\frac{\partial P}{\partial x_1}\right)_T = 0 \qquad (10)$$

or equivalently

$$x_1 = y_1 \quad \text{at constant temperature} \qquad (11)$$

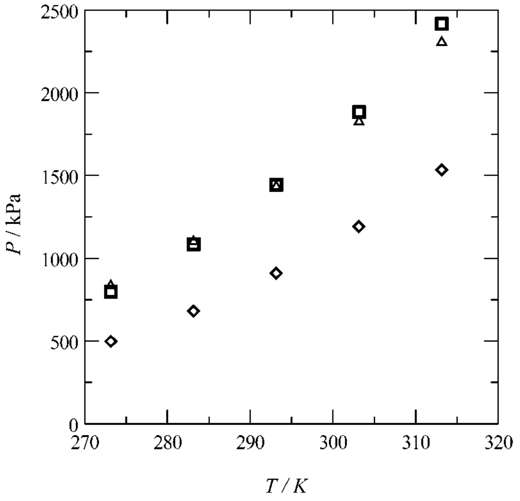

Figure 7. Saturation vapor pressure for HCFC-22, zeotropic mixture R-410a, and azeotropic mixture of HFC-125 + propane.: (◇) HCFC-22; (□) R-410a; (△) azeotropic mixture of HFC-125 + propane.

Table 6. Coefficients of the Polynomial Equation Fitting the Difference between Vapor and Liquid Mole Fracions HFC-125: $(y_1 - x_1) = a_1x_1^3 + a_2x_1^2 + a_3x_1 + a_4$

T (K)	a_1	a_2	a_3	a_4
273.15	2.0206	−3.4238	1.3548	0.0732
283.15	1.1674	−2.1420	0.8049	0.1230
293.15	1.5357	−2.8982	1.3382	−0.0123
303.15	1.6870	−2.9621	1.2485	0.0236
313.15	1.0203	−1.9258	0.8296	0.0400

Table 7. Azeotropic Compositions and Pressures of the HFC-125 + Propane System

T (K)	azeotropic composition HFC-125	P (kPa)		
		CSD	PR	RKS
273.15	0.8019	784.2	779.8	782.5
283.15	0.7696	1054.7	1051.5	1054.1
293.15	0.7722	1362.5	1360.8	1363.9
303.15	0.7666	1750.4	1752.8	1755.3
313.15	0.7789	2207.6	2216.0	2218.6

In this study, the latter condition was used. The difference between the measured vapor composition (y_1) and the liquid composition (x_1) are shown in Figure 6 and were fitted with a cubic polynomial equation in Table 6. The azeotropic composition is a solution of the polynomial equation meeting eq 11 and can be determined graphically. The azeotropic compositions are given at varying temperatures in Table 7. Over the temperature range from 273.15 K to 313.15 K, the azeotropic composition was found to be about 0.77 mole fraction HFC-125. In Figure 2, it can be seen that, around this azeotropic composition, the VLE prediction deviated from the measured VLE data. This indicated that, around this azeotropic composition, the calculation algorithm was not stable. In Figure 7, the vapor pressures of HCFC-22, the azeotropic mixture of HFC-125 + propane, and the zeotropic mixture of difluoroethane (HFC-32) + HFC-125 (50–50) (alternative refrigerant blend R-410a) were compared. The vapor pressure of the azeotropic system HFC-125 + propane was lower than that of R-410a and higher than that of HCFC-22. In terms of vapor pressure, the azeotropic HFC-125 + propane may therefore be a suitable alternative refrigerant to replace HCFC-22. Further experimental investigations are recommended for this composition.

Conclusions

Isothermal vapor−liquid equilibrium data of the binary system HFC-125 + propane were obtained at 30 conditions over the temperature range from 273.15 K to 313.15 K at 10 K intervals. The experimental data were correlated with the CSD, PR, and RKS equations of state. The CSD equation of state correlates the experimental data slightly better than the PR and RKS equations of state. It was found that this mixture exhibited azeotropic behavior at a composition near 0.77 mole fraction HFC-125. It was observed that the vapor pressures of the azeotropic system HFC-125 + propane were between those of HCFC-22 and those of the zeotropic system HFC-32 + HFC-125 (50−50). The azeotropic system may be a promising alternative refrigerant to replace HCFC-22. Further experimental investigation is proceeding in this laboratory to establish its suitability.

Nomenclature

a, a_0, a_1, a_2 = coefficients of the equation of state
b, b_0, b_1, b_2 = coefficients of the equation of state
k_{12} = interaction parameter
obj = objective function
N = number of data
P = pressure
T = temperature
x = liquid-phase mole fraction
y = vapor-phase mole fraction

Subscripts

1 = composition 1
2 = composition 2
c = critical point
cal = calculation
exp = experiment
i = composition i
j = composition j

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