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Vapor−Liquid Equilibria for Isobutane + Pentafluoroethane (HFC-125) at 293.15 to 313.15 K and + 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) at 303.15 to 323.15 K

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Isothermal vapor−liquid equilibria were determined for binary systems of pentafluoroethane (HFC-125) + isobutane (R600a) at 293.15, 303.15 and 313.15 K and 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) + isobutane (R600a) at 303.15, 313.15 and 323.15 K in a circulation-type equilibrium apparatus. The experimental data were well correlated with the Peng−Robinson−Stryjek−Vera (PRSV) equation of state combined with the NRTL excess Gibbs free-energy model and Huron-Vidal original mixing rules.

Introduction

Hydrofluorocarbons (HFCs) such as HFC-125 and HFC-227ea are promising alternative refrigerants to replace dichlorodifluoromethane (CFC-12; CCl_2F_2) and chlorodifluoromethane (HCFC-22; $CHClF_2$). Isobutane is a hydrocarbon refrigerant which is widely used in Europe. The ozone depletion potentials (ODPs) of HFC-125, HFC-227ea and isobutane are zero since they do not contain chlorine. Their global warming potentials (GWPs) are less than those of CFC-12 and HCFC-22 because they contain more hydrogen atoms and thus have a shorter atmospheric lifetime.[1] HFCs are stable but very expensive, on the other hand, hydrocarbons are flammable but not expensive. Mixtures of the two compounds may have good potential as alternative refrigerants. Vapor−liquid equilibrium data are required as one of the most important types of information in evaluating the performance of refrigeration cycles and determining their optimal compositions. Azeotropic mixtures have merit since their behaviors are similar to pure compounds. However, no or very few experimental data have been reported previously in the literature.

In this study, we measured isothermal vapor−liquid equilibria for binary systems HFC-125 + isobutane at 293.15, 303.15 and 313.15 K and HFC-227ea + isobutane at 303.15, 313.15 and 323.15 K. The experimental data were correlated with the Peng−Robinson−Stryjek−Vera (PRSV) equation of state[2] combined with the NRTL excess free-energy model[3] and Huron-Vidal original mixing rules.[4]

Experimental Section

Chemicals. High-grade chemicals having purities greater than 99.8 mass %, shown in Table 1, 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.

Table 1. Suppliers and Purities of the Chemicals

component	supplier	purity/mass %
HFC-125	Dupont, USA	>99.8
HFC-227ea	Lancaster, U.K.	>99.9
isobutane	Jeongil Chemical Co., Korea	>99.9

Experimental Apparatus. Vapor−liquid equilibria were measured in a circulation-type apparatus in which both vapor and liquid phases were continuously recirculated. The explanation of the experimental apparatus and the procedure has been reported in our previous publications[5,6] and are briefly summarized here. The stainless steel equilibrium cell with an inner volume of about 80 cm^3 was equipped with dual glass windows in order to make it possible to observe the inside during operation. The temperature of the equilibrium cell in the water bath was maintained constant by a circulator from Jeio Tech, Korea. The temperature in the cell was measured with a platinum resistance sensor from Automatic Systems Laboratories Ltd. and the uncertainty was estimated to be ±0.01 K. The pressure was measured with a pressure transducer-model PC 106 Digital Pressure Gauge, Beamex and the uncertainty was estimated to be ±0.001MPa. The vapor and liquid phases in the equilibrium cell were continuously recirculated by a dual-head circulation pump from Milton Roy company. After the equilibrium was reached, the vapor and liquid samples were taken from the recycling loop and on-line injected into the gas chromatograph of Gow-Mac model 550P. The gas chromatograph was equipped with a thermal conductivity detector and a Porapak Q column from Alltech Company.

Experimental Procedure. Experiments for a binary system were performed by the following procedure. The whole system was vacuum pumped to a pressure of 3×10^{-4} Torr. A certain amount of isobutane was introduced into the cell, and then the temperature of the entire system was maintained constant by controlling the temperature of the water bath. After the desired temperature was

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attained, the pressure of the pure component was measured. A proper amount of HFC-125 (for isobutane + HFC-125) or HFC-227ea (for isobutane + HFC-227ea) was supplied to the cell from a charging cylinder. Both vapor and liquid phases were allowed to circulate for about an hour to ensure equilibrium. When the equilibrium was attained, pressure was measured and then vapor and liquid samples were taken 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 gas chromatograph which is connected on-line to both vapor and liquid sampling valves. The gas chromatograph was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. The analysis uncertainty of the liquid and vapor phase composition is estimated to be within ± 0.5 mol %, including the uncertainty of the calibration curve. We measured the equilibrium concentration at least three times in a row to obtain reliable average values.

Correlation

Stryjek and Vera[2] proposed the temperature dependence of the α term in Peng−Robinson equation of state. The Stryjek−Vera modification of the α term was known to take care of the inaccuracies in temperature dependence of the α term at low temperatures.

In this study, the VLE experimental data were correlated with the Peng−Robinson−Stryjek−Vera (PRSV) equation of state. The PRSV equation of state can be expressed as follows:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \tag{1}$$

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

$$\alpha(T) = [1 + \kappa(1 - \sqrt{T/T_c})]^2 \tag{3}$$

$$b = 0.077796\frac{RT_c}{P_c} \tag{4}$$

Here, we use the temperature dependence of the α term proposed by Stryjek and Vera.

$$\kappa = \kappa_0 + \kappa_1(1 + T_r^{0.5})(0.7 - T_r) \tag{5}$$

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.1713184\omega^2 + 0.0196554\omega^3 \tag{6}$$

where k_1 is a specific constant for each pure compound. The k_1 value of the PRSV equation is obtained by fitting pure component saturation pressure (P^{vap}) versus temperature data.

The Huron−Vidal original mixing rule was used, in this work, to obtain equation of state parameters for a mixture from those of the pure components. This mixing rule for a cubic equation of state can be written as

$$a = b\left[\sum x_i\left(\frac{a_i}{b_i}\right) + \frac{G^{ex}{}_{\gamma}}{C^*}\right] \tag{7}$$

$$b = \sum x_i b_i \tag{8}$$

where $C^* = \ln(\sqrt{2} - 1)/\sqrt{2} = -0.62323$ and G^{ex} is an excess Gibbs free energy.

Table 2. Comparison between Measured Vapor Pressures of Pure Components and Calculated Values from the Database REFPROP 6.01[7]

		P/MPa			
component	T/K	measd	REFPROP[7]	ΔP^a/MPa	AAD(%)[b]
isobutane	293.15	0.3045	0.3018	0.0027	0.888
	303.15	0.4070	0.4043	0.0027	0.663
	313.15	0.5300	0.5308	0.0008	0.151
	323.15	0.6832	0.6843	0.0011	0.161
HFC-125	293.15	1.2036	1.2050	0.0014	0.116
	303.15	1.5700	1.5670	0.0030	0.191
	313.15	2.0030	2.0060	0.0030	0.150
HFC-227ea	303.15	0.5257	0.5299	0.0042	0.799
	313.15	0.7015	0.7058	0.0043	0.613
	323.15	0.9167	0.9215	0.0048	0.524

[a] $\Delta P = |P_{exp} - P_{cal}|$. [b] AAD(%) $= |(P_{exp} - P_{cal})/P_{exp}| \times 100$.

Table 3. Vapor−Liquid Equilibrium Measurements for the HFC-125 (1) + Isobutane (2) System

P/MPa	x_1	y_1	P/MPa	x_1	y_1
T/K = 293.15					
0.3045	0.0000	0.0000	1.1982	0.8884	0.9092
0.4279	0.0379	0.2714	1.2067	0.9507	0.9563
0.5529	0.0848	0.4411	1.2093	0.9647	0.9676
0.6988	0.1590	0.5697	1.2102	0.9707	0.9727
0.8354	0.2634	0.6608	1.2108	0.9716	0.9734
0.9333	0.3693	0.7138	1.2106	0.9807	0.9797
1.1092	0.6454	0.8056	1.2036	1.0000	1.0000
1.1750	0.8146	0.8736			
T/K = 303.15					
0.4070	0.0000	0.0000	1.2240	0.4115	0.7125
0.6900	0.0816	0.3998	1.3412	0.5371	0.7611
0.7376	0.0977	0.4474	1.4530	0.6894	0.8200
0.8492	0.1492	0.5277	1.5372	0.8510	0.8920
0.9714	0.2085	0.5977	1.5652	0.9260	0.9384
1.0858	0.2889	0.6515	1.5700	1.0000	1.0000
T/K = 313.15					
0.5300	0.0000	0.0000	1.6742	0.5387	0.7476
0.6488	0.0260	0.1673	1.7590	0.6191	0.7774
0.7672	0.0566	0.2955	1.9006	0.7690	0.8469
1.2016	0.2259	0.5729	1.9934	0.8983	0.9539
1.3296	0.2846	0.6216	2.0008	0.9314	0.9722
1.3958	0.3298	0.6449	2.0030	1.0000	1.0000
1.4790	0.3947	0.6820			

Results and Discussion

Table 2 is a comparison of measured vapor pressures of pure isobutane, HFC-125, and HFC-227ea with those calculated from the database REFPROP 6.01,[7] which is considered to be reliable for the pure compounds considered and consistent with other literature data. The average absolute deviation between measured and calculated values from the data of REFPROP 6.01 is 0.42%. The experimental data for isothermal vapor liquid equilibria (VLE) for the binary systems of HFC-125 + isobutane and HFC-227ea + isobutane are shown in Tables 3 and 4, respectively. Each table lists the measured mole fraction of the liquid and vapor phases, pressures and temperatures in equilibrium. The vapor−liquid equilibrium data of HFC-125 + isobutane and HFC-227ea + isobutane systems were predicted with Huron-Vidal mixing rules combined with NRTL excess free-energy models and the PRSV equation of state. The critical properties (T_c, P_c) and acentric factors (ω) of the pure components (HFC-125, HFC-227ea, and isobutane) used to calculate the parameters for the PRSV equation of state are given in Table 5. The parameter k_1 of each pure component in the range of experimental tem-

Table 4. Vapor−Liquid Equilibrium Measurements for the HFC-227ea (1) + Isobutane (2) System

P/MPa	x_1	y_1	P/MPa	x_1	y_1
		T/K = 303.15			
0.4070	0.0000	0.0000	0.6582	0.6061	0.6031
0.4416	0.0199	0.0838	0.6442	0.6978	0.6456
0.5214	0.0975	0.2530	0.6308	0.7929	0.7066
0.5680	0.1584	0.3331	0.6140	0.8575	0.7682
0.6003	0.2365	0.4018	0.5880	0.9095	0.8459
0.6314	0.3783	0.4878	0.5597	0.9631	0.9181
0.6470	0.4649	0.5309	0.5257	1.0000	1.0000
0.6566	0.5883	0.5937			
		T/K = 313.15			
0.5300	0.0000	0.0000	0.8446	0.6095	0.6103
0.5804	0.0249	0.0849	0.8456	0.6259	0.6162
0.6694	0.0967	0.2375	0.8426	0.6879	0.6566
0.7504	0.1975	0.3568	0.8254	0.7917	0.7319
0.7878	0.2822	0.4221	0.7890	0.8820	0.8222
0.8260	0.4084	0.4986	0.7430	0.9555	0.9160
0.8384	0.5002	0.5481	0.7015	1.0000	1.0000
0.8440	0.5907	0.5969			
		T/K = 323.15			
0.6832	0.0000	0.0000	1.0778	0.6411	0.6291
0.8666	0.1059	0.2427	1.0706	0.7202	0.6854
0.9752	0.2306	0.3752	1.0470	0.8111	0.7592
1.0354	0.3548	0.4625	1.0128	0.8787	0.8258
1.0690	0.5007	0.5457	0.9752	0.9337	0.8933
1.0806	0.6107	0.6118	0.9167	1.0000	1.0000
1.0809	0.6239	0.6201			

Table 5. Characteristic Properties of the Chemicals[a]

component	chemical formula	MW	T_c/K	P_c/MPa	ω
isobutane	$C(CH_3)_3$	58.12	407.85	3.640	0.1853
HFC-125	C_2HF_5	120.03	339.33	3.629	0.3035
HFC-227ea	CF_3CHFCF_3	170.03	375.95	2.980	0.3632

[a] Data source: REFPROP(V. 6.01).[7]

Table 6. Optimum k_1 Values of Pure Components in the PRSV Equation of State[a]

component	range of T/K	k_1
isobutane	293.15−313.15	−0.1231
	303.15−323.15	−0.0025
HFC-125	293.15−313.15	−0.1061
HFC-227ea	303.15−323.15	0.0979

[a] Data source: REFPROP(V. 6.01).[7]

Table 7. NRTL Parameters and Deviations between Calculated and Experimental Pressures and Vapor Phase Mole Fractions

mixture	T/K	A_{12}[a]	A_{21}[a]	AAD%(P)[b]	AAD(y)[c]
HFC-125 + isobutane	293.15	2.855	1.751	0.614	0.0045
	303.15	2.785	1.641	0.5779	0.0042
	313.15	3.198	0.958	0.8036	0.0091
HFC-227ea+ isobutane	303.15	2.055	2.758	0.666	0.0061
	313.15	1.913	2.611	0.463	0.0044
	323.15	1.653	2.703	0.265	0.0027

[a] The units of A_{12} and A_{21} are $kJ \cdot mol^{-1}$. [b] $AAD\%(P) = 1/N\sum|(P_{exp} - P_{cal})/P_{exp}| \times 100$. [c] $AAD(y) = 1/N\sum|Y_{exp} - Y_{cal}|$.

peratures is listed in Table 6. All the binary parameters of the NRTL model and the average absolute deviations of pressure (AAD%(P)) and vapor phase composition (AAD(y)) between measured and calculated values are listed in Table 7.

Figures 1 and 2 show the comparison of measured and calculated values for HFC-125 (1) + isobutane (2) at 293.15, 303.15, and 313.15 K and HFC-227ea (1) + isobutane (2) at 303.15, 313.15, and 323.15 K. As shown in these figures and by the low AAD in Table 7, the calculated values give good agreement with the experimental data.

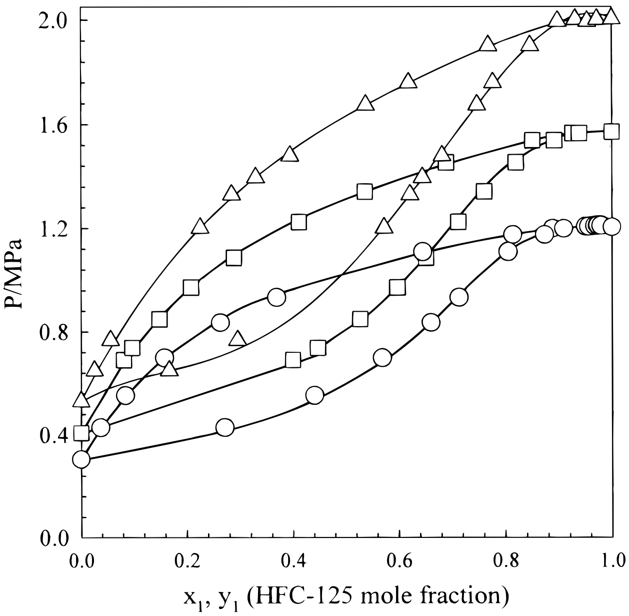

Figure 1. Comparison between experimental and calculated values of the HFC-125 + isobutane binary system: (○) exp at 293.15 K; (□) exp at 303.15 K; (△) exp at 313.15 K; (−) calculated by the PRSV-EOS with HVO mixing rules.

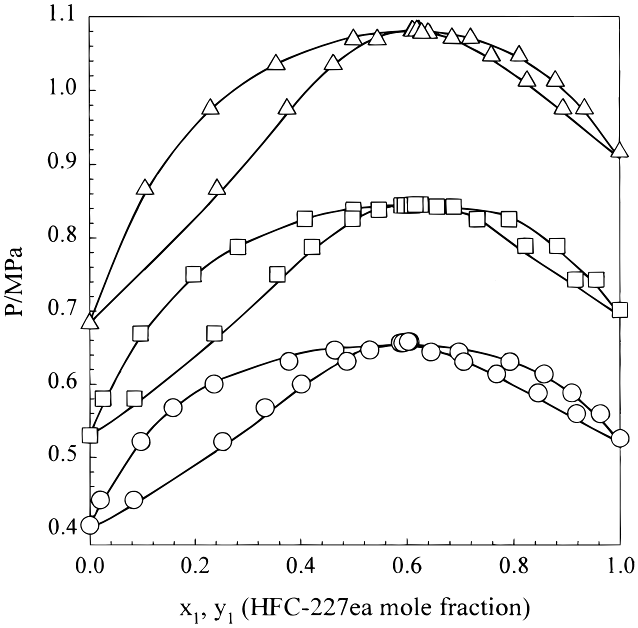

Figure 2. Comparison between experimental and calculated values of the HFC-227ea + isobutane binary system: (○) exp at 293.15 K; (□) exp at 303.15 K; (△) exp at 313.15 K; (−) calculated by the PRSV-EOS with HVO mixing rules.

Table 8. Azeotropic Data

system	T/K	x_1	P/MPa
HFC-125 + isobutane	293.15	0.976	1.211
HFC-227ea + isobutane	303.15	0.601	0.659
	313.15	0.611	0.846
	323.15	0.616	1.082

For HFC-125 + isobutane system, azeotropic point was observed only at 293.15 K, and at 303.15 and 313.15 K there was no azeotrope but shows near-azeotropic behavior. For the HFC-227ea + isobutane system, there were azeotropes at all temperatures studied in this work. The azeotropic data (temperature, composition and pressure) of HFC-125 + isobutane and HFC-227ea + isobutane

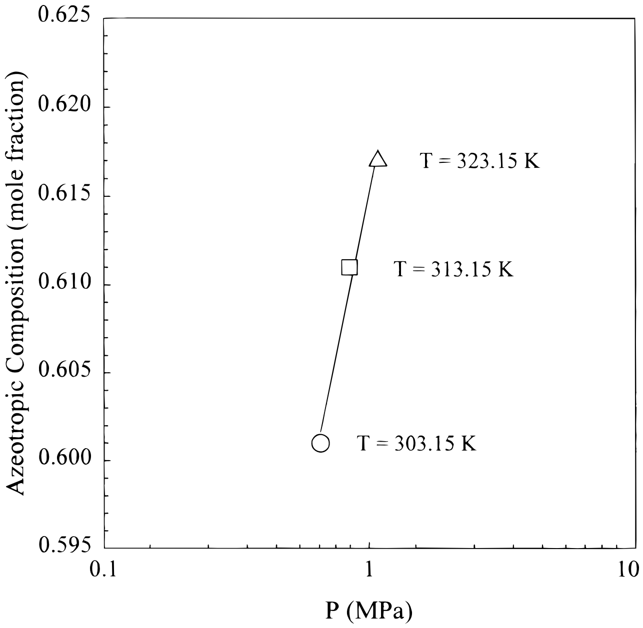

Figure 3. Variation of the azeotropic composition with pressure for the HFC-227ea (1) + isobutane (2) system.

systems are listed in Table 8. Figure 3 represents the variation of the azeotropic composition with pressure for HFC-227ea + isobutane system. As can be seen in Figure 3, a logarithmic plot between the mole fractions of the HFC-227ea in the azeotropic points and pressures shows linear in the interval of pressure studied.

Literature Cited

(1) Lisal, M.; Vacek, V. Effective Potentials for Liquid Simulation of the Alternative Refrigerants HFC-32: CH_2F_2 and HFC-23: CHF_3. *Fluid Phase Equilibria* **1996**, *118*, 61−76.

(2) Stryjek, R.; Vera, J. H. An improved Peng−Robinson equation of state for pure components and for mixtures. *Can. J. Chem. Eng.* **1986**, *64*, 323−333.

(3) Orbey, H.; Sandler, S. I. *Modeling Vapor-Liquid Equilibria-cubic equation of state and their mixing rules*; Cambridge University Press: 1998.

(4) Huron, M.; Vidal, J. New mixing rules in simple equations of state for representing vapor-liquid equilibria of strongly nonideal mixtures. *Fluid Phase Equilib.* **1979**, *3*, 255−271

(5) Lee, B. G.; Park, J. Y.; Lim, J. S.; Cho, S. Y.; Park, K. Y. Phase Equilibria of Chlorofluorocarbon Alternative Refrigerant Mixtures *J. Chem. Eng. Data* **1999**, *44*, 190−192

(6) Lim, J. S.; Park, J. Y.; Lee, B. G.; Lee, Y. W.; Kim, J. D. Phase Equilibria of CFC Alternatives Refrigerant Mixtures; Binary systems of Trifluoromethane + isobutane at 283.15 and 293.15K and 1,1,1-Trifluoroethane + isobutane at 323.15 and 333.15 K. *J. Chem. Eng. Data* **1999**, *44*, 1226−1230.

(7) Huber, M.; Gallagher, J.; McLinden, M. O.; Morrison, G. Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), V.6.01, NIST, 1996.

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