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Vapor−Liquid Equilibria of the 1,1,1-Trifluoroethane + *n*-Butane System

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Binary vapor−liquid equilibrium data were measured for the 1,1,1-trifluoroethane (HFC-143a) + *n*-butane (HC-600) system at temperatures from (313.15 to 363.15) K. This experiment was carried out with a circulating-type apparatus with online gas chromatography. The experimental data were correlated well by Peng−Robinson−Stryjek−Vera equation of state with the Wong−Sandler mixing rules. The average absolute deviation of pressure and vapor composition between the measured data and the correlation was below 0.98 % and 0.0128, respectively.

Introduction

Our previous works were to measure binary vapor−liquid equilibrium (VLE) data of the alternative refrigerant mixtures for substitution in the chlorofluorocarbons regulated.[1,2] Those data would be useful information to design and operate refrigerant processes. This study is a part of the series work of our studies. In this work, we measured the isothermal VLE data for the binary system 1,1,1-trifluoroethane (HFC-143a) + *n*-butane (HC-600) at a temperature range from (313.15 to 363.15) K at 10 K intervals. The experimental data were correlated by the Peng−Robinson−Stryjek−Vera[3,4] equation of state (PRSV EOS) with the Wong−Sandler mixing rules.[5]

Experimental Section

Chemicals. HFC-143a of 99.9 % purity was supplied by Ulsan Chemical Co. HC-600 of 99.5 % purity was obtained from Korea Industrial Gases. Both chemicals were used without further purification in these experiments.

Apparatus. The measurement of the VLE data was conducted in a circulation-type apparatus. Details of this apparatus were given in a previous work.[6] The equilibrium cell was made of 316 stainless steel with an inner volume of about 320 mL. It was equipped with two windows. Two magnetic pumps were used to circulate vapor and liquid phase separately. Because two magnetic pumps were used to circulate both phases, equilibrium was quickly reached. Figure 1 shows a cross section of the magnetic pump. The pump consists of four parts: a piston, two stainless steel (SUS) balls, a magnet, and a cylinder. The piston was made of iron and was plated with chrome. A role of the SUS balls is similar to a ball in a check valve. As the magnet moves up and down, the piston in the cylinder moves. Thus, vapor or liquid phases can circulate. The temperature in the cell was measured with a 100 Ω platinum resistance thermometer (Hart Scientific Co., model 5627) and a digital indicator (Hart Scientific Co., model 1502A) with an accuracy of 0.05 K. The pressure of the cell was measured with a pressure transducer (Sensotec Co., model Super TJE, (0 to 1500) psia) connected to a digital indicator (Laurel, model L20010WM1). Accuracy of the digital pressure gauge is 0.05 %. Calibration of the pressure gauge and the thermometer was done by the Korea Testing Laboratory. The temperature can be read to an uncertainty of ± 0.02 K, and the estimated uncertainty of the pressure is ± 1.0 kPa. In order to measure compositions of the liquid and the vapor samples, we used two sampling valves (Rheodyne Instruments, model 7413 with a 1.0 μL sampling loop for the liquid phase and model 7010 with a 10 μL sampling loop for the vapor phase). A gas chromatograph (GC) was connected online to the equilibrium apparatus. The GC was

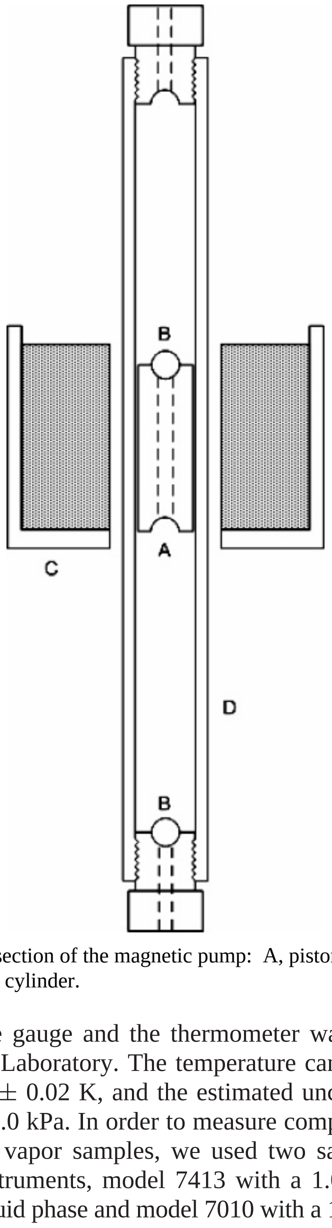

Figure 1. Cross section of the magnetic pump: A, piston; B, SUS ball; C, magnet; D, pump cylinder.

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Table 1. Vapor−Liquid Equilibrium Data for the HFC-143a (1) + HC-600 (2) System

P_{exp}/MPa	$x_{1,exp}$	$y_{1,exp}$	P_{cal}/MPa	$y_{1,cal}$	ΔP^{a}/MPa	$\Delta y_1{}^{b}$
			$T = 313.15$ K			
0.377	0.0000	0.0000				
0.753	0.1020	0.5203	0.753	0.5009	0.000	−0.0194
0.990	0.2093	0.6581	0.980	0.6340	−0.010	−0.0241
1.160	0.3130	0.7242	1.154	0.7079	−0.006	−0.0163
1.361	0.4815	0.7908	1.378	0.7858	0.017	−0.0050
1.599	0.7364	0.8719	1.610	0.8665	0.011	−0.0054
1.740	0.9050	0.9450	1.748	0.9386	0.008	−0.0064
1.831	1.0000	1.0000				
			$T = 323.15$ K			
0.495	0.0000	0.0000				
0.742	0.0499	0.3376	0.748	0.3284	0.006	−0.0092
1.141	0.1823	0.5952	1.149	0.5774	0.008	−0.0178
1.496	0.3600	0.7169	1.509	0.7080	0.013	−0.0089
1.834	0.6066	0.8107	1.868	0.8110	0.034	0.0003
1.964	0.7162	0.8479	1.994	0.8494	0.030	0.0015
2.103	0.8294	0.8960	2.119	0.8959	0.016	-0.0001
2.232	0.9370	0.9548	2.239	0.9554	0.007	0.0006
2.302	1.0000	1.0000				
			$T = 333.15$ K			
0.639	0.0000	0.0000				
0.949	0.0536	0.3149	0.940	0.3075	−0.009	−0.0074
1.310	0.1548	0.5168	1.326	0.5120	0.016	−0.0048
1.671	0.2885	0.6408	1.678	0.6306	0.007	−0.0102
2.000	0.4507	0.7237	2.013	0.7191	0.013	−0.0046
2.317	0.6430	0.8064	2.339	0.8007	0.022	−0.0057
2.672	0.8728	0.9055	2.692	0.9109	0.020	0.0054
2.754	0.9333	0.9399	2.783	0.9498	0.029	0.0099
2.802	0.9615	0.9588	2.825	0.9701	0.023	0.0113
2.874	1.0000	1.0000				
			$T = 343.15$ K			
0.810	0.0000	0.0000				
1.271	0.0789	0.3504	1.265	0.3390	−0.006	−0.0114
1.808	0.2204	0.5503	1.819	0.5378	0.011	−0.0125
2.476	0.4783	0.6993	2.474	0.6862	−0.002	−0.0131
2.814	0.6415	0.7728	2.822	0.7618	0.008	−0.0110
3.015	0.7412	0.8176	3.033	0.8136	0.018	−0.0040
3.145	0.8085	0.8508	3.176	0.8535	0.031	0.0027
3.272	0.8734	0.8873	3.311	0.8971	0.039	0.0098
3.352	0.9136	0.9129	3.393	0.9271	0.041	0.0142
3.553	1.0000	1.0000				
			$T = 353.15$ K			
1.012	0.0000	0.0000				
1.372	0.0506	0.2429	1.363	0.2339	−0.009	−0.0090
1.872	0.1570	0.4497	1.895	0.4381	0.023	−0.0116
2.650	0.3797	0.6317	2.654	0.6145	0.004	−0.0172
3.092	0.5384	0.7044	3.101	0.6974	0.009	−0.0070
3.443	0.6680	0.7601	3.446	0.7612	0.003	0.0011
3.718	0.7776	0.8068	3.736	0.8197	0.018	0.0129
			$T = 363.15$ K			
1.250	0.0000	0.0000				
1.621	0.0454	0.2072	1.620	0.1980	−0.001	−0.0092
2.163	0.1470	0.4044	2.186	0.3890	0.023	−0.0154
2.541	0.2299	0.4950	2.541	0.4750	0.000	−0.0200
3.134	0.3863	0.5976	3.133	0.5897	−0.001	−0.0079
3.638	0.5383	0.6632	3.662	0.6749	0.024	0.0117

[a] $\Delta P = P_{cal} - P_{exp}$. [b] $\Delta y_1 = y_{cal} - y_{exp}$.

Table 2. Critical Properties, Acentric Factors, and κ_1 of Pure Components

components	$T_c{}^{a}$ K	$P_c{}^{a}$ MPa	ω^{a}	κ_1
HFC-143a	346.04	3.776	0.2611	−0.04663
HC-600	425.16	3.796	0.1995	0.03443

[a] REFPROP 6.01.[7]

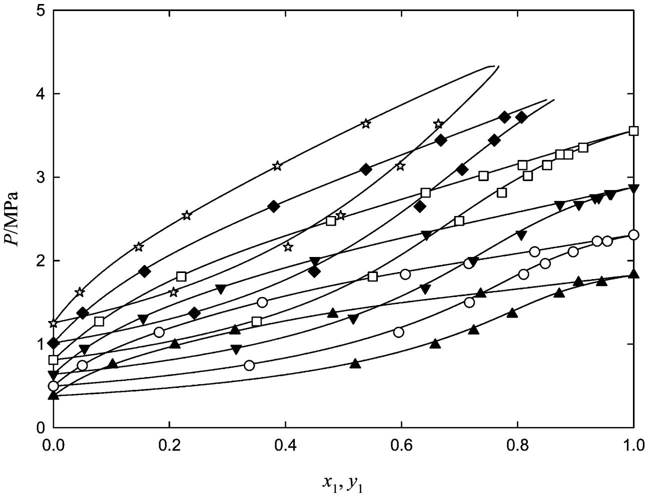

Figure 2. Vapor−liquid equilibria of the HFC-143a (1) + HC-600 (2) system. —, PRSV EOS using Wong−Sandler mixing rules; ▲, experimental data at 313.15 K; ○, 323.15 K; ▼, 333.15 K; □, 343.15 K; ◆, 353.15 K; ☆, 363.15 K.

equipped with a thermal conductivity detector (TCD), and a Porapak-Q column (1.83 m long; 3.18 mm diameter; mesh range, 80/100) was used.

Experimental Procedure. The whole parts of the apparatus were evacuated with a vacuum pump to remove all the impurities. Next, a certain amount of HC-600 was injected into the cell. Then, a proper amount of HFC-143a was charged. After the target temperature was reached, two magnetic pumps were started to circulate vapor and liquid phases. When the equilibrium was reached, the vapor and liquid samples were taken into the gas chromatograph, and the composition was measured. The equilibrium composition of each phase was measured at least five times in a row to obtain reliable average values. The uncertainty of the equilibrium compositions in the mole fraction was estimated to less than ± 0.0002.

Results and Discussion

VLE data for the binary system HFC-143a (1) + HC-600 (2) were measured in a temperature range from (313.15 to 363.15) K. Experimental data are given in Table 1. Experimental data were correlated with the PRSV EOS[3,4] with the Wong−Sandler mixing rules.[5] The PRSV EOS is expressed as follows:

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

$$a(T) = 0.45724\,\frac{R^2 T_c{}^2}{P_c}\,\alpha(T) \tag{2}$$

$$b(T_c) = 0.07780\frac{RT_c}{P_c} \tag{3}$$

$$\alpha(T) = [1 + \kappa(1 - T_r^{0.5})]^2 \tag{4}$$

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

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{6}$$

where T_c is the critical temperature, P_c is the critical pressure, T_r is the reduced temperature, and ω is the acentric factor. κ_1 is a characteristic pure component parameter. The correlation value, κ_1, provided by Stryjek and Vera[4] was used for HC-600, and the value of HFC-143a was obtained by fitting vapor pressure data.[7] The critical properties, acentric factors, and κ_1 are listed in Table 2.

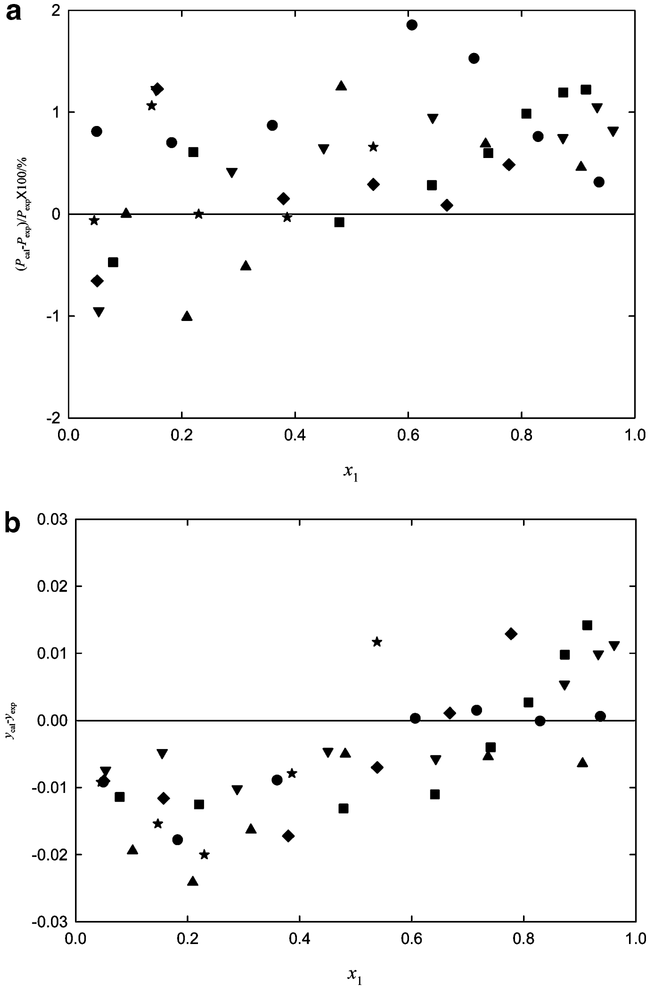

Figure 3. Deviation of the HFC-143a (1) + HC-600 (2) system. Deviation of pressure (a) and vapor mole fraction (b): ▲, 313.15 K; ●, 323.15 K ; ▼, 333.15 K; ■, 343.15 K ; ◆, 353.15 K; ★, 363.15 K.

Table 3. Binary Parameters and AAD

	binary parameters				
T/K	k_{ij}	A_{ij}/K	A_{ji}/K	AAD − P^a/%	AAD − y^b
313.15	0.4409	−374.55	909.41	0.65	0.0127
323.15	0.4023	−352.01	872.70	0.98	0.0054
333.15	0.3287	−255.55	738.08	0.85	0.0074
343.15	0.2096	25.81	431.33	0.68	0.0098
353.15	0.2660	−202.55	681.72	0.48	0.0098
363.15	0.3062	−357.36	951.78	0.36	0.0128

[a] AAD − P/% = $(100/N)\sum_i^N(|P_{i,\mathrm{cal}} - P_{i,\mathrm{exp}}|/P_{i,\mathrm{exp}})$. [b] AAD − y = $(1/N)\sum_i^N|y_{i,\mathrm{cal}} - y_{i,\mathrm{exp}}|$.

The Wong−Sandler mixing rule is represented as

$$b_\mathrm{m} = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{CRT}} \tag{7}$$

$$a_\mathrm{m} = b_\mathrm{m}\left(\sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^\mathrm{E}}{C}\right) \tag{8}$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij}) \tag{9}$$

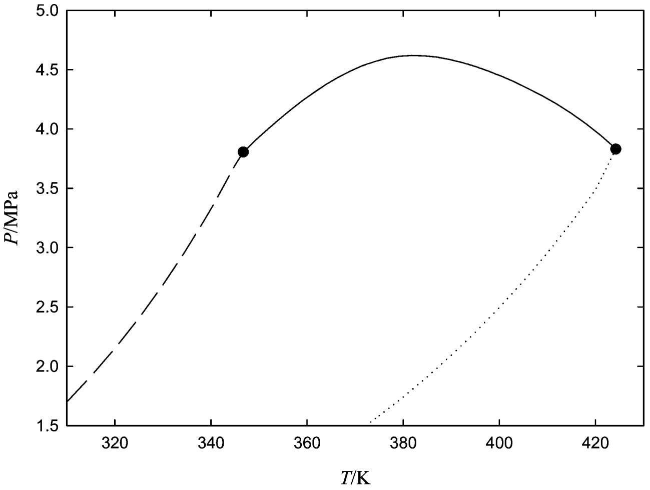

Figure 4. Critical locus and pure vapor pressure curve for the HFC-143a (1) + HC-600 (2) system: —, critical locus; - - -, vapor pressure line of HFC-143a; ···, vapor pressure line of HC-600; ●, critical points of pure components.

where $C = \ln(\sqrt{2} - 1)/\sqrt{2}$ for the PR EOS. Because the excess Helmholtz free energy of mixing at infinite pressure is assumed equal to the excess Gibbs free energy (G^E) at low pressure, the G^E model is used in place of A_∞^E. We used NRTL model[8] as a G^E model in this study:

$$\frac{G^\mathrm{E}}{RT} = \sum_i x_i \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} \tag{10}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})\ \alpha_{ij} = \alpha_{ji} \tag{11}$$

$$\tau_{ij} = A_{ij}/T \tag{12}$$

where τ_{ij} and τ_{ji} are the interaction parameters, and α_{ij} is the nonrandomness parameter. We fixed the nonrandomness parameter α_{ij} to 0.3 in this study. The Simplex algorithm was used to minimize the following objective function:

$$\mathrm{OF} = \sum_i^N \left(\sum_j^\mathrm{NC}\left(\frac{y_{ij,\mathrm{exp}} - y_{ij,\mathrm{cal}}}{y_{ij,\mathrm{exp}}}\right)^2 + \left(\frac{P_{i,\mathrm{exp}} - P_{i,\mathrm{cal}}}{P_{i,\mathrm{exp}}}\right)^2\right) \tag{13}$$

where N is the number of experimental data points, and NC is the number of components. $P_{i,\mathrm{exp}}$ and $P_{i,\mathrm{cal}}$ are the experimental and the calculated pressure, respectively. $y_{ij,\mathrm{exp}}$ is the measured vapor mole fraction, and $y_{ij,\mathrm{cal}}$ is the calculated vapor mole fraction.

As shown in Figure 2, the calculated results give a good agreement with the experimental data at each temperature. The average absolute deviation of pressure and vapor composition were below 0.98 % and 0.0128. Figure 3 shows the deviations of P and y between the measured data and the calculated values. Binary parameters and the average absolute deviations of P and y are given in Table 3. Figure 4 presents calculated critical locus. For the critical point calculation, we applied the method reported by Castier and Sandler.[9] This system shows type I fluid phase behavior according to the classification of van Konynenburg and Scott.[10]

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