J. Chem. Eng. Data **2008,** *53,* 2193–2196

Vapor−Liquid Equilibria of the Fluoroethane (R161) + 1,1,1,2-Tetrafluoroethane (R134a) System at Various Temperatures from (253.15 to 292.92) K

Xueqiang Dong,[†,‡] Maoqiong Gong,*[,†] Yu Zhang,[†] and Jianfeng Wu[†]

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, P.O. Box 2711, Beijing 100190, China, and Graduate University of Chinese Academy of Sciences, Beijing 100039, China

---

The vapor−liquid equilibrium data for the binary system of fluoroethane (R161) + 1,1,1,2-tetrafluoroethane (R134a) at a temperature range from (253.15 to 292.92) K were measured with a recirculation method. The experimental results including temperatures, pressures, and compositions were correlated using the Peng−Robinson equation of state with two different mixing rules, the van der Waals mixing rule with a single binary interaction parameter, and the Huron−Vidal mixing rule in which the mole excess Gibbs free energy was obtained with the NRTL activity coefficient model. The calculated results agree well with the experimental data, and the largest deviations of the pressure and vapor mole fraction between the experimental data and the correlated results are 0.3642 % and 0.0073, respectively.

Introduction

The traditionally used halogenated hydrocarbons, especially those with chlorine, have been or should be phased out in the refrigeration industry as refrigerants because of their ozone depletion effects. So searching for the environmentally friendly alternative refrigerants has become a crucial work in the refrigeration industry. The former investigations show that it is very hard to find pure substance candidates with appropriate properties. Therefore, mixed refrigerants are becoming more and more attractive. The vapor−liquid equilibrium data are one of the most important fundamental parameters in evaluating mixed refrigerants. Xuan and Chen's[1] study shows that fluoroethane (R161) is a good component in some mixtures for refrigeration applications. In this work, the vapor−liquid equilibrium data for the binary system of fluoroethane (R161) + 1,1,1,2-tetrafluoroethane (R134a) were measured with a recirculation method at the temperature range from (253.15 to 292.92) K.

Experimental Section

Materials. R161 (fluoroethane) was supplied by Zhejiang Lantian Company with a declared mole fraction purity of 99.7 %. R134a (1,1,1,2-tetrafluoroethane) was provided by Arkema with a mole fraction of > 99.6 %. Both of the materials were used without further purification.

Apparatus. The VLE (vapor−liquid equilibrium) data of R161 + R134a were measured with an apparatus based on the vapor-phase recirculation method. The details of the apparatus have been introduced in the previous work.[2−5] A stainless steel equilibrium cell with a volume of 300 cm^3 was immerged in the liquid bath. The vapor phase in the cell was circulated into the liquid phase by a self-made electromagnetic pump. The liquid bath filled with R12 (dichlorodifluoromethane) was cooled by a liquid nitrogen coil and heated with an electric heater. A stirrer was used to obtain a uniform temperature distribution in the liquid bath. A Shimaden SR 253 digital controller was used to control the liquid bath temperature. The liquid bath temperature fluctuation is less than ± 0.01 K. The phase composition was measured by a gas chromatograph (Beifen SP3400) equipped with a thermal conductivity detector (TCD). The uncertainty of the composition measurement was estimated to be ± 0.004 in mole fraction after the careful calibration (different from previous data due to difference of the material purity). The temperature in the equilibrium cell was measured by a 25 Ω standard platinum resistance thermometer which was calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences with an uncertainty of ± 0.003 K. The combined standard uncertainty of the temperature measurement was estimated to be ± 0.01 K. The pressure in the cell was measured by a Druck PMP 4010 pressure transducer with a full

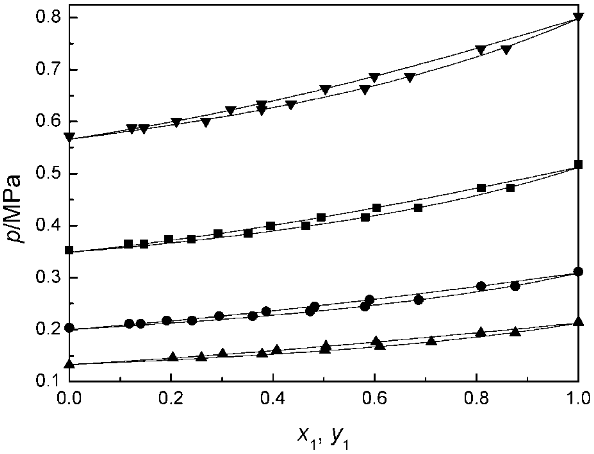

Figure 1. Vapor−liquid equilibrium for the R161 (1) + R134a (2) system at four temperatures: ▲, 253.15 K; ●, 263.15 K; ■, 278.15 K; ▼, 292.92 K; —, calculated using the PR-HV-NRTL model.

Table 1. Critical Parameters and Acentric Factors for R161 (Fluoroethane) and R134a (1,1,1,2-Tetrafluoroethane)[9]

compound	T_c/K	p_c/MPa	ω
R161	375.28	5.027	0.217
R134a	374.26	4.059	0.326

---

* Corresponding author. E-mail: gongmq@mail.ipc.ac.cn. Tel.: +86 10 82543728. Fax: +86 10 82543728.

[†] Technical Institute of Physics and Chemistry.

[‡] Graduate University of Chinese Academy of Sciences.

10.1021/je800505y CCC: $40.75

Table 2. Experimental and Literature Vapor Pressure of R161 and R134a

T/K	p_{exp}/MPa	p_{ref}/MPa	Δp^a/MPa	$\Delta p/p^b$
		R161		
253.16	0.214_1	0.2162^{10}	−0.0021	−0.9809
263.15	0.311_3	0.3119^{10}	−0.0006	−0.1927
278.15	0.517_1	0.5171^{10}	0.0000	0.0000
292.92	0.802_9	0.8012^{10}	0.0017	0.2117
		R134a		
253.15	0.131_7	0.1327^{11}	−0.0010	−0.7593
263.15	0.203_7	0.2006^{11}	0.0031	1.5218
278.15	0.353_0	0.3497^{11}	0.0033	0.9348
292.92	0.571_7	0.5676^{11}	0.0041	0.7172

[a] $\Delta p = p_{exp} - p_{ref}$. [b] $\Delta p/p = 100 \cdot (p_{exp} - p_{ref})/p_{exp}$.

Table 4. Binary Parameters and AAD for R161 + R134a

T/K	253.15	263.15	278.15	292.92
		PR-vdW		
k_{ij}	−0.0110	−0.0122	−0.0142	−0.0142
[a]AAD-p	0.3063	0.3242	0.2574	0.1757
[b]AAD-y	0.0073	0.0064	0.0028	0.0051
		PR-HV-NRTL		
A_{ij}/K	−14.1027	−14.4187	−16.5886	−16.1422
A_{ji}/K	−13.1070	−14.5216	−16.9932	−16.1439
[a]AAD-p	0.3308	0.3642	0.2826	0.1816
[b]AAD-y	0.0073	0.0066	0.0031	0.0052

[a] AAD-p = $100/N \sum_{i=1}^{N} (|P_{exp} - P_{cal}|)/P_{exp}$. [b] AAD-$y$ = $\sum_{i=1}^{N} (|y_{iexp} - y_{ical}|)/N$.

scale of 6 MPa and an uncertainty of ± 0.002 MPa. The combined standard uncertainty of the pressure measurement was estimated to be within ± 0.005 MPa.

Experimental Procedure. The cell and the recirculation loop were first evacuated to remove the remaining gas at room temperature. While the liquid bath was cooled down, a certain amount of the pure less volatile component (R134a in this work) was charged to the equilibrium cell. After the desired temperature was reached and maintained constant for 1 h, the vapor pressure of the less volatile component was obtained. The more volatile component (R161 in this work) was then charged to

Table 3. Experimental Data and Correlated Data for the Binary System of R161 (1) + R134a (2)

experimental data			calculated data							
			PR-vdW model				PR-HV-NRTL model			
p_{exp}/MPa	x_{1exp}	y_{1exp}	p_{cal}/MPa	y_{1cal}	Δp^a/MPa	Δy^b	p_{cal}/MPa	y_{1cal}	Δp^a/MPa	Δy^b
253.15 K										
0.131_7	0.000_0	0.000_0	0.1326	0.0000	−0.0009	0.0000	0.1326	0.0000	−0.0009	0.0000
0.145_7	0.203_4	0.259_6	0.1456	0.2733	0.0001	−0.0137	0.1454	0.2728	0.0003	−0.0132
0.153_2	0.301_5	0.378_7	0.1525	0.3928	0.0007	−0.0141	0.1523	0.3930	0.0009	−0.0143
0.159_9	0.408_0	0.502_2	0.1605	0.5130	−0.0006	−0.0108	0.1603	0.5139	−0.0004	−0.0117
0.168_0	0.503_8	0.609_9	0.1681	0.6126	−0.0001	−0.0028	0.1680	0.6138	0.0000	−0.0039
0.176_3	0.602_5	0.710_9	0.1763	0.7068	0.0000	0.0041	0.1763	0.7078	0.0000	0.0031
0.186_8	0.705_9	0.801_2	0.1853	0.7962	0.0015	0.0050	0.1854	0.7968	0.0014	0.0044
0.193_8	0.808_4	0.876_2	0.1946	0.8755	−0.0008	0.0007	0.1947	0.8757	−0.0009	0.0005
0.214_1	1.000_0	1.000_0	0.2126	1.0000	0.0015	0.0000	0.2126	1.0000	0.0015	0.0000
263.15 K										
0.203_7	0.000_0	0.000_0	0.2001	0.0000	0.0036	0.0000	0.2001	0.0000	0.0036	0.0000
0.211_2	0.117_9	0.140_6	0.2096	0.1562	0.0016	−0.0156	0.2095	0.1559	0.0017	−0.0153
0.217_3	0.191_4	0.241_2	0.2161	0.2493	0.0012	−0.0081	0.2159	0.2493	0.0014	−0.0081
0.226_0	0.294_4	0.360_4	0.2257	0.3736	0.0003	−0.0132	0.2256	0.3742	0.0004	−0.0138
0.234_9	0.387_0	0.473_3	0.2349	0.4788	0.0000	−0.0055	0.2349	0.4799	0.0000	−0.0066
0.244_2	0.482_4	0.581_0	0.2450	0.5803	−0.0008	0.0007	0.2451	0.5815	−0.0009	−0.0005
0.256_8	0.590_1	0.686_4	0.2571	0.6861	−0.0003	0.0003	0.2574	0.6871	−0.0006	−0.0007
0.271_1	0.697_4	0.785_2	0.2699	0.7820	0.0012	0.0032	0.2702	0.7824	0.0009	0.0028
0.283_2	0.809_2	0.876_4	0.2839	0.8715	−0.0007	0.0049	0.2841	0.8714	−0.0009	0.0050
0.311_3	1.000_0	1.000_0	0.3088	1.0000	0.0025	0.0000	0.3088	1.0000	0.0025	0.0000
278.15 K										
0.353_0	0.000_0	0.000_0	0.3484	0.0000	0.0046	0.0000	0.3485	0.0000	0.0045	0.0000
0.364_3	0.116_1	0.147_0	0.3617	0.1459	0.0026	0.0011	0.3615	0.1456	0.0028	0.0014
0.373_2	0.195_5	0.240_2	0.3716	0.2427	0.0016	−0.0030	0.3714	0.2428	0.0018	−0.0026
0.384_7	0.292_4	0.352_0	0.3847	0.3570	0.0000	−0.0050	0.3846	0.3577	0.0001	−0.0057
0.399_6	0.395_4	0.465_0	0.3999	0.4729	−0.0003	−0.0080	0.3999	0.4741	−0.0003	−0.0091
0.416_0	0.494_8	0.581_8	0.4157	0.5785	0.0003	0.0033	0.4160	0.5798	0.0000	0.0020
0.434_3	0.603_7	0.685_4	0.4343	0.6863	0.0000	−0.0009	0.4349	0.6873	−0.0006	−0.0019
0.454_4	0.701_0	0.774_6	0.4521	0.7751	0.0023	−0.0005	0.4527	0.7756	0.0017	−0.0010
0.471_9	0.809_8	0.866_8	0.4731	0.8655	−0.0010	0.0013	0.4737	0.8654	−0.0018	0.0014
0.517_1	1.000_0	1.000_0	0.5120	1.0000	0.0051	0.0000	0.5120	1.0000	0.0051	0.0000
292.92 K										
0.571_7	0.000_0	0.000_0	0.5661	0.0000	0.0056	0.0000	0.5662	0.0000	0.0055	0.0000
0.587_7	0.122_9	0.146_6	0.5860	0.1489	0.0017	−0.0023	0.5855	0.1485	0.0022	−0.0019
0.601_0	0.210_5	0.268_1	0.6017	0.2524	−0.0007	0.0157	0.6011	0.2524	0.0001	0.0157
0.623_5	0.317_2	0.378_0	0.6225	0.3745	0.0010	0.0035	0.6220	0.3751	0.0015	0.0029
0.633_9	0.378_1	0.435_4	0.6352	0.4419	−0.0013	−0.0065	0.6349	0.4428	−0.0010	−0.0074
0.663_4	0.503_2	0.580_8	0.6633	0.5744	0.0001	0.0064	0.6634	0.5756	0.0000	0.0052
0.686_6	0.599_1	0.669_0	0.6866	0.6699	0.0000	−0.0009	0.6870	0.6708	−0.0004	−0.0018
0.716_8	0.706_8	0.765_8	0.7146	0.7700	0.0022	−0.0042	0.7151	0.7705	0.0017	−0.0047
0.740_2	0.808_4	0.858_6	0.7425	0.8570	−0.0023	0.0016	0.7430	0.8570	−0.0028	0.0016
0.802_9	1.000_0	1.000_0	0.7983	1.0000	0.0046	0.0000	0.7984	1.0000	0.0045	0.0000

[a] $\Delta p = p_{exp} - p_{cal}$. [b] $\Delta y = y_{1exp} - y_{1cal}$.

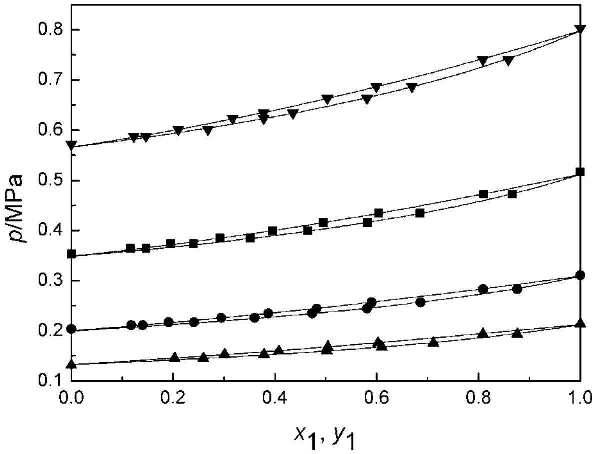

Figure 2. Vapor−liquid equilibrium for the R161 (1) + R134a (2) system at four temperatures: ▲, 253.15 K; ●, 263.15 K; ■, 278.15 K; ▼, 292.92 K; −, calculated using the PR-vdW model.

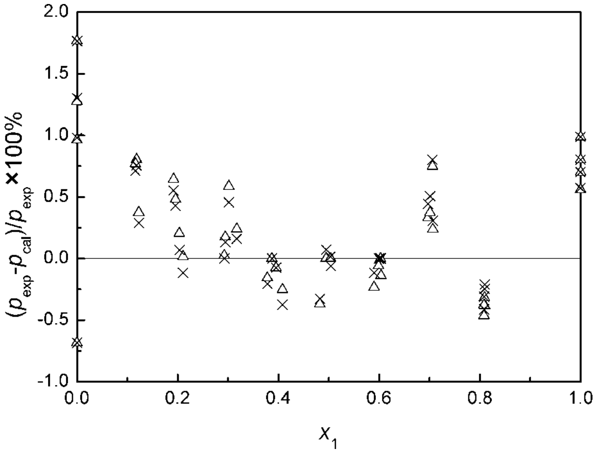

Figure 3. Deviations of the pressure for the system R161 (1) + R134a (2): ×, calculated with the PR-vdW model; Δ, calculated with the PR-HV-NRTL model.

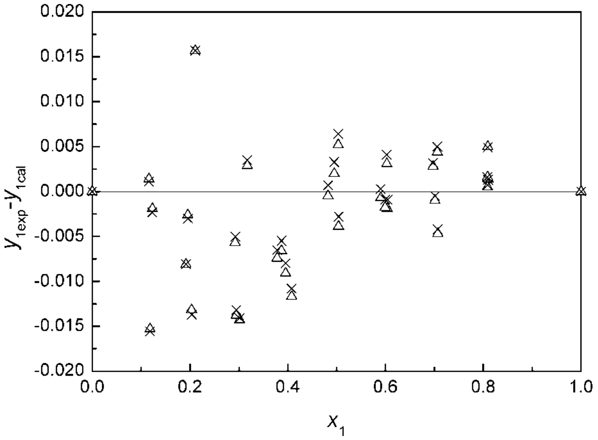

Figure 4. Deviations of the vapor phase composition for the system R161 (1) + R134a (2): ×, calculated with the PR-vdW model; Δ, calculated with the PR-HV-NRTL model.

the cell and mixed with R134a sufficiently through the circulation of the vapor phase driven by the pump. After the vapor phase was recirculated by the pump for at least 2 h and the fluctuation of the pressure was less than ± 0.001 MPa in 0.3 h, the equilibrium state was considered to be established. The pressure in the cell was recorded. The vapor and liquid mole fractions were measured, respectively, by the gas chromatograph at least three times, and then the average value was recorded. Repeating this process by adding the more volatile component step by step, the VLE data at other compositions were measured. At last, the equilibrium cell and recirculation loop were evacuated again, and the pure more volatile component was charged to measure its vapor pressure. Finally, the whole phase equilibrium curve was obtained.

Results and Correlation

The VLE data of R161 + R134a were measured at four temperature points from (253.15 to 292.92) K. All the experimental data were correlated by the Peng−Robinson[6] equation of state (PR EoS) with two different mixing rules, the van der Waals (vdW) mixing rule with a single binary interaction parameter, and the Huron−Vidal (HV) mixing rule[7] involving the NRTL[8] activity coefficient model. The critical parameters and acentric factors for R161 (fluoroethane) and R134a (1,1,1,2-tetrafluoroethane) used in the correlation were listed in Table 1.[9] The vapor pressure data of R161 and R134a were compared with reference data[10] or data calculated from Refprop 8.0,[11] and good agreement was obtained. These data were shown in Table 2. The last digits of the pressures are written as subscripts because the least significant digits of the pressures are 0.001 MPa.

The PR EoS was used in this form

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

where p is the pressure; R is the gas constant; v is the mole volume; T is the temperature; and a and b are EoS constants.

In the PR EoS, constants a and b can be given in the form

$$a(T)=0.457235\frac{R^2T_c^2\alpha(T)}{p_c} \tag{2}$$

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

$$T_r=\frac{T}{T_c} \tag{4}$$

$$b=0.077796\frac{RT_c}{p_c} \tag{5}$$

where p_c and T_c are the critical pressure and temperature and ω is the acentric factor.

The classical van der Waals (vdW) mixing rule with a single adjustable interaction parameter was used in the form below

$$a=\sum_i\sum_j x_ix_ja_{ij} \tag{6}$$

$$a_{ij}=(1-k_{ij})\sqrt{a_{ii}a_{jj}} \tag{7}$$

$$b=\sum_i x_ib_{ii} \tag{8}$$

where k_{ij} is the interaction parameter.

The Huron−Vidal (HV) mixing rule was employed in the form

$$a=b\left[\sum_i x_i\left(\frac{a_{ii}}{b_{ii}}\right)-\frac{g_\infty^E}{C}\right] \tag{9}$$

$$b=\sum_i x_ib_{ii} \tag{10}$$

where g_∞^E is the excess Gibbs energy at infinite pressure and $C$is a constant. For the PR EoS, C is 0.623225.

The NRTL model activity coefficient model was used to calculate the excess Gibbs energy in the form:

$$\frac{g^{\mathrm{E}}}{RT} = \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l} \tag{11}$$

$$\tau_{ji} = \frac{A_{ji}}{T} \tag{12}$$

$$A_{ji} = \frac{\Delta g_{ji}}{RT} \tag{13}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{14}$$

$$\alpha_{ji} = \alpha_{ij} \tag{15}$$

where $\tau_{ii} = 0$; $\alpha_{ii} = 0$; and α_{ji}, A_{ij}, and A_{ji}[12] are adjustable parameters. In this work, $\alpha_{ji} = 0.3$.

k_{ij} in the vdW mixing rule and A_{ij} and A_{ji} in the HV mixing rule were regressed from the experimental data using the gradient method to minimize the objective function listed as follows

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

where N is the number of the experimental data points and p_{exp} and p_{cal} are the pressures obtained from the experiment and calculation, respectively.

All the experimental and correlated results are presented in Table 3 and plotted in Figure 1 and Figure 2. The last digits of the pressures and compositions are written as subscripts in Table 3, because the least significant digits are 0.001 MPa and 0.001 in composition. $x_{1\mathrm{exp}}$ and $y_{1\mathrm{exp}}$ are the mole fractions of the liquid and vapor phases for R161. $y_{1\mathrm{cal}}$ is the mole fractions of the liquid phase obtained from the calculation. $\triangle p$ and $\triangle y$ are the deviations between the experimental data and the calculated data. They are also shown in Figure 3 and Figure 4, respectively. The binary interaction parameters regressed from the VLE data, and the average absolute deviations (AAD) of pressures and vapor phase compositions are presented in Table 4. The results show that both models represent the VLE of the R161 + R134a system quite well, and the PR-vdW model shows a better correlation for this system.

Conclusions

In this work, isothermal VLE data of the R161 + R134a system were measured at four temperature points from (253.15 to 292.92) K. These data were correlated by the Peng−Robinson equation of state using the van der Waals (vdW) mixing rule with a single binary interaction parameter and the Huron−Vidal (HV) mixing rule involving the NRTL activity coefficient model. The correlated results show good agreement with the experimental data. The deviations of the pressure and vapor mole fraction are less than 0.3642 % and 0.0073, respectively.

Literature Cited

(1) Xuan, Y. M.; Chen, G. M. Experimental study on HFC-161 mixture as an alternative refrigerant to R502. *Int. J. Refrig.* **2005**, *28*, 436–441.

(2) Zhang, Y.; Gong, M. Q.; Zhu, H. B.; Wu, J. F. Vapor−liquid equilibrium measurements for the ethane + hexafluoroethane system over a temperature range from (199.64 to 242.93) K. *J. Chem. Eng. Data* **2005**, *50*, 2074–2076.

(3) Zhang, Y.; Gong, M. Q.; Zhu, H. B.; Wu, J. F. Vapor-liquid equilibrium measurements and correlations for an azeotropic system of ethane + hexafluoroethane. *Fluid Phase Equilib.* **2006**, *240*, 73–78.

(4) Zhang, Y.; Gong, M. Q.; Zhu, H. B.; Wu, J. F. Vapor−liquid equilibrium data for the ethane + trifluoromethane system at temperatures from (188.31 to 243.76) K. *J. Chem. Eng. Data* **2006**, *51*, 1411–1414.

(5) Zhu, H. B.; Gong, M. Q.; Zhang, Y.; Wu, J. F. Isothermal vapor−liquid equilibrium data for tetrafluoromethane + ethane over a temperature range from (179.68 to 210.03) K. *J. Chem. Eng. Data* **2006**, *51*, 1201–1204.

(6) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

(7) Huron, M. J.; Vidal, J. New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilib.* **1979**, *3*, 255–271.

(8) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(9) Poling, B E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.

(10) Cui, X. L.; Chen, G. M.; Han, X. H.; Wang, Q. Experimental vapor pressure data and a vapor pressure equation for fluoroethane (HFC-161). *Fluid Phase Equilib.* **2006**, *245*, 155–157.

(11) Lemmon, E. W.; Huber, M. L.; Mclinden, M. O. *Reference Fluid Thermodynamic and Transport Properties (REFPROP)*, NIST Standard Reference Database 2.3, version 8.0; Physical and Chemical Properties Division, National Institute of Standards and Technology: Gaithersburg, MD, 2007.

(12) Im, J.; Lee, G.; Lee, J.; Kim, H. Vapor-liquid equilibria of the 1,1,1-trifluoroethane (HFC-143a) + dimethyl ether (DME) system. *Fluid Phase Equilib.* **2007**, *251*, 59–62.

Received for review July 1, 2008. Accepted July 23, 2008. This work is financially supported by the National Natural Sciences Foundation of China under the contract number of 50576102.

JE800505Y