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Vapor−Liquid Equilibria for the Binary System Pentafluoroethane (HFC-125) + Isobutane (HC-600a) at Temperatures from (243.15 to 333.15) K

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An experimental method was presented for vapor liquid equilibrium measurement by improving the PVT measurement apparatus. Isothermal vapor liquid equilibrium data for pentafluoroethane (HFC-125) + isobutane (HC-600a) were measured at (243.15, 253.15, 263.15, 272.15, 283.15, 293.15, 303.15, 313.15, 323.15, and 333.15) K at pressures up to 3.2 MPa. The experimental data were correlated with the Peng−Robinson equation of state with van der Waals mixing rules. The overall average absolute deviation between measured pressures and calculated results from the Peng−Robinson (PR) equation of state is 0.87 %. The interaction parameters k_{12} were obtained for different temperatures, and the values of k_{12} increase from 0.12 to 0.22 as the temperature increases.

Introduction

HFC + HC refrigerant mixtures are considered as promising alternative refrigerants for their zero ozone depletion potential. Vapor−liquid equilibria (VLE) data are essential for evaluating the performance of refrigeration or heat pump cycles and determining their optimal compositions. Pentafluoroethane (HFC-125) + isobutane (HC-600a) is the possible alternative refrigerant but limited experimental VLE data have been reported in the literatures.[1,2]

In this work, isothermal VLE for binary systems HFC-125 + HC-600a were measured at (243.15, 253.15, 263.15, 272.15, 283.15, 293.15, 303.15, 313.15, 323.15, and 333.15) K. The experimental data were correlated with the Peng−Robinson (PR) equation of state[3] (EoS) using van der Waals mixing rules.

Experimental Section

Chemicals. HFC-125 and HC-600a of mass fraction 99.8 % purity were supplied by the Zhejiang Chemical Industry Research Institute of China. The purities of the chemicals were guaranteed by the manufacturers, and they were used without further purification.

The pressures of the pure components were measured and compared with calculated values from the database REFPROP 6.01[4] at some temperatures. The comparison of results are shown in Table 1.

Apparatus. The apparatus consists of a mixing part and PVT measurement part. The measurement apparatus was presented by Hu.[5,6] A schematic diagram of the measurement apparatus used in this study is given in Figure 1. It includes a thermostatic bath, a temperature measurement and control system with total uncertainty ± 5 mK from (233 to 453) K, a pressure measurement system with measuring range from (0 to 6) MPa and the maximum uncertainty of ± 1.5 kPa at 6 MPa, and a vacuum system.

The schematic diagram of the mixing apparatus is shown in Figure 2. It includes three sample cells (S1, S2, and S3), a vacuum system, and a vessel filled with liquid nitrogen. The vacuum sample cells S2 and S3 were filled with different pure refrigerants, respectively, and the masses of refrigerants were determined by a precise standard balance (TG-31B, Shanghai Balance Factory, China) with measuring range from 0 to 1 kg and accuracy 1 mg. The mixing ratio was determined by masses of pure refrigerants. After the system was evacuated and the valve VL was closed, the vessel V was cooled down by filling with liquid nitrogen, and valves S2 and S3 were opened and the binary mixture would be obtained within several minutes.

Table 1. Comparison of Results of Vapor Pressure of HFC-125 and HC-600a

refrigerants	T/K	P/KPa p_{exp}[a]	 p_{REF}[a]	100 δ_P[b]
HFC-125	272.15	650.64	650.07	0.09
	295.47	1282.6	1282.3	0.02
	313.15	2004.1	2005.6	−0.07
HC-600a	272.15	151.55	150.92	0.42
	298.42	354.40	353.1	0.37
	313.15	531.85	530.79	0.20

[a] p_{exp} are the experimental values measured in this work, p_{REF} comes from REFPROP 6.01.[4] [b] $\delta_P = (p_{exp}/p_{REF} - 1)$.

Some binary mixtures of different mixing ratios were blended by the mixing system. The mass of the mixture was about 20 g. The lost of mass were all less than 10 mg during the mixing process, which is because of tiny residual refrigerants in the sample cells S2, S3, and pipes. Therefore the absolute deviation of mass fraction w of one component is below 0.05 %.

The experimental method is shown in Figure 3. A binary mixture of mole fraction x_1^t of component 1 is the measurement object. The point b is the bubble point corresponding to VLE state point e at the same pressure and temperature. The sample cell S1 was initially filled with the binary mixture with liquid volume fraction greater than 70 % at a temperature 243.15 K, and the volume increased with temperature increase. The moles in the vapor are small compared with the moles in the liquid. So the liquid mole fraction x_1 is almost equal to the overall mole fraction x_1^t, namely the points a, b, and e are very close to each other in Figure 3.

To correct the experimental bubble point pressure, the pseudo bubble point pressures of binary mixture were calculated as the mole fraction average of the vapor pressures of pure components

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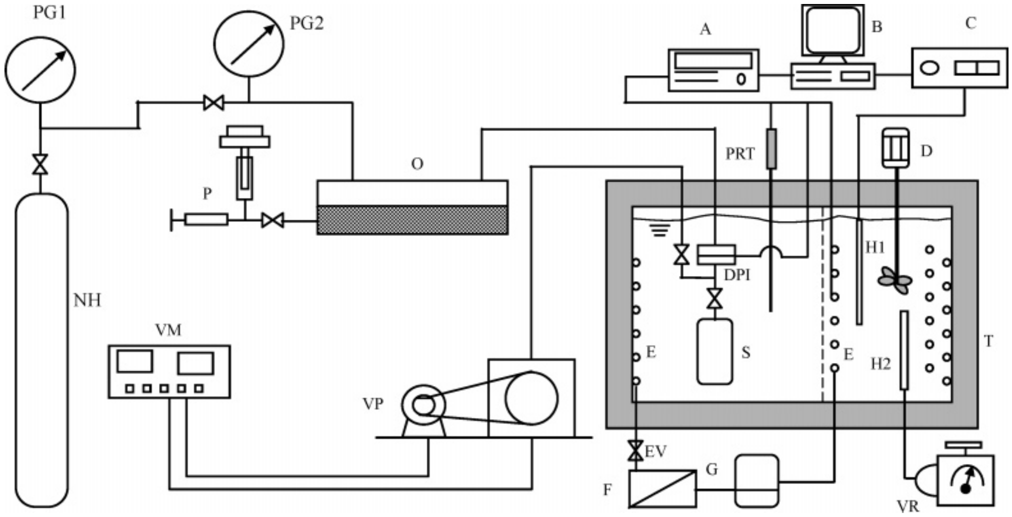

Figure 1. The PVT experimental apparatus. A, HP34970A data acquisition/switch unit; B, computer; C, silicon-controlled switch; D, stirrer; DPI, differential pressure detector; E, evaporator; EV, expansion valve; F, condenser; G, compressor; H1(H2), heaters; NH, nitrogen bottle; O, oil−vapor separator; P, oil−piston type dead-weight pressure gauge; PG1(PG2), pressure gauges; PRT, platinum resistance thermometer; S, sample cell; T, thermostatic bath; VM, vacuum gauge; VP, vacuum pump; VR, voltage regulator.

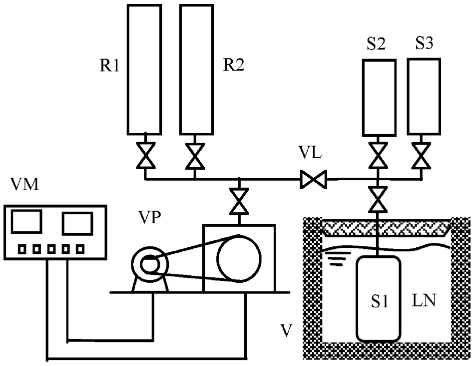

Figure 2. Mixing system of binary mixtures. VM, vacuum gauge; VP, vacuum pump; S (S1,S2,S3), sample cells; R1(R2), sample bottle; VL, valve; V, vessel; LN, liquid nitrogen.

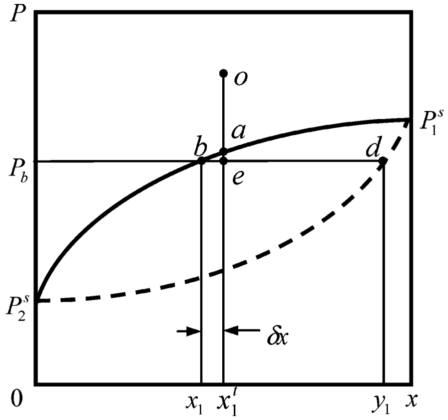

Figure 3. Experimental principle diagram.

at isocorresponding temperature,[7] and the pseudo saturated vapor and liquid densities of binary mixture were calculated by isocorresponding principle.[8] The liquid mole fraction x_1 was calculated by correcting the total mole fraction x_1^t using isocorresponding parameters:

$$x_1 = \frac{x_1^t m / \sum x_i^t M_i - y_1 \rho_m^v \phi / \sum y_i M_i}{m / \sum x_i^t M_i - \rho_m^v \phi / \sum y_i M_i} \qquad (1)$$

In eq 1, m is the total mixing mass of the binary mixture in the cell, which values are shown in Table 2, x_i^t are total mole fractions of each of the components, M_i is the molar mass of pure components, and ϕ is vapor volume fraction, which is shown as

Table 2. Total Composition of HFC-125 (1) + HC-600a (2) in the Cell

w_1	x_1^t	m(g)
0.10	0.0511	16.757
0.20	0.1080	17.642
0.30	0.1719	18.612
0.40	0.2440	19.674
0.50	0.3263	19.825
0.60	0.4208	22.087
0.70	0.5305	23.427
0.80	0.6595	24.819

$$\phi = \frac{\rho_m^l - m/V}{\rho_m^l - \rho_m^v} \qquad (2)$$

where, V is the volume of sample cell, $V = 31.726$ mL.

Vapor mole fraction y_i was calculated by the following:

$$y_1 = \frac{x_1 p_1^0}{p_2^0 + x_1(p_1^0 - p_2^0)}, \qquad y_2 = 1 - y_1 \qquad (3)$$

where p_i^0 are the saturated pressures of pure components of the binary mixture at measurement temperature T.

Saturated vapor density ρ_m^v was calculated by the generalized corresponding equation:

$$\frac{\ln z_m}{\ln z_{c,m}} = [{\rho_{r,m}^{v}}^{n} + 0.0198 - 0.11|T_{r,m} - 0.82| + 0.07(1 - T_{r,m})^2] \qquad (4)$$

where

$$n = 0.256 + 1.85 z_{c,m} + 0.05(1 - {p_{r,m}}^{40}) \qquad (5)$$

$$z_{c,m} = \frac{p_{c,m}}{\rho_{c,m} R T_{c,m}} \qquad (6)$$

and corresponding temperature, pressure, and saturated vapor density were defined as

$$T_{r,m} = T_m/T_{c,m}, \qquad p_{r,m} = p_m/p_{c,m}, \qquad \rho^{\mathrm{v}}_{r,m} = \rho^{\mathrm{v}}_m/\rho_{c,m} \tag{7}$$

Pseudo-critical properties of mixtures were determined by the following:

$$T_{c,m} = 1/\sum (y_i/T_{c,i}) \tag{8}$$

$$p_{c,m} = \sum y_i p_{c,i} \tag{9}$$

$$\rho_{c,m} = \sum (x_{i,\mathrm{mass}}\rho_{c,i}) - \sum_{i=1}^{n-1}\sum_{j=2}^{n}(0.72x_{i,\mathrm{mass}}x_{j,\mathrm{mass}}|\rho_{c,i} - \rho_{c,j}|) \tag{10}$$

Saturated liquid density ρ^{l}_m was calculated by the following equation:

$$\rho^{\mathrm{l}}_{r,m} = T_{r,m}^{(0.444+0.017\cdot\ln T_{\mathrm{r,m}})} \tag{11}$$

with

$$\rho^{\mathrm{l}}_{r,m} = \frac{\rho^{\mathrm{l}}_m - \rho_{c,m}}{\rho^{\mathrm{l}}_{b,m} - \rho_{c,m}} \tag{12}$$

$$T_{r,m} = \frac{T_{c,m} - T_m}{T_{c,m} - T_{b,m,B}} \tag{13}$$

Pseudo-normal boiling temperature of mixtures is

$$T_{b,m,B} = 1/\sum (x_i/T_{b,i}) \tag{14}$$

and pseudo-saturated liquid density at normal boiling temperature is

$$\rho^{\mathrm{l}}_{b,m} = \sum (x_{i,\mathrm{mass}}\rho^{\mathrm{l}}_{b,i}) - \sum_{i=1}^{n-1}\sum_{j=2}^{n}(0.1x_{i,\mathrm{mass}}x_{j,\mathrm{mass}}|\rho^{\mathrm{l}}_{b,i} - \rho^{\mathrm{l}}_{b,j}|) \tag{15}$$

The average absolute deviations of eqs 4 and 5 are 0.72 % and 0.77 % compared with the data of R404A, R407A, R407B, R410A, R32/R134a (25/75, mass %) in literature.[9] The uncertainty of liquid mole fraction x_i is estimated within ± 1.5 %.

Measurements. VLE measurements on the binary system HFC-125 (1) + HC-600a (2) were performed at the temperature range from (243.15 to 333.15) K and at pressures up to 3.2 MPa. The isothermal experimental data are shown in Table 3.

Results and Discussion

VLE Correlations. In this work, the PR EoS[3] was used to correlate VLE data. The critical temperature T_{c}, critical pressure P_{c}, and the acentric factor ω used are summarized in Table 4.

The mixing rule used to predict the VLE data was the one parameter van der Waals rule. In van der Waals rule, the binary interaction parameters k_{ij} was determined by applying the least-square method to fit the experimental bubble point pressure data. The object function was

$$\mathrm{Obj} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{p_{\mathrm{cal}} - p_{\mathrm{exp}}}{p_{\mathrm{exp}}}\right| \tag{16}$$

where p_{exp} and p_{cal} are the experimental pressure and calculated pressure, respectively.

The correlation results are shown in Table 5. $|\delta_{\mathrm{p}}|$ is the average absolute deviation of pressures, and its definition is the same with the object function Obj.

The calculated values are in good agreement with the experimental data of this work and Lee[1] from Figures 4 and 5. The relative deviations between the experimental values and calculated pressures are within ± 3 % and all average absolute deviations are less than 2 % at temperature from (243.15 to 333.15) K. The overall average absolute deviation of pressure is 0.87 %.

Interaction Parameters and Temperature. The interaction parameters k_{12} increases as the temperature T increases, and the relationship between k_{12} and $1/T$ is approximately linear as shown in Figure 6. It was fitted by the following expression

$$k_{12} = 0.3787 - 63.43/(T/K) \tag{17}$$

where T is from (243.15 to 333.15) K. The correlated k_{12} and the predicted k_{12} by eq 17 were shown in Figure 6. The deviation

Table 3. VLE Data for HFC-125 (1) + HC-600a (2)

$T = 243.15$ K		$T = 253.15$ K		$T = 263.15$ K		$T = 272.15$ K		$T = 283.15$ K	
p/kPa	x_1	p/kPa	x_1	p/kPa	x_1	p/kPa	x_1	p/kPa	x_1
46.2	0	72.0	0	107.9	0	150.9	0	220.1	0
78.2	0.0509	117.1	0.0509	172.9	0.0509	238.1	0.0508	339.4	0.0508
109.0	0.1077	165.1	0.1076	240.5	0.1076	326.2	0.1075	458.3	0.1074
137.9	0.1714	205.1	0.1713	293.8	0.1711	395.9	0.1710	550.7	0.1709
161.8	0.2435	238.2	0.2433	339.8	0.2431	455.3	0.2429	634.7	0.2427
186.2	0.3254	275.8	0.3252	394.7	0.3249	518.8	0.3246	697.6	0.3243
203.9	0.4198	297.0	0.4195	417.5	0.4192	551.5	0.4188	754.6	0.4184
216.8	0.5295	315.6	0.5291	444.2	0.5287	589.1	0.5282	804.9	0.5277
226.3	0.6584	330.5	0.6580	465.4	0.6576	618.9	0.6570	856.2	0.6564
228.5	1	337.9	1	483.1	1	650.1	1	908.8	1

$T = 293.15$ K		$T = 303.15$ K K		$T = 313.15$ K K		$T =323.15$ K		$T = 333.15$ K	
p/kPa	x_1	p/kPa	x_1	p/kPa	x_1	p/kPa	x_1	p/kPa	x_1
301.8	0	404.3	0	530.8	0	684.3	0	868.3	0
460.0	0.0508	580.0	0.0507	725.6	0.0507	903.8	0.0508	1115.8	0.0509
607.1	0.1073	765.8	0.1073	932.4	0.1073	1157.6	0.1074	1398.0	0.1076
720.0	0.1707	909.0	0.1707	1088.9	0.1707	1343.4	0.1708	1624.6	0.1712
830.0	0.2425	1039.0	0.2424	1253	0.2424	1550.0	0.2426	1863.7	0.2432
914.5	0.3240	1150.4	0.3238	1400.7	0.3237	1715.6	0.3239	2079.8	0.3246
980.1	0.4180	1245.3	0.4177	1534.8	0.4176	1873.9	0.4178	2257.7	0.4188
1045.8	0.5272	1339.5	0.5267	1659.3	0.5265	2055.3	0.5266	2488.8	0.5277
1116.0	0.6557	1431.4	0.6551	1802.0	0.6546	2229.3	0.6545	2704.4	0.6557
1204.5	1	1566.8	1	2005.6	1	2533.2	1	3167.4	1

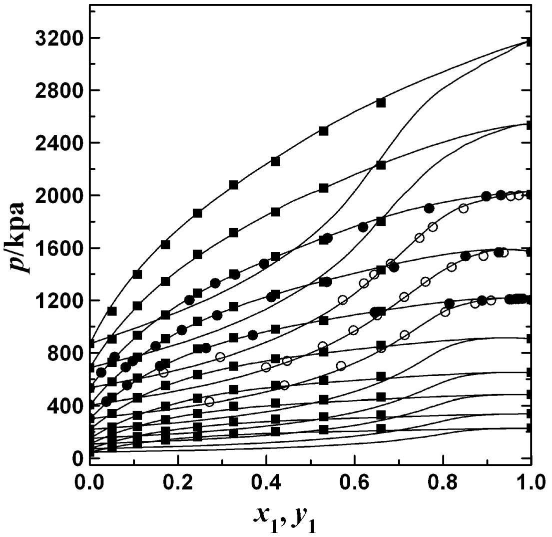

Figure 4. Comparison between experimental and calculated values of the HFC-125 (1) + HC-600a (2) binary system. ■, experimental points of this work; ——, calculated values; ● ○, experimental points of literature.[1] Lowest temperature, 243.15 K; highest temperature, 333.15 K.

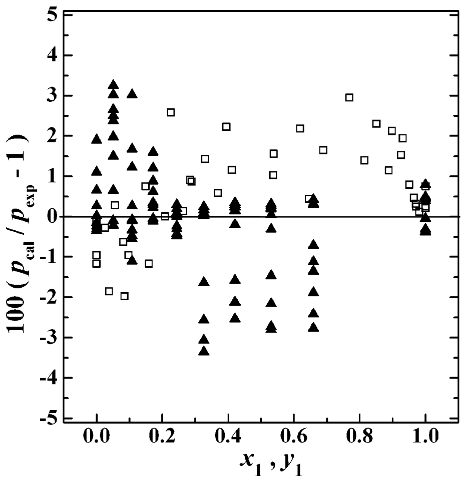

Figure 5. The deviations of pressure of the HFC-125 (1) + HC-600a (2) binary system.

Table 4. Critical Properties and Acentric Factors of Pure Refrigerants

refrigerants	T_c/K	P_c/kPa	ω	source
HFC-125	339.33	3629	0.3035	REFPROP[4]
isobutane	407.85	3640	0.1853	REFPROP[4]

Table 5. Interaction Parameter k_{12} of HFC-125 (1) + HC-600a (2) and the Average Absolute Deviations of Pressure

T/K	no. points	k_{12}[a]	$100\|\delta_p\|$
243.15	10	0.119	1.40
253.15	10	0.127	1.86
263.15	10	0.137	1.60
272.15	10	0.145	1.50
283.15	10	0.155	0.48
293.15	10	0.163	0.35
303.15	10	0.171	0.45
313.15	10	0.177	0.49
323.15	10	0.181	0.24
333.15	10	0.188	0.34
Average			0.87

between the correlated values and predicted values of k_{12} are within ± 1% at the ten temperatures from (243.15 to 333.15) K.

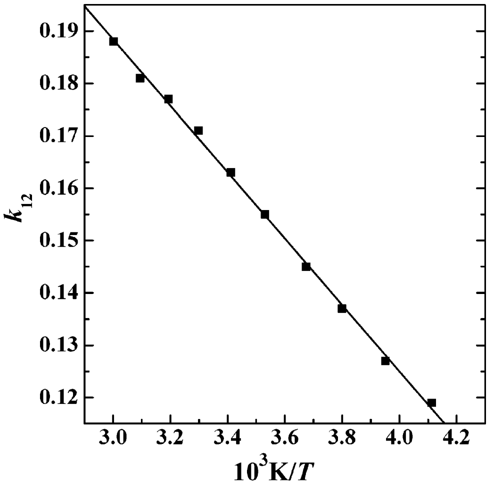

Figure 6. The relationship between the interaction parameters and temperature. ■, correlated k_{12}; ——, predicted k_{12}.

Conclusions

Isothermal VLE data for the pentafluoroethane (HFC-125) + 2-methyl-propane (HC-600a) binary system were measured at (243.15, 253.15, 263.15, 272.15, 283.15, 293.15, 303.15, 313.15, 323.15, and 333.15) K and pressures up to 3.2 MPa. Experimental data were well correlated with the PR equation of state and the van der Waals mixing rules. The overall average absolute deviation between the experimental values and the calculated values of pressure are 0.87 %. The interaction parameters k_{12} were obtained at different temperatures, and the relationship between the interaction parameter and the temperature is present.

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