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Vapor−Liquid Equilibrium Data of the Methane + Tetrafluoromethane System at Temperatures from (159.61 to 178.93) K

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Isothermal vapor−liquid equilibrium (VLE) data for the binary mixture of methane (R50) + tetrafluoromethane (R14) were measured at (159.61, 161.58, 169.38, 173.90, and 178.93) K. The experiments were carried out with a recirculation-method apparatus including the measurements of temperatures, pressures, and compositions of the liquid and vapor phases. The experimental VLE data were correlated by the Peng−Robinson equation with the Panagiotopoulos−Reid mixing rule and its modified form. The calculated results by these two models were compared with the experimental data.

Introduction

Great achievements have been made on the multicomponent mixed-gases Joule−Thomson refrigerator (MJTR),[1−5] which has many merits over other kinds of cryocoolers, such as high flexibility, high efficiency, low cost, and easily built on an industrial scale. For different refrigeration applications, different components will need to be used in the MJTR to obtain the appropriate mixed refrigerant. As a rule, there are four to seven components used to obtain the mixtures,[5,6] which are generally selected from inert gases (neon, nitrogen, argon, etc.), hydrocarbons (methane, ethane, propane, isobutane, etc.), fluorocarbons (tetrafluoromethane, hexafluoroethane, etc.) and hydrofluorocarbons (trifluoromethane, 1,1,1,2-tetrafluoroethane, etc.) according to the required temperature. These components are all ozone-friendly materials, including methane and tetrafluoromethane. However, tetrafluoromethane has a GWP (global warming potential) value of 5700 and atmospheric lifetime of about 5000 years, and these two values are relatively larger for the refrigerants. Precise prediction of the mixture's properties including the vapor−liquid equilibrium (VLE) behavior is one of the most important and difficult tasks in the design of MJTRs. Many of the above components do not have binary VLE data available. So we have built an experimental rig to measure the required data.[7−9] As part of our series work, the binary VLE data of the methane and tetrafluoromethane system were measured over a temperature range from (159.61 to 178.93) K. The experimental data were fitted by the Peng−Robinson equation of state (PR-EOS) with the Panagiotopoulos−Reid mixing rule and its modified form. The interaction parameters and average deviations of pressures and vapor-phase compositions obtained from the two models are also presented.

Experimental Section

Chemicals. High-purity chemicals of methane and tetrafluoromethane were used in this investigation. Methane of purity higher than 99.995 % by mole fraction was supplied by Dalian DaTe Gas Inc. (China). Tetrafluoromethane supplied by Special Chemical Product Inc. (U.S.A.) has a purity higher than 99.97 % by mole fraction. Both materials were used without further purification.

Table 1. Critical Parameters and Acentric Factors for Tetrafluoromethane and Methane

compound	T_C/K	P_C/MPa	ω
methane	190.564	4.600	0.0115
tetrafluoromethane	227.600	3.739	0.1800

Table 2. Comparison of the Vapor Pressrues (*P*) of Pure Components between Experimental and Calculated Data for Methane (R50) and Tetrafluoromethane (R14)

	T	P	P_{REF}	$\Delta P^a/P$	P_{cal}	$\Delta P^b/P$
component	K	MPa	MPa	%	MPa	%
R14	159.61	0.243	0.254	4.5	0.244	0.4
	161.58	0.269	0.283	5.2	0.274	1.9
	169.38	0.413	0.427	3.4	0.418	1.2
	173.90	0.517	0.532	2.9	0.523	1.2
	178.90	0.651	0.670	2.9	0.661	1.5
				avg 3.8		avg 1.2
R50	159.61	1.566	1.567	0.1		
	161.58	1.694	1.695	0.1		
	169.38	2.275	2.277	0.1		
	173.90	2.671	2.673	0.1		
	178.90	3.170	3.171	0.0		
				avg 0.1		

[a] $\Delta P/P(\%) = 100 \times |P - P_{REF}|/P(\%)$. P_{REF} is obtained from database REFPROP 7.0. [b] $\Delta P/P(\%) = 100 \times |P - P_{cal}|/P(\%)$. P_{cal} is calculated by the Wagner vapor pressure equation for R14 (see text).

Experimental Apparatus. VLE data were measured with a vapor-circulation apparatus, in which the vapor phase was circulated by a self-made electromagnetic pump.[7] The experimental apparatus used in this work is the same as that used in previous work[7−9] and is briefly summarized here. The equilibrium cell is made of stainless steel with an inner volume of about 300 cm^3. It was immersed in a liquid dichlorodifluoromethane bath. In this bath, a stirrer, rotated at a fixed speed by an external magnet, was used to obtain an

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Table 3. Experimental Vapor−Liquid Equilibrium Data at Various Temperatures for the Mixture of Methane (1) + Tetrafluoromethane (2)

T/K	x_1	y_1	P/MPa	T/K	x_1	y_1	P/MPa
159.61	0.000	0.000	0.243	173.90	0.000	0.000	0.517
	0.069	0.440	0.431		0.048	0.268	0.722
	0.134	0.594	0.589		0.079	0.373	0.844
	0.204	0.682	0.735		0.238	0.615	1.332
	0.363	0.776	0.971		0.397	0.717	1.704
	0.647	0.856	1.202		0.617	0.808	2.062
	0.781	0.897	1.326		0.769	0.866	2.308
	0.887	0.938	1.429		0.882	0.923	2.481
	1.000	1.000	1.567		1.000	1.000	2.672
161.58	0.000	0.000	0.269	178.93	0.000	0.000	0.651
	0.066	0.421	0.470		0.052	0.255	0.896
	0.114	0.549	0.598		0.078	0.338	1.016
	0.174	0.635	0.728		0.106	0.403	1.118
	0.316	0.741	0.977		0.312	0.639	1.790
	0.635	0.850	1.330		0.609	0.785	2.443
	0.771	0.887	1.440		0.765	0.854	2.726
	0.886	0.936	1.528		0.880	0.916	2.944
	1.000	1.000	1.695		1.000	1.000	3.170
169.38	0.000	0.000	0.431				
	0.054	0.313	0.606				
	0.105	0.473	0.791				
	0.182	0.595	1.020				
	0.329	0.709	1.326				
	0.625	0.822	1.791				
	0.770	0.878	1.970				
	0.884	0.928	2.112				
	1.000	1.000	2.276				

uniform temperature distribution for accelerating equilibrium process.

The temperature of the liquid bath was controlled by a digital controller from Shimaden, Japan. The temperature in the cell was measured with a platinum resistance thermometer calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences. The uncertainty in the temperature measurement is estimated to be within ± 0.01 K.

The pressure in the equilibrium cell was measured with a pressure transducer, (model PMP4010) from Druck, United Kingdom, and a digital pressure indicator, (model 2700) from Keithley, United States. The uncertainty was estimated to be ± 0.002 MPa after a careful calibration with a dead weight piston pressure tester (model YU60) from Shanghai Fourth Automation Instrument plant, China.

After equilibrium was reached, the vapor and liquid phases were withdrawn separately from the recycling loop and the cell and injected into an on-line gas chromatograph (GC) (Beifen model SP3400). A thermal conductivity detector (TCD) and a stainless steel capillary column from the Beifen Company were used to analyze the compositions.

Procedures. The system was first evacuated to remove impurities. When the thermostatic bath was cooled down from room temperature, a certain amount of tetrafluoromethane was charged into the cell, and then the temperature of the entire system was maintained constant by controlling the temperature of the liquid bath. After the desired temperature was attained, the pressure of the pure component was measured (the pressures of pure methane were measured in the same way). A proper amount of methane was supplied to the cell from a cylinder. The liquid bath was stirred continuously for over 1 h, and the vapor phase was circulated by the electromagnetic pump until equilibrium was established.

After that, the pressure in the cell was measured; then vapor and liquid samples were withdrawn from the recycling line and the cell by the vapor and liquid sampling valves, respectively. The compositions of the samples were measured by the GC, which was connected on-line to the vapor and liquid sampling valves with stainless steel capillaries. The GC was calibrated with mixtures of known composition that were prepared gravimetrically. At least four measurements were performed for each phase, and the average value was considered as the corresponding composition at each equilibrium point. Considering the margin of error and the reproducibility of GC, the overall uncertainty in the measurements of compositions for both the liquid and vapor phases was estimated to be ± 0.001 in the mole fraction.

Table 4. Deviation of Pressures and Vapor-Phase Compositions Calculated by the PR-EOS with the Panagiotopoulos−Reid Mixing Rule and Its Modified Form for the Mixture of R50 (1) + R14 (2) at Various Temperatures

T/K	x_1	$(\Delta P_{\mathrm{PRP}}/P)/\%^{a}$	$\Delta y_{1,\mathrm{PRP}}{}^{b}$	$(\Delta P_{\mathrm{PRM}}/P)/\%^{c}$	$\Delta y_{1,\mathrm{PRM}}{}^{d}$
159.61	0.000	5.7	0.000	5.8	0.000
	0.069	3.4	0.000	2.5	0.004
	0.134	3.2	0.004	2.4	0.007
	0.204	1.5	0.008	0.7	0.009
	0.363	1.0	0.006	0.2	0.007
	0.647	5.0	0.003	2.3	0.001
	0.781	3.9	0.004	0.1	0.004
	0.887	3.0	0.003	1.1	0.001
	1.000	0.3	0.000	0.3	0.000
161.58	0.000	6.7	0.000	6.7	0.000
	0.066	3.4	0.007	2.8	0.010
	0.114	2.2	0.009	1.2	0.013
	0.174	2.5	0.004	1.7	0.007
	0.316	1.7	0.003	0.8	0.003
	0.635	1.8	0.000	0.3	0.003
	0.771	3.0	0.007	0.4	0.000
	0.886	4.3	0.003	0.5	0.000
	1.000	0.3	0.000	0.3	0.000
169.38	0.000	4.8	0.000	4.8	0.000
	0.054	2.9	0.004	2.1	0.001
	0.105	1.5	0.009	0.6	0.012
	0.182	0.1	0.009	0.5	0.010
	0.329	1.5	0.006	1.4	0.005
	0.625	0.6	0.000	0.1	0.000
	0.770	1.2	0.001	0.3	0.005
	0.884	1.5	0.002	0.5	0.000
	1.000	0.4	0.000	0.4	0.000
173.90	0.000	4.3	0.000	4.3	0.000
	0.048	2.4	0.001	1.7	0.005
	0.079	1.5	0.004	0.7	0.008
	0.238	1.6	0.003	1.4	0.001
	0.397	0.4	0.004	0.8	0.001
	0.617	1.7	0.004	1.8	0.004
	0.769	1.4	0.001	0.7	0.002
	0.882	1.4	0.001	0.2	0.002
	1.000	0.5	0.000	0.5	0.000
178.93	0.000	4.3	0.000	4.3	0.000
	0.052	2.6	0.000	1.8	0.005
	0.078	1.4	0.003	0.5	0.008
	0.106	2.2	0.002	1.4	0.005
	0.312	0.7	0.003	1.2	0.001
	0.609	0.7	0.004	1.6	0.003
	0.765	1.4	0.002	1.7	0.004
	0.880	1.3	0.000	1.0	0.002
	1.000	0.6	0.000	0.5	0.000

[a] $(\Delta P_{\mathrm{PRP}}/P)(\%) = 100 \times |P - P_{\mathrm{PRP}}|/P(\%)$. PRP, result caculated by the PRP model. [b] $\Delta y_{1,\mathrm{PRP}} = |y_1 - y_{1,\mathrm{PRP}}|$. [c] $(\Delta P_{\mathrm{PRM}}/P)(\%) = 100 \times |P - P_{\mathrm{PRM}}|/P(\%)$. PRM, result caculated by the PRM model. [d] $\Delta y_{1,\mathrm{PRM}} = |y_1 - y_{1,\mathrm{PRM}}|$.

Correlations

In this work, the experimental VLE data of methane + tetrafluoromethane were measured at five temperatures of (159.61, 161.58, 169.38, 173.90, and 178.93) K and were correlated with the PR-EOS[10] combined with the Panagiotopoulos−Reid[11] mixing rule and its modified form proposed by Simulation Sciences Inc. (SimSci).[12] For each pure component,

Table 5. Interaction Parameters, Average Deviations of Pressures, AD(*P*), and Average Deviations of Vapor-Phase Compositions, AD(*y*), for the Mixture of R50 (1) + R14 (2) at Various Temperatures

	PRP				PRM					
T/K	k_{12}	k_{21}	AD(P)^a/%	AD(y)^b	k_{12}	k_{21}	C_{12}	C_{21}	AD(P)^a/%	AD(y)^b
159.61	0.13	0.11	3.01	0.003	0.12	−0.01	10.003	0.257087	1.70	0.004
161.58	0.13	0.11	2.87	0.004	0.13	0.00	10.003	0.257087	1.63	0.004
169.38	0.13	0.11	1.63	0.003	0.13	0.04	10.003	0.257087	1.19	0.004
173.90	0.13	0.11	1.68	0.002	0.13	0.06	10.003	0.257087	1.35	0.003
178.93	0.13	0.11	1.67	0.002	0.13	0.09	10.003	0.257087	1.55	0.003

[a] $\mathrm{AD}(P)(\%) = 1/N \sum_{i=1}^{N} [100 \times (\Delta P_i/P_i)](\%)$.

[b] $\mathrm{AD}(y) = 1/N \sum_{i=1}^{N} (\Delta y_{1,i})$.

the critical temperature (T_C), critical pressure (P_C), and acentric factor (ω) were all obtained from a commercial software of ProII from SimSci[12] and are listed in Table 1. The correlation was conducted with ProII. The interaction parameters in the Panagiotopoulos−Reid mixing rule for the PR-EOS has such expressions as:

$$a_{ij} = (a_i a_j)^{1/2}\{(1 - k_{ij}) + (k_{ij} - k_{ji})x_i\} \tag{1}$$

The two adjustable interaction parameters are k_{ij} and k_{ji}. The Panagiotopoulos−Reid mixing rule, however, is fundamentally inconsistent for multicomponent systems. In the limit of an infinite number of components so that all the x_i approach zero, the mixing rule reduces to the original Van der Waals mixing rule:

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{2}$$

Equation 1 was modified in a way that eliminated the flaw noted above. This improvement provided better predictions of properties for multicomponent systems:

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) + (k_{ij} - k_{ji})[x_i/(x_i + x_j)]^{c_{ij}} \tag{3}$$

The expression for a_{ji}, which is similar to eq 3, can be obtained by interchanging subscripts i and j. The four adjustable interaction parameters are k_{ij}, k_{ji}, c_{ij}, and c_{ji}. When c_{12} and c_{21}

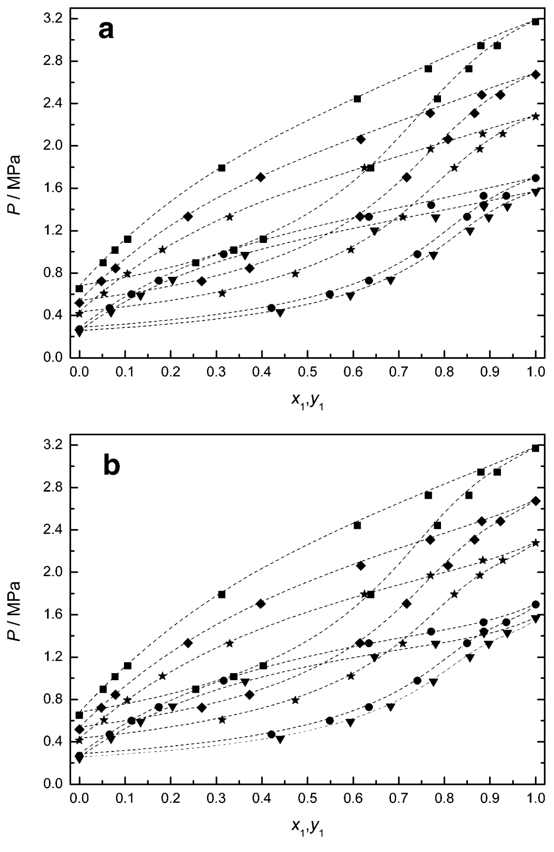

Figure 1. *P*, *x*, *y* curves for the mixture of R50 (1) + R14 (2) at various temperatures: ▼, 159.61 K; ●, 161.58 K; ★, 169.38 K; ◆, 173.90 K; ■, 178.93 K; - - -, calculated data. (a) Calculated by the PRP model. (b) Calculated by the PRM model.

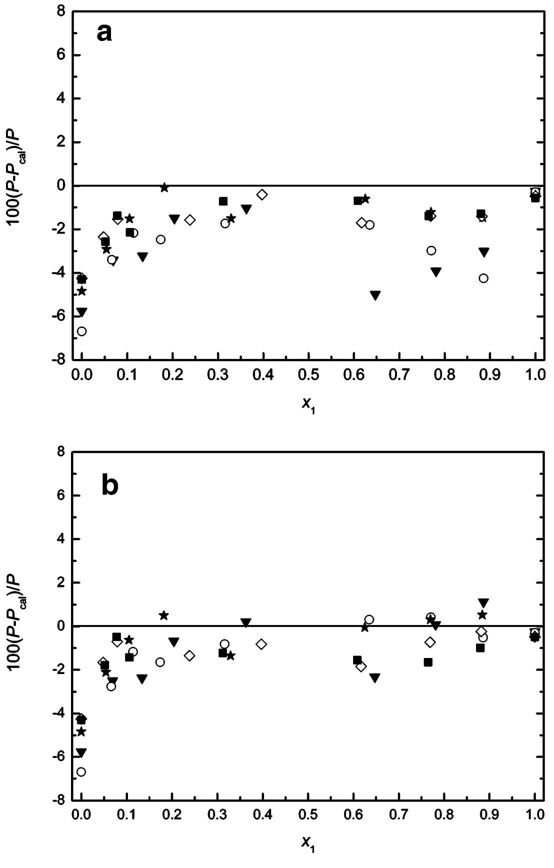

Figure 2. Deviations between experimental and calculated pressures for the mixture of R50 (1) + R14 (2) at various temperatures: ▼, 159.61 K; ○, 161.58 K; □, 169.38 K; □, 173.90 K; ■, 178.93 K. (a) Calculated by the PRP model. (b) Calculated by the PRM model.

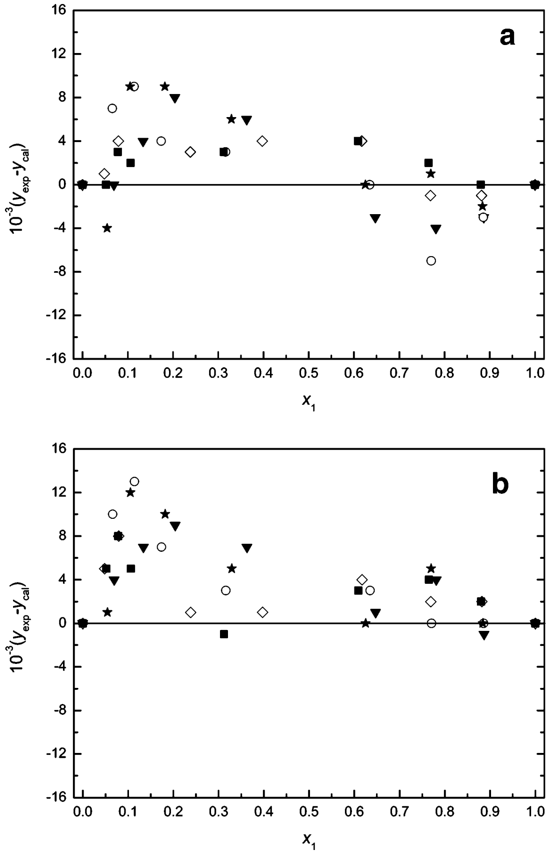

Figure 3. Deviations between experimental and calculated vapor phase compositions for the mixture of R50 (1) + R14 (2) at various temperatures: ▼, 159.61 K; ○, 161.58 K; □, 169.38 K; □, 173.90 K; ■, 178.93 K. (a) Calculated by the PRP model. (b) Calculated by the PRM model.

are equal to 1, eq 3 becomes identical to the mixing rule proposed (also for the purpose of overcoming the flaw of Panagiotopoulos−Reid mixing rule) by Harvey and Prausnitz.[13]

The parameters of these two mixing rules were obtained by minimizing the following objective function:

$$F = \sum_{i=1}^{N} \left[\sum_{j=1}^{\mathrm{NOC}} \left(1.0 - \frac{y_{ij\mathrm{cal}}}{y_{ij}}\right)^2 + \left(1.0 - \frac{P_{i\mathrm{cal}}}{P_i}\right)^2 \right] \tag{4}$$

where N is the number of experimental points, P_i is the experimental pressure, and $P_{i\mathrm{cal}}$ is the calculated pressure. NOC is the number of components. y_{ij} is the experimental vapor mole fraction, and $y_{ij\mathrm{cal}}$ is the calculated vapor mole fraction.

Results and Discussion

The comparison of the saturated vapor pressures of the pure components between experimental data and calculated results by REFPROP 7.0[14] is listed in Table 2, in which the absolute deviation of vapor pressure for methane was within ± 0.002 MPa and the average relative deviation was 0.1 %, but the relevant values for R14 were from (0.011 to 0.019) MPa and 3.8 %. The values for tetrafluoromethane were too large to be acceptable. So, in order to improve the correlation accuracy of pure tetrafluoromethane vapor pressure, a specific (Wagner[15]) vapor pressure equation was built. The Wagner vapor pressure equation has such expression as:

$$\ln(P_\mathrm{r}) = \frac{(A_1\tau + A_2\tau^{1.5} + A_3\tau^3 + A_4\tau^6)}{T_\mathrm{r}} \tag{5}$$

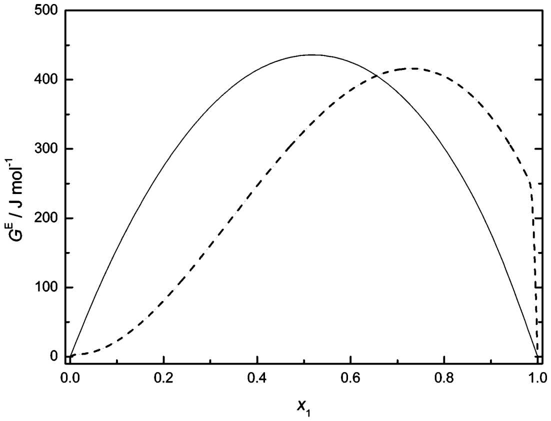

Figure 4. G^E for CF_4 (1) + CH_4 (2) at 98 K. —, ref 17; - - -, calculated data with the measured values in this work.

where $P_\mathrm{r} = P/P_\mathrm{C}$, $T_\mathrm{r} = T/T_\mathrm{C}$, $\tau = 1 - T_\mathrm{r}$, and the critical temperature and pressure for R14 are listed in Table 1. The dimensionless coefficients of A_1, A_2, A_3, and A_4 were all correlated with experimental data from (139.53 to 217.53) K and are equal to −7.38059, 2.81980, −7.15617, and 24.85656, respectively.[16] The comparison between experimental data and calculated results by the Wagner vapor pressure equation are also listed in Table 2, which shows that the absolute deviation of vapor pressure for R14 was from (0.001 to 0.010) MPa and the average relative deviation was 1.2 %. These two values were relatively low and acceptable.

The experimental VLE data for the binary mixture R50 + R14, including the mole fractions of methane in the liquid and vapor phases, and the pressures in equilibrium at (159.61, 161.58, 169.38, 173.90, and 178.93) K are listed in Table 3. The VLE results calculated by the PR-EOS combined with the Panagiotopoulos−Reid mixing rule and its modified form (PRM) and their deviations in pressure and in vapor-phase compositions (Δy_1) as compared with experimental data at various temperatures are given in Table 4. With regression from the experimental data, the two interaction parameters of k_{ij} and k_{ji} in eq 1 were defined as functions of temperatures with following forms:

$$k_{ij} = 0.265134 - 35.1637/T + 2108.6/T^2 \tag{6}$$

$$k_{ji} = -0.023173 + 53.1286/T - 5158.52/T^2 \tag{7}$$

Four interaction parameters of k_{ij}, k_{ji}, C_{ij}, and C_{ji} in eq 3 were also determined by the experimental data. The values of C_{ij} and C_{ji} at (159.61, 161.58, 169.38, 173.90, and 178.93) K were 10.003 and 0.257087, respectively. k_{ij} and k_{ji} have such expressions as

$$k_{ij} = 0.296078 - 51.9899/T + 3938.82/T^2 \tag{8}$$

$$k_{ji} = 0.358886 + 39.932/T - 15859/T^2 \tag{9}$$

The interaction parameters and the average deviations in pressures, AD(P), and average deviations in vapor-phase compositions, AD(y), between measured and calculated data for the mixture are listed in Table 5.

The P, x, y diagrams for the mixture of methane + tetrafluoromethane at various temperatures are shown in Figure 1, where the experimental VLE data at (159.61, 161.58, 169.38, 173.90, and 178.93) K are shown as triangles, closed circles, pentacles, diamonds, and squares, respectively. The black dash lines indicated the calculated results by the PR-EOS with the

Panagiotopoulos–Reid mixing rule (PRP, Figure 1a) or by the PR-EOS with the modified Panagiotopoulos–Reid mixing rule (PRM, Figure 1b). The deviations of pressures and vapor-phase compositions of calculated results compared with experimental data can be demonstrated clearly at each point, which are shown in Figures 2 and 3, respectively.

From Table 5, the values of AD(P) varied from (1.6 to 3.0) % for the PRP model and from (1.2 to 1.7) % for the PRM model. Meanwhile, the AD(y) varied from 0.002 to 0.004 for the PRP model and from 0.003 to 0.004 for the PRM model. In detail, for pressures, the PRM model was more accurate than the PRP model, especially in low temperatures. However, for vapor-phase compositions, the PRM model was less accurate than the PRP model.

In addition, to test the validity of the experimental data measured in this work, comparison with the excess Gibbs energy for methane + tetrafluoromethane at 98 K[17] was made after the VLE data were extrapolated to 98 K, and the result is shown in Figure 4. As seen from Figure 4, there were relatively large differences between the experimental data by Simon and Knobler[17] and calculated data with the measured values in this work. Because the lowest experimental temperature was 159.61 K, which was 61.61 K higher than 98 K, too large a difference in temperature of extrapolation may result in a big difference here.

Conclusions

Measurements of the VLE for the mixture of R50 + R14 at five temperatures, (159.61, 161.58, 169.38, 173.90, and 178.93) K, were carried out with a recirculation-method equilibrium apparatus. The experimental VLE data were correlated with the PRP and PRM models. According to the comparison results between the experimental data and calculated results, the deviations with two models were relatively low and acceptable. In low temperatures, the PRM model is recommended to get high-accuracy calculation results.

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