Isothermal Vapor−Liquid Equilibrium Data for the Binary Mixture Trifluoroethane (HFC-143a) + Ethyl Fluoride (HFC-161) over the Temperature Range (253.15 to 303.15) K

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This work presents experimental data of vapor−liquid phase behavior in the binary system of trifluoroethane (HFC-143a) + ethyl fluoride (HFC-161) with a single-phase circulation over the temperature range (253.15 to 303.15) K. The correlated results of the vapor−liquid equilibrium data with the Peng−Robinson (PR) equation of state (EoS), combined with the first Modified Huron−Vidal (MHV1) mixing rule and Wilson model, are presented. It is shown that there is a good agreement between the correlated results and the experimental data. The average and maximum absolute derivations of vapor mole fraction are within 0.0209 and 0.0437, respectively, and the average and maximum relative derivations of pressure are within 1.14 % and 2.88 %, respectively. In addition, from the correlation results, it is revealed that there is no azeotrope in the binary system, and the system exhibits from slightly negative deviations to slightly positive deviations when the temperature increases.

Introduction

Production of chlorinated refrigerants, like chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), will cease over the next few decades because of the propensity of these fluids to deplete ozone in the Earth’s stratosphere. Therefore, it is urgent to find suitable replacements in various processes. Ethyl fluoride (HFC-161) has excellent environmental characteristics among the halogenated hydrocarbons of methane and ethane, such as an ozone depletion potential (ODP) of zero, a global warming potential (GWP) of 12, and a lifespan of 3 years in the atmosphere. Some of the mixtures with HFC-161, such as ternary mixtures (HFC-125 + HFC-143a + HFC-161) and (HFC-32 + HFC-125 + HFC-161), were actually proposed as promising alternative refrigerants for R404A and monochlorodifluoromethane HCFC-22.[1−3] It was found that the COP of the new mixture (HFC-125 + HFC-143a + HFC-161) is equal to or higher than that of R404A, and its discharge temperature and GWP are lower than those of the latter.[1] Therefore, the new mixtures of HFC-161 will find more and more applications as the global awareness of environmental protection grows.

To apply these new refrigerants in designing and operating new processes of cyclic refrigerating machines, it is extremely important to collect the information of vapor−liquid equilibrium (VLE) data and build up the models furnishing reliable information. Therefore, in this paper, VLE data for refrigerant mixture trifluoroethane (HFC-143a) and HFC-161 are reported. In addition, the accurate thermodynamic models are also reported to predict the behavior of the binary mixture (HFC-143a + HFC-161), which are the basis for predicting the behavior of the ternary mixture (HFC-125 + HFC-143a + HFC-161) in the future.

Experimental Section

HFC-143a and HFC-161 were provided by Zhejiang Lantian Environment Protection Hi-Tech Co. Ltd. with a minimum mass fraction purity of 99.99 % and 99.74 %, respectively. No further purification was done on these chemicals before use.

The apparatus used in this investigation is a circulation-type still described in detail by Han and Cui.[3−5] The temperature of the stainless steel equilibrium cell in the thermostat bath was maintained by the refrigeration subsystem and the heater subsystem. The temperature fluctuation in the bath was less than ± 5 mK/30 min. The temperature measurement system consists of a four-head 25-platinum resistance thermometer (model: WZPB-2, China) with an uncertainty of ± 10 mK (ITS) and a Keithley 2010 data acquisition/switch unit with an uncertainty of ± 1 mK. The overall temperature uncertainty for the bath and the temperature measurement system was ± 15 mK. The pressure measurement system includes a pressure transducer (model: PMP4010, Drunk), a differential pressure null transducer (model: 1151DP, China), an oil-piston type dead-weight pressure gauge (model: YS-6•60•250•600, China), and an atmospheric pressure gauge (model: DYM-1, China). The pressure transducer was calibrated by the oil-piston-type dead-weight pressure gauge before the experiments. The total uncertainty of the pressure measurement system is ± 1.6 kPa.

The equilibrium compositions of the vapor and liquid phase were measured by a gas chromatograph (GC), which was equipped with a Flame Ionization Detector (FID) (model: GC112A, China). The GC was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. Considering the margin of error and reproducibility of GC, we generally estimated that an overall uncertainty in the measurements of the composition is ± 0.003 in mole fraction for both the liquid and vapor phases.

The experimental procedure was as follows. The system was evacuated to remove inert gases. A targeted amount of HFC-

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161 and HFC-143a was added into the equilibrium cell, and the vapor in the cell was circulated continuously by the magnetic circulation pump. The temperature of the entire system was maintained by the temperature controlling system of the thermostatted bath. It was believed that 2 h or more was sufficient to establish a thermal equilibrium state between the cell and thermostatted bath. After the desired equilibrium temperature was attained, the pressure in the equilibrium cell was measured. Then, vapor and liquid samples were withdrawn from the recycling lines by the vapor−liquid sampling valves and were measured in the GC, respectively.

Experimental Results and Discussion

The VLE experimental results for the binary system HFC-143a + HFC-161 are given in Table 1.

In this paper, the Peng−Robinson (PR) equation-of-state (EOS) and Modified Huron−Vidal (MHV1) mixing rule were used to correlate the vapor−liquid equilibrium data of the (HFC-143a + HFC-161) system in which the Wilson activity coefficient model was used to calculate the excess Gibbs free energy.

The expression of the PR equation-of-state is[6]

$$p = \frac{RT}{v - b} - \frac{a}{v^2 + 2vb - b^2} \tag{1}$$

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

$$\alpha(T) = (1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5}))^2 \tag{3}$$

$$b = 0.07780RT_c/p_c \tag{4}$$

where p is the pressure; v is the molar volume; T is the absolute temperature; p_c is the critical pressure; T_c is the critical temperature; R is the general gas constant; and a and b are equation of state dependent parameters, respectively.

In our equation of state approach, the MHV1 mixing rule was used to correlate the vapor−liquid equilibrium[7]

$$\frac{a_m}{b_m RT} = \frac{1}{C}\frac{G^E}{RT} + \frac{1}{C}\sum_i x_i \ln\left(\frac{b_m}{b_i}\right) + \sum_i x_i \frac{a_i}{b_i RT} \tag{5}$$

$$b_m = \sum_i x_i b_i \tag{6}$$

where G^E is excess Gibbs energy; subscripts m and i denote the parameters of the mixture and ith component, respectively; C is determined by the equation of state; and x is the liquid mole fraction.

The excess Gibbs energy G^E was calculated by the Wilson model[8]

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(\Lambda_{21}x_1 + x_2) \tag{7}$$

where Λ_{12} and Λ_{21} are adjustable parameters.

Activity coefficients were obtained by the Wilson model

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + \beta x_2 \tag{8}$$

$$\ln \gamma_2 = -\ln(\Lambda_{21}x_1 + x_2) - \beta x_1 \tag{9}$$

where

$$\beta = \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \tag{10}$$

In the correlation, the necessary conditions of vapor−liquid equilibrium are

$$y_i\hat{\varphi}_i^V p = x_i\gamma_i p_i^{sat}\varphi_i^{sat} \tag{11}$$

where y is the mole fraction in the vapor phase; φ is the fugacity coefficient; γ is the activity coefficient; and the superscript sat denotes the parameter of the saturated property of the pure refrigerants, respectively.

Table 1. Experimental VLE Results for the Binary Mixture of (HFC-143a (1) + HFC-161(2)) from T = (253.15 to 303.15) K

x_1	y_1	p/MPa	x_1	y_1	p/MPa
	T/K = 253.15			T/K = 283.15	
0.0808	0.1120	0.2203	0.0784	0.1004	0.6215
0.1697	0.2315	0.2307	0.1850	0.2294	0.6502
0.2653	0.3277	0.2399	0.3002	0.3513	0.6789
0.4043	0.4705	0.2538	0.4046	0.4371	0.7088
0.5319	0.6105	0.2681	0.4749	0.5140	0.7202
0.7137	0.7628	0.2846	0.7013	0.7356	0.7729
0.7607	0.8221	0.2912	0.8351	0.8567	0.8008
0.8755	0.9049	0.3009	0.8905	0.9010	0.8129
0.9422	0.9586	0.3078	0.9653	0.9677	0.8263
	T/K = 258.15			T/K = 288.15	
0.0699	0.0829	0.2650	0.0760	0.0982	0.7217
0.2068	0.2544	0.2791	0.1855	0.2271	0.7540
0.2933	0.3634	0.2939	0.2944	0.3449	0.7870
0.3816	0.4415	0.3034	0.3788	0.4324	0.8102
0.5002	0.5780	0.3197	0.4636	0.5034	0.8329
0.6408	0.7061	0.3345	0.5944	0.6305	0.8658
0.7557	0.8027	0.3480	0.6997	0.7297	0.8932
0.8919	0.9155	0.3631	0.8189	0.8440	0.9243
0.9379	0.9521	0.3679	0.8877	0.8983	0.9375
			0.9624	0.9662	0.9545
	T/K = 263.15			T/K = 293.15	
0.0551	0.0755	0.3180	0.0745	0.0967	0.8343
0.1306	0.1731	0.3300	0.1820	0.2214	0.8698
0.1699	0.2162	0.3339	0.2907	0.3377	0.9062
0.2209	0.2743	0.3414	0.3749	0.4249	0.9345
0.3191	0.3850	0.3565	0.4517	0.4896	0.9568
0.4454	0.5112	0.3730	0.6099	0.6251	0.9957
0.5072	0.5684	0.3804	0.7055	0.7234	1.0259
0.5767	0.6390	0.3903	0.8126	0.8350	1.0614
0.7429	0.7895	0.4132	0.8854	0.8964	1.0764
0.8433	0.8738	0.4261	0.9623	0.9662	1.0955
0.9242	0.9393	0.4365			
	T/K = 268.15			T/K = 298.15	
0.0266	0.0362	0.3745	0.0731	0.0946	0.9573
0.1236	0.1565	0.3900	0.1880	0.2170	0.9984
0.2289	0.2827	0.4108	0.2918	0.3294	1.0398
0.2511	0.3117	0.4175	0.3956	0.4113	1.0685
0.3929	0.4618	0.4364	0.4480	0.4791	1.0939
0.5363	0.6006	0.4600	0.5782	0.6025	1.1399
0.6542	0.7135	0.4799	0.7032	0.7154	1.1738
0.7216	0.7732	0.4883	0.8209	0.8244	1.2132
0.8002	0.8412	0.5008	0.8884	0.8921	1.2301
0.8545	0.8800	0.5097	0.9634	0.9645	1.2513
0.9203	0.9396	0.5178			
	T/K = 273.15			T/K = 303.15	
0.0927	0.1015	0.4429	0.0789	0.0905	1.0865
0.1530	0.1778	0.4646	0.1599	0.1995	1.1279
0.2275	0.2783	0.4821	0.2611	0.3046	1.1789
0.2715	0.3207	0.4886	0.4168	0.4521	1.2360
0.3830	0.4548	0.5144	0.5348	0.5746	1.2922
0.4704	0.5256	0.5254	0.6793	0.6969	1.3358
0.5640	0.6307	0.5449	0.7505	0.8019	1.3685
0.7576	0.7888	0.5758	0.8778	0.8841	1.3980
0.8204	0.8712	0.5938	0.9569	0.9604	1.4207
0.8758	0.8998	0.6007			
0.9444	0.9542	0.6117			
	T/K = 278.15				
0.0178	0.0181	0.5205			
0.0865	0.1098	0.5362			
0.1187	0.1447	0.5446			
0.1566	0.1899	0.5530			
0.2774	0.3405	0.5855			
0.3798	0.4526	0.6038			
0.5883	0.6247	0.6420			
0.7026	0.7521	0.6672			
0.8906	0.9180	0.7066			
0.9374	0.9524	0.7129			

Table 2. Critical Parameters and Acentric Factors for HFC-143a and HFC-161[9,10]

substance	molecular formula	molecular weight	T_c K	p_c MPa	ω
HFC-143a	CH_3-CF_3	84.04	346.04	3.77	0.2611
HFC-161	CH_3-CH_2F	48.06	375.30	5.02	0.2155

Table 3. Correlated Results of Vapor-Liquid Equilibrium Using the PR + MHV1 Model for HFC-143a + HFC-161 from T = (253.15 to 303.15) K

		PR + MHV1				interaction parameters	
T/K	N_p	Δy	max$\lvert y_{cal} - y_{exp}\rvert$	δp	max 100·[$(p_{cal} - p_{exp})/p_{exp}$]	Λ_{12}	Λ_{21}
253.15	11	0.0092	0.0216	0.5057	0.9820	0.5184	1.6868
258.15	11	0.0102	0.0217	0.8100	1.5263	1.6331	0.5565
263.15	13	0.0092	0.0193	0.4179	0.7964	0.3990	1.8898
268.15	13	0.0076	0.0143	0.4007	1.1857	0.8739	1.1232
273.15	13	0.0121	0.0252	1.0284	2.4996	1.9364	0.3886
278.15	14	0.0082	0.0308	0.3941	0.9619	0.5052	1.6330
283.15	11	0.0149	0.0315	0.8204	1.4892	0.3218	2.0520
288.15	12	0.0129	0.0265	0.6762	1.6362	0.3544	1.9683
293.15	12	0.0161	0.0437	0.6539	1.8273	0.3104	2.0727
298.15	12	0.0209	0.0399	1.0175	2.0306	0.2207	2.3391
303.15	11	0.0132	0.0328	1.1395	2.8800	0.2190	2.3233

In the correlation, the used parameters, such as the critical temperature T_c, critical pressure p_c, and acentric factor ω for each pure component, are listed in Table 2. The saturated pressures of pure substances HFC-143a and HFC-161 are from the Refrop 7.0[9] and Chen,[11] respectively.

For the correlation of the experimental data, a computer program has been developed applying the least-squares method for fitting an objective function as follows

$$\mathrm{OF} = \frac{1}{N_p}\sum_{j}^{N_p}\left(\left(\frac{p_{exp} - p_{cal}}{p_{exp}}\right)_j^2 + (y_{1,exp} - y_{1,cal})_j^2 + (y_{2,exp} - y_{2,cal})_j^2\right) \qquad (12)$$

where the subscripts exp and cal denote the calculated and experimental data, respectively; N_p is the number of experimental points; and j denotes the jth experimental point.

The correlated results are shown in Table 3 and Figures 1 to 3. The average absolute deviations of vapor mole fraction Δy and average relative deviations of pressure δp in Table 3 are defined as follows

$$\Delta y = \sum_j \lvert y_{cal} - y_{exp}\rvert_j / N_p \qquad (13)$$

$$\delta p = 100 \cdot \sum_j \lvert (p_{cal} - p_{exp})/p_{exp}\rvert_j / N_p \qquad (14)$$

From the results in Table 3, we can see that within a wide range of temperatures and pressures the mixing rule MHV1 with the PR EOS has a good agreement with the experimental data. The average and maximum absolute derivations of vapor mole fraction are within 0.0209 and 0.0437, respectively, and the average and maximum relative derivations of pressure are within 1.14 % and 2.88 %, respectively. From Figure 1, the binary system exhibits slightly negative deviations in low temperature but slightly positive deviations in high temperature from ideality and has no azeotropes. In the composition range (0 to 1), the temperature glides are small.

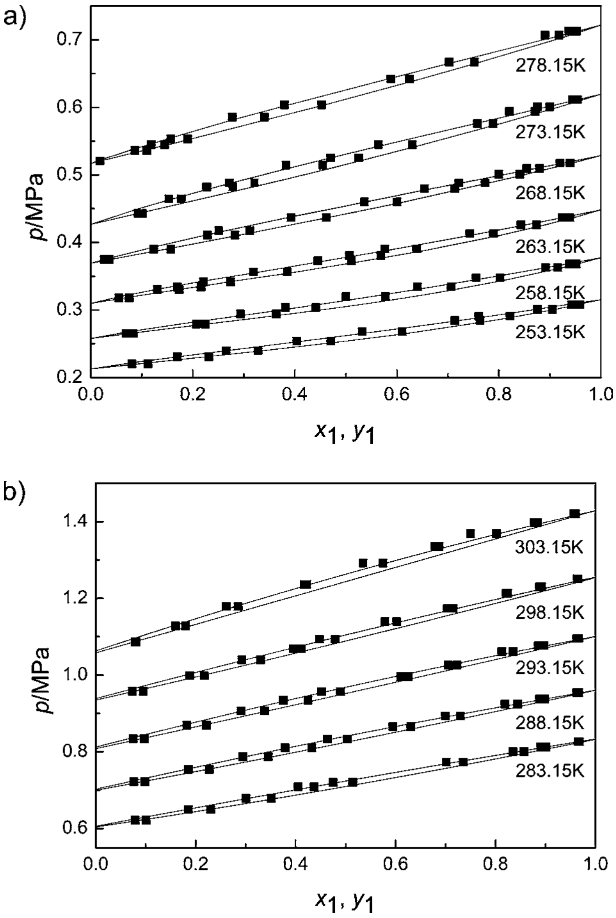

Figure 1. (a) P, x, y curve for the binary mixture (HFC-143a (1) + HFC-161 (2)) from T = (253.15 to 278.15) K. Symbols: ■, experimental data; —, PR + MHV1 model. (b) P, x, y curve for the binary mixture (HFC-143a (1) + HFC-161 (2)) from T = (283.15 to 303.15) K. Symbols: ■, experimental data; —, PR + MHV1 model.

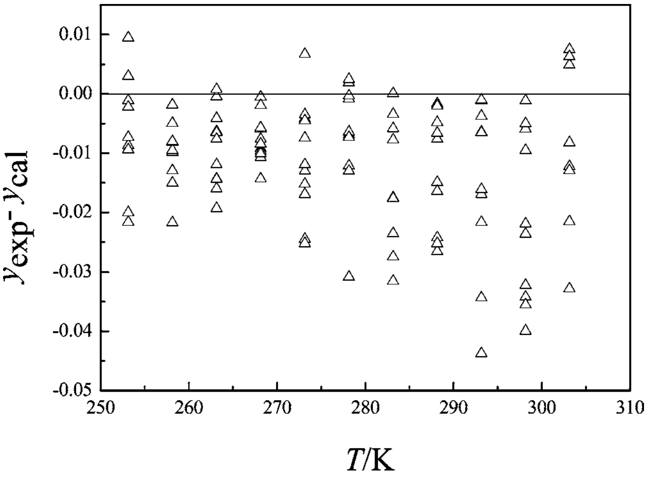

Figure 2. Absolute deviations of vapor mole fraction for the binary mixture (HFC-143a + HFC-161).

Conclusions

In this paper, isothermal vapor−liquid equilibrium data of the binary refrigerant mixture (HFC-143a + HFC-161) over the temperature range (253.15 to 303.15) K were obtained. Using the PR equation of state, combined with the MHV1 mixing rule and Wilson model, the vapor−liquid equilibrium data were correlated, and the interaction parameters of the Wilson model were given. It shows that there is a good agreement between the correlated results and experimental data. In addition, no azeotrope was found in the binary system, and temperature glides of the binary system are small. The system exhibits from

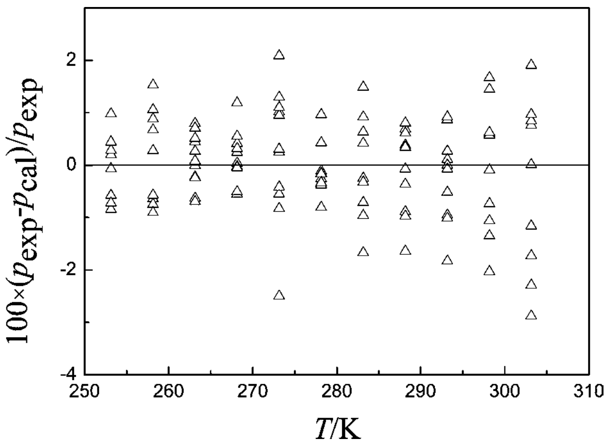

Figure 3. Relative deviations of vapor pressure for the binary mixture (HFC-143a + HFC-161).

slightly negative deviations to slightly positive deviations when the temperature increases.

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