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# Measurements of isothermal (vapor + liquid) equilibrium for the (propane + cis-1,3,3,3-tetrafluoropropene) system at temperatures from (253.150 to 293.150) K



# Maoqiong Gong<sup>a,\*</sup>, Yanxing Zhao<sup>a,b</sup>, Xueqiang Dong<sup>a,\*</sup>, Hao Guo<sup>a</sup>, Jun Shen<sup>a</sup>, Jianfeng Wu<sup>a</sup>

<sup>a</sup> Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, P. O. Box 2711, Beijing 100190, China <sup>b</sup> University of Chinese Academy of Sciences, Beijing 100039, China

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# 1. Introduction

From an environmental perspective, switching from conventional refrigerants to low-GWP (global warming potential) refrigerants is the most important consideration for high temperature heat pumping, organic Rankine cycles (ORC), air-conditioning and refrigeration systems. R1234ze(Z) (cis-1,3,3,3-tetrafluoropropene), with the 10 days atmospheric life time and <1 GWP values [1], has been investigated in recent years. Brown et al. [2] predicted the critical temperature, critical pressure and acentric factor for R1234ze(Z) with group contribution methods, which gave 426.8 K, 3970 kPa and 0.333, respectively. Zhang et al. [3] evaluated non-azeotropic mixtures containing R1234ze(Z) as potential refrigerants in refrigeration and high-temperature heat pump systems. It was identified that among the fluorinated propene isomers, R1234ze(Z) delivered similar volumetric refrigerating capacity as R114 (1,2-dichloro-1,1,2,2-tetrafluoroethane) and exhibited the highest COP, although the discharge temperature was higher than that of R114. In the research of Hihara [4], the fundamental information about R1234ze(Z) was provided. Its compatibility with various materials and its flammability and toxicity had been clarified. Additionally, data on its thermodynamic and transport properties were presented. The critical temperature and critical pressure were 423.27 K and 3533 kPa in Hihara's work

# ABSTRACT

cis-1,3,3,3-Tetrafluoropropene, with zero ozone depleting potential and low global warming potential, has received much attention in recent years. In this work, the (vapor + liquid) phase equilibrium for the (propane + cis-1,3,3,3-tetrafluoropropene) binary system was investigated using an apparatus based on the recirculation method over the temperature range from (253.150 to 293.150) K. The VLE results were correlated by the PR-VDW model and PR-HV-NRTL model. Both models can give satisfactory results and the PR-HV-NRTL model exhibits better performance than PR-VDW model on the VLE description for this binary system. No azeotropic behavior was observed during the experiment.

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[4]. Fedele et al. [5] measured the saturation pressure of R1234ze (Z) over the temperature range from 238.13 K to 372.61 K, and the NBP (normal boiling point) temperature and the acentric factor for R1234ze(Z) were estimated to be 282.73 K and 0.3257, respectively. Higashi et al. [6] measured the PpT properties, vapor pressures, saturated densities and the critical parameters for R1234ze (Z). The results of the critical parameters are as same as those of Hihara.

At the same time, many researchers had investigated the heat transfer characteristic and frictional pressure drop of R1234ze(Z) for both the condensation and evaporation. The pressure gradient of R1234ze(Z) was approximately three times greater than those of R1234ze(E) (trans-1,3,3,3-tetrafluoropropene) and the conventional refrigerant R134a (1,1,1,2-tetrafluoroethane), and the HTC (heat transfer coefficient) of R1234ze(Z) was approximately 2.6 times higher than those of R1234ze(E) and R134a according to Kondou et al. [7]. A similar conclusion was obtained from Longo et al. [8]. Then reported that the heat transfer coefficients of R1234ze(Z) were much greater than those of all the refrigerants now used in heat pump applications and the frictional pressure drop was similar to R600a. Fukuda et al. [9] and Petr and Raabe [10] also indicated the superiority of R1234ze(Z) in hightemperature heat pump and ORC applications. In conclusion, R1234ze(Z) is a potential low-GWP and low-flammable refrigerant with high HTC while its frictional pressure drop is higher than conventional refrigerants. R290 (propane) is also a natural working fluid, which is cheap and conveniently available. The drawback of

<sup>\*</sup> Corresponding authors. E-mail address: gongmq@mail.ipc.ac.cn (M. Gong).

R290 is flammability. Therefore, it may be an effective way to blend R1234ze(Z) with other R290 to integrate the advantages of both fluids and may achieve a better coefficient of performance [11,12].

(Vapor + liquid) equilibrium (VLE) of these interesting mixtures plays an important role in calculating and optimizing performance of vapor compression refrigeration cycles. In this paper, the VLE values for the {R290 + R1234ze(Z)} system will be presented at five temperatures ranging from 253.150 K to 293.150 K. The results will be correlated by two thermodynamic models: Peng–Robinson (PR) [13] equation of state (EoS) with Van der Waals (VDW) [14] mixing rule and PR EoS with non-random two liquids (NRTL) [15] activity coefficient model combined Huron–Vidal (HV) [16] mixing rule.

# 2. Experimental

#### 2.1. Materials

R290 and R1234ze(Z) were supplied by Beijing AP BAIF Gases Industry Co., Ltd. and Beijing Yuji Science & Technology Co., Ltd. respectively. The purities of the chemicals stated as a mole fraction by the suppliers are 0.999 and 0.995, respectively. In order to eliminate the non-condensable gases, each sample underwent several cycles of freezing with liquid nitrogen, evacuation, and thawing. The fluids were used with no further purification. The critical temperatures, critical pressures, and acentric factors for R290 and R1234ze(Z) used in this work are taken from REFPROP 9.1 [17] and provided in Table 1.

### 2.2. Apparatus

The experimental set up used in this paper has been described in previous works [18–20], and used without modification, so only essential information is supplied here. The VLE was achieved in a cell with a magnetic pump used to force the vapor through the liquid. A 25  $\Omega$  standard platinum resistance thermometer and a Mensor Series 6000 digital pressure transducer were used to measure the temperature and pressure in the equilibrium cell. The combined standard uncertainties of the temperature and pressure measurement were estimated to be less than ±5 mK and ±0.0005 MPa, respectively. A gas chromatograph (Shimadzu GC2014) equipped with a thermal conductivity detector was used to analyze the compositions of the vapor and liquid phases. At least three analyses were performed for each sample until the deviations among them was less than 0.001. Taking into account the uncertainties from the calibration and the dispersion of analyses, the uncertainty on vapor and liquid mole fractions is estimated to be within ±0.005 over the whole range of concentration.

#### 2.3. Experimental procedure

First the pipeline and the equilibrium cell were evacuated and then purged by R1234ze(Z) for three times. Second, an amount of R1234ze(Z) was injected into the cell. When a desired temperature

# Table 1

Mole fraction purity, critical parameters ( $T_c$ ,  $p_c$ ) and a centric factors  $\omega$  for R290 and R1234ze(Z).

 Components	CAS No.	Mole fraction purity	$T_{\rm c}/{\rm K}^{\rm c}$	p <sub>c</sub> /MPa <sup>c</sup>	ω <sup>c</sup>
 R290 <sup>a</sup>	74-98-6	0.999 <sup>d</sup>	369.89	4.2512	0.1521
R1234ze(Z) <sup>b</sup>	29118-25-0	0.995 <sup>d</sup>	423.27	3.5330	0.3274

<sup>a</sup> Supplied by Beijing AP BAIF Gases Industry Co., Ltd.

<sup>b</sup> Supplied by Beijing Yuji Science & Technology Co., Ltd.

<sup>c</sup> Ref. [17].

<sup>d</sup> As stated by the supplier.

was reached and the fluctuations of the temperature and the pressure were less than  $\pm 3$  mK,  $\pm 100$  Pa, respectively, for more than 20 min in the cell, the equilibrium state was established. The saturated pressure of R1234ze(Z) was recorded. Then an estimated amount of R290 was injected into the equilibrium cell. When the same equilibrium state was achieved, the mole fractions of the vapor and liquid phases of {R290 + R1234ze(Z)} were collected by the gas chromatograph. The process above was repeated and the VLE measurements were accomplished.

### 3. Thermodynamic models

The experimental values were regressed by both PR-VDW model and PR-HV-NRTL model. The PR EoS is employed in the following form:

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

$$a = 0.457235 \\ \times \frac{R^2 T_c^2}{p_c} \Big[ 1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) \Big( 1 - \sqrt{T/T_c} \Big) \Big]^2,$$
(2)

$$b = 0.077796 \frac{RT_c}{p_c},$$
 (3)

where *p* is the pressure in Pa, *v* the mole volume in  $m^3 \cdot mol^{-1}$ , *T* the temperature in K, R is the gas constant in  $J \cdot mol^{-1} \cdot K^{-1}$ ,  $p_c$  and  $T_c$  are the critical pressure and temperature, respectively, and  $\omega$  is the acentric factor of the pure component.

NRTL activity coefficient model is used to calculate the excess molar Gibbs energy, which is given by:

$$\frac{G^{\rm E}}{RT} = \sum_{i} x_i \frac{\sum_{j} \tau_{ji} G_{ji} x_j}{\sum_{l} G_{li} x_l},\tag{4}$$

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

where  $\tau_{ij}$ ,  $\tau_{ij}$  and  $\alpha_{ij} = \alpha_{ji}$  are adjustable parameters and  $\tau_{ii} = 0$ ,  $\alpha_{ii} = 0$ . The parameter  $\alpha_{ij}$  was used as a fixed value 0.3 in present work.

Activity coefficients obtained by NRTL model for a binary system are

$$\ln \gamma_1 = x_2^2 \left[ \frac{\tau_{21} G_{21}^2}{\left( x_1 + x_2 G_{21} \right)^2} + \frac{\tau_{12} G_{12}}{\left( x_2 + x_1 G_{12} \right)^2} \right],\tag{6}$$

$$\ln \gamma_2 = x_1^2 \left[ \frac{\tau_{12} G_{12}^2}{\left( x_2 + x_1 G_{12} \right)^2} + \frac{\tau_{21} G_{21}}{\left( x_1 + x_1 G_{21} \right)^2} \right].$$
(7)

The Van der Waals mixing rule is expressed as

$$a_{\rm m} = \sum_{i} \sum_{i} x_i x_j \sqrt{a_{ii} a_{jj}} (1 - k_{ij}), \tag{8}$$

$$b_{\rm m} = \sum_{i} x_i b_i,\tag{9}$$

with  $k_{ii} = k_{ii}$  and  $k_{ii} = 0$ .

The HV mixing rule can be rewritten as

$$a = b \left[ \sum_{i} x_{i} \left( \frac{a_{ii}}{b_{ii}} \right) - \frac{g_{\infty}^{E}}{C} \right], \tag{10}$$

$$b = \sum_{i} x_i b_{ii},\tag{11}$$

where *C* is a numerical constant with the value 0.623225 in PR EoS and  $g_{i}^{E}$  is the excess molar Gibbs energy calculated by NRTL activity coefficient model at infinite pressure.

The thermodynamic condition for the VLE is the equality of the fugacities of each component in each phase, which is expressed as:

$$f_i^{\rm V} = f_i^{\rm L},\tag{12}$$

where  $f_i^{V}$  and  $f_i^{L}$  represent the fugacity of the vapor phase and liquid phase, respectively.

The parameters  $\tau_{ij}$  and  $\tau_{ji}$  in the NRTL model and  $k_{ij}$  in the VDW model were obtained by minimizing the objective function (OF) as expressed below

$$OF = \sum_{i}^{N} |p_{exp} - p_{cal}|, \qquad (13)$$

where *N* is the number of the experiment points,  $p_{exp}$  and  $p_{cal}$  are the experimental and calculated pressures, respectively.

The point test [21,22] was performed to test thermodynamic consistency of the VLE measurements. The thermodynamic consistency test of VLE values is passed when the average absolute deviation (AAD) of vapor composition must be less than 0.01 for the point test:

$$AADy = 1/N \sum_{i}^{N} \left| y_{exp} - y_{cal} \right| \le 0.01$$
(14)

## 4. Results and discussion

# 4.1. VLE data measurements

In this part, the measured saturated vapor pressures of pure R290 and R1234ze(Z) were compared with the referenced data, as listed in Table 2. The experimental and calculated VLE values of the {R290 + R1234ze(Z)} system by the PR-VDW model and PR-HV-NRTL model are presented, as shown in Table 3 and Figs. 1 and 2. Figs. 1 and 2 show the experimental values at five temperatures T = (253.150, 263.150, 273.150, 283.150, 293.150) K and the calculated values by both thermodynamic models, respectively. Good agreements were found between the calculated and experimental values. Meanwhile, the pressure and vapor phase deviations between the calculated and experimental values at each experimental point are shown in Figs. 3 and 4, respectively. The {R290 + R1234ze(Z)} mixture exhibits zeotropic behavior at the experimental temperature range. Figs. 5 and 6 give the activity coefficients calculated with the NRTL model and the excess Gibbs

Table 2
Comparison of the experimental and referenced saturated vapor pressures ( $p_{exp}$ and
$p_{ref}$ ) of pure components {R290 and R1234ze(Z)} with the literature data.

_					
	T/K	$p_{\mathrm{exp}}/\mathrm{MPa}$	$p_{\rm ref}/{ m MPa}$	$\Delta p^{ m b}/{ m MPa}$	$\Delta p/p^{c}  imes 100$
	R290 <sup>a</sup>				
	293.150	0.8363	0.8365	-0.0002	-0.02
	283.150	0.6364	0.6366	-0.0002	-0.03
	273.150	0.4744	0.4745	-0.0001	-0.02
	263.150	0.3451	0.3453	-0.0002	-0.06
	253.150	0.2441	0.2445	-0.0004	-0.16
	R1234ze(Z) <sup>a</sup>				
	293.150	0.1489	0.149	-0.0001	-0.07
	283.150	0.1025	0.103	-0.0005	-0.49
	273.150	0.0685	N/A	N/A	N/A

<sup>a</sup> Referenced data of R290 are taken from Ref. [17], and referenced data of R1234ze(Z) are taken from Ref. [23].

<sup>b</sup>  $\Delta p = p_{\exp} - p_{ref}$ .

<sup>c</sup>  $\Delta p/p = \left(p_{\exp} - p_{\mathrm{ref}}\right)/p_{\exp}$  .

#### Table 3

VLE results for the experimental pressures ( $p_{exp}$ ), liquid phase mole fractions of R290 ( $x_{1exp}$ ), vapor phase mole fractions ( $y_{1exp}$ ), and the activity coefficients ( $\gamma$ ) and excess Gibbs energies( $G^{E}$ ) for the {R290 (1) + R1234ze(Z) (2)} system.<sup>a</sup>

T/K	$p_{\rm exp}/{ m MPa}$	x <sub>1exp</sub>	$y_{1 \exp}$	γ <sub>1</sub>	γ2	$G^{E}/(J \cdot mol^{-1})$
293.150	0.1489	0.000	0.000	4.1260	1.0000	0.0000
	0.3520	0.106	0.591	3.3502	1.0119	338.0990
	0.4542	0.170	0.688	2.9655	1.0319	513.9071
	0.5350	0.240	0.746	2.6039	1.0671	680.2011
	0.5704	0.283	0.772	2.4084	1.0971	768.1878
	0.6587	0.414	0.817	1.9168	1.2406	964.4411
	0.7584	0.661	0.875	1.3140	1.9464	990.2358
	0.7720	0.685	0.879	1.2733	2.0766	964.4542
	0.7908	0.755	0.895	1.1706	2.5800	855.7734
	0.8001	0.798	0.900	1.1189	3.0190	762.4661
	0.8126	0.853	0.918	1.0655	3.8074	610.8669
	0.8224	0.876	0.927	1.0475	4.2446	535.9728
	0.8302	0.930	0.953	1.0159	5.6506	331.3106
	0.8363	1.000	1.000	1.0000	8.8317	0.0000
283.150	0.1025	0.000	0.000	4.5264	1.0000	0.0000
	0.2750	0.104	0.638	3.6138	1.0126	340.8892
	0.3515	0.171	0.729	3.1442	1.0353	528.9344
	0.4107	0.241	0.781	2.7319	1.0739	697.5325
	0.4452	0.285	0.804	2.5073	1.1073	788.2604
	0.5114	0.415	0.841	1.9697	1.2618	982.6335
	0.5814	0.662	0.889	1.3254	2.0268	1001.2296
	0.5883	0.685	0.893	1.2845	2.1622	975.6451
	0.6028	0.757	0.905	1.1743	2.7286	860.5421
	0.6101	0.798	0.913	1.1231	3.1885	769.5985
	0.6176	0.853	0.925	1.0677	4.0539	615.9606
	0.6255	0.875	0.930	1.0498	4.5132	543.6633
	0.6307	0.931	0.955	1.0160	6.1324	329.4089
	0.6364	1.000	1.000	1.0000	9.6660	0.0000
273.150	0.0685	0.000	0.000	4.9825	1.0000	0.0000
	0.2091	0.104	0.681	3.8972	1.0137	348.9413
	0.2717	0.171	0.766	3.3528	1.0383	540.6641
	0.3132	0.243	0.797	2.8708	1.0813	716.4579
	0.3409	0.286	0.831	2.6251	1.1167	805.8997
	0.3865	0.414	0.861	2.0400	1.2801	998.9155
	0.4358	0.661	0.901	1.3447	2.1021	1016.6563
	0.4402	0.683	0.901	1.3031	2.2420	991.9517
	0.4494	0.753	0.914	1.1888	2.8344	880.2034
	0.4528	0.799	0.920	1.1281	3.4000	777.3386
	0.4602	0.852	0.929	1.0720	4.3310	627.1698
	0.4656	0.875	0.933	1.0523	4.8699	550.7111
	0.4697	0.928	0.958	1.0182	6.5906	346.4365
	0.4744	1.000	1.000	1.0000	10.8268	0.0000
263.150	0.1545	0.105	0.729	4.0713	1.0142	350.1965
	0.2013	0.170	0.806	3.5084	1.0386	535.6601
	0.2335	0.241	0.839	3.0010	1.0815	709.6015
	0.2549	0.279	0.861	2.7676	1.1127	789.9276
	0.2957	0.413	0.886	2.1108	1.2853	997.4382
	0.3192	0.663	0.914	1.3651	2.1641	1020.6545
	0.3215	0.682	0.916	1.3269	2.2939	999.7063
	0.3277	0.756	0.923	1.1985	2.9793	882.2482
	0.3297	0.798	0.928	1.1394	3.5539	788.2648
	0.3349	0.855	0.933	1.0749	4.6945	625.7753
	0.3388	0.879	0.941	1.0533	5.3601	544.3837
	0.3413	0.931	0.960	1.0183	7.4088	339.2916
	0.3451	1.000	1.000	1.0000	12.4774	0.0000
253.150	0.1135	0.105	0.773	4.4107	1.0154	356.7334
	0.1490	0.171	0.840	2 1 0 0 0	1.0421	710.0590
	0.1730	0.240	0.070	3.1898 2.0072	1 1220	7 19.0380 806 E010
	0.1864	0.281	0.886	2.90/3	1.1229	800.3919 1014 1573
	0.∠008	0.415	0.903	2.184/	1.5090	1014,15/2
	0.2271	0.003	0.926	1.3885	2.2544	1034.0208
	0.2295	0.084	0.927	1.3430	2.4125	1010,9853
	0.2333	0.755	0.930	1.212/	3.1409	090,0710 700,0100
	0.2348	0.798	0.935	1.1483	3./9//	/99.6190
	0.2379	0.855	0.943	1.0798	5.0955	035.1820
	0.2397	0.8/9	0.945	1.0568	5.863/	552./46/
	0.2419	0.93 I 1 000	0.903 1.000	1.0196	0.27 IU 17 7415	244,7908 0,0000
	0.2441	1.000	1.000	1.0000	14.4417	0.0000

<sup>a</sup> Standard uncertainties u are u(T) = 5 mK and u(p) = 0.0005 MPa and u(x) = u(y) = 0.005. Declared mole fraction purities: R290 (0.999), R1234ze(Z) (0.995).



**Fig. 1.** VLE plot of pressure against mole fraction for the  $\{R290(1) + R1234ze(Z)(2)\}$  system at five temperatures *T* = (253.150, 263.150, 273.150, 283.150, 293.150) K. The symbols represent the experimental values. The solid lines are predicted by the PR-HV-NRTL model.



**Fig. 2.** VLE plot of pressure against mole fraction for the  $\{R290(1) + R1234ze(Z)(2)\}$  system at at five temperatures *T* = (253.150, 263.150, 273.150, 283.150, 293.150) K. The symbols represent the experimental values. The solid lines are predicted by the PR-VDW model.



**Fig. 3.** Plot of the relative deviations of pressure between the calculated and experimental values against mole fraction for the {R290 (1)+R1234ze(Z) (2)} system at five temperatures *T* = (253.150, 263.150, 273.150, 283.150, 293.150) K. (■):  $(p_{cal} - p_{exp})/p_{exp} \times 100\%$  calculated using the PR-VDW model; (○):  $(p_{cal} - p_{exp})/p_{exp} \times 100\%$  calculated using the PR-HV-NRTL model.

energy calculated with the PR-HV-NRTL model, respectively. It can been seen that  $\gamma_1$ ,  $\gamma_1$  are greater than 1, which indicates that the binary system {R290 + R1234ze(Z)} exhibits a positive deviation from Raoult's law.



**Fig. 4.** Plot of the deviations of vapor compositions between the calculated and experimental values against mole fraction for the {R290 (1)+R1234ze(Z) (2)} system at five temperatures *T* = (253.150, 263.150, 273.150, 283.150, 293.150) K. (**■**):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{cal} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{exp} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{exp} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{exp} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{exp} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{exp} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):  $y_{exp} - y_{exp}$  calculated using the PR-VDW model; ( $\bigcirc$ ):



**Fig. 5.** Activity coefficients calculated using the NRTL model for the {R290 (1) + R1234ze(Z) (2)} systems at *T*/K = 293.150 ( $\blacksquare$ ,  $\gamma_1$ ;  $\Box$ ,  $\gamma_2$ ), 283.150 ( $\blacklozenge$ ,  $\gamma_1$ ;  $\bigcirc$ ,  $\gamma_2$ ), 273.150 ( $\bigstar$ ,  $\gamma_1$ ;  $\triangle$ ,  $\gamma_2$ ), 263.150 ( $\blacktriangledown$ ,  $\gamma_1$ ;  $\bigtriangledown$ ,  $\gamma_2$ ) and 253.150 ( $\bigstar$ ,  $\gamma_1$ ;  $\Leftrightarrow$ ,  $\gamma_2$ ).



**Fig. 6.** Excess Gibbs energy calculated using the PR-HV-NRTL model for the {R290 (1) + R1234ze(Z) (2)} systems at T/K = 293.150 (-), 283.150(-), 273.150(···), 263.150(---) and 253.150(---).

The binary interaction coefficients  $k_{ij}$  in the PR-model and  $\tau_{ij}$ and  $\tau_{ji}$  in PR-HV-NRTL at each experimental temperature are shown in Table 3. Notably, the regressed parameters show monotonicity with the temperature. The  $K_{ij}$  decreases as the temperature increases while  $\tau_{ij}$  and  $\tau_{ji}$  show the opposite tendency. The average

#### Table 4

Adjustable parameters and deviation values of different models at each temperature for the {R290 (1) + R1234ze(Z) (2)} system.

T/K	AARDp <sup>a</sup>	ARDy <sup>b</sup>	<i>k</i> <sub>12</sub>	AARDp <sup>a</sup>	ARDy <sup>b</sup>	$\tau_{12}$	$\tau_{21}$
	PR-VDW			PR-HV-NRTL			
293.150	0.84	0.006	0.1415	0.47	0.005	1.8613	0.3524
283.150	0.93	0.007	0.1406	0.44	0.006	1.8834	0.4395
273.150	0.99	0.007	0.1395	0.53	0.007	1.9349	0.5231
263.150	1.31	0.007	0.1367	0.41	0.007	2.0602	0.5463
253.150	1.11	0.008	0.1358	0.48	0.007	2.1486	0.6300

<sup>a</sup> AARD $p = \frac{1}{N} \sum_{i}^{N} \text{abs} \left( p_{\text{exp}} - p_{\text{cal}} \right) / p_{\text{exp}} \times 100\%.$ 

<sup>b</sup> AADy =  $\frac{1}{N} \sum_{i}^{N} abs(y_{exp} - y_{cal})$ .

absolute relative deviation of pressure (AARDp) and the average absolute deviation of the vapor phase mole fraction (AADv) for the binary system are reported in Table 4. The maximum AARDp is 1.31 for the PR-VDW model is 0.53 for PR-HV-NRTL model. The maximum AADy is 0.008 for the PR-VDW model and is 0.007 for PR-HV-NRTL model. As the experimental vapor phase numbers were not used in the regression, a comparison of the experimental vapor phase values with those predicted by the model represents a measure of thermodynamics consistency. The results show that the VLE measurements for the {R290 + R1234ze(Z)} system meet the thermodynamic consistency test, which demonstrates that both thermodynamics models can describe nicely the {R290 + R1234ze (Z)} binary system, although PR-HV-NRTL model gives much smaller values of AARDp than the PR-VDW model.

## 5. Conclusions

In this paper, the investigation of the (vapor + liquid) equilibrium for the {R290 + R1234ze(Z)} system at temperatures from 253.150 K to 293.150 K was conducted. The PR-VDW and PR-HV-NRTL models were employed to describe the VLE properties of the system concerned. Both models can give satisfactory results. The maximum AARDp is 1.31 for the PR-VDW model and is 0.53 for the PR-HV-NRTL model. The maximum AADy is 0.008 for the PR-VDW model and is 0.007 for the PR-HV-NRTL model. The {R290 + R1234ze(Z)} mixture exhibits zeotropic behavior at the experimental temperatures.

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