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High-Pressure Vapor−Liquid Equilibria for the Binary Mixtures of Carbon Dioxide + Isopropanol (IPA)

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Isothermal high-pressure vapor−liquid equilibrium data were measured for the binary mixtures of CO_2 + isopropanol (IPA) at various temperatures [(323.15 ∼ 353.15) K]. The vapor and liquid compositions and pressures were measured in a circulation-type apparatus. To facilitate easy equilibration, both vapor and liquid phases were circulated separately in the experimental apparatus, and the equilibrium composition was analyzed by an on-line gas chromatograph. The experimental data were compared with literature results and correlated with the Peng−Robinson equations of state (PR EOS) combined with the Wong−Sandler mixing rules. Calculated results with the PR EOS showed good agreement with our experimental data.

1. Introduction

Thermodynamic knowledge of high-pressure phase equilibrium data of pure fluids and fluid mixtures plays an essential role in the efficient basic design of various separation processes in such fields as natural gas, oil, and numerous fine chemical industries. As a result, attention has been placed on the thermodynamic understanding of fluid systems.[1,2] Also, during the last two decades, efforts have been focused on the understanding of phase equilibrium behaviors of fluids near the critical region of mixtures as well as of pure fluids due to the emerging technology of supercritical fluids. The information of the high-pressure behavior of fluids at the supercritical state has been valuably used to design new separation processes in various fields such as food, pharmaceutical, and fine chemical industries.[3]

In the semiconductor manufacturing fields, isopropanol (IPA) is used as one of the rinsing and drying agents after the wet cleaning process. Recently, many attempts have been made to replace the wet cleaning process because it has many problems such as a huge amount of wastewater, the enormous cost of ultrapure water (UPW), a technical limit in applying it to the water having a line-width narrower than 45 nm due to the surface tension of water, etc. The SCORR (supercritical carbon dioxide resist removal) process, which uses supercritical CO_2 instead of UPW, is considered to be the alternative one. To develop such a new process, the knowledge of the solubility of high-boiling components at elevated pressures and temperatures near the critical temperature of the solvents is essential. However, very few data have been reported in the literature.[4,5] The extents of prior vapor−liquid equilibrium (VLE) measurements of this system were (293.2, 313.2, and 333.1) K for Bamberger and Maurer's data[4] and (317, 335, 354, and 394) K for Radosz's data.[5] In developing the SCORR process in our lab, more intensive VLE data were needed at a temperature range between (323.15 and 353.15) K. So, in the present study, we measured the isothermal vapor−liquid equilibrium data for the binary CO_2 + isopropanol (IPA) system at (323.15, 333.15, 343.15, and 353.15) K. At each temperature, we reported 10 or more measured data points except at 353.15 K. The measured VLE data were correlated with the classical Peng−Robinson equations of state[6] combined with the Wong−Sandler mixing rules,[7] and the relative accuracy was discussed.

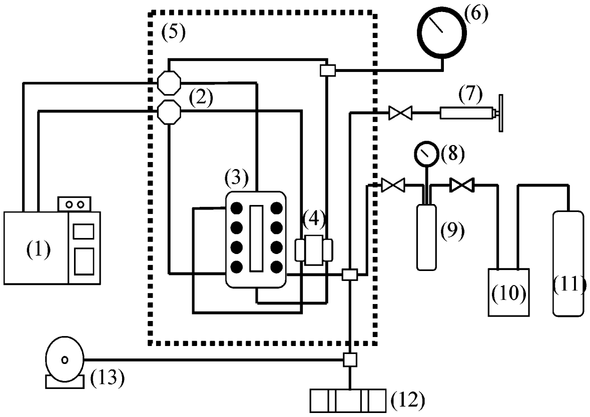

Figure 1. Schematic diagram of the experimental apparatus: 1, gas chromatograph; 2, sampling valve; 3, equilibrium cell; 4, circulation pump; 5, air bath; 6, pressure gauge; 7, hand pump; 8, pressure transducer; 9, reservoir; 10, CO_2 charging pump; 11, CO_2 gas cylinder; 12, vacuum pump; 13, liquid sample charging pump.

2. Experimental Section

Chemicals. CO_2 was supplied by Seoul Special Gas Co. (Seoul, Korea) with a guaranteed purity in mass fraction higher than 0.999, and isopropanol was purchased from the DukSan Pure Chemical Co. Ltd. (Ansan, Kyungi-do, Korea) with a guaranteed purity in mass fraction higher than 0.995. Furthermore, we also analyzed these two pure components with a gas chromatograph. The resulted mass fraction purities of CO_2 and isopropanol were higher than 0.9995 and 0.999, respectively. So, they were used without any further purification.

Apparatus and Procedure. A schematic diagram of the experimental apparatus that was designed and constructed for this work is shown in Figure 1. The equipment consists of four major parts: high-pressure equilibrium cell, pressure and temperature control parts, air-bath, and the feeding and sampling devices. The equilibrium cell is equipped with a pair of sapphire glass windows to allow a view to the inside of the cell. The

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Table 1. Vapor−Liquid Equilibrium Measurements for the CO_2 (1) + IPA (2) System at (323.15 to 353.15) K at Various Temperatures

experimental data			PR EOS				
P_{exptl} MPa	$x_{1,exptl}$	$y_{1,exptl}$	P_{calcd} MPa	$y_{1,calcd}$	ΔP MPa	$\Delta P/P$ (%)[a]	Δy
			T/K = 323.15				
1.06	0.0585	0.9709	1.059	0.9707	0.001	0.064	0.0002
1.57	0.0884	0.9822	1.574	0.9787	−0.004	−0.184	0.0035
2.17	0.1231	0.9845	2.159	0.9829	0.011	0.290	0.0016
3.79	0.2270	0.9876	3.811	0.9871	−0.021	−0.386	0.0005
5.44	0.3430	0.9873	5.438	0.9875	0.002	0.027	−0.0002
7.32	0.5167	0.9859	7.310	0.9851	0.010	0.127	0.0008
7.86	0.5839	0.9851	7.824	0.9835	0.036	0.432	0.0016
8.34	0.6845	0.9840	8.376	0.9807	−0.036	−0.401	0.0033
8.97	0.8631	0.9754	8.953	0.9744	0.017	0.187	0.0010
9.08	0.9014	0.9720	9.086	0.9715	−0.006	−0.066	0.0005
			T/K = 333.15				
2.01	0.1026	0.9719	2.013	0.9713	−0.003	−0.102	0.0006
2.94	0.1529	0.9791	2.935	0.9770	0.005	0.133	0.0021
3.75	0.1989	0.9806	3.743	0.9790	0.007	0.160	0.0016
4.37	0.2370	0.9818	4.383	0.9791	−0.013	−0.256	0.0027
5.07	0.2803	0.9813	5.074	0.9799	−0.004	−0.065	0.0014
6.16	0.3538	0.9826	6.145	0.9801	0.015	0.216	0.0025
6.95	0.4168	0.9805	6.943	0.9793	0.007	0.087	0.0012
8.05	0.5297	0.9794	8.063	0.9779	−0.013	−0.157	0.0015
8.27	0.5609	0.9753	8.302	0.9740	0.032	−0.374	0.0013
8.56	0.5950	0.9724	8.530	0.9727	0.030	0.350	−0.0003
8.91	0.6647	0.9691	8.907	0.9683	0.003	0.034	0.0008
			T/K = 343.15				
1.99	0.0807	0.9574	1.992	0.9556	−0.002	−0.101	0.0018
2.64	0.1098	0.9643	2.632	0.9626	0.008	0.303	0.0017
3.43	0.1485	0.9686	3.436	0.9671	−0.006	−0.175	0.0015
4.18	0.1864	0.9702	4.169	0.9691	0.011	0.263	0.0011
5.05	0.2365	0.9711	5.057	0.9699	−0.007	−0.139	0.0012
6.80	0.3584	0.9693	6.825	0.9679	−0.025	−0.368	0.0014
8.21	0.4933	0.9652	8.186	0.9628	0.024	0.292	0.0024
9.18	0.6364	0.9574	9.167	0.9560	0.013	0.142	0.0014
9.68	0.7209	0.9516	9.677	0.9505	0.003	0.031	0.0011
9.97	0.7702	0.9451	9.991	0.9457	−0.021	−0.211	−0.0006
			T/K = 353.15				
5.13	0.2226	0.9589	5.133	0.9579	−0.003	−0.058	0.001
5.82	0.2582	0.9586	5.808	0.9580	0.012	0.206	0.0006
6.91	0.3219	0.9571	6.905	0.9564	0.005	0.072	0.0007
7.95	0.3949	0.9544	7.979	0.9527	−0.029	−0.365	0.0017
9.33	0.5155	0.9464	9.323	0.9436	0.007	0.075	0.0028
10.09	0.6124	0.9349	10.067	0.9346	0.023	0.228	0.0003
10.77	0.7358	0.9167	10.779	0.9189	−0.009	−0.084	−0.0022

[a] $\Delta P = P_j^{exptl} - P_j^{calcd}$; $\Delta P/P\ (\%) = (P_j^{exptl} - P_j^{calcd})/P_j^{exptl}\cdot 100$; $\Delta y = y_j^{exptl} - y_j^{calcd}$.

cell volume was 50 mL, and it was designed to operate safely up to 30 MPa and 400 K. The system temperature was maintained within ± 0.5 K by controlling the temperature in the air-bath using a PID controller (Hanyoung Electronic Co. Ltd., Seoul, Korea). Temperature was measured within the accuracy of ± 0.05 K by a PRT-type thermocouple. The equilibrium pressure was measured by a Heise guage (Heise Co., Newtown, Connecticut) within ± 0.01 MPa. To adjust the pressure accurately, a hand pump (HIP Co., Erie, Pennsylvania) was used. By using a dual-head high-pressure pump (Milton Roy Co.), the vapor and liquid phases were circulated separately until the system reached an equilibrium state.

CO_2 was fed by the Isco Syringe Pump (ISCO 260DM, Lincoln, Nebraska), and the isopropanol was fed by a liquid pump (Milton Roy Co.). The equilibrated compositions of vapor and liquid phases were sampled separately by the six-port sampling valves (Rheodyne L.P., Rohnert Park, California), and the compositions were analyzed by an on-line gas chromatograph (GL Science Inc., Tokyo, Japan). The internal volume of the sampling loop of the vapor sampling valve was 5 μL, and that of the liquid sampling valve was 1 μL.

Experiments were carried out in the following manner. The entire internal loop of the apparatus including the equilibrium cell was rinsed several times by liquid CO_2, and the degree of the cleanness was checked by analyzing the rinsing liquid CO_2 with the gas chromatograph. Then, the equilibrium cell was evacuated by a vacuum pump (Sinku Kiko Co. Ltd., Yokohama, Japan), and subsequently, the isopropyl alcohol and CO_2 were fed into the cell. By the dual-head circulation pumps, the vapor and liquid phases were recirculated separately until the system reached the equilibrium state. We confirmed the equilibrium state when the GC peak area percents come out constantly. In general, the equilibrium state was reached within 4 h. After equilibration, the 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, 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 technique was used for preparing a standard sample. The two gases were injected into the manometer and made a mixture. It took more than 2 h when the two gases were completely mixed and became a standard sample. A microsyringe 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. Sampling and analysis were repeated more than five times until the GC area % coincided down to two places of decimals and the mean values were taken as the final composition. When one experiment at a fixed pressure was finished, the next experiment was continued by adding CO_2 to the equilibrium cell until the system pressure increased up to (0.5 ∼ 1.0) MPa. When the system pressure went up to near the critical point of the binary mixture, the circulation rate of each phase was quite lowered to minimize the possible fluctuation of an equilibrium state, and the final equilibrium state was maintained by controlling the hand pump while sampling. Considering the margin of error and the reproducibility of 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.

3. Correlation

In this work, the experimental VLE data were correlated with the Peng−Robinson equation of state (PR EOS)[6] combined with the Wong−Sandler mixing rule,[7] which is expressed as follows

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

with

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

$$b = 0.077796RT_c/P_c \tag{3}$$

$$\alpha(T) = [1 + k(1 - {T_r}^{0.5})]^2 \tag{4}$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

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

Table 2. Values of Binary Parameters and Average Absolute Deviations of *P* and *y*

T (K)	k_{12}[a]	A_{12}[b]	A_{21}[b]	AAD-P (%)[c]	δy[d]
323.15	0.4667	4690.94	−235.97	0.275	0.0013
333.15	0.4227	5475.18	−290.09	0.176	0.0015
343.15	0.4081	4100.42	797.94	0.607	0.0015
353.15	0.4000	4896.44	308.77	0.450	0.0014
average				**0.377**	**0.0014**

[a] k_{12} is the interaction parameter. [b] The unit of A_{12} and A_{21} is $\text{kJ}\cdot\text{g}^{-1}\cdot\text{mol}^{-1}$. [c] AAD-$P$ (%) $= 1/N \sum|(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}|\cdot 100$. [d] $\delta y = 1/N \sum|y_{\text{exptl}} - y_{\text{calcd}}|$.

temperature; T_r is the reduced temperature; and v ($\text{cm}^3\cdot\text{mol}^{-1}$) is molar volume.

The Wong−Sandler mixing rule[6] was used in this work to obtain the equation of state parameters for a mixture from those of the pure components. Wong and Sandler equated the excess Helmholtz free energy at infinite pressure from an equation of state to the excess Helmholtz free energy from any activity coefficient model, in such a way that a mixing rule is obtained which simultaneously satisfies the quadratic composition dependence of the second virial coefficient and behaves like an activity coefficient model at high density. This mixing rule for a cubic equation of state can be written

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

with

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

and

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

where C is a constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the PR EOS used in this work and k_{ij} is the binary interaction parameter. Also, A_∞^E is an excess Helmholtz free energy model at infinite pressure which can be equated to a low-pressure excess Gibbs free energy.[8] In this study we use the NRTL model[9] given by

$$\frac{A_\infty^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \tag{9}$$

with

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

and

$$A_{ij} = (g_{ij} - g_{jj}), \quad A_{ji} = (g_{ji} - g_{ii}) \tag{11}$$

where G_{ji} is the local composition factor for the NRTL model; τ_{ji} is the NRTL model binary interaction parameter; g_{ji} is an interaction energy parameter of the $i-j$ component; A_{ij} is an adjustable binary parameter; α_{ji} is a nonrandomness parameter; and R is the universal gas constant ($8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The critical properties (T_c, P_c) and acentric factors (ω) of CO_2 and isopropanol are used in calculating the parameters for the PR EOS. We have set the nonrandomness parameter, α_{ij}, equal to 0.3 for the binary mixture investigated here. Thus, this model contains three adjustable binary parameters (k_{ij}, A_{ij}, and A_{ji}). The parameters of these equations were obtained by minimizing the following objective function

$$\text{objective function} = \frac{1}{N}\sum_{i=1}^{N}\left[\left(\frac{P_{i,\text{exptl}} - P_{i,\text{calcd}}}{P_{i,\text{exptl}}}\right)\cdot 100\right]^2 \tag{12}$$

where N is the number of experimental points; P_{exptl} is the experimental pressure; and P_{calcd} is the calculated pressure.

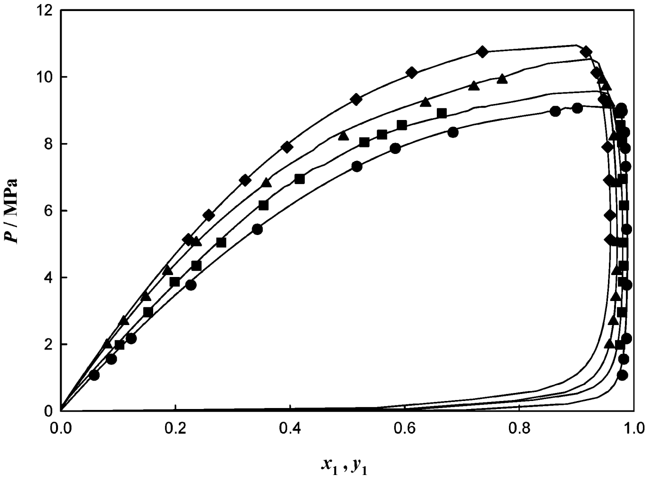

Figure 2. $P-xy$ diagram for the CO_2 (1) + isopropanol (2) binary system (x_1, y_1: CO_2 mole fraction): ●, measured data at 323.15 K; ■, at 333.15 K; ▲, at 343.15 K; ◆, at 353.15 K; −, calculated with PR EOS.[6]

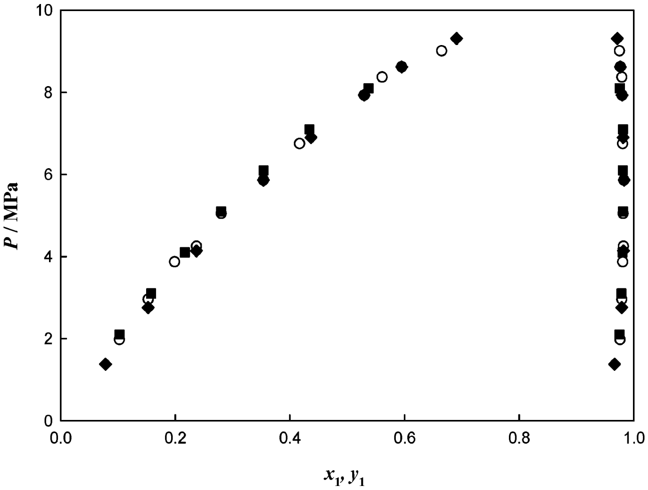

Figure 3. Comparison of the measured and the literature data for the CO_2 (1) + isopropanol (2) system (x_1, y_1: CO_2 mole fraction): ○, this work at 333.15 K; ■, Bamberger and Maurer[4] at 333.1 K; ◆, Radosz[5] at 334.88 K.

4. Results and Discussion

In this work, the equilibrium compositions for the binary system of CO_2 (1) + isopropanol (2) were measured at four equally spaced temperatures from (323.15 to 353.15) K. Table 1 shows the experimental VLE data for this system. This table lists the measured mole fraction of the vapor and liquid phases, pressures, and temperatures in equilibrium and the deviations between measured and calculated pressures ($\Delta P/P_{\text{exptl}}$ %) and vapor-phase compositions (Δy_1), point by point. Table 2 lists the interaction parameters of binary mixtures for each isotherm and the average absolute deviations in pressure (AAD-P (%))

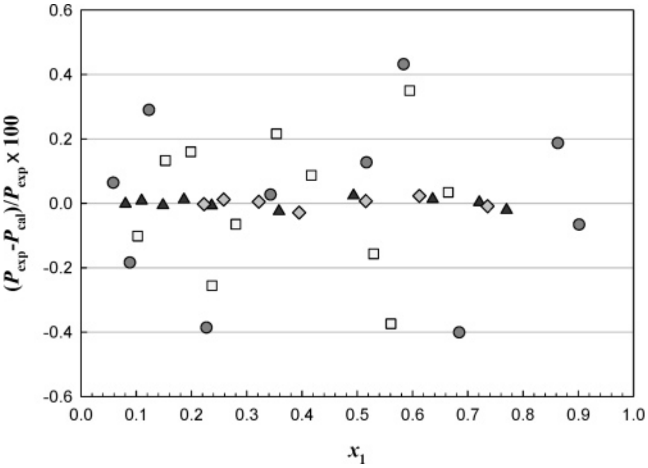

Figure 4. Deviation of pressure for the system CO_2 (1) + isopropanol (2) from the PR EOS[6] using the W−S mixing rule[7] (x_1: CO_2 mole fraction): ●, at 323.15 K; ■, at 333.15 K; ▲, at 343.15 K; ◆, at 353.15 K.

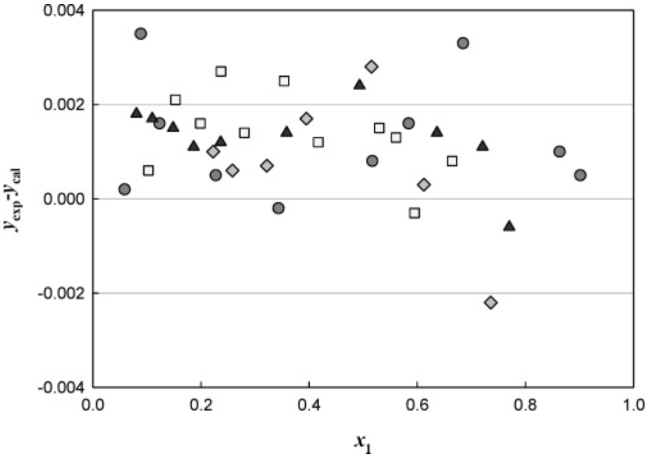

Figure 5. Deviation of vapor composition for the system CO_2 (1) + isopropanol (2) from the PR EOS[6] using the W−S mixing rule[7] (x_1, y_1: CO_2 mole fraction): ●, at 323.15 K; ■, at 333.15 K; ▲, at 343.15 K; ◆, at 353.15 K.

and average absolute deviations in vapor-phase compositions (AAD-y_1) between measured and calculated values for the mixture of CO_2 (1) + isopropanol (2). The values of binary parameters (κ_{12}) determined at (323.15, 333.15, 343.15, and 353.15) K were 0.4667, 0.4227, 0.4081, and 0.4000, respectively, for the PR EOS. The $P-x-y$ diagram for the system of CO_2 (1) + isopropanol (2) at various temperatures is shown in Figure 2, where the experimental VLE data at (323.15, 333.15, 343.15, and 353.25) K are shown as closed circles, squares, triangles, and diamonds, respectively. The black solid lines represent the calculated data by the PR EOS. Figure 3 shows the comparison of our experimental VLE data at 333.15 K with literature data at similar temperatures that have already been reported by Bamberger and Maurer[4] (at 333.1 K) and Radosz[5] (at 334.88 K) for the CO_2 (1) + isopropanol (2) binary system. As can be seen in this figure, the literature data reported by Bamberger and Maurer[9] almost coincided with our data; however, the data reported by Radosz[5] showed slightly lower pressure values at the same compositions. These literature data were also correlated with the PR EOS. The AAD-P (%) of the VLE data from Bamberger and Maurer[4] (at 333.1 K) was 0.168 and from Radosz[5] (at 334.88 K) was 1.154, while our data was 0.176. This means that the accuracy of Bamberger and Maurer's literature data[4] and our experimental data is almost the same and relatively higher than Radosz's data.[5] Also, the values of binary parameters (κ_{12}) of our data (at 333.15 K), Bamberger and Maurer's data[4] (at 333.1 K), and Radosz's data.[5] (at 334.88 K) were 0.4227, 0.4586, and 0.4243, respectively. In Figures 4 and 5, the average absolute deviation of pressure ($\Delta P/P_{exptl}$ %) and vapor-phase compositions (Δy_1) were plotted point by point. The overall average values of AAD-P (%) and AAD-y through the temperature range from (323.15 to 353.15) K were 0.377 % and 0.0014, respectively. All values are small and acceptable. From these figures and the low average deviations of P and y, we conclude that the calculated values using the PR EOS give good agreement with the experimental data.

5. Conclusions

The vapor−liquid equilibrium data for the binary systems of CO_2 (1) + isopropanol (2) were measured at four equally spaced temperatures between (313.15 and 353.15) K using a circulation-type equilibrium apparatus. The experimental VLE data were correlated with the Peng−Robinson equations of state combined with the Wong−Sandler mixing rules. The calculated results with these equations showed good agreement with our experimental data. These data could be useful for the basic design of various separation processes in the SCORR (supercritical carbon dioxide resist removal) system.

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