Vapor–liquid equilibrium of difluoromethane +1,1,1,2-tetrafluoroethane systems over a temperature range from 258.15 to 343.15 K

Xiaolong Cui [a], Guangming Chen [a,*], Changsheng Li [b], Xiaohong Han [a]

[a] *Institute of Cryogenics and Refrigeration, Zhejiang University, Hangzhou 310027, China*
[b] *Institute of Chemical Engineering, Zhejiang University, Hangzhou 310027, China*

Abstract

Isothermal vapor–liquid equilibrium data for the binary system of difluoromethane (HFC-32) +1,1,1,2-tetrafluoroethane (HFC-134a) were measured at temperature from 258.15 to 343.15 K in a circulation-type equilibrium apparatus. The experimental data were correlated with the Peng–Robinson–Stryjek–Vera equation of state using the Wong–Sandier mixing rule. The overall deviation of the pressure by the PRSV equation of state was 0.940%, and the average deviation of vapor phase composition by the PRSV equation of state was 0.0063.
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Keywords: Vapor–liquid equilibrium; Difluoromethane; 1,1,1,2-Tetrafluoroethane; Refrigerants

1. Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which are used as working fluids for different refrigeration applications due to their outstanding properties, will be restricted or completely phased out within the near future, because of global environment concerns. Hydrofluorocarbons (HFCs) mixtures HFC-32 (CH_2F_2) + HFC-134a (CH_2F-CF_3) have been considered as promising candidates for the replacement of CFCs and HCFCs compounds since their ozone depletion potentials arc zero [1–3]. The composition of mixtures recommended for a particular application is determined mainly by the vapor pressure, non-flammability, and contribution to the global warming potential [4–6]. As a prerequisite for process calculations for different conditions, reliable knowledge of the thermodynamic properties within the relevant range of temperature and composition is necessary.

The binary isothermal vapor–liquid equilibria (VLE) for systems composed of HFC-32 and HFC-134a have been studied extensively. McLinden et al. [1] and Duan and Wang [7] summarized some researches in their papers. Table 1 gives out the

summary of experimental data for HFC-32 + HFC-134a mixtures.

In this work, we measured isothermal VLE for the binary systems of HFC-32 + HFC-134a at temperature from 258.15 to 343.15 K in an equilibrium apparatus with a continuous vapor phase circulation. The experimental data were correlated with the Peng–Robinson–Stryjek–Vera (PRSV) cubic equation of state [20] using the Wong–Sandler (WS) mixing rule [21].

2. Experimental

2.1. Materials

The chemicals or HFC-32 (w > 0.999) and HFC-134a (w > 0.999) were supplied by Zhejiang Chemical Industry Research Institute, China and Honeywell Co., USA, respectively. They were used without any further purification.

2.2. Apparatus

VLE data were measured in an apparatus in which vapor phase was continuously recirculated. The schematic diagram of the experimental apparatus is shown in Fig. 1. The apparatus includes a thermostat bath, an equilibrium cell, temperature and pressure controllers and measurement device, etc. The equi-

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Table 1
Summary of experimental data for HFC-32 + HFC-134a mixtures

Author	No. of points	Pressure range (MPa)	Temperature (K)	x_1 mole (%)	Source
Cluing	28	0.289–3.316	263.15–323.15	0.208–0.760	[8]
Lee	10	0.783–3.111	303.15–323.15	0.043–0.626	[9]
Takagi	10	0.273–3.934	248.15–333.15	0.0593–0.816	[10]
Widiatmo	30	0.580–3.100	280.00–340.00	0.33–0.89	[11]
Defibaugh	25	0.26–4.47	253–358	0.50–0.55	[12]
Fujiwara	6	0.38–0.76	273–273	0.20–0.2	[13]
Higash	39	0.57–1.91	283–365	0.12–0.67	[14]
Holcomb	48	0.38–4.56	280–340	0.16–0.78	[15]
Kleemiss	16	0.07–3.15	223–343	0.42–0.52	[16]
Nagel	50	0.01–5.42	203–369	0.21–0.77	[17]
Oguchi	34	0.13–1.29	238–301	0.27–0.71	[18]
Piao	10	0.24–0.93	261–283	0.33–0.89	[19]

librium cell made of stainless steel with an inner volume of about 80 cm^3 was immersed in the thermostat bath. In its middle part, a pair of Pyrex glass windows of 20 mm thickness was installed so that the liquid level, mixing and circulating behaviors could be observed during operation. A motor blender, rotated at variable speeds, was used to accelerate the equilibrium process.

The temperature of the equilibrium cell in the thermostat bath was maintained by the refrigeration subsystem and heater subsystem. The temperature fluctuation in the bath is less than ±4 mK in 1 h. The temperature measurement is made with a four-head 25-Ω platinum resistance thermometer (Yunnan Instrument) with an uncertainty of ±5 mK (ITS) and a Keithley 2010 data acquisition/switch unit with an uncertainty of ±1 mK. The overall temperature uncertainty for the bath and the temperature measurement system was ±10 mK.

The pressure measurement system includes a pressure transducer (Druck PMP4010), a differential pressure null transducer (Xi'an Instrument, 1151DP), an oil-piston type dead-weight pressure gauge (Xi'an Instrument, YS-60), and an atmospheric pressure guage (Ningbo Instrument, DYM-1). A sensitive dif-ferential pressure null transducer separates the sample from the N$_2$-filled system. The accuracy of the null transducer is 0.25% within the range from 0 to 7.5 kPa. Its maximum uncertainty is 0.18 kPa. The accuracy of the oil-piston type dead-weight pressure gauge is 0.02% within the range from 0.1 to 6.0 MPa. The accuracy of the pressure transducer is 0.04%, and its maximum allowable pressure is 3.5 MPa, which was calibrated by the oil-piston type dead-weight pressure gauge before the experiments. The maximum uncertainty of the atmosphere gauge is ±0.05 kPa. The whole pressure measurement system has an uncertainty of ±1.6 kPa.

Table 2
Critical parameters, acentric factors and k_1 value of pure components in the PRSV equation of state [22]

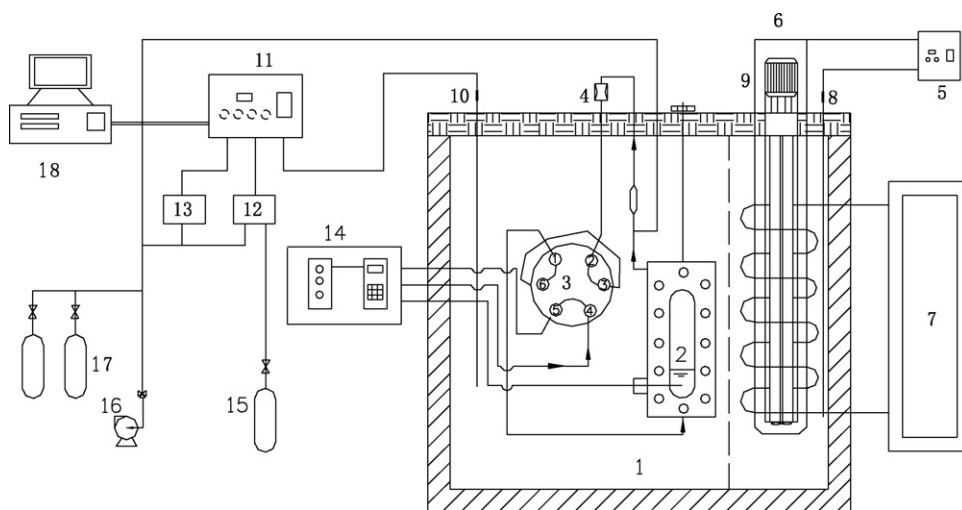| Component	T_c (K)	p_c (MPa)	ω	k_1
HFC-32	351.26	5.782	0.2768	−0.1258[a]
HFC-134a	374.21	4.059	0.3268	−0.0103[b]

[a] Kleiber [23].
[b] Lim et al. [24].

Fig. 1. Experimental apparatus for the VLE measurement: (1) thermostat bath; (2) equilibrium cell; (3) six-way valve; (4) vapor circulation pump; (5) temperature controller; (6) heater; (7) refrigeration system; (8) platinum resistance thermometer; (9) motor blender; (10) high accuracy platinum resistance thermometer; (11) Keithley 2010 data acquisition/switch unit; (12) differential pressure null transducer; (13) pressure transmitter; (14) gas chromatograph; (15) high pressure nitrogen container; (16) vacuum pump; (17) sample reservoir; (18) computer.

Table 3
Vapor–liquid equilibrium measurements for the HFC-32 (1) + HFC-134a (2) system

$T = 258.15$ K				$T = 263.15$ K		
p (MPa)	x_1	y_1		p (MPa)	x_1	y_1
0.1639	0.0000	0.0000		0.2006	0.0000	0.0000
0.2781	0.1982	0.4021		0.2934	0.2363	0.4534
0.2966	0.2851	0.5452		0.3175	0.3067	0.5335
0.3228	0.3875	0.6693		0.3552	0.3869	0.6368
0.3456	0.4630	0.7191		0.3964	0.4929	0.7423
0.3679	0.5567	0.7723		0.4255	0.5777	0.7978
0.3953	0.6539	0.8574		0.4667	0.6912	0.8623
0.4223	0.7370	0.8990		0.4927	0.7508	0.9053
0.4452	0.8402	0.9443		0.5219	0.8247	0.9313
0.4631	0.8948	0.9698		0.5387	0.8741	0.9519
0.4735	0.9436	0.9835		0.5526	0.9134	0.9640
0.4881	1.0000	1.0000		0.5628	0.9446	0.9749
		0.5826		1.0000	1.0000	

$T = 268.15$ K				$T = 275.15$ K		
p (MPa)	x_1	y_1		p (MPa)	x_1	y_1
0.2433	0.0000	0.0000		0.3146	0.0000	0.0000
0.3383	0.2030	0.3941		0.3797	0.1432	0.2605
0.4094	0.3431	0.6022		0.4457	0.2322	0.4371
0.4624	0.4654	0.7245		0.5401	0.3644	0.6232
0.5223	0.6096	0.8097		0.5957	0.4501	0.7039
0.5566	0.6809	0.8524		0.6705	0.5834	0.7975
0.5786	0.7201	0.8811		0.7172	0.6898	0.8566
0.6056	0.7744	0.9208		0.7452	0.7616	0.8877
0.6397	0.8654	0.9488		0.7718	0.8114	0.9148
0.6595	0.9251	0.9722		0.8007	0.8591	0.9446
0.6689	0.9524	0.9811		0.8285	0.9207	0.9704
0.6906	1.0000	1.0000		0.8665	1.0000	1.0000

$T = 283.15$ K				$T = 293.15$ K		
p (MPa)	x_1	y_1		p (MPa)	x_1	y_1
0.4146	0.0000	0.0000		0.5717	0.0000	0.0000
0.5261	0.1627	0.3108		0.8000	0.2763	0.4619
0.5732	0.2186	0.4133		0.8726	0.3589	0.5556
0.6503	0.3320	0.5540		0.9553	0.4358	0.6742
0.7115	0.4339	0.6856		1.0257	0.5328	0.7361
0.8230	0.5838	0.7885		1.1478	0.6596	0.8220
0.9126	0.7095	0.8534		1.1946	0.6974	0.8632
0.9657	0.7772	0.8951		1.2712	0.7643	0.9100
0.9946	0.8343	0.9154		1.3523	0.8548	0.9532
1.0298	0.8729	0.9529		1.3905	0.8943	0.9720
1.0728	0.9459	0.9773		1.4526	0.9637	0.9929
1.1070	1.0000	1.0000		1.4750	1.0000	1.0000

$T = 303.15$ K				$T = 313.15$ K		
p (MPa)	x_1	y_1		p (MPa)	x_1	y_1
0.7702	0.0000	0.0000		1.0170	0.0000	0.0000
1.1014	0.2797	0.4800		1.3655	0.2504	0.4543
1.1605	0.3377	0.5437		1.4144	0.2742	0.4975
1.3032	0.4347	0.6670		1.6165	0.4202	0.6604
1.4123	0.5329	0.7549		1.7699	0.5207	0.7208
1.5509	0.6747	0.8308		1.9809	0.6586	0.8322
1.5789	0.7023	0.8613		2.0253	0.6993	0.8608
1.6627	0.7756	0.9002		2.1482	0.7649	0.9047
1.7515	0.8496	0.9356		2.2467	0.8366	0.9385
1.7914	0.8949	0.9565		2.3311	0.8931	0.9652
1.8906	0.9824	0.9913		2.4486	0.9804	0.9929
1.9280	1.0000	1.0000		2.4780	1.0000	1.0000

Table 3 (*Continued*)

T = 323.15 K			T = 333.15 K		
p (MPa)	x_1	y_1	p (MPa)	x_1	y_1
1.3180	0.0000	0.0000	1.6820	0.0000	0.0000
1.6385	0.1800	0.3255	2.0355	0.1691	0.3047
1.7862	0.2561	0.5093	2.2617	0.2567	0.4184
2.1302	0.4277	0.6098	2.6133	0.4009	0.5886
2.3113	0.5212	0.7111	2.8546	0.5050	0.6597
2.4968	0.6495	0.7288	3.1595	0.6412	0.7399
2.6343	0.6919	0.8312	3.1916	0.6511	0.8266
2.7277	0.7740	0.8759	3.4164	0.7652	0.8609
2.8878	0.8310	0.8974	3.5743	0.8292	0.9114
2.9762	0.8909	0.9506	3.9330	1.0000	1.0000
3.0884	0.9785	0.9954			
3.1410	1.0000	1.0000			

T = 343.15 K		
p (MPa)	x_1	y_1
2.1170	0.0000	0.0000
2.5739	0.1770	0.3071
2.8098	0.2583	0.4342
3.1679	0.3843	0.5601
3.5093	0.4983	0.6842
4.8770	1.0000	1.0000

The vapor phase in the equilibrium cell was continuously recirculated by a vapor circulation pump. After equilibrium was reached, the vapor sample was withdrawn from the recycling loop and the liquid sample was taken from the sample cell to the liquid sample line. And then they were sent and injected on-line into a gas chromatograph (GC) model 112A. The gas chromatograph was calibrated with pure components of known purity and with mixture of known composition that were prepared gravimetrically. The experimental data at the equilibrium state were measured at least three times in order to ensure repeatability. Considering the margin of error and the reproducibility of GC, we generally estimated an overall accuracy in the measurements of the composition of ±0.001 in mole fraction for both liquid and vapor phases.

3. Correlation model

In this work, the experimental data were correlated with the PRSV equation of state using the WS mixing rule. The PRSV equation of state is expressed as follows:

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

with

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

$$b = \frac{0.077796 R T_c}{p_c} \tag{3}$$

$$\alpha(T) = [1 + k(1 - T_r^{1/2})]^2 \tag{4}$$

$$k = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r) \tag{5}$$

$$k_0 = 0.378893 + 1.48971539\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{6}$$

where the parameter a is a function of temperature, b the constant, ω the acentric factor, p the pressure, p_c the critical pressure, T the absolute temperature, T_c the critical temperature, T_r the reduced temperature (T/T_c), k_1 the specific constant for each pure component, and v is the mole volume. The value of critical temperature T_c, critical pressure p_c, acentric factor ω and k_1, for HFC-23 and HFC-134a in Eqs. (1)–(6) are given in Table 2. The Wong–Sandler mixing rules can be expressed as follows [21]:

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - (a/RT))_{ij}}{1 - \left(\left(\sum_i (x_i(a_i/b_i))/RT \right) + (A_\infty^E/CRT) \right)} \tag{7}$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_i}{RT} \right) \right] (1 - k_{ij}) \tag{8}$$

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \tag{9}$$

where k_{ij} is a binary interaction parameter and C is a numerical constant equal to $\ln \left(\sqrt{2} - 1 \right) / \sqrt{2}$ for the PRSV equation of stale used in this work.

The excess Gibbs energy function is based on the NRTL [25] local composition model:

$$\frac{A_\infty^E}{RT} = \sum_i x_i \sum_j \frac{x_j \exp(-a_{ji}(\tau_{ji}/RT))}{\sum_k x_k \exp(-\alpha_{ki}(\tau_{ki}/RT))} \tau_{ji} \tag{10}$$

where $\tau_{ii} = 0$, $\alpha_{ii} = 0$. $\alpha_{ij} = \alpha_{ji}$, τ_{ij} and τ_{ji} are adjustable parameters and. As it is recommended [25] to use $\alpha_{ij} = 0.3$ for the system like the current one, only τ_{ij} and τ_{ji} are correlated directly by
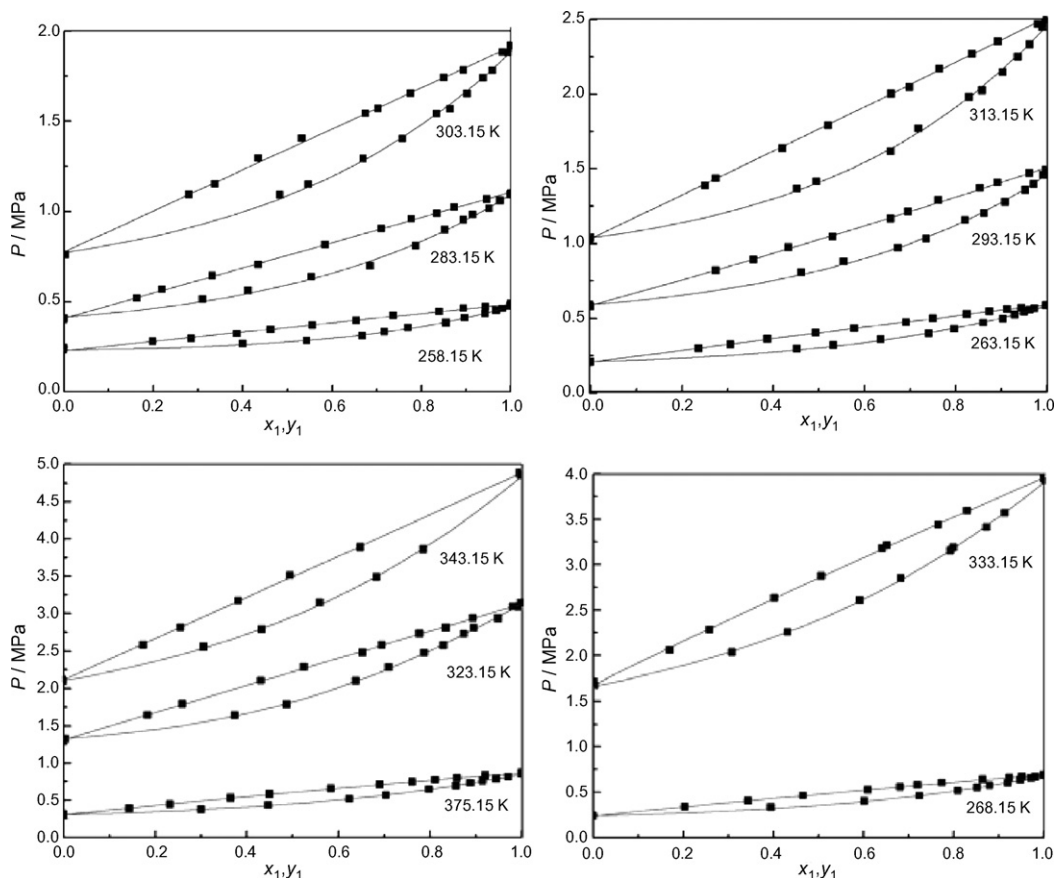
Fig. 2. p–x–y diagram for the HFC-32 (1) + HFC-13a (2) system from 258 to 343 K; (–) for PRSV equation of state.

VLE experimental data. The correlation is performed through a simplex algorithm using the objective function:

$$OBF = \sum_{i=1}^{N}[(y_{e1} - y_{c1})^2 + (y_{e2} - y_{c2})^2] \qquad (11)$$

where N is the number of experimental points, y_e the experimental vapor phase fraction and y_c is the calculated vapor phase fraction. With objective function given in Eq. (11), we determine binary interaction parameters that allow calculating vapor composition in very good agreement with experimental ones.

4. Results and discussions

The experimental isothermal VLE data for the binary system of HFC-32 + HFC-134a are shown in Table 3. The table lists the measured mole fraction of the liquid and vapor phases, pressures, and temperatures in equilibrium. Table 4 lists the interaction parameters of binary mixtures for each isotherm, the binary parameters of NRTL model with Wong–Sandler mixing rules, and the average deviation of pressure (δp) and vapor phase composition (δy) between measured and calculated values. The overall deviation of the pressure by the PRSV equation of state was 0.940%, and average deviation of vapor phase composition by the PRSV equation of state was 0.0063. Azeotropic behavior has not been found in any of the binary system.

Pressure-composition diagrams for the binary system of HFC-32 + HFC-134a are presented in Fig. 2. Figs. 3 and 4 show the comparisons of relative pressure and vapor-phase mole fraction of HFC-32 between the measured data and the calculated results from the PRSV equation of state. From these figures and the low average deviation, we conclude that the values calculated with the PRSV equation of state and the WS mix-
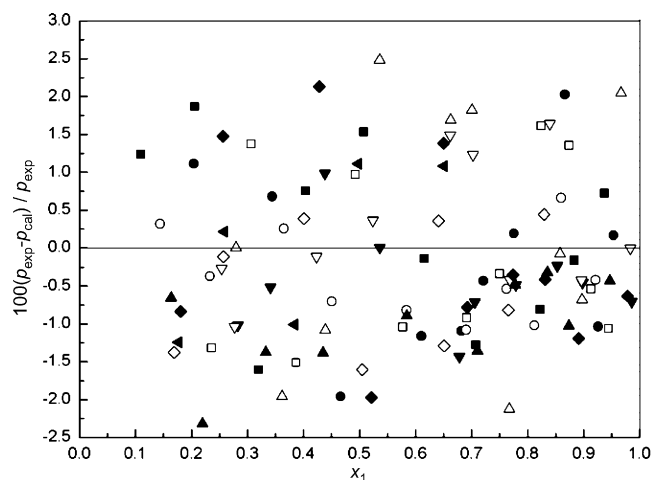

Fig. 3. Deviation of saturated pressure for HFC-32 for the HFC-32 + HFC-134a system: (■) 258.15 K; (□) 263.15 K; (●) 268.15 K; (○) 275.15 K; (▲) 283.15 K; (△) 293.15 K; (▼) 303.15 K; (▽) 313.15 K; (♦) 323.15 K; (◇) 333.15 K; (◄) 343.15 K.

Table 4
Interaction parameters and average absolute deviation of p and y

T (K)	τ_{12}[a]	τ_{21}[a]	k_{12}	δp[b] (%)	δy[c]
258.15	1.1107	−0.8731	0.0505	1.010	0.0082
263.15	1.1186	−0.8956	0.0506	1.095	0.0062
268.15	1.1265	−0.9009	0.0507	0.986	0.0067
275.15	1.1379	−0.9015	0.0509	0.619	0.0044
283.15	1.1686	−0.9133	0.0513	1.006	0.0095
293.15	1.1898	−0.9325	0.0529	1.396	0.0051
303.15	1.2018	−0.9542	0.0543	0.668	0.0053
313.15	1.2344	−0.9678	0.0566	0.702	0.0040
323.15	1.3699	−1.0235	0.0599	1.122	0.0037
333.15	1.4354	−1.2181	0.0661	0.803	0.0089
343.15	1.5191	−1.4203	0.0723	0.932	0.0074

[a] The unit of τ_{12} and τ_{21} is $J\,mol^{-1}$.

[b] $\delta p = \dfrac{1}{N}\sum (|p_{exp}-p_{cal}|/p_{exp}) \times 100$.

[c] $\delta y = \dfrac{1}{N}\sum |y_{exp}-y_{cal}|$.
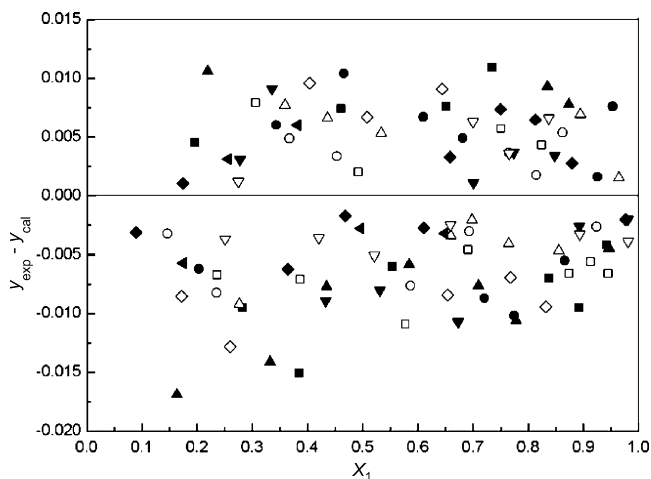
Fig. 4. Deviation of the vapor-phase mole fraction of HFC-32 for the HFC-32 + HFC-134a system: (■) 258.15 K; (□) 263.15 K; (●) 268.15 K; (○) 275.15 K; (▲) 283.15 K; (△) 293.15 K; (▼) 303.15 K; (▽) 313.15 K; (◆) 323.15 K; (◇) 333.15 K; (◀) 343.15 K.
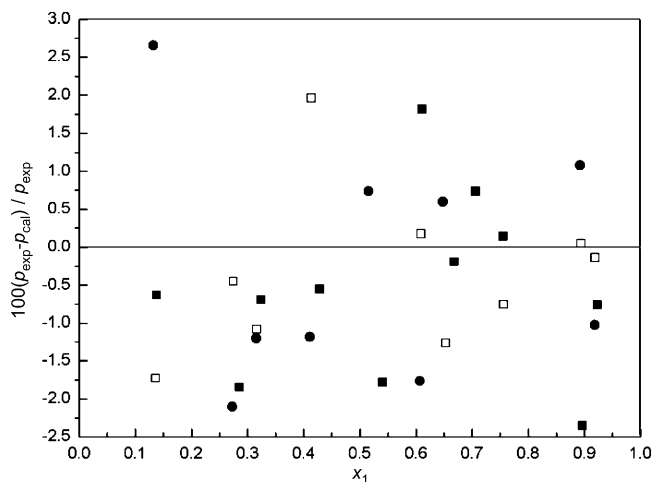

Fig. 5. Relative deviation of bubble-point pressure p_{cal}. p_{cal} was calculated based on the calculated parameters listed in Table 4. (■) 263.15 K; (□) 283.15 K; (●) 293.15 K.

ing rules give comparatively good agreement with experimental data.

As can be seen in Fig. 5, the experimental measurements for the binary system of HFC-32 + HFC-134a show good agreement with the literature data of Shimawaki et al. [26]. At 263.15, 283.15 and 293.15 K, the overall deviations of pressure (δp) that calculated based on the parameters listed in Table 4 were found to be 1.046%, 0.837% and 1.371%, respectively.

5. Conclusions

An apparatus based on the recirculation method is presented in this work. The VLE data for binary systems of HFC-32 + HFC-134a were measured at temperature from 258.15 to 343.15 K. The model of PRSV equation of state with the WS mixing rule was used to correlate the experimental data. The overall deviation of the pressure by the PRSV equation of state was 0.940% and average deviation of vapor phase composition by the PRSV equation of state was 0.0063. The predicted results show a good agreement with the experimental data.

List of symbols

a	parameter of equation of state
b	parameter of equation of state
C	numerical constant −0.6232, Eq. (6)
k_{ij}	binary interaction parameter
k_1	specific constant of pure component in the PRSV equation of state
p	pressure (MPa)
δp	relative deviation of pressure
p_c	critical pressure (MPa)
R	gas constant
T	temperature (K)
T_c	critical temperature (K)
T_r	reduce temperature
v	molar volume
x	liquid mole fraction
y	vapor mole fraction
δy	deviation of vapor-phase mole fraction

Greek letters

α_{ij}	NRTL model parameter, Eq. (9)
τ_{ij}	NRTL model binary interaction parameter, Eq. (9)
ω	acentric factor

Subscript

c	critical property
cal	calculation
exp	experiment
i, j	molecular species

Acknowledgements

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