

CO₂ + alcohol 혼합물 계의 고압 기-액 상평형 데이터 측정

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High Pressure VLE Measurement of CO₂ + alcohol Systems

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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. 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 [2].

In the present study the binary CO₂+Alcohol systems at various isotherms (313.15 ~ 353.15 K) used in the Super Critical Carbon Dioxide Resist Removal (SCORR) process have been measured.

The measured data was correlated by the classical Peng-Robinson equations of state.

2 EXPERIMENT**2.1 Chemicals**

CO₂ (>99.9% purity) was purchased from Seoul Special Gas Co. (Seoul, Korea) and used without further purification. Isopropanol (HPLC grade >99.5% purity) was obtained from the DukSan Pure Chemical co. ltd.. (Ansan, Kyungi-do, Korea), n-propanol and n-butanol (HPLC grade >99.9% purity) were obtained from The Sigma Aldrich.

2.2 Apparatus and Procedure

The equipment consists of four major parts as the high-pressure equilibrium cell, pressure and temperature control parts, air-bath, and the feeding and sampling devices. The equilibrium cell equipped with a sapphire glass window in order to allow a view to the inside of the cell. The cell volume was 50 ml and it was designed to operate safely up to 250 bar. The temperature was controlled within accuracy of ± 0.1 K by a PID controller (Hanyoung Electronic Co. Ltd., Seoul, Korea) with an forced-circulation type air bath. Temperature was measured within the accuracy of ± 0.05 K by a Pt-100 Ω thermocouple. The equilibrium pressure was measured by a Heise gauge (Heise Co., Newtown, Connecticut, USA) within ± 0.1 bar. To control pressure accurately, a hand pump (HIP Co., Erie, Pennsylvania, USA) was used. By separate two circulation pumps (Thermo Separation Products Inc., Riviera Beach, Florida, USA), the vapor and liquid phases were circulated until the system reaches to an equilibrium state.

CO₂ was fed by the Isco Syringe Pump (ISCO 260DM, Lincoln, Nebraska, USA). The equilibrated compositions of vapor and liquid phase were separately sampled by circulation pumps (Rheodyne L.P., Rohnert Park, California, USA) and the compositions were analyzed by an on-line gas chromatograph (GL science Inc., Tokyo, Japan). The internal volume of the sampling loop of vapor stream was 5 μ l and that of liquid stream was 1 μ l.

The entire internal loop of the apparatus including the equilibrium cell was rinsed several times by liquid CO₂ and the degree of the cleanness was checked by analyzing the rinsed liquid CO₂ with the gas

chromatograph. Then, the equilibrium cell was evacuated by a vacuum pump (Sinku Kiko Co. Ltd., Yokohama, Japan) and subsequently the CO₂ and alcohol sample were fed into the cell. The vapor and liquid phase was sampled by the sampling valves and they were analyzed by the on-line gas chromatograph. Sampling and analysis was repeated more than three times and the mean values were taken as the finally measured composition.

2.3 Correlation

The experimental binary VLE data were correlated with the PR-EOS [2].

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

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

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

$$\alpha(T) = \left[1 + \kappa (1 - T/T_c)^{0.5} \right]^2 \quad (4)$$

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

where the parameter a is a function of temperature, b and κ are constants characteristic of each substance, κ is a constant characteristic of each substance, ω is the acentric factor, P is the pressure, P_c is the critical pressure, T is absolute temperature, T_c is the critical temperature and $v(\text{cm}^3\text{mol}^{-1})$ is molar volume.

In this work the Wong-Sandler mixing rule [3] was used to obtain equation of state parameters

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

with

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

and

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

for the mixture. These mixing rules for a cubic equation of state can be written as where C is a numerical constant equal to $\ln(2^{1/2} - 1/2^{1/2})$ for the PR-EOS used in this work.

Figure 1 and 2, 3 shows the comparison of the experimental VLE data with data reported by A. Bamberger et. al. [4], Radosz M. [5], Kazuhiko Suzuki et al. [6], David W. et. al. [7], Katsuo Ishihara et. al. [8]. The experimental shown in Figure 5, 6 and 7 were correlated with the PR-EOS.

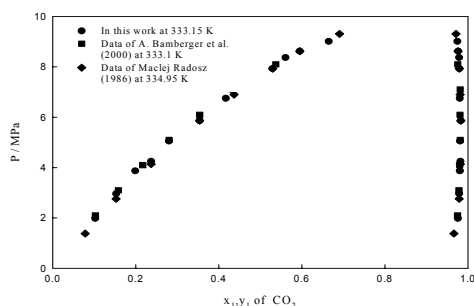


Figure 1. Comparison of measured and literature vapor-liquid equilibrium data for the CO₂ + 2-propanol system at 313.15K

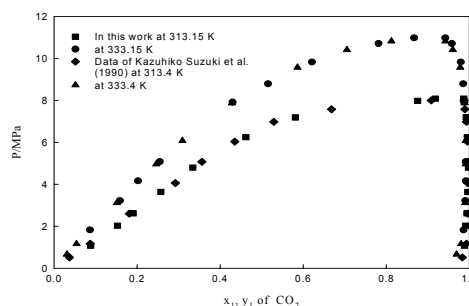


Figure 2. Comparison of measured and literature vapor-liquid equilibrium data for the CO₂ + n-propanol system at 313.15K

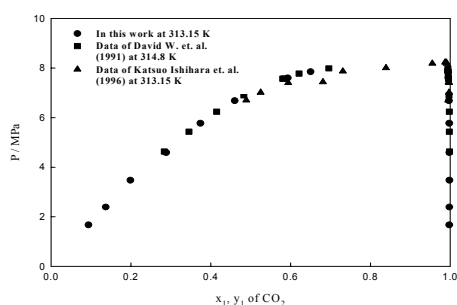


Figure 3. Comparison of measured and literature vapor-liquid equilibrium data for the CO₂ + n-butanol system at 313.15 K

3 Conclusion

The results of those references agree with our experimental data. The equilibrium compositions for the carbon dioxide + 2-propanol, n-propanol, n-butanol binary systems were measured at 313.15 K to 353.15 K., and the results are shown in Figure 4, 5 and 6.

The vapor-liquid equilibrium data for the binary systems of CO₂ + Alcohols (2-propanol, n-propanol, n-butanol) were measured at four temperatures between 313.15 and 353.15 K using a circulation-type equilibrium apparatus. The VLE data of CO₂ + Alcohol systems were used for correlation with PR Equation of State involving the Wong-Sandler mixing rule and the NRTL excess Helmholtz free energy model. This mixing rule combined with PR equation of state and an activity coefficient model (NRTL) for the A^{ex} term showed good agreements with the measured data

The calculated results with these PR EOS [9] have given satisfactory results in comparison with the experimental data.

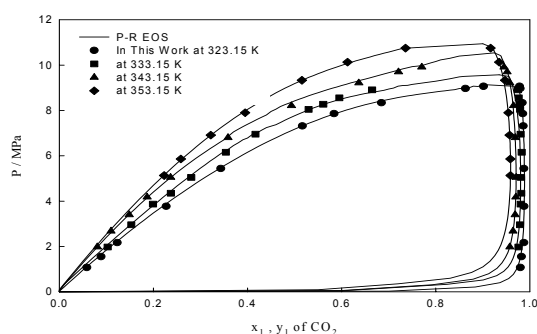


Figure 4. Pxy diagram for the carbon dioxide + 2-propanol system

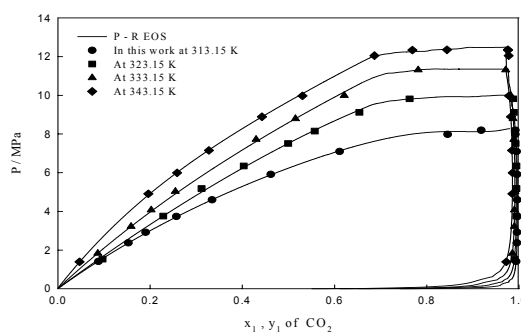


Figure 5. Pxy diagram for the carbon dioxide + n-propanol system

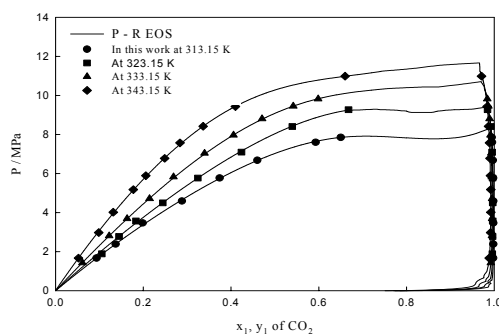


Figure 6. Pxy diagram for the carbon dioxide + n-butanol system

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