

Vapor-liquid equilibria of carbon dioxide+n-propanol at elevated pressure

Jun-Hyuk Yim, Youn Geun Jung, and Jong Sung Lim[†]

Department of Chemical and Biomolecular Engineering, Sogang University, 1142, Seoul 121-742, Korea
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Abstract—High-pressure vapor-liquid equilibrium data were measured for the binary mixtures of CO₂+n-propanol at various isotherms (313.15-343.15 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 (PR) equations of state using the Wong-Sandler mixing rules. Calculated results with PR EOS showed good agreement with our experimental data.

Key words: High-pressure VLE, Carbon Dioxide, n-Propanol, 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 given to the thermodynamic understanding of fluid systems [1,2]. Also, during the last two decades, efforts have been focused on an understanding of the phase equilibrium behavior 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 valuably 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-propanol 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-propanol 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 the 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 on the literature [4]. 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-propanol system at (313.15, 323.15, 333.15 and 343.15) K. At each temperature, 8-9 measured data points were

reported. The measured VLE data was correlated with the classical Peng-Robinson equations of state [5] combined with the Wong-Sandler mixing rules [6], and the relative accuracy was discussed.

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-propanol 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-propanol 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 apparatus used in this work was the same as that used in our previous works [7,8], and the experimental procedure was also well described in them.

3. Correlation

In this work, the experimental VLE data were correlated with the Peng-Robinson equation of state (PR-EOS) [5] combined with the Wong-Sandler mixing rule [6] which is expressed as follows:

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

with

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

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

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

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

where the parameter 'a' is a function of temperature, 'b' is constant, k is a constant characteristic of each substance, ω is the acentric

[†]To whom correspondence should be addressed.
E-mail: limjs@sogang.ac.kr

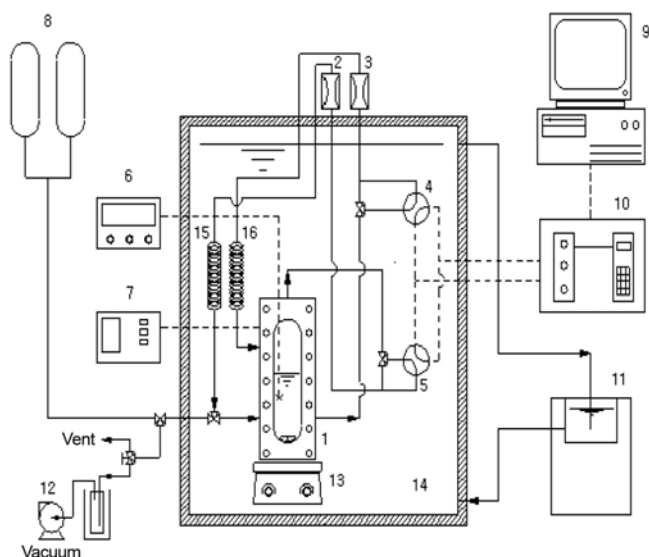


Fig. 1. Schematic diagram of the experimental apparatus.

1. Equilibrium cell
2. Vapor circulation pump
3. Liquid circulation pump
4. Liquid sample valve
5. Vapor sample valve
6. Temperature indicator
7. Pressure indicator
8. Sample reservoir
9. Computer
10. Gas Chromatograph
11. Circulator
12. Vacuum pump
13. Magnetic stirrer
14. Constant temperature water bath
15. Vapor phase heat exchanger
16. Liquid phase heat exchanger

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 [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 but also behaves like an activity coefficient model at high density. This mixing rule for a cubic equation of state can be written,

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

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 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 [9]. In this

study we used the NRTL model [10] given by:

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

Table 1. Characteristic properties of carbon dioxide and n-propanol^a

Characteristic property	Carbon dioxide	n-Propanol
Chemical formula	CO ₂	(CH ₃) ₃ OH
Molar mass	44.01	60.10
Boiling point, T_b /K	226.6	370.3
Critical temperature, T_c /K	304.1	536.8
Critical pressure, P_c /MPa	7.38	5.169
Acentric factor, ω	0.239	0.623

^aSource: database REFPROP 6.01 [11]

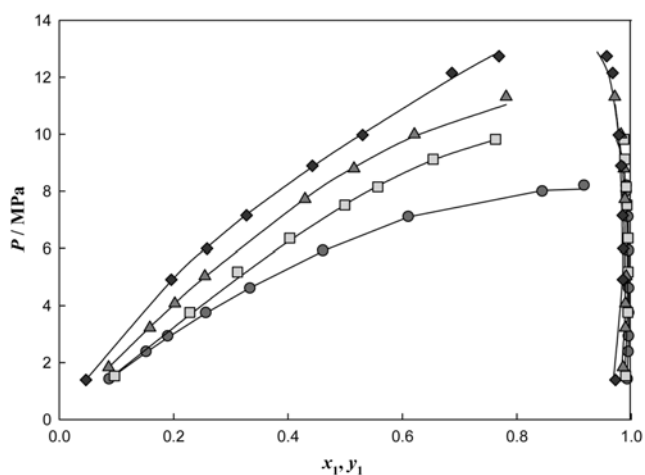


Fig. 2. P-xy diagram for the CO₂ (1)+n-propanol (2) binary system (x_1, y_1 : CO₂ mole fraction): (●), measured data at 313.15 K; (■), at 323.15 K; (▲), 333.15 K; (◆), 343.15 K; (—), calculated with PR EOS⁵.

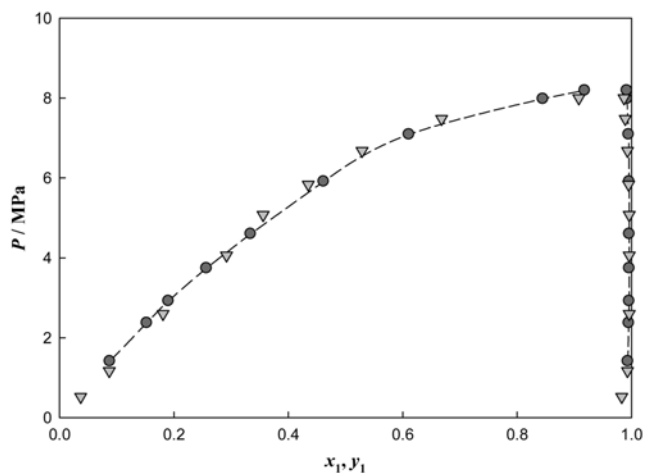


Fig. 3. Comparison of the measured and the literature data for the CO₂ (1)+n-propanol (2) system (x_1, y_1 : CO₂ mole fraction): (●), this work at 313.15 K; (▼), Suzuki et al. [4] at 313.4 K.

with

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

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, 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 n-propanol used in calculating the parameters for the PR-EOS are given in Table 1. We set the non-randomness parameter, α_{ji} , 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 fol-

lowing objective function:

$$\text{objective function} = \frac{1}{N} \sum_{i=1}^N \left[\left(\frac{P_{i,\text{exp}} - P_{i,\text{cal}}}{P_{i,\text{exp}}} \right) \times 100 \right]^2 \quad (21)$$

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 CO_2 (1)+n-propanol (2) binary systems were measured at four equally spaced temperatures from 313.15 K to 343.15 K. Fig. 3 shows a comparison of our data for the CO_2 (1)+n-propanol (2) system at 313.15 K with the litera-

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

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							
1.41	0.0881	0.9939	1.422	0.9927	-0.012	-0.851	0.0012
2.37	0.1526	0.9954	2.365	0.9949	0.005	0.211	0.0005
2.92	0.1904	0.9960	2.883	0.9954	0.037	1.267	0.0006
3.74	0.2571	0.9963	3.736	0.9958	0.004	0.107	0.0005
4.60	0.3342	0.9963	4.630	0.9959	-0.030	-0.652	0.0004
5.91	0.4619	0.9960	5.910	0.9956	0.000	0.000	0.0004
7.09	0.6111	0.9951	7.092	0.9945	-0.002	-0.028	-0.0094
7.98	0.8453	0.9921	8.020	0.9916	-0.040	-0.501	0.0005
8.19	0.9183	0.9920	8.073	0.9912	0.117	1.429	0.0008
T/K=323.15							
1.53	0.0967	0.9902	1.577	0.9888	-0.047	-3.079	0.0014
3.76	0.2284	0.9943	3.676	0.9932	0.084	2.243	0.0011
5.18	0.3166	0.9944	5.024	0.9935	0.156	3.004	0.0009
6.35	0.4030	0.9944	6.267	0.9930	0.083	1.302	0.0014
7.51	0.4993	0.9927	7.519	0.9917	-0.009	-0.120	0.0010
8.15	0.5571	0.9913	8.181	0.9902	-0.031	-0.376	0.0011
9.12	0.6538	0.9889	9.094	0.9857	0.026	0.289	0.0032
9.82	0.7628	0.9873	9.807	0.9741	0.013	0.134	0.0132
T/K=333.15							
1.83	0.0864	0.9858	1.823	0.9836	0.007	0.372	0.0022
3.22	0.1587	0.9901	3.247	0.9883	-0.027	-0.844	0.0018
4.07	0.2023	0.9901	4.065	0.9892	0.005	0.126	0.0009
5.03	0.2546	0.9912	5.001	0.9895	0.029	0.573	0.0017
7.72	0.4299	0.9889	7.740	0.9874	-0.020	-0.259	0.0015
8.79	0.5152	0.9872	8.825	0.9847	-0.035	-0.396	0.0025
9.99	0.6211	0.9821	9.926	0.9788	0.064	0.645	0.0033
11.01	0.7813	0.9713	11.034	0.9721	-0.024	-0.216	-0.0008
T/K=343.15							
1.39	0.0469	0.9724	1.390	0.9689	0.000	0.000	0.0035
4.91	0.1961	0.9856	4.872	0.9847	0.038	0.774	0.0009
5.99	0.2585	0.9863	6.036	0.9848	-0.046	-0.768	0.0015
7.15	0.3275	0.9851	7.178	0.9841	-0.028	-0.392	0.0010
8.89	0.4426	0.9827	8.852	0.9814	0.038	0.427	0.0013
9.97	0.5304	0.9785	10.013	0.9777	-0.043	-0.431	0.0008
12.15	0.6864	0.9677	11.956	0.9624	0.194	1.597	0.0053
12.74	0.7689	0.9572	12.883	0.9407	-0.143	-1.122	0.0165

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

ture data of Suzuki et al. [4] for the corresponding temperature. As can be seen, our experimental data agreed well with the literature data reported by Suzuki et al. [4].

The experimental data of the isothermal VLE for the binary system of CO₂ (1)+n-propanol (2) are shown in Table 2. 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 ($\Delta P/P_{exp}$ %) and vapor phase compositions (Δy_1), point by point. 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-y₁) between measured and calculated values for the mixture of CO₂ (1)+n-propanol (2) are reported in Table 3. The binary parameters (κ_{12}) for the PR-EOS determined at (313.15, 323.15, 333.15, and 343.15) K were 0.4932, 0.4772, 0.4687 and 0.4952, respectively, and the mean value was 0.4836. The P-x-y diagram for the system of CO₂ (1)+n-propanol (2) at various temperatures is shown in Fig. 3, where the experimental VLE data at (313.15, 323.15, 333.15 and 343.15) K are shown as closed circles, squares, triangles, and diamonds, respectively. The black solid lines represent the calculated data by the PR-EOS. The average ab-

Table 3. Values of binary parameters and average absolute deviations of P and y

T (K)	κ_{12}^a	A_{12}^b	A_{21}^b	AAD-P (%) ^c	δy^d
313.15	0.4932	579.88	2233.52	0.561	0.0016
323.15	0.4772	-893.69	4467.71	1.318	0.0028
333.15	0.4687	30.49	3644.46	0.429	0.0019
343.15	0.4952	2300.77	1237.25	0.689	0.0036
Average				0.749	0.0025

^a κ_{12} is interaction parameter

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

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

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

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

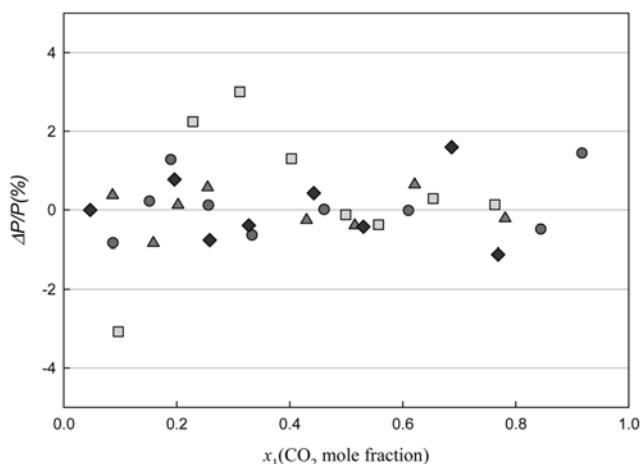


Fig. 4. Deviation of pressure for the system CO₂ (1)+n-propanol (2) from the PR-EOS⁵ using W-S mixing rule⁶ (x_1 : CO₂ mole fraction): (●), at 313.15 K; (■), at 323.15 K; (▲), 333.15 K; (◆), 343.15 K.

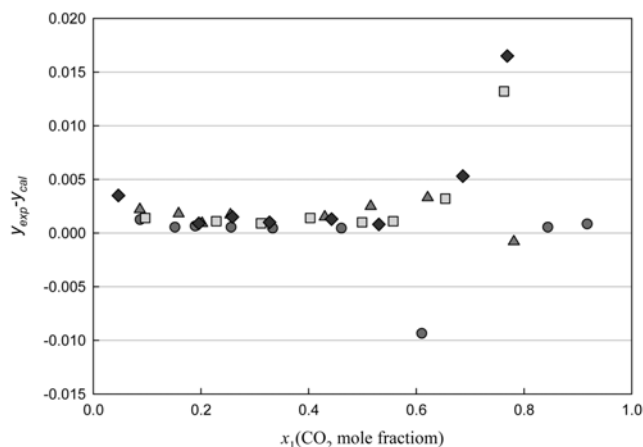


Fig. 5. Deviation of vapor composition for the system CO₂ (1)+n-propanol (2) from the PR-EOS⁵ using W-S mixing rule⁶ (x_1 , y_1 : CO₂ mole fraction): (●), at 313.15 K; (■), at 323.15 K; (▲), 333.15 K; (◆), 343.15 K.

solute deviation of pressure and vapor phase compositions, point by point are shown in Figs. 4 and 5, respectively. The overall average values of AAD-P (%) and AAD-y were 0.749% and 0.0025, 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-propanol (2) were measured at four equally spaced temperatures between 313.15 and 343.15 K by 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.

ACKNOWLEDGMENT

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NOMENCLATURE

- a(T) : temperature dependent constant of equation of state
- a : attraction parameter
- A_{ij} : adjustable parameters
- $\alpha_0, \alpha_1, \alpha_2$: coefficients for the temperature dependence of a
- b : molecular volume
- $\beta_0, \beta_1, \beta_2$: coefficients for the temperature dependence of b
- g_{ij} : an energy parameter characteristic of the i-j interaction
- f_{12} : PR equation of state parameter
- P, P_c : pressure, critical pressure [MPa]
- R : gas constant 8.3144 [J·mol⁻¹ K⁻¹]

T, T_c , T_r : absolute temperature, critical temperature, reduced temperature [K]
 v : liquid molar volume
 x : liquid mole fraction
 y : vapor mole fraction
 y : $b/4V$

Greek Letters

Δ : deviation
 ω : acentric factor

Subscripts

c : critical property
cal : calculated
exp : experimental
i, j : i th, j th component of the mixture

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