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Vapor−Liquid Equilibria of the *trans*-1,3,3,3-Tetrafluoropropene (R1234ze(E)) + Isobutane (R600a) System at Various Temperatures from (258.150 to 288.150) K

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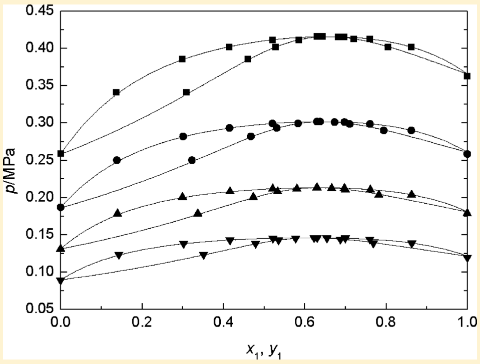
ABSTRACT: Vapor−liquid equilibrium (VLE) data for the binary system of *trans*-1,3,3,3-tetrafluoropropene (R1234ze(E)) + isobutane (2-methylpropane, R600a) were measured using a recirculation apparatus with view windows at four temperatures [(258.150, 268.150, 278.150, and 288.150) K]. The measured uncertainties of the temperature, pressure, and compositions are ± 5 mK, ± 0.0005 MPa, and ± 0.005, respectively. All of the experimental data were correlated with the Peng−Robinson (PR) EoS using the Huron−Vidal (HV) mixing rule involving the nonrandom two-liquid (NRTL) activity coefficient model. The maximum average absolute relative deviation of pressure is 0.32 %, while the maximum average absolute deviation of vapor phase mole fraction is 0.0029. Azeotropic behavior can be found at the measured temperature range.



INTRODUCTION

Traditional chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants have been or will be phased out with the implementation of the Montreal protocol and its modifications because of their high ozone depletion potential (ODP) values. Therefore, it is urgent to find highly efficient and environmentally friendly alternative refrigerants for the refrigeration industry. Hydrofluorocarbons (HFCs) and hydrocarbons (HCs) were used as alternative refrigerants. However, the HFCs are to some degree expensive, and most of them have high global warming potential (GWP) values; the HCs are flammable. In this case, the mixtures of HFCs and HCs are considered as promising alternatives since HFCs can reduce the flammability of the HCs, while the HCs can reduce the GWPs of the mixtures. Furthermore, azeotropic mixtures behave like pure substances at their azeotropic compositions. The performance and the optimal concentration of the mixed refrigerants can be estimated by their thermodynamic properties, such as vapor−liquid equilibrium (VLE) data. VLE data of some binary mixtures have been measured in our previous work.[1−3] In this study, isothermal VLE data for *trans*-1,3,3,3-tetrafluoropropene (R1234ze(E)) + isobutane (2-methylpropane, R600a) systems were measured by a recirculation apparatus at four temperatures [(258.150, 268.150, 278.150, and 288.150) K]. All of the experimental data were correlated with the Peng−Robinson (PR) EoS[4] using the Huron−Vidal (HV) mixing rule[5] involving the nonrandom two-liquid (NRTL) activity coefficient[6] model. R1234ze(E) and R600a are good components with zero ODP and very low GWP values. Their mixtures are friendly to the environment.

EXPERIMENTAL SECTION

Materials. R1234ze(E) was supplied by Nanjing Yuji Tuohao Co. with a declared mole fraction of 0.995. R600a was provided by Dalian Special Gas Industry Company with a declared mole fraction of >0.999. Both of the materials were used without further purification.

Apparatus. The apparatus based on the vapor-phase recirculation method is shown in Figure 1. The details have been presented in our previous work.[2,3] A visual VLE cell made of stainless steel was immersed in an isothermal liquid bath which was full of alcohol. A magnetic pump was used to ensure intensive circulation of the vapor phase through the liquid phase in the cell. It was operated by a step motor with a digital controller. A copper tube with distributed nozzles lying at the bottom of the cell was used to make the return vapor phase mix evenly with the liquid phase. The isothermal liquid bath was heated with an electric heater and cooled with a cold coil of a refrigerating machine. The temperature of the liquid bath was controlled with the Shimaden SR 253 digital controllers by adjusting the heat loads of the electric heater. To accelerate the equilibrium process and obtain a uniform temperature distribution, two stirrers with speed controllers were located in the liquid bath. A stainless steel vacuum vessel was used outside the isothermal liquid bath to reduce the heat exchange with the environment and prevent frosting on the surface of the liquid bath. One vapor-phase capillary at the

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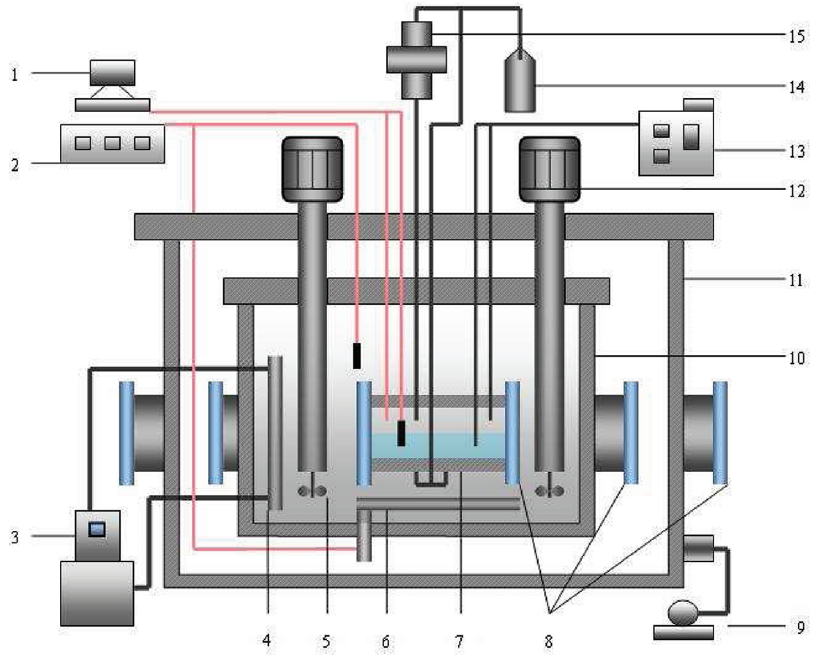

Figure 1. Schematic diagram of the experimental system: 1, temperature and pressure indicator; 2, digital controller; 3, refrigerating machine; 4, evaporator; 5, stirrer; 6, electric heater; 7, equilibrium cell; 8, view windows; 9, vacuum pump; 10, isothermal liquid bath; 11, vacuum vessel; 12, motor; 13, gas chromatograph; 14, feed system; 15, magnetic pump.

top of the cell and three liquid-phase capillaries at different elevations in the cell were employed for sampling. The compositions of the samples were analyzed by a gas chromatograph (Shimadzu GC2014) equipped with a thermal conductivity detector (TCD). The gas chromatograph was calibrated by the mixtures that were preprepared gravimetrically. An uncertainty of the composition measurement is estimated to be less than ± 0.005 in mole fraction. The WZPB-1 25 Ω standard platinum resistance thermometer supplied by Kunming Temperature Instruments was used to measure the temperatures of the equilibrium cell. It was calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences based on the 1990 International Temperature Scale (ITS 90) with an uncertainty less than ± 3 mK. The temperatures in the cell were measured by the Guildline 6622A DC resistance/thermometry bridge. The combined standard uncertainty of the temperature measurement is estimated to be less than ± 5 mK. The pressures of the cell were measured by the Mensor CPT6000 digital pressure transducer with full scales of 1.25 MPa. An uncertainty of the pressure transducer is 0.02 %. The combined standard uncertainty of the pressure measurement is estimated to be less than ± 0.0005 MPa.

Experimental Procedure. The whole system was evacuated at first to remove all of the residual impurities. A small amount of the pure, less volatile component was then put into the cell and degassed from the cell at least three times to purge the total system. After that, the pure less volatile component (R600a in this work) was added to the equilibrium cell to obtain the saturated vapor pressure data. When the desired temperatures were reached and maintained for at least 1 h with the continuous work of the magnetic pump, and the temperature fluctuation in the cell was less than ± 3 mK and the pressure fluctuation was less than ± 200 Pa for at least 10 min, the equilibrium state was considered to be established, and the saturated vapor pressure data were recorded. Adjusting the equilibrium state of the cell, the saturated vapor pressure data at different temperatures were obtained. A suitable amount of the pure more volatile component (R1234ze(E) in this work) was charged into the cell next. It was mixed sufficiently with the less volatile component under the work of the magnetic pump. After the desired temperatures were maintained for at least 1 h and the fluctuations of the temperature and pressure in the cell were less than ± 3 mK and ± 200 Pa, respectively, for at least 10 min, the equilibrium state was considered to be reached. The vapor and liquid compositions were measured by the gas chromatograph at least three times, and then the average value was recorded. Then right amount of R1234ze was charged into the cell again and mixed with the original mixture. When the equilibrium state was established, the values of temperature, pressure, and composition at this molar ratio were recorded. Repeating this process by adding the more volatile component, VLE data of other concentration were measured. At last, the content of the cell was evacuated again, and the pure more volatile component was charged into the cell to measure the saturated vapor pressure.

Table 1. Critical Parameters and Acentric Factors for R1234ze(E) and R600a

compound	T_c/K	p_c/MPa	ω
R1234ze(E)	382.51[7]	3.632[7]	0.3086[8]
R600a[9]	407.81	3.629	0.184

RESULTS AND CORRELATION

The VLE data for the binary system of R1234ze(E) + R600a were measured at four temperature points of (258.150, 268.150, 278.150, and 288.150) K. All of the experimental data were correlated with the PR EoS[4] using the HV mixing rule[5] involving the NRTL activity coefficient model[6] (PR-HV-NRTL model). The critical properties and the acentric factors of R1234ze(E) and R600a are listed in Table 1.[7−9]

Table 2. Experimental Data and Correlated Data for the Binary System of R1234ze (1) + R600a (2)

			calculated data			
experimental data			PR-HV-NRTL model			
p_{exp}/MPa	x_{1exp}	y_{1exp}	p_{cal}/MPa	$y_{1\ cal}$	Δp^a/MPa	Δy^b
258.150 K						
0.0889	0.000	0.000	0.0892	0.0000	−0.0003	0.0000
0.1233	0.143	0.351	0.1224	0.3484	0.0009	0.0026
0.1381	0.303	0.480	0.1378	0.4819	0.0003	−0.0029
0.1427	0.417	0.536	0.1428	0.5373	−0.0001	−0.0013
0.1451	0.522	0.578	0.1451	0.5800	0.0000	−0.0020
0.1458	0.631	0.623	0.1458	0.6253	0.0000	−0.0023
0.1452	0.700	0.655	0.1452	0.6588	0.0000	−0.0038
0.1438	0.760	0.688	0.1439	0.6939	−0.0001	−0.0059
0.1385	0.863	0.769	0.1387	0.7775	−0.0002	−0.0085
0.1193	1.000	1.000	0.1212	1.0000	−0.0019	0.0000
268.150 K						
0.1308	0.000	0.000	0.1308	0.0000	0.0000	0.0000
0.1781	0.140	0.337	0.1765	0.3345	0.0016	0.0025
0.2002	0.300	0.474	0.1996	0.4750	0.0006	−0.0010
0.2077	0.417	0.534	0.2077	0.5365	0.0000	−0.0025
0.2116	0.522	0.581	0.2115	0.5831	0.0001	−0.0021
0.2129	0.630	0.631	0.2129	0.6317	0.0000	−0.0007
0.2123	0.698	0.667	0.2123	0.6667	0.0000	0.0003
0.2102	0.762	0.700	0.2104	0.7057	−0.0002	−0.0057
0.2034	0.863	0.783	0.2036	0.7889	−0.0002	−0.0059
0.1784	1.000	1.000	0.1806	1.0000	−0.0022	0.0000
278.150 K						
0.1867	0.000	0.000	0.1861	0.0000	0.0006	0.0000
0.2496	0.138	0.323	0.2473	0.3213	0.0023	0.0017
0.2816	0.301	0.468	0.2811	0.4696	0.0005	−0.0016
0.2929	0.415	0.532	0.2929	0.5338	0.0000	−0.0018
0.2991	0.521	0.584	0.2991	0.5847	0.0000	−0.0007
0.3015	0.630	0.638	0.3015	0.6376	0.0000	0.0004
0.3010	0.698	0.674	0.3010	0.6747	0.0000	−0.0007
0.2983	0.761	0.711	0.2987	0.7146	−0.0004	−0.0036
0.2897	0.862	0.795	0.2900	0.7982	−0.0003	−0.0032
0.2581	1.000	1.000	0.2605	1.0000	−0.0024	0.0000
288.150 K						
0.2587	0.000	0.000	0.2578	0.0000	0.0009	0.0000
0.3409	0.137	0.309	0.3378	0.3086	0.0031	0.0004
0.3855	0.299	0.461	0.3845	0.4611	0.0010	−0.0011
0.4019	0.414	0.529	0.4020	0.5303	−0.0001	−0.0013
0.4114	0.521	0.586	0.4114	0.5859	0.0000	0.0001
0.4155	0.630	0.643	0.4155	0.6427	0.0000	0.0003
0.4153	0.697	0.682	0.4152	0.6813	0.0001	0.0007
0.4123	0.761	0.721	0.4125	0.7235	−0.0002	−0.0025
0.4015	0.862	0.805	0.4017	0.8080	−0.0002	−0.0030
0.3628	1.000	1.000	0.3654	1.0000	−0.0026	0.0000

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

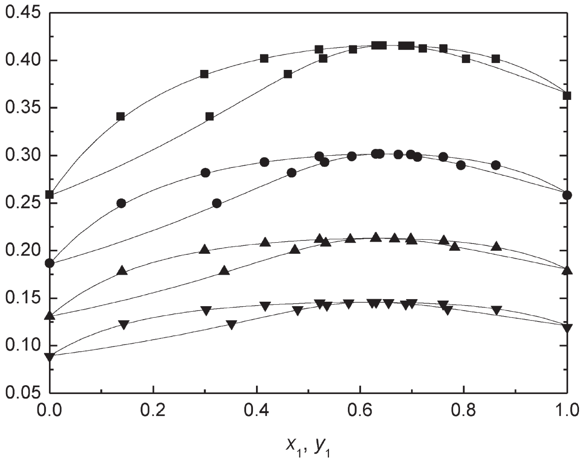

Figure 2. VLE data for the R1234ze(E) (1) + R600a (2) system at four temperatures: ▼, 258.150 K; ▲, 268.150 K; ●, 278.150 K; ■, 288.150 K; —, calculated using the PR-HV-NRTL model.

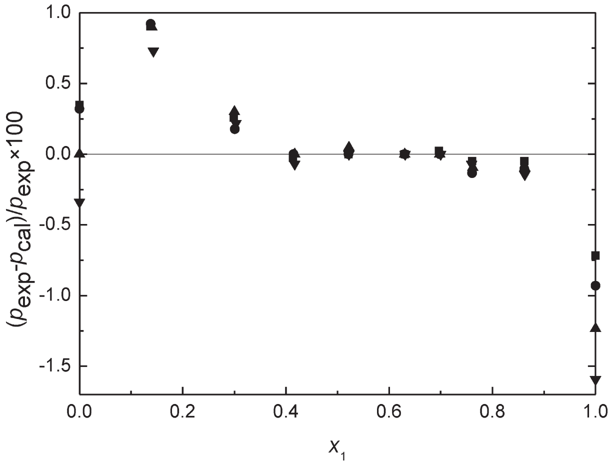

Figure 3. Deviations of the pressure between the experimental data and the calculated data: ▼, 258.150 K; ▲, 268.150 K; ●, 278.150 K; ■, 288.150 K.

The adjustable parameters in the NRTL model can be regressed from the experimental data by minimizing the following objective function using a gradient method

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

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

All of the experimental and correlated VLE data are shown in Table 2 and plotted in Figure 2. The symbol p_{exp} refers to the equilibrium pressures; x_{1exp} and y_{1exp} refer to the mole fractions of the liquid and vapor phases for R1234ze(E), respectively; y_{1cal} represents to the correlated mole fraction of the vapor phase; Δp and Δy represent the deviations between the experimental data and the correlated data. Figure 2 shows that the correlated results agree well with the experimental data. The relative deviations of the pressures and vapor-phase mole fraction are shown in Figures 3 and 4, respectively. The average absolute deviations (AADs) of vapor-phase mole fraction and the average absolute relative deviations (AARDs) of pressure are presented in Table 3. The values of the adjustable parameters A_{ij} and A_{ji} in the NRTL model are also shown in Table 3.[2]

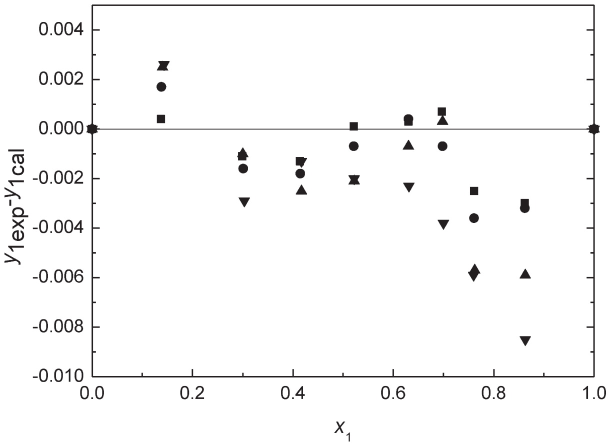

Figure 4. Deviations of the mole fraction of the vapor phase between the experimental data and the calculated data: ▼, 258.150 K; ▲, 268.150 K; ●, 278.150 K; ■, 288.150 K.

Table 3. Binary Parameters and Deviations for the R1234ze + R600a System

T/K	258.150	268.150	278.150	288.150
A_{ij}/K	218.605	215.430	211.476	205.267
A_{ji}/K	223.352	220.396	217.252	214.315
AARD p^a	0.32	0.26	0.26	0.24
AAD y^b	0.0029	0.0021	0.0014	0.0009

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

Table 4. Azeotropic Composition $x_{1,\text{az}}$ and Pressure p_{az} for the R1234ze (1) + R600a (2) System at Each Experimental Temperature

T/K	$x_{1,\text{az}}$	p_{az}/MPa	T/K	$x_{1,\text{az}}$	p_{az}/MPa
258.150	0.619	0.1458	278.150	0.643	0.3016
268.150	0.631	0.2129	288.150	0.656	0.4157

Azeotropic behavior is observed from both the experimental data and the calculated results at these four temperatures. The azeotropic pressure and composition at each temperature can be determined by solving the following equation:[10]

$$\frac{dp}{dx_1} = 0 \tag{2}$$

The calculated results are shown in Table 4. The symbols $x_{1,\text{az}}$ and p_{az} represent the calculated compositions of R1234ze(E) and pressures at azeotropic points, respectively.

CONCLUSIONS

The VLE data for the binary system of R1234ze(E) + R600a were measured with a recirculation method at four temperatures from (258.150 to 288.150) K at 10 K intervals. All of the data were correlated with the PR EoS using the HV mixing rule involving the NRTL activity coefficient model. The correlated results show good agreement with the experimental data at each temperature. The maximum average relative deviation of pressure is 0.32 %, while the maximum average absolute deviation of vapor phase mole fraction is 0.0029. Azeotropic behavior was found at the measured temperature range.

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