

High-pressure vapor-liquid equilibrium measurement for the binary mixtures of carbon dioxide+n-butanol

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Abstract—High-pressure vapor-liquid equilibrium data for the binary mixtures of CO₂+n-butanol were measured at various isotherms of (313.15, 323.15, 333.15 and 343.15) K, respectively. The equilibrium compositions of vapor and liquid phases and pressures at each temperature were measured in a circulation-type equilibrium 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 (PR) equations of state using the Wong-Sandler mixing rules. Calculated results with the PR EOS showed good agreement with our experimental data.

Key words: High-pressure VLE, Carbon Dioxide, n-Butanol, Peng-Robinson Equation of State, Wong-Sandler Mixing Rule, SCORR

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]. 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 pure fluids due to the emerging technology of supercritical fluids. The information of high-pressure behavior of fluids at supercritical state has been used to design new separation processes in various fields such as food, pharmaceutical and fine chemical industries [3].

In the present study, the isothermal vapor-liquid equilibrium data for the binary CO₂+n-butanol system have been measured at various temperatures (313.15-343.15 K). In the semiconductor manufacturing fields, alcohols are used as a rinsing and drying agent after the wet cleaning process and n-butanol is one of the candidates. Recently, many attempts have made to replace the wet cleaning process because it has many problems such as huge amount of waste water, enormous cost of ultra-pure water (UPW), technical limit in applying it to a wafer having 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 CO₂ instead of UPW, is considered to be the alternative one. To develop such a new process, a 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 [4-8]. The extents of prior VLE

measurements of this system were (323.15, 333.14, 343.15) K for the data from Ishihara et al. [4] and Hiaki et al. [5], (313.15, 323.15, 333.15, 343.15) K for Jennings et al.'s data [6]. The temperature range of Elizalde-Solis et al.'s work [7], that was 354-430 K, was beyond our experimental range, and the Stevens et al.'s data [8] contains only vapor phase composition data, so we could not use them. In developing the SCORR process in our lab, more intensive VLE data were needed at a temperature range between (313.15 and 343.15) K. So, in the present study, we measured the isothermal vapor-liquid equilibrium data for the binary CO₂+n-butanol system at (313.15, 323.15, 333.15 and 343.15) K. At each temperature, about 10 measured data points were reported. The measured VLE data were correlated with the classical Peng-Robinson equations of state [9] combined with the Wong-Sandler mixing rules [10] and the relevant parameters were presented.

EXPERIMENTAL

1. Chemicals

CO₂ was supplied by Seoul Special Gas Co. (Seoul, Korea) with a guaranteed purity in mass fraction higher than 0.999, and n-butanol was purchased from the Sigma Aldrich (USA) with a guaranteed purity in mass fraction higher than 0.999. Furthermore, we also analyzed these two pure components with a gas chromatograph. The resulting mass fraction purities of CO₂ and n-butanol were higher than 0.9995 and 0.999, respectively, so they were used without any further purification.

2. Apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus for measuring high-pressure vapor-liquid equilibrium data. The experimental apparatus used in this work was the same that used in our previous works [11,12], and the experimental procedure is also well described in them.

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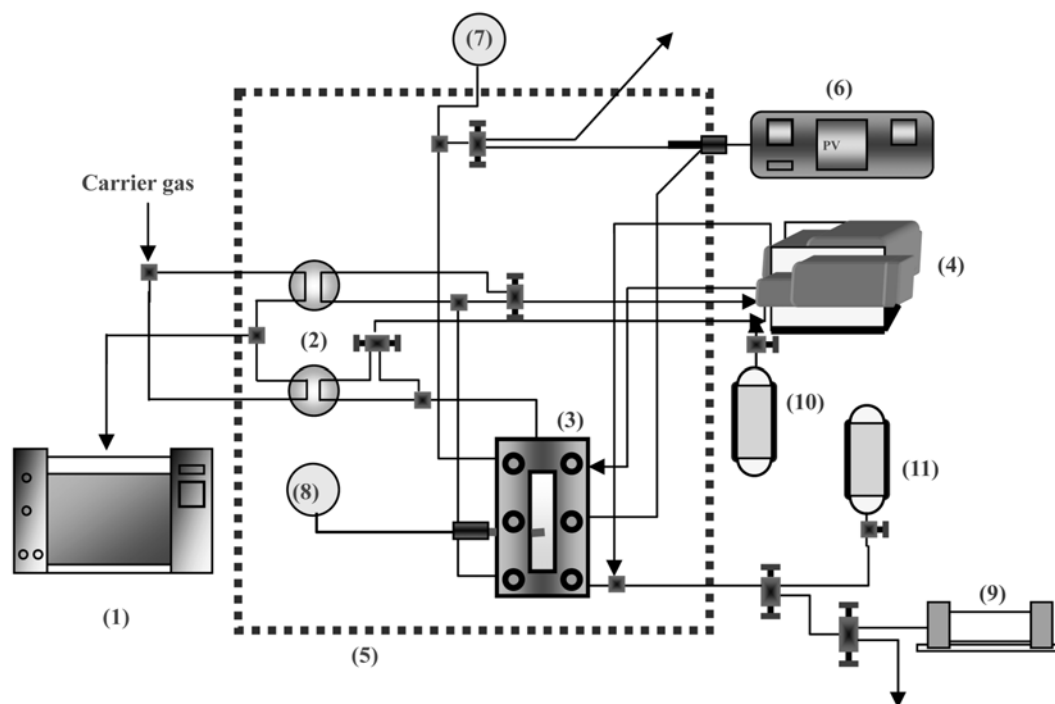


Fig. 1. The schematic diagram of the experimental apparatus.

- | | | | |
|----------------------|---------------------------|--------------------------|---|
| 1. Gas Chromatograph | 4. Circulation pump | 7. Pressure gauge | 10. n-Butanol cylinder |
| 2. Sampling valve | 5. Air bath | 8. Temperature indicator | 11. CO ₂ gas cylinder & syringe pump |
| 3. Equilibrium cell | 6. Temperature controller | 9. Vacuum pump | |

3. Correlation

The experimental VLE data were correlated with the Peng-Robinson equation of state (PR-EOS) [9] combined with the Wong-Sandler mixing rule [10] which is expressed as follows:

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

with

$$a = (0.457235R^2T_c^2/P_c)\alpha(T) \quad (2)$$

$$b = 0.077796RT_c/P_c \quad (3)$$

$$\alpha(T) = [1 + k(1 - T_r^{0.8})]^2 \quad (4)$$

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

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

The Wong-Sandler mixing rule [10] was used 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 but also behaves like an activity coefficient model at high density.

This mixing rule for a cubic equation of state can be written as

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

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 constant equal to $\ln(\sqrt{2}-1)/\sqrt{2}$ for the PR-EOS used in this work, and k_{ij} is 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 [13]. In this study we use the NRTL model [14] given by:

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

with

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

and

$$A_{ij} = (g_{ij} - g_j), A_{ji} = (g_{ji} - g_i) \quad (11)$$

where G_{ji} is the local composition factor for the NRTL model, τ_{ji} is

the NRTL model binary interaction parameter, g_{ij} is an interaction energy parameter of the i - j component, A_{ij} is adjustable binary parameter, α_{ij} 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 n-butanol used in calculating the parameters for the PR-EOS are given in Table 1 [15]. We have set the non-randomness parameter, α_{ij} , equal to 0.3 for the binary mixture investigated here. Thus, this model contains three adjustable

Table 1. Thermodynamic properties of components [15]

Chemical	Chemical formula	Molecular weight	T_c/K	P_c/MPa	ω
Carbon dioxide (1)	CO_2	44.01	304.1	7.38	0.239
n-Butanol (2)	$(\text{CH}_3)_4\text{OH}$	74.12	563.00	4.414	0.593

Table 2. Vapor-liquid equilibrium measurements for the CO_2 (1)+n-butanol (2) system at 313.15 to 343.15 K

Experimental data			PR EOS				
$P_{\text{exp}}/\text{MPa}$	$x_{1,\text{exp}}$	$y_{1,\text{exp}}$	$P_{\text{cal}}/\text{MPa}$	$y_{1,\text{cal}}$	$\Delta P/\text{MPa}$	$\Delta P/P$ (%)	Δy
T/K=313.15							
1.67	0.0936	0.9972	1.670	0.9970	0.000	0.000	0.0002
2.39	0.1370	0.9978	2.392	0.9975	-0.002	-0.084	0.0003
3.36	0.1987	0.9981	3.357	0.9978	0.003	0.089	0.0003
4.62	0.2883	0.9978	4.616	0.9977	0.004	0.087	0.0001
5.64	0.3740	0.9977	5.646	0.9974	-0.006	-0.106	0.0003
6.49	0.4601	0.9969	6.495	0.9969	-0.005	-0.077	0.0002
7.44	0.5930	0.9951	7.427	0.9956	0.013	0.175	-0.0001
7.68	0.6503	0.9945	7.687	0.9949	-0.007	-0.091	0.0003
T/K=323.15							
2.03	0.1055	0.9956	2.034	0.9955	-0.004	-0.197	0.0001
2.76	0.1447	0.9964	2.757	0.9961	0.003	0.109	0.0003
3.45	0.1833	0.9967	3.448	0.9963	0.002	0.058	0.0004
4.50	0.2444	0.9966	4.495	0.9963	0.005	0.111	0.0003
5.77	0.3244	0.9963	5.762	0.9959	0.008	0.139	0.0004
7.10	0.4238	0.9951	7.132	0.9948	-0.032	-0.451	0.0003
8.41	0.5398	0.9923	8.386	0.9923	0.024	0.285	0.0000
9.27	0.6679	0.9867	9.275	0.9868	-0.005	-0.054	0.0001
T/K=333.15							
1.43	0.0612	0.9922	1.435	0.9906	-0.005	-0.350	0.0016
2.81	0.1223	0.9947	2.804	0.9934	0.006	0.214	0.0013
3.69	0.1631	0.9951	3.683	0.9939	0.007	0.190	0.0012
4.73	0.2143	0.9950	4.735	0.9938	-0.005	-0.106	0.0012
5.80	0.2689	0.9945	5.787	0.9932	0.013	0.224	0.0013
7.03	0.3397	0.9934	7.020	0.9919	0.010	0.140	0.0015
7.99	0.4057	0.9917	8.009	0.9900	-0.019	-0.238	0.0017
8.80	0.4709	0.9894	8.810	0.9875	-0.010	-0.114	0.0019
9.45	0.5419	0.9867	9.458	0.9840	-0.008	-0.085	0.0027
9.82	0.5987	0.9842	9.805	0.9810	0.015	0.153	0.0032
T/K=343.15							
1.68	0.0523	0.9874	1.687	0.9865	-0.007	-0.417	0.0009
3.06	0.0985	0.9917	3.060	0.9901	0.000	0.000	0.0016
4.00	0.1315	0.9922	3.980	0.9906	0.020	0.500	0.0016
5.18	0.1772	0.9920	5.164	0.9904	0.016	0.309	0.0016
5.84	0.2058	0.9913	5.852	0.9900	-0.012	-0.205	0.0013
6.79	0.2489	0.9893	6.805	0.9889	-0.015	-0.221	0.0004
7.52	0.2837	0.9893	7.501	0.9878	0.019	0.253	0.0015
8.42	0.3364	0.9871	8.424	0.9856	-0.004	-0.048	0.0015
9.43	0.4101	0.9829	9.447	0.9817	-0.017	-0.180	0.0012
10.98	0.6601	0.9711	10.974	0.9680	0.006	0.055	0.0031

$$\Delta P = P_j^{\text{exp}} - P_j^{\text{cal}}, \Delta P/P (\%) = (P_j^{\text{exp}} - P_j^{\text{cal}})/P_j^{\text{exp}} \times 100, \Delta y = y_j^{\text{exp}} - y_j^{\text{cal}}$$

binary parameters (k_{ij} , A_{ij} and A_{ji}). The parameters of these equations were obtained by minimizing the following objective function:

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

where N is the number of experimental points, P_{exp} is the experimental pressure, and P_{cal} is the calculated pressure.

RESULTS AND DISCUSSION

The equilibrium compositions for the CO₂ (1)+n-butanol (2) binary systems were measured at four equally spaced temperatures from (313.15 to 343.15) K. Table 2 shows the experimental VLE data for this system and lists the measured mole fraction of the vapor and liquid phases, pressures, and temperatures in equilibrium and the deviations between measured and calculated pressures ($\Delta P/P_{\text{exp}}$ %) and vapor phase compositions (Δy_1), point by point. Table 3 lists the interaction parameters of binary mixtures for each isotherm and the average absolute deviations in pressure (AAD-P (%)) and average absolute deviations in vapor phase compositions (AAD- y_1) between measured and calculated values for the mixture of CO₂ (1)+

Table 3. 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
313.15	0.5392	4353.97	256.55	0.089	0.0002
323.15	0.5283	4990.48	-86.84	0.175	0.0002
333.15	0.4943	5584.62	157.78	0.181	0.0018
343.15	0.4986	4501.14	1336.73	0.219	0.0015
Average				0.166	0.0009

^a k_{12} is interaction parameter

^bThe unit of A_{12} and A_{21} is kJ/g-mol

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

^d $\delta y = 1/N \sum |y_{\text{exp}} - y_{\text{cal}}|$

We have set the non-randomness parameter, α_{ij} , equal to 0.3

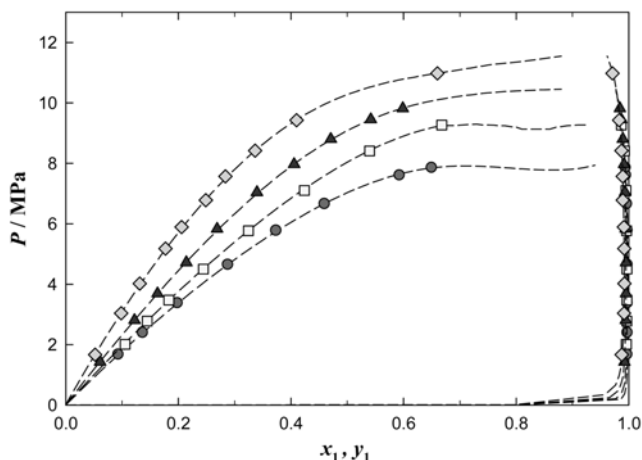


Fig. 2. P-xy diagram for the CO₂ (1)+n-butanol (2) binary system (x_1, y_1 : CO₂ mole fraction): (●), measured data at 313.15 K; (■), at 323.15 K; (▲), 333.15 K; (◆), 343.15 K; (—), calculated with PR EOS [9].

n-butanol (2). The values of binary parameters (k_{12}) determined at (313.15, 323.15, 333.15, and 343.15) K were 0.5392, 0.5283, 0.4943 and 0.4986, respectively, for the PR-EOS. The P-x-y diagram for the system of CO₂ (1)+n-butanol (2) at various temperatures is shown in Fig. 2, where the experimental VLE data at (313.15, 323.15, 333.15 and 343.25) K are shown as closed circles, squares, triangles, and diamonds, respectively. The black solid lines represent the calculated data by the PR-EOS. Fig. 3 shows the comparison of our experimental VLE data at 313.15 K with literature data at similar temperatures that were already reported by Ishihara et al. [4] (at 313.15 K), Hiaki et al. [5] (at 313.2 K) and Jennings et al. [6] (at 314.8 K) for the CO₂ (1)+n-butanol (2) binary system. As can be seen in this figure, our experimental data agreed well with the literature data and, especially, the literature data reported by Ishihara et al. [4] (at 313.15 K) and Hiaki et al. [5] (at 313.2 K) almost coincided with our data. However, Jennings et al.'s data [6] (at 314.8 K) showed a little bit

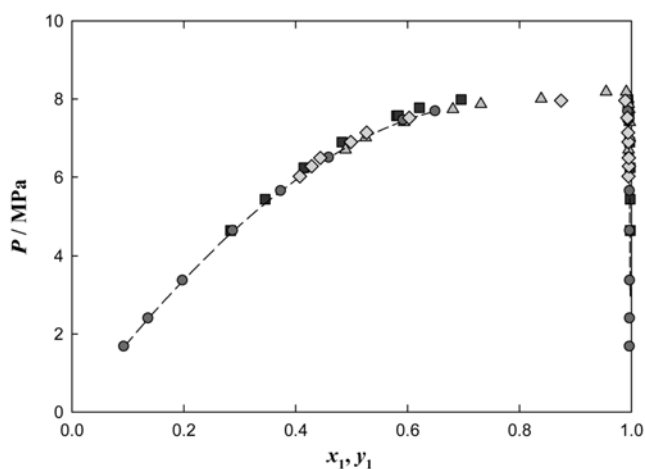


Fig. 3. Comparison of the measured and the literature data for the CO₂ (1)+n-butanol (2) system (x_1, y_1 : CO₂ mole fraction): (—●—), this work at 313.15 K; (▲), Ishihara et al. [4] at 313.15 K; (◆), Hiaki et al. [5] at 313.2 K; (■), Jennings et al. [6] at 314.8 K.

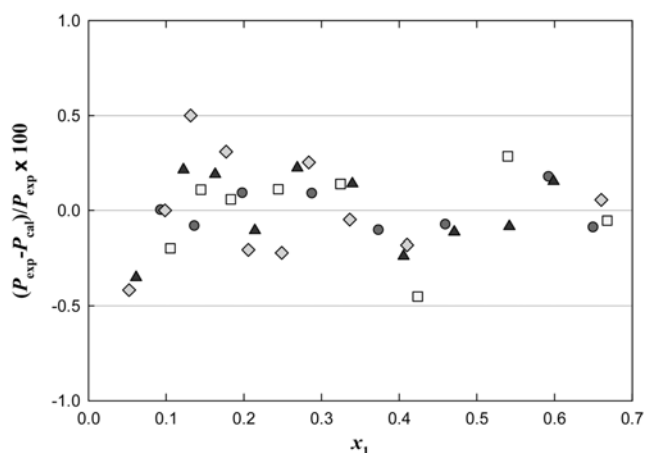


Fig. 4. Deviation of pressure for the system CO₂ (1)+n-butanol (2) from the PR-EOS [9] using W-S mixing rule [10] (x_1 : CO₂ mole fraction): (●), at 313.15 K; (■), at 323.15 K; (▲), at 333.15 K; (◆), at 343.15 K.

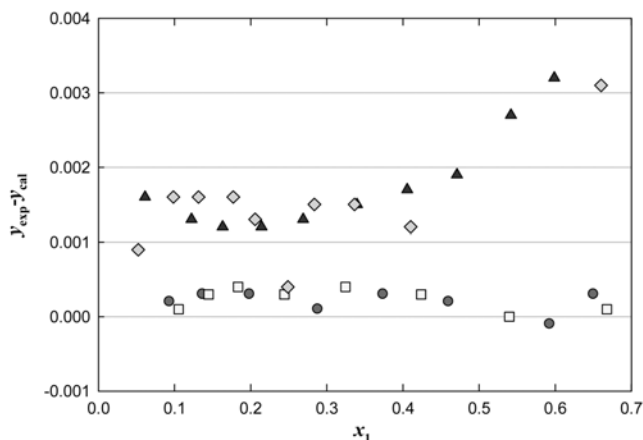


Fig. 5. Deviation of vapor composition for the system CO₂ (1)+n-butanol (2) from the PR-EOS [9] using W-S mixing rule [10] (x_1, y_1 : CO₂ mole fraction): (●), at 313.15 K; (■), at 323.15 K; (▲), at 333.15 K; (◆), at 343.15 K.

higher pressure values at the same compositions because their system temperature was slightly higher than ours by 1.65 K. These literature data were also correlated with the P-R EOS. The AAD-P (%) of the VLE data from Ishihara et al. [4] (at 313.15 K) was 0.172 and Jennings et al. [6] (at 314.8 K) was 0.085, while that of our data was 0.089. The values of binary parameters (κ_{12}) of our data (at 313.15 K), Ishihara et al.'s data [4] (at 313.15 K) and Jennings et al.'s data [6] (at 334.8 K) were 0.539, 0.539 and 0.525, respectively. In Figs. 4 and 5, the average absolute deviation of pressure ($\Delta P/P_{exp}$ %) 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 313.15 to 343.15 K were 0.166% and 0.0009, 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 gives good agreement with the experimental data.

CONCLUSIONS

The vapor-liquid equilibrium data for the binary systems of CO₂ (1)+n-butanol (2) were measured at four equally spaced temperatures between 313.15 and 343.15 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 system.

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