J. Chem. Eng. Data **2006,** *51,* 1411−1414

Vapor−Liquid Equilibrium Data for the Ethane + Trifluoromethane System at Temperatures from (188.31 to 243.76) K

Yu Zhang,[†,‡] Maoqiong Gong,*[,†] Hongbo Zhu,[†,‡] and Jianfeng Wu[†]

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, P.O. Box 2711, Beijing 100080, China, and Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

Isothermal vapor−liquid equilibrium (VLE) data for ethane (R170) + trifluoromethane (R23) system were measured at six temperatures from (188.31 to 243.76) K and pressures up to 1.62 MPa. The measurements were performed with a recirculation method. The experimental data were correlated with the Soave−Redlich−Kwong equation of state using the Huron−Vidal mixing rule and the NRTL model. The calculated results agree well with the experimental data. Azeotropic VLE behaviors can be observed at certain compositions from the experimental and calculated data.

Introduction

Generally, the lowest effective cooling temperature for a single-stage vapor-compression cycle is about 233 K. To achieve a lower temperature range of (193 to 233) K, two-stage cascade refrigeration systems are usually used.[1,2] In most traditional cascade refrigeration systems for an refrigerating temperature of 193 K, the refrigerants used in the lower temperature stage are mostly chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), or their mixtures, which are listed in Table 1. These have high ozone depletion potential (ODP) or large global warming potential (GWP) or both detrimental facets.[3] It is one of the most important tasks in current refrigeration industry to search for more effective and environment-friendly substitutes to replace the CFC and HCFC refrigerants.

There have been some achievements in searching for these refrigerants; for example, an azeotrope R508B (trifluoromethane/hexafluoroethane) is popularly used to achieve the refrigerating temperature of 193 K. However, as listed in Table 1, this refrigerant has very high GWP value. Moreover, this kind of refrigerant has low solubility in compressor lubricants, which could result in blocks in throttling elements due to solidification of lubricants at low temperatures, and consequently lead to a reduction of system reliability. Therefore, in practical applications, propane (R290) or isobutane (R600a) are usually added to the lower temperature stage to increase the reliability of the refrigeration system. However, doing so reduces the efficiency of the refrigerator. Thus alternatives to these refrigerants are required for cascade refrigeration systems that achieve temperatures of 193 K, and a search has been conducted by the authors. A new azeotrope ethane (R170) + hexafluoroethane (R116) has been discussed in our previous work.[4,5] Moreover, ethane + trifluoromethane also has the potential to be a refrigerant for the lower temperature stage of cascade refrigeration systems, because it exhibits zero ODP value and lower GWP value as compared with the current refrigerants. Vapor−liquid equilibrium (VLE) data are important for evaluation of the refrigerant, and none are available in open publications for the ethane + trifluoromethane system. Therefore, the VLE data were measured for this system at temperatures from (188.31 to 243.76) K, in which azeotropic behaviors were observed.

Table 1. Traditional Refrigerants Used in Cascade Refrigeration Systems for 193 K Applications

name	chemical name	formula	ODP[3]	GWP[3]
R13	chlorotrifluoromethane	$CClF_3$	1.0	14000
R23	trifluoromethane	CHF_3	0.0	12000
R503 (R23/R13) (0.4997/0.5003)	trifluoromethane/ chlorotrifluoromethane	$CHF_3/CClF_3$	0.599	13000
R508B (R23/R116) (0.6268/0.3732)	trifluoromethane/ hexafluoroethane	CHF_3/C_2F_6	0.0	12000

Table 2. Critical Parameters and Acentric Factors[10]

compound	T_C/K	P_C/MPa	ω
R170	305.45	4.8839	0.09860
R23	299.06	4.8290	0.26400

Experimental Section

Chemicals. Ethane was supplied by Airgas with a declared mole fraction purity of > 99.95 %, and trifluoromethane was supplied by DuPont with a declared mole fraction purity of > 99.97 %. All samples were checked by the gas chromatograph and used without further purification.

Apparatus. The VLE measurements were carried out with a recirculation apparatus. Details of this apparatus have been reported previously.[4,5] A stainless steel equilibrium cell with a volume of about 300 cm^3 was immersed in a cryostat. The cryostat was filled with dichlorodifluoromethane as a liquid bath. A magnetic stirrer was used to mix the liquid bath to ensure an even temperature distribution in the cryostat. The liquid bath was cooled by liquid nitrogen coils and heated with an electric heater, and its temperature was controlled by a Shimaden SR 253 digital controller. The fluctuation of the cryostat temperature is less than ± 0.01 K. An electromagnetic pump was used to recirculate the vapor phase to mix with the liquid phase in the cell to accelerate the thermodynamic equilibrium process.

A standard platinum resistance thermometer, with a nominal resistance of 25 Ω and calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences was inserted into

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* Corresponding author. E-mail: gongmq@cl.cryo.ac.cn. Tel: +86 10 82543728. Fax: +86 10 62627843.

[†] Technical Institute of Physics and Chemistry.

[‡] Graduate School of the Chinese Academy of Sciences.

10.1021/je0601107 CCC: $33.50

Table 3. VLE Data for the Ethane (1) + Trifluoromethane (2) System

experimental data			calculated data with the SRK-HV-NRTL model				experimental data			calculated data with the SRK-HV-NRTL model			
P_{exp}/MPa	$x_{1,exp}$	$y_{1,exp}$	P_{cal}/MPa	$y_{1,cal}$	ΔP/MPa	Δy	P_{exp}/MPa	$x_{1,exp}$	$y_{1,exp}$	P_{cal}/MPa	$y_{1,cal}$	ΔP/MPa	Δy
T = 188.31 K													
0.085_4	0.000_0	0.000_0	0.0858	0.0000	−0.0004	0.0000	0.191_6	0.575_5	0.584_4	0.1908	0.5868	0.0008	−0.0024
0.179_8	0.143_9	0.534_0	0.1834	0.5544	−0.0036	−0.0204	0.191_6	0.591_9	0.586_2	0.1908	0.5879	0.0008	−0.0017
0.189_9	0.277_4	0.569_9	0.1892	0.5741	0.0007	−0.0042	0.191_4	0.622_1	0.587_2	0.1908	0.5894	0.0006	−0.0022
0.191_4	0.393_6	0.579_5	0.1902	0.5789	0.0012	0.0006	0.189_2	0.796_8	0.606_9	0.1891	0.6052	0.0001	0.0017
0.191_5	0.502_3	0.582_9	0.1907	0.5834	0.0008	−0.0005	0.123_8	1.000_0	1.000_0	0.1232	1.0000	0.0006	0.0000
T = 193.28 K													
0.115_2	0.000_0	0.000_0	0.1144	0.0000	0.0008	0.0000	0.244_4	0.573_7	0.580_6	0.2439	0.5797	0.0005	0.0009
0.216_2	0.103_7	0.488_0	0.2202	0.5008	−0.0040	−0.0128	0.244_5	0.582_5	0.581_1	0.2439	0.5809	0.0006	0.0002
0.241_2	0.286_1	0.562_5	0.2406	0.5575	0.0006	0.0050	0.244_1	0.631_9	0.585_1	0.2438	0.5849	0.0003	0.0002
0.244_1	0.402_2	0.575_5	0.2426	0.5660	0.0015	0.0095	0.239_7	0.796_7	0.608_9	0.2406	0.6076	−0.0009	0.0013
0.244_3	0.517_1	0.578_5	0.2438	0.5754	0.0005	0.0031	0.159_0	1.000_0	1.000_0	0.1581	1.0000	0.0009	0.0000
T = 198.66 K													
0.153_3	0.000_0	0.000_0	0.1534	0.0000	−0.0001	0.0000	0.313_3	0.568_7	0.571_4	0.3134	0.5725	0.0001	−0.0011
0.273_5	0.094_1	0.446_8	0.2724	0.4569	0.0011	−0.0101	0.313_3	0.575_3	0.572_0	0.3134	0.5733	0.0001	−0.0013
0.306_4	0.271_7	0.536_3	0.3068	0.5374	−0.0004	−0.0011	0.312_5	0.624_2	0.576_8	0.3132	0.5793	−0.0007	−0.0025
0.312_1	0.396_2	0.556_3	0.3112	0.5526	0.0009	0.0037	0.305_3	0.795_7	0.612_8	0.3077	0.6105	−0.0024	0.0023
0.313_0	0.506_3	0.566_1	0.3131	0.5650	0.0001	0.0011	0.204_7	1.000_0	1.000_0	0.2040	1.0000	0.0007	0.0000
T = 212.84 K													
0.307_8	0.000_0	0.000_0	0.3072	0.0000	0.0006	0.0000	0.568_9	0.550_5	0.549_8	0.5684	0.5520	0.0005	−0.0022
0.469_1	0.087_1	0.352_6	0.4707	0.3681	−0.0016	−0.0155	0.568_7	0.568_8	0.555_1	0.5684	0.5570	0.0003	−0.0019
0.546_1	0.246_8	0.479_1	0.5455	0.4834	0.0006	−0.0043	0.566_5	0.612_0	0.564_4	0.5677	0.5667	−0.0012	−0.0023
0.564_4	0.392_5	0.516_7	0.5630	0.5209	0.0014	−0.0042	0.544_6	0.803_6	0.627_4	0.5487	0.6254	−0.0041	0.0020
0.568_5	0.511_4	0.542_2	0.5681	0.5455	0.0004	−0.0033	0.374_3	1.000_0	1.000_0	0.3737	1.0000	0.0006	0.0000
T = 228.50 K													
0.591_5	0.000_0	0.000_0	0.5933	0.0000	−0.0018	0.0000	1.000_8	0.524_7	0.531_7	1.0030	0.5305	−0.0022	0.0012
0.864_1	0.120_8	0.342_4	0.8649	0.3434	−0.0008	−0.0010	1.001_2	0.538_5	0.534_9	1.0031	0.5371	−0.0019	−0.0022
0.968_8	0.285_8	0.453_0	0.9680	0.4513	0.0008	0.0017	0.998_4	0.616_4	0.558_6	0.9993	0.5612	−0.0009	−0.0026
0.995_4	0.425_8	0.503_7	0.9968	0.5005	−0.0014	0.0032	0.940_8	0.816_6	0.646_0	0.9458	0.6505	−0.0050	−0.0045
1.000_2	0.500_9	0.525_1	1.0025	0.5247	−0.0023	0.0004	0.665_4	1.000_0	1.000_0	0.6659	1.0000	−0.0005	0.0000
T = 243.76 K													
1.028_0	0.000_0	0.000_0	1.0339	0.0000	−0.0059	0.0000	1.620_6	0.506_9	0.510_0	1.6257	0.5114	−0.0051	−0.0014
1.389_6	0.118_2	0.278_7	1.3895	0.2861	0.0001	−0.0074	1.620_4	0.519_5	0.514_7	1.6258	0.5182	−0.0054	−0.0035
1.548_1	0.261_7	0.397_1	1.5498	0.3991	−0.0017	−0.0020	1.610_4	0.611_9	0.553_7	1.616	0.5581	−0.0056	−0.0044
1.609_5	0.404_9	0.472_1	1.6123	0.4690	−0.0028	0.0031	1.484_9	0.825_5	0.673_0	1.4964	0.6791	−0.0115	−0.0061
1.619_2	0.495_6	0.504_3	1.6254	0.5080	−0.0062	−0.0037	1.084_0	1.000_0	1.000_0	1.0875	1.0000	−0.0035	0.0000

the liquid phase in the cell to measure the temperature of the phase equilibrium. The uncertainty of the temperature was estimated to be ± 0.01 K. The pressure was measured by a Druck PMP 4010 pressure transducer with a maximum operating temperature of 6 MPa, which was calibrated against a piston pressure gauge (Shanghai Automation, model YU 60) and has an uncertainty of ± 0.002 MPa. The compositions of the liquid and vapor phases were analyzed by a Beifen SP 3400 gas chromatograph. The gas chromatograph was calibrated with gas mixtures of known compositions that were prepared gravimetrically by a Sartorius BS 4000S precision balance, and the uncertainty of the composition was ± 0.002 in mole fraction (different from previous data due to different chromatograph column adopted). The experimental apparatus has been tested and verified by measuring the vapor pressure of propane and VLE data of the ethane + propane system, the results of which were presented elsewhere.[6]

Experimental Procedure. The system was first evacuated to remove the remaining gas in the equilibrium cell and recirculation loop. Then the cryostat was cooled; meanwhile, a certain amount of the pure less volatile component 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 measured. A proper amount (to ensure that the level of the liquid inside the cell is much higher than the entry of the liquid sampling capillary) of more volatile component was then charged to the cell from the feed cylinder. After the vapor phase was recirculated by the pump for at least 2 h and the fluctuation of the pressure is less than ± 0.001 MPa in 0.3 h, the equilibrium state was confirmed to be established. The pressure in the cell was measured. After sweeping the sampling lines, at least four samples of both vapor and liquid phase were withdrawn and analyzed by the gas chromatograph, and the average value was recorded. The interval of every two sampling processes is about 0.3 h. The pressure drop caused by the vapor sampling process is less than 0.001 MPa, and the pressure would reinstate soon due to vapor recirculation.

After the measurement at one concentration was finished, this procedure was repeated at other concentrations by adding the more volatile component to the equilibrium cell. At last, after evacuating the equilibrium cell and recirculation loop, the more volatile component was charged to measure its vapor pressure. So the phase envelop curve at one temperature was obtained.

Correlations

All the experimental results were correlated with the Soave−Redlich−Kwong[7] (SRK) equation of state using the Huron−Vidal (HV) mixing rule[8] involving the NRTL model.[9] The critical and acentric parameters of the two pure components used in the correlations are shown in Table 2 and taken from a commercial software of PROVISION.[10]

In the HV mixing rule, the parameters a and b of the SRK equation of state have the following forms:

$$a = b\left[\sum_i x_i\left(\frac{a_i}{b_i}\right) - \frac{g_\infty^E}{C}\right] \tag{1}$$

$$b = \sum_i x_i b_i \tag{2}$$

where C is a numerical constant. For the SRK equation of state, C = ln 2. The NRTL local composition model was used to

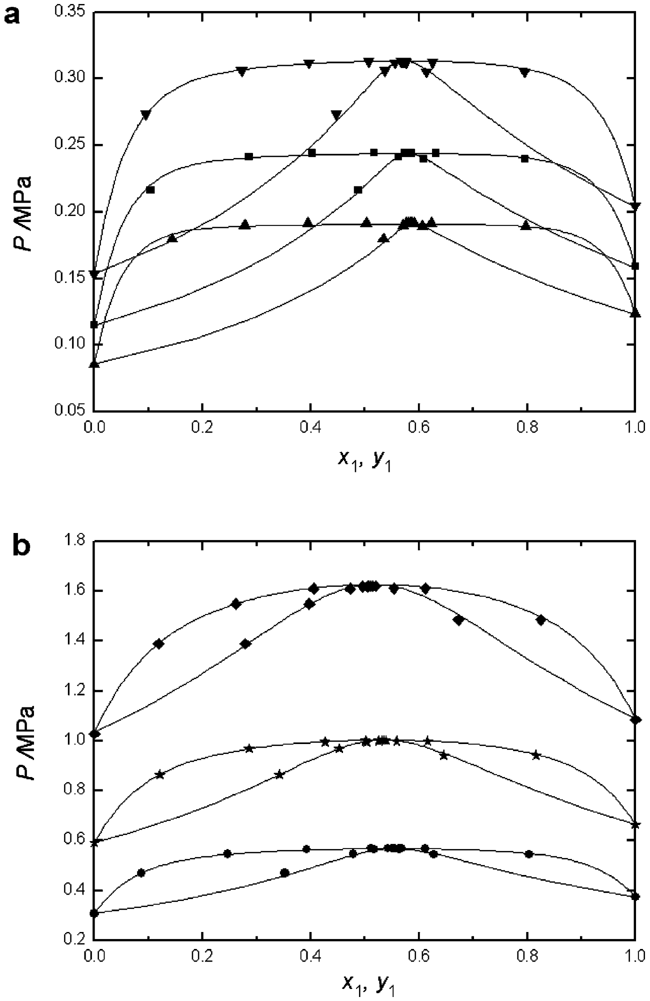

Figure 1. Vapor−liquid equilibrium for the ethane (1) + trifluoromethane (2) system at different temperatures: ▲, 188.31 K; ■, 193.28 K; ▼, 198.66 K; ●, 212.84 K; ★, 228.50 K; ◆, 243.76 K; −, calculated with the SRK-HV-NRTL model.

calculate the excess Gibbs energy:

$$\frac{g^{\mathrm{E}}}{RT} = \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l} \tag{3}$$

where

$$\tau_{ji} = \Delta g_{ji}/(RT) = (g_{ji} - g_{ii})/(RT) \tag{4}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{5}$$

$$\alpha_{ij} = \alpha_{ji} \tag{6}$$

In the NRTL model, α_{ij}, Δg_{ij}, and Δg_{ji} are adjustable parameters and can be regressed from the experimental data.

Results and Discussion

In this work, the $P-T-x-y$ data for the ethane + trifluoromethane system were measured at six temperatures (188.31, 193.28, 198.66, 212.84, 228.50, and 243.76) K. All the experimental data are presented in Table 3 and plotted in Figure 1. In the experiments, the last digits of pressure and composition data are recorded to 0.0001 MPa and 0.0001 in mole fraction, which are written as subscripts in Table 3. But the least significant digits are 0.001 MPa and 0.001 in mole fraction.

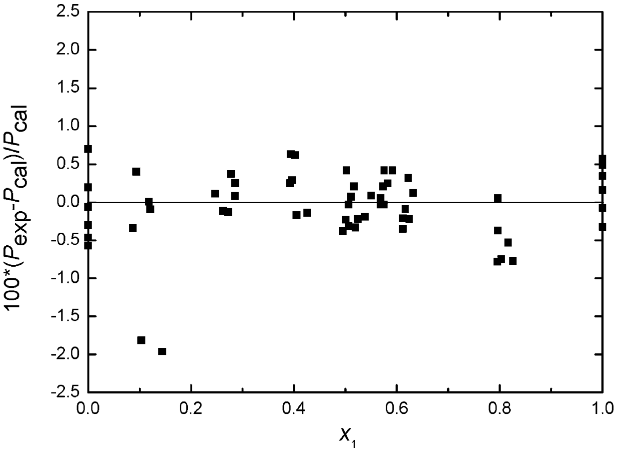

Figure 2. Pressure deviations of the experimental data from the calculated results of the SRK equation with HV mixing rule and NRTL model.

Table 4. Experimental and Calculated Vapor Pressure for Ethane (1) and Trifluoromethane (2)

T	$P_{1,\mathrm{exp}}$	$P_{1,\mathrm{cal}}$	ΔP	$P_{2,\mathrm{exp}}$	$P_{2,\mathrm{cal}}$	ΔP
K	MPa	MPa	MPa	MPa	MPa	MPa
188.31	0.123$_8$	0.1236	0.0002	0.085$_4$	0.0858	−0.0004
193.28	0.159$_0$	0.1585	0.0005	0.115$_2$	0.1145	0.0007
198.66	0.204$_7$	0.2045	0.0002	0.153$_3$	0.1537	−0.0004
212.84	0.374$_3$	0.3744	−0.0001	0.307$_8$	0.3075	0.0003
228.50	0.665$_4$	0.6658	−0.0004	0.591$_5$	0.5924	−0.0009
243.76	1.084$_0$	1.0846	−0.0006	1.028$_0$	1.0284	−0.0004

Table 5. Azeotropic Compositions and Pressures for the Ethane (1) + Trifluoromethane (2) System

T/K	$x_{1,\mathrm{az}}$	P_{az}/MPa	T/K	$x_{1,\mathrm{az}}$	P_{az}/MPa
188.31	0.5874	0.1908	212.84	0.5540	0.5685
193.28	0.5805	0.2439	228.50	0.5337	1.0031
198.66	0.5728	0.3134	243.76	0.5170	1.6259

To check the data consistency, the vapor pressures of pure ethane and trifluoromethane were compared with the values estimated from REFPROP 7.0,[11] and the differences, listed in Table 4, are within ± 0.001 MPa.

In the correlations, the two adjustable parameters Δg_{ij} and Δg_{ji} were regressed as functions of temperature to ensure that they can be used in the entire temperature range, which have such forms as:

$$\Delta g_{ij}/\mathrm{J{\cdot}mol^{-1}} = 1403.7 - 2.1912(T/\mathrm{K}) + 512192/(\mathrm{K}/T) \tag{7}$$

$$\Delta g_{ji}/\mathrm{J{\cdot}mol^{-1}} = -182.8 + 0.5183(T/\mathrm{K}) + 725721/(\mathrm{K}/T) \tag{8}$$

The third parameter α_{ij} of the NRTL model was also regressed as a function of temperature as shown in eq 9, although it is commonly regarded as a numerical constant gained from recommendation of literatures according to the mixture type:

$$\alpha_{ij} = 0.1033 + 0.0013976(T/\mathrm{K}) \tag{9}$$

The VLE data at temperatures (188.31, 193.28, 198.66, 212.84, 228.50, and 243.76) K were calculated with the functions presented above and compared with the experimental data, which can be found in Table 3 and Figure 1. The deviations of the calculated results from the experimental data are shown in Figures 2 and 3.

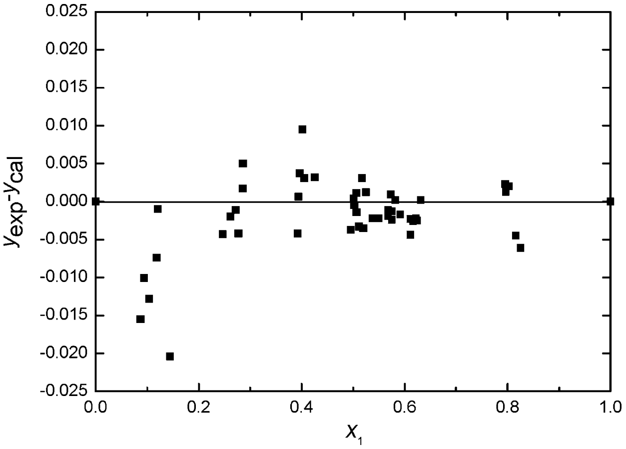

Figure 3. Vapor phase composition deviations of the experimental data from the calculated results of the SRK equation with HV mixing rule and NRTL model.

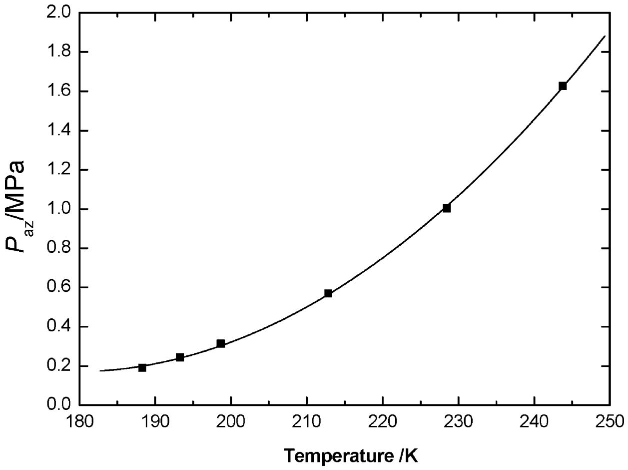

Figure 4. Azeotropic pressure: ■, calculated results at measured temperatures; −, eq 10.

Azeotropic behaviors can be observed from both the experimental data and the calculated results. The calculated azeotropic pressures and compositions are presented in Table 5 and plotted in Figures 4 and 5. Two temperature-dependent functions were used to represent the relation between T, P_{az}, and $x_{1,az}$:

$$P_{az}/\text{MPa} = 11.3125 - 0.1244(T/\text{K}) + (3.4711 \cdot 10^{-4})(T/\text{K})^2 \tag{10}$$

$$x_{az} = 0.9858 - 0.00276(T/\text{K}) + (3.4396 \cdot 10^{-4})\,(T/\text{K})^2 \tag{11}$$

The R170 + R23 system can be regarded as a pressure maximum (or positive) azeotrope, and its azeotropic compositions move toward the less volatile component (trifluoromethane) as the temperature increases.

Conclusions

Isothermal VLE data for the ethane + trifluoromethane system were measured at six temperatures and pressures up to 1.62 MPa. The SRK-HV-NRTL model was used to correlate experimental data. According to the results, the pressure range of this azeotrope at temperatures from (193 to 243) K, which is the evaporating and condensation temperature range of the refrigeration cycle, is about (0.24 to 1.6) MPa. These characteristics are very suitable to achieve a high efficiency of the compressor. Therefore, it suggests that this fluid is potentially useful as refrigerant in the cascade refrigeration system for an operating temperature of 193 K.

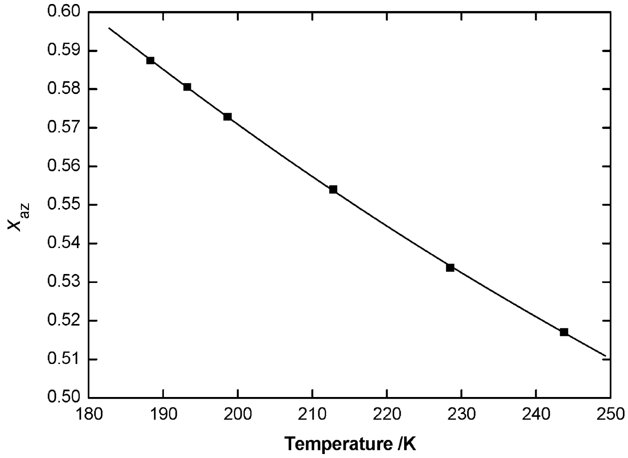

Figure 5. Azeotropic composition: ■, calculated results at measured temperatures; −, eq 11.

Note Added after ASAP Publication. There was an error in the last terms of eqs 7 and 8 in the version published ASAP June 17, 2006; the corrected version was published ASAP June 21, 2006.

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Received for review March 9, 2006. Accepted April 19, 2006. We thank the National Natural Sciences Foundation of China for the financial support under Contract No. 50576102.

JE0601107