

High pressure isothermal vapor-liquid equilibria of carbon dioxide+1,1-difluoroethane

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Abstract—Vapor-liquid equilibrium data for the binary mixture of carbon dioxide (CO₂)+1,1-difluoroethane (HFC-152a) were measured at five evenly spaced temperatures of (273.15, 283.15, 293.15, 303.15 and 313.15) K by using a circulation-type equilibrium apparatus in which both vapor and liquid phases were recirculated. The experimental data were correlated with the Peng-Robinson equation of state (PR-EoS) using the Wong-Sandler mixing rules combined with the NRTL excess Gibbs free energy model and the Carnahan-Starling-DeSantis equation of state (CSD EoS). Almost all the calculated values with these two models showed good agreement with the experimental data.

Key words: Carbon Dioxide (CO₂), HFC-152a, Vapor-liquid Equilibria (VLE), Carnahan-Starling-DeSantis Equation of State (CSD EoS), Peng-Robinson Equation of State (PR EoS)

INTRODUCTION

For many years, chlorofluorocarbons (CFCs) were extensively used as refrigerants due to many advantages such as non-toxicity, non-flammability, thermodynamic properties and so on. However, their use has been restricted by the Montreal Protocol (1989) because of their harmfulness to the ozone layer [1]. So, many researchers investigated CFCs alternatives such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). However, the use of HCFCs has also been banned by the Kyoto Protocol (2005) because of their high global warming potential (GWP). HFCs are synthetic refrigerants which consist of hydrogen, fluorine, and carbon. They are considered as alternative refrigerants for CFCs and HCFCs because they have zero ozone depletion potential (ODP) [2]. HFC-152a (1,1-Difluoroethane, C₂H₄F₂) is the halogenated aliphatic group. It has zero ODP; thus HFC-152a is used as a good refrigerant even though it is considered to be flammable. On the other hand, carbon dioxide (CO₂) is a representative compound of the carbon cycle. It is natural refrigerant and often used in air conditioners and other cooling processes. To develop optimal alternative refrigerants for CFCs and HCFCs, many mixtures have been investigated. These mixtures satisfy the properties of original refrigerants conditions such as flammability, toxicity, but with less environmental impact (ozone depletion and global warming). Vapor-liquid equilibrium (VLE) data is necessary to design appropriate refrigeration process and determine optimal process conditions [3,4]; however, few experimental data were reported in the literature for CO₂ (1)+HFC-152a system [3,5].

In this work, isothermal VLE data for binary mixture of Carbon dioxide (CO₂)+1,1-difluoroethane (HFC-152a) at five temperatures from 273.15 K to 313.15 K were measured by using a circulation-type equilibrium apparatus in which both phases were continuously recirculated. The experimental data were correlated with the Peng-Robinson equation of state (PR EoS) [6] using the Wong-Sandler mixing rule [7] combined with the NRTL excess Gibbs free energy

model and the Carnahan-Starling-DeSantis equation of state (CSD EoS) [8]. In the range of experimental temperature, the average absolute deviations of pressure and vapor phase compositions between experimental and calculated values were determined and the relevant parameters were presented.

EXPERIMENTAL

1. Chemicals

High-grade chemicals of carbon dioxide and HFC-152a were used for VLE measurement. Carbon dioxide was purchased from Dong-A special gas co. (Korea) with 99.9 mass% purity. HFC-152a was obtained DuPont (USA) with the purity higher than 99.9 mass%. They were used without any further purification.

2. Apparatus

The experimental apparatus used in this study was a circulation type equilibrium apparatus, where both liquid and vapor phases were recirculated continuously. This apparatus was explained well in our previous works [9-12], so the explanation was omitted here.

3. Procedure

Experiments to measure vapor-liquid equilibrium data for the binary system of CO₂ (1)+HFC-152a (2) were performed by the following procedures. The system was first evacuated to remove all inert gases. A certain amount of HFC-152a was supplied to the cell, and then the temperature of the entire system was held constant by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. A proper amount of CO₂ was introduced into the cell from a sample reservoir. Both the vapor and liquid phases were recirculated by the dual-head circulation pump until an equilibrium state was established. It is believed that 1 hour or more is sufficient to obtain thermal equilibrium between the cell fluid and the thermostatic bath as well as the vapor and liquid phases. After equilibration, the pressure in the equilibrium cell was measured and then vapor and liquid samples were withdrawn from the recycling lines by the vapor and liquid sampling valves. The compositions of the samples were measured by immediately injecting them into the GC,

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which was connected online to the vapor and liquid sampling valves. The GC was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. A manometer was used for preparing a standard sample. The two were injected into the manometer and made a mixture. It took more than 2 hours when the two gases were completely mixed and became a standard sample. A micro syringe was used to inject the sample into the GC. These two gases were assumed as ideal gases, so the pressure ratio is approximately equal to its mole fraction here. At least five analyses were performed for each phase and the average values were considered to correspond to the equilibrium values. Considering the margin of error and the reproducibility of the GC, we generally estimated an overall accuracy in the measurements of the composition of ± 0.002 in the mole fraction for both the liquid and the vapor phases.

4. Correlation

The experimental VLE data were correlated with the Peng-Robinson equation of state (PR-EoS) [6] using the Wong-Sandler mixing rule [7] and the Carnahan-Starling-DeSantis equation of state (CSD-EoS) [8].

5. PR-EoS

The experimental VLE data were correlated with the PR-EoS [6].

$$P = \frac{RT}{v_M - b} - \frac{a(T)}{v_M(v_M + b) + b(v_M - b)} \quad (1)$$

with

$$a(T) = \left(0.457235 \frac{R^2 T_c^2}{P_c}\right) \alpha(T) \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha(T) = [1 + k(1 - \sqrt{T/T_c})]^2 \quad (4)$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

where the parameter a is a function of temperature, b is constant, k is a constant characteristic of each substance, ω is the acentric factor, P (MPa) is the pressure, P_c (MPa) is the critical pressure, T (K) is the absolute temperature, T_c (K) is the critical temperature, and v_M is the molar volume of the mixture.

The Wong-Sandler mixing rules [7] were used in this work to obtain EoS parameters for a mixture from those of the pure components. These mixing rules for a cubic equation of state can be written as

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{\left(1 - A_{\infty}^E / CRT - \sum_i x_i a_i / RT b_i\right)} \quad (6)$$

with

$$(b - a/RT)_{ij} = \frac{1}{2}[(b - a/RT)_i + (b - a/RT)_j](1 - k_{ij}) \quad (7)$$

and

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_{\infty}^E}{C} \quad (8)$$

where C is a numerical constant equal to $\ln(\sqrt{2}-1)/\sqrt{2}$ for the PR

Table 1. Thermodynamic properties of components [16]

Chemical	Chemical formula	T_c/K	P_c/MPa	ω
Carbon dioxide (1)	CO_2	304.21	7.384	0.2239
HFC-152a (2)	CF_3CHF_2	386.41	4.517	0.2752

EoS used in this work. The single adjustable parameter (k_{ij}) for each binary pair is referred to as the Wong-Sandler mixing rule parameter. Also, A_{∞}^E is an excess Helmholtz free energy model at infinite pressure that can be equated to a low-pressure excess Gibbs energy model [13]. In this study, we used the nonrandom two-liquid (NRTL) model [14] given by

$$\frac{A_{\infty}^E}{RT} = \frac{\sum_i x_i \sum_j G_{ji} \tau_{ji}}{\sum_i x_i \sum_r G_{ri}} \quad (9)$$

with

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad \text{and} \quad \tau_{ji} = (g_{ji} - g_{ii}) / (RT) \quad (10)$$

where

$$A_{ij} = (g_{ij} - g_{ii}) \quad (11)$$

The critical temperature (T_c), critical pressure (P_c), and acentric factor (ω) for both propane and HFC-152a that were used to calculate the parameters for the PR EoS are provided in Table 1. We have set the non-randomness parameter, a_{ij} equal to a fixed value of 0.3 for all of the binary mixtures studied here. The parameters of the PR EoS were obtained by minimizing the following objective function.

$$\text{objective function} = \frac{1}{N} \sum_j \left[\left(\frac{P_{j,exp} - P_{j,cal}}{P_{j,exp}} \right) \times 100 \right]^2 \quad (12)$$

6. CSD-EoS

The CSD-EoS [8] is expressed as follows:

$$\frac{PV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(V + b)} \quad (13)$$

$$\text{where } y = \frac{b}{4V}, \quad V: \text{molar volume} \quad (14)$$

In case of pure component, the temperature dependence of 'a' and 'b' is represented by the following form:

$$a = \alpha_0 \exp(\alpha_1 T + \alpha_2 T^2) \quad (15)$$

$$b = \beta_0 + \beta_1 T + \beta_2 T^2 \quad (16)$$

The coefficients of α_0 , α_1 , α_2 in Eq. (15) and β_0 , β_1 , β_2 in Eq. (16) were cited from REFPROP 5.0 [15].

In the application of CSD-EoS to mixture, there exist the effective molecular parameters a_m and b_m defined by using the following mixing rules:

$$a_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij} \quad (17)$$

$$b_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_{ij} \quad (18)$$

When $i=j$, the value of a_{ii} and b_{ii} are those of 'a' and 'b' of the pure components which are determined by Eq. (15) and (16). The

values of a_{12} and b_{12} can be expressed as the following forms:

$$a_{12} = (1 - f_{12})(a_{11}a_{22})^{1/2} \quad (19)$$

$$b_{12} = \frac{1}{8}(b_{11}^{1/3} + b_{22}^{1/3})^3 \quad (20)$$

The model involves the adjustable binary parameters, f_{12} , which must be determined from experimental data. In the CSD-EoS calculation, the same objective function that used in the PR-EoS calculation was used.

RESULTS AND DISCUSSION

Table 2 shows a comparison of the measured vapor pressures of pure HFC-152a and CO₂ with those calculated from the database REFPROP 6.01 [16], which are considered to be reliable for the pure compounds considered and consistent with literature data. The absolute average relative deviation ($\sum|\Delta P/P|/N(\%)$) between measured and calculated values from the data of REFPROP 6.01 [16] was 0.007% for CO₂ and 0.012% for HFC-152a. The experimental vapor-liquid equilibrium data and the results of the correlation are reported in Table 3. This table lists the measured mole fraction of the liquid and vapor phases, pressures and temperatures in equilibrium and the deviations between measured and calculated pressures (ΔP) and vapor compositions (Δy). The interaction parameters

Table 2. Comparison of the measured pure component vapor pressures with the database REFPROP 6.01 [16]

Component	T/K	P_{exp}/MPa	P_{ref}/MPa	ΔP	$ \Delta P /P_{exp}$
CO ₂ (1)	273.15	3.482	3.481	0.001	0.0003
	283.15	4.495	4.497	-0.002	0.0004
	293.15	5.729	5.722	0.007	0.0012
	303.15	7.198	7.205	-0.007	0.0010
	313.15				
					Ave 0.0007
HFC-152a (2)	273.15	0.262	0.264	-0.002	0.008
	283.15	0.379	0.373	0.006	0.016
	293.15	0.517	0.513	0.004	0.008
	303.15	0.676	0.690	0.014	0.021
	313.15	0.903	0.909	-0.006	0.007
					Ave 0.012

of the binary mixtures for each temperature, the binary parameters of the NRTL model with the Wong-Sandler mixing rules, and the absolute average relative deviations of pressure (AAD-P (%)) and average absolute deviations of vapor-phase composition (AAD-y) between measured and calculated values are reported in Table 4.

Fig. 1 shows the comparison of measured and calculated values

Table 3. Vapor-liquid equilibrium measurements for the CO₂ (1)+HFC-152a (2) system

Experimental data			PR EoS				CSD EoS			
P_{exp}/MPa	$x_{1,exp}$	$y_{1,exp}$	P_{cal}/MPa	$y_{1,cal}$	$^a\Delta P/\text{MPa}$	$^b\Delta y_1$	P_{cal}/MPa	$y_{1,cal}$	$^a\Delta P/\text{MPa}$	$^b\Delta y_1$
T/K=273.15										
0.262	0.000	0.000	0.263	0.000	-0.001	0.000	0.264	0.000	-0.002	0.000
0.634	0.163	0.605	0.651	0.634	-0.017	-0.030	0.754	0.669	-0.120	-0.064
0.924	0.244	0.717	0.877	0.746	0.047	-0.029	0.997	0.759	-0.073	-0.043
1.262	0.367	0.818	1.255	0.842	0.007	-0.025	1.366	0.838	-0.104	-0.020
1.482	0.437	0.854	1.482	0.877	0.000	-0.023	1.577	0.867	-0.095	-0.013
1.765	0.521	0.888	1.765	0.907	0.001	-0.019	1.833	0.895	-0.068	-0.006
2.006	0.592	0.910	2.008	0.927	-0.001	-0.017	2.052	0.914	-0.045	-0.004
2.213	0.663	0.929	2.250	0.942	-0.037	-0.014	2.275	0.931	-0.062	-0.002
2.517	0.747	0.948	2.537	0.958	-0.021	-0.010	2.547	0.949	-0.030	-0.001
2.882	0.836	0.965	2.845	0.973	0.037	-0.007	2.849	0.966	0.033	-0.001
3.151	0.907	0.979	3.098	0.984	0.052	-0.004	3.108	0.981	0.043	-0.001
3.482	1.000	1.000	3.476	1.000	0.006	0.000	3.483	1.000	-0.001	0.000
T/K=283.15										
0.379	0.000	0.000	0.372	0.000	0.007	0.000	0.373	0.000	0.007	0.000
0.696	0.103	0.433	0.696	0.484	0.000	-0.051	0.721	0.497	-0.024	-0.064
1.048	0.208	0.642	1.050	0.676	-0.002	-0.034	1.084	0.680	-0.036	-0.038
1.386	0.302	0.744	1.384	0.769	0.002	-0.024	1.419	0.767	-0.033	-0.023
1.793	0.408	0.819	1.784	0.835	0.009	-0.016	1.809	0.830	-0.016	-0.011
2.151	0.504	0.867	2.163	0.876	-0.012	-0.009	2.176	0.870	-0.025	-0.003
2.634	0.622	0.902	2.650	0.914	-0.017	-0.012	2.651	0.908	-0.017	-0.007
3.006	0.705	0.926	3.012	0.935	-0.006	-0.009	3.004	0.930	0.002	-0.005
3.372	0.782	0.941	3.361	0.952	0.010	-0.011	3.355	0.949	0.017	-0.008
3.627	0.829	0.952	3.578	0.962	0.049	-0.010	3.573	0.960	0.054	-0.008
4.495	1.000	1.000	4.503	1.000	-0.008	0.000	4.493	1.000	0.003	0.000

Table 3. Continued

Experimental data			PR EoS				CSD EoS			
P_{exp}/MPa	$x_{1,exp}$	$y_{1,exp}$	P_{cal}/MPa	$y_{1,cal}$	$^a\Delta P/\text{MPa}$	$^b\Delta y_1$	P_{cal}/MPa	$y_{1,cal}$	$^a\Delta P/\text{MPa}$	$^b\Delta y_1$
T/K=293.15										
0.517	0.000	0.000	0.513	0.000	0.004	0.000	0.512	0.000	0.005	0.000
1.124	0.165	0.554	1.133	0.573	-0.010	-0.019	1.190	0.585	-0.066	-0.031
1.662	0.290	0.714	1.662	0.728	-0.000	-0.014	1.728	0.728	-0.066	-0.014
2.082	0.379	0.783	2.073	0.795	0.009	-0.012	2.127	0.790	-0.045	-0.007
2.565	0.486	0.840	2.450	0.837	0.115	0.003	2.490	0.830	0.075	0.011
2.944	0.559	0.867	2.973	0.879	-0.029	-0.011	2.988	0.870	-0.044	-0.003
3.144	0.588	0.877	3.126	0.889	0.018	-0.011	3.134	0.881	0.010	-0.003
3.627	0.685	0.908	3.654	0.917	-0.028	-0.009	3.646	0.911	-0.019	-0.003
3.896	0.727	0.921	3.895	0.928	0.001	-0.008	3.879	0.923	0.017	-0.002
4.164	0.777	0.934	4.182	0.940	-0.018	-0.006	4.167	0.937	-0.003	-0.002
5.729	1.000	1.000	5.741	1.000	-0.012	0.000	5.696	1.000	0.033	0.000
T/K=303.15										
0.676	0.000	0.000	0.691	0.000	-0.015	0.000	0.689	0.000	-0.013	0.000
0.979	0.075	0.309	0.999	0.319	-0.020	-0.010	1.053	0.348	-0.074	-0.039
1.489	0.181	0.551	1.484	0.558	0.005	-0.007	1.587	0.576	-0.098	-0.025
2.068	0.290	0.688	2.037	0.694	0.031	-0.006	2.158	0.698	-0.089	-0.010
2.503	0.372	0.754	2.491	0.761	0.012	-0.007	2.607	0.758	-0.104	-0.005
2.972	0.450	0.800	2.946	0.808	0.026	-0.008	3.048	0.801	-0.076	-0.010
3.358	0.517	0.831	3.358	0.840	-0.001	-0.009	3.443	0.832	-0.085	-0.000
3.751	0.592	0.857	3.839	0.870	-0.088	-0.013	3.902	0.861	-0.151	-0.004
4.695	0.717	0.900	4.690	0.909	0.005	-0.008	4.722	0.903	-0.027	-0.002
5.026	0.763	0.912	5.023	0.922	0.003	-0.009	5.048	0.917	-0.021	-0.005
5.419	0.816	0.926	5.426	0.936	-0.006	-0.009	5.443	0.934	-0.024	-0.007
5.792	0.860	0.939	5.780	0.948	0.011	-0.009	5.792	0.948	-0.001	-0.009
7.198	1.000	1.000	7.217	1.000	-0.019	0.000	6.399	1.000	0.799	0.000
T/K=313.15										
0.903	0.000	0.000	0.912	0.000	-0.009	0.000	0.909	0.000	-0.005	0.000
1.358	0.095	0.343	1.383	0.348	-0.025	-0.005	1.423	0.363	-0.065	-0.020
1.889	0.184	0.528	1.875	0.529	0.014	-0.001	1.933	0.537	-0.044	-0.010
2.337	0.262	0.628	2.336	0.631	0.002	-0.004	2.396	0.633	-0.058	-0.005
3.068	0.373	0.725	3.047	0.730	0.021	-0.004	3.091	0.725	-0.023	-0.000
3.565	0.447	0.772	3.558	0.777	0.006	-0.005	3.585	0.771	-0.020	0.001
4.613	0.586	0.835	4.599	0.841	0.014	-0.006	4.593	0.836	0.019	-0.001
5.075	0.649	0.858	5.095	0.864	-0.021	-0.005	5.083	0.861	-0.009	-0.002
5.716	0.723	0.877	5.714	0.887	0.002	-0.010	5.704	0.887	0.012	-0.010
6.329	0.793	0.895	6.333	0.907	-0.004	-0.012	6.337	0.911	-0.008	-0.017
6.984	0.858	0.909	6.946	0.925	0.038	-0.016	6.940	0.936	-0.050	-0.022

$$^a\Delta P = P_{exp} - P_{cal}$$

$$^b\Delta y_1 = y_{exp} - y_{cal}$$

Table 4. Values of binary parameters and average absolute deviations of P and y

T/K		273.15	283.15	293.15	303.15	313.15
PR-EoS	Binary parameter $^ak_{12}$	0.2645	0.2228	0.2324	0.2301	0.2329
	$^b\text{AAD-P} (\%)$	1.213	0.531	0.872	0.817	0.526
	$^c\text{AAD-y}$	0.015	0.016	0.009	0.007	0.006
CSD-EoS	Binary parameter f_{12}	0.0100	-0.0036	-0.0036	0.0002	-0.0093
	$^b\text{AAD-P} (\%)$	4.573	1.439	1.743	3.558	1.196
	$^c\text{AAD-y}$	0.013	0.015	0.007	0.008	0.008

$$^b\text{AAD-P} (\%) = (1/N) \sum |P_{exp} - P_{cal}| / P_{exp} \times 100$$

$$^c\text{AAD-y} = (1/N) \sum |y_{exp} - y_{cal}|$$

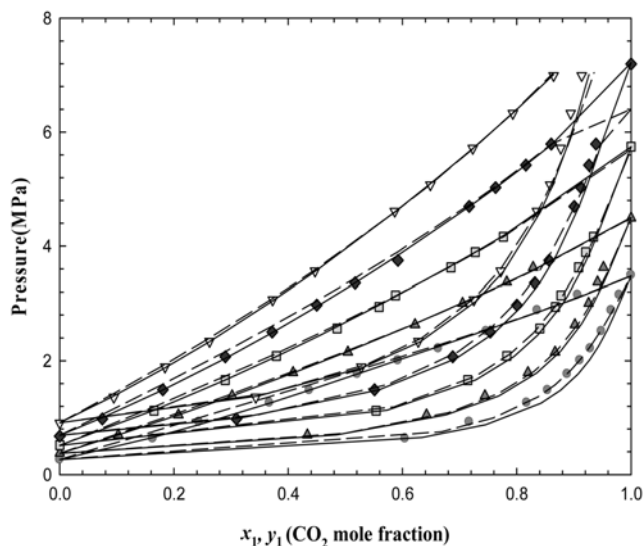


Fig. 1. P-x-y diagram for the CO₂ (1)+HFC-152a (2) system. Experimental data at 273.15 K (●); 283.15 K (▲); 293.15 K (■); 303.15 K (◆); 313.15 K (▼); calculated with the PR-EoS using W-S mixing (—); calculated with the CSD-EoS (---).

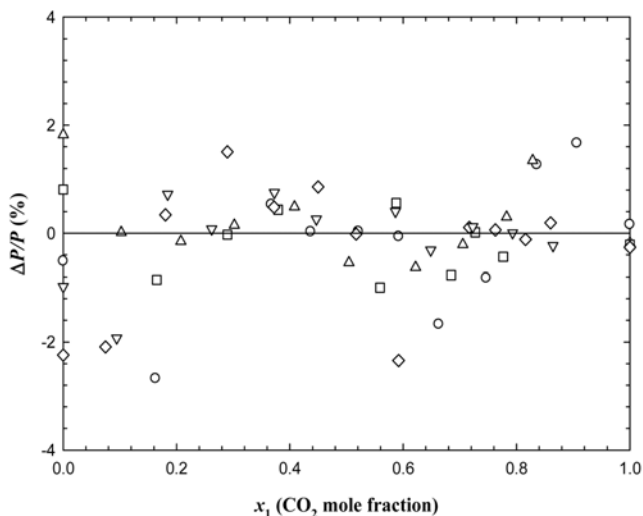


Fig. 2. Deviation of pressure for the system CO₂ (1)+HFC-152a (2) from the PR-EoS using W-S mixing rule at 273.15 K (○); 283.15 K (△); 293.15 K (□); 303.15 K (◇); 313.15 K (▽).

with the PR and CSD EoSs for CO₂ (1)+HFC-152a (2) at (273.15, 283.15, 293.15, 303.15, and 313.15) K.

Binary parameter (f_{12}) of CSD-EoS was temperature independent and its value was 0.125. The average values of AAD-P and AAD-y were 0.792% and 0.011 for the PR EoS and 2.502% and 0.010 for the CSD EoS, respectively. The AAD-P values of the PR EoS were less than those of the CSD EoS and AAD-y values of the PR EoS were almost the same as those of the CSD EoS. The PR EoS based results are shown in Figs. 2 and 3 and the CSD EoS based results are shown in Figs. 4 and 5. From these figures and the regular tendency of the average deviations of P and y, we conclude that the calculated values using the PR EoS and the CSD EoS give

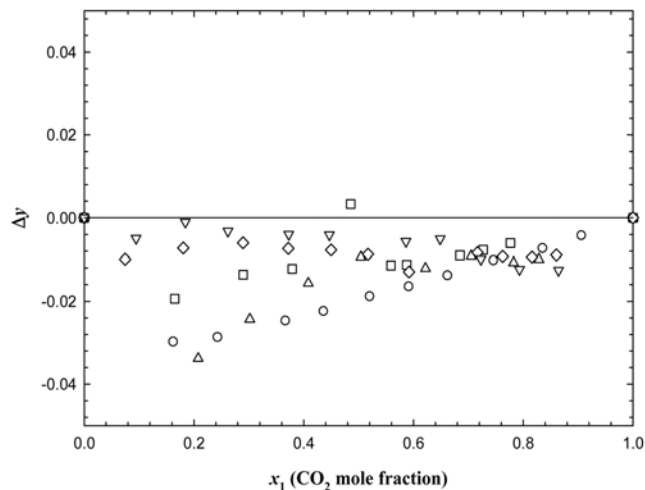


Fig. 3. Deviation of vapor composition for the system CO₂ (1)+HFC-152a (2) from the PR-EoS using W-S mixing rule at 273.15 K (○); 283.15 K (△); 293.15 K (□); 303.15 K (◇); 313.15 K (▽).

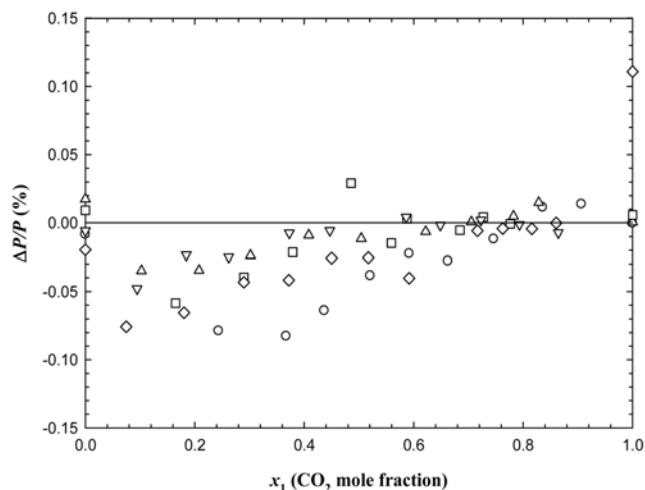


Fig. 4. Deviation of pressure for the system CO₂ (1)+HFC-152a (2) from the CSD-EoS at 273.15 K (○); 283.15 K (△); 293.15 K (□); 303.15 K (◇); 313.15 K (▽).

good agreement with the experimental data; however, PR EoS gives a somewhat better result for this CO₂ (1)+HFC-152a (2) system.

CONCLUSIONS

The isothermal vapor-liquid equilibrium data for the binary systems of CO₂ (1)+HFC-152a (2) were measured at five equally spaced temperatures of (273.15, 283.15, 293.15, 303.15, and 313.15) K by using a circulation-type equilibrium apparatus. The experimental VLE data were correlated with the PR-EoS using the W-S mixing rule and the CSD-EoS. Calculated results with these equations have given satisfactory results in the comparison with the experimental data. According to the results of this work, the PR EoS shows better correlation results than CSD EoS at high temperature, while the CSD EoS reproduces the experimental data well at low temperature.

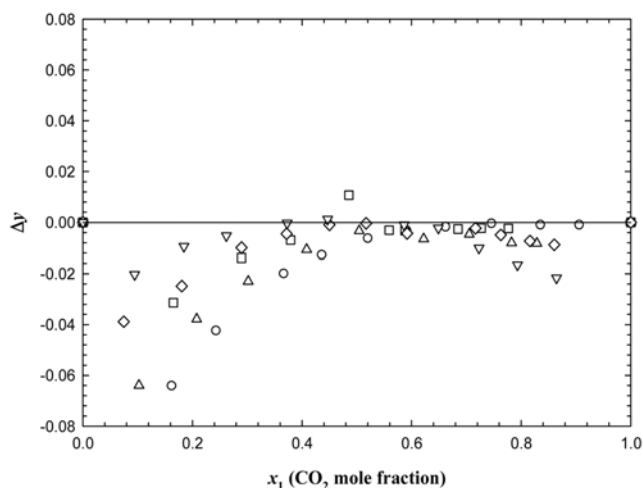


Fig. 5. Deviation of vapor composition for the system CO₂ (1)+HFC-152a (2) from the CSD-EoS at 273.15 K (○); 283.15 K (△); 293.15 K (□); 303.15 K (◇); 313.15 K (▽).

NOMENCLATURE

- a(T) : temperature-dependent constant of EoS
 A : adjustable parameters of NRTL model [kJ/g-mol]
 b : molecular volume [l/g-mol]
 g : an energy parameter [kJ/g-mol]
 f : CSD parameter
 k : PR EoS parameter
 N : the number of components in mixture
 P : pressure [MPa]
 R : gas constant, 8.3144 [J/mol·K]
 T : temperature [K]
 V : molar volume [l/g-mol]
 x : liquid mole fraction
 y : vapor mole fraction

Greek Letters

- α : attraction parameter
 Δ : deviation
 τ : dimensionless form of A/RT
 ω : acentric factor

Subscripts

- c : critical property
 cal : calculated

- exp : experimental
 i, j : ith and jth components of the mixture
 azeo : azeotropic point
 m : mixtures
 r : reduced property

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