HIGH PRESSURE VAPOR LIQUID EQUILIBRIUM FOR CARBON DIOXIDE + ETHANOL + 2-BUTANONE SYSTEM

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Vapor-liquid equilibrium was measured for three binary systems, carbon dioxide + ethanol, carbon dioxide + 2-butanone, and ethanol + 2-butanone, and a ternary system, carbon dioxide + ethanol + 2-butanone, at 313.2K. A circulation type apparatus was used in case of the high pressure systems, carbon dioxide + ethanol, carbon dioxide + 2-butanone, and carbon dioxide + ethanol + 2-butanone, and a flow type one in case of low pressure system, ethanol + 2-butanone. The binary data measured were correlated with improved Peng-Robinson equation of state combined with Adachi-Sugie type mixing rule. Using the optimized binary parameters in the mixing rule, the phase equilibrium was predicted for the ternary system.

INTRODUCTION

Supercritical carbon dioxide (CO_2) has been paid much attention to be a new type of earth-friendly solvent. Many researchers have proposed various separation processes using supercritical carbon dioxide [1]. Especially, extraction of biomass ethanol (C_2H_5OH) from fermentation is expected to establish a sustainable process. Though the knowledge of vapor-liquid equilibrium (VLE) is essential for the design and the operation for the process, few data are available except for the system containing, CO_2, C_2H_5OH, and water. In this study, we focused on a byproduct, 2-butanone ($CH_3COC_2H_5$), and measured the VLE for three binary systems and a ternary system containing CO_2, C_2H_5OH, and $CH_3COC_2H_5$ at 313.2K. The experimental data for the three binary systems were correlated with improved Peng-Robinson equation of state combined with Adachi-Sugie type mixing rule. Using the optimized binary parameters, the VLE was predicted for the ternary system.

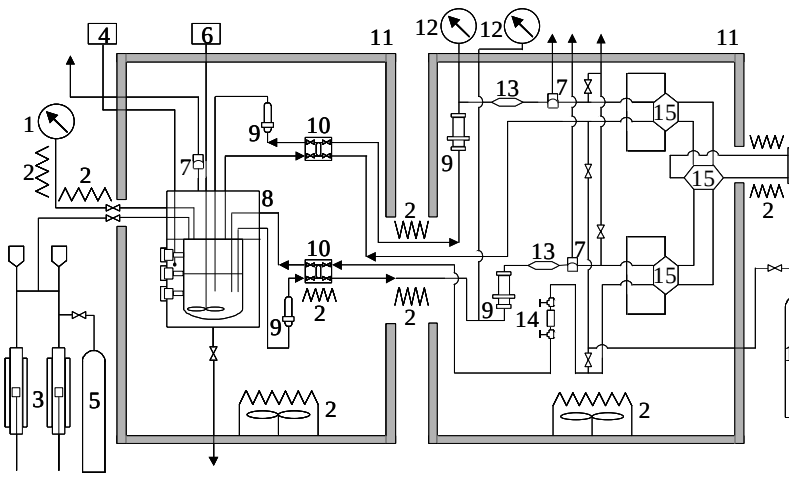
EXPERIMANTAL

Materials

CO_2 used in this study was purchased from Showa Tansan Co. Ltd. Tokyo, and the mass purity was no less than 99.99%. C_2H_5OH and $CH_3COC_2H_5$ used were special grade reagents supplied from Wako Puer Chemical Industries Ltd., Osaka, Japan, and the mass purities were 99.5 and 99.0%, respectively. All reagents were used as received.

Equipment and Procedures

VLE was measured for three binary systems, CO_2 (1) + C_2H_5OH (2), CO_2 (1) + $CH_3COC_2H_5$ (3), and C_2H_5OH (2) + $CH_3COC_2H_5$ (3), and a ternary system, CO_2 (1) + C_2H_5OH (2) + $CH_3COC_2H_5$ (3), at 313.2K. Two different types of apparatus were employed corresponding to the experimental pressure range. One is a circulation type apparatus for the system containing CO_2 (1), and the other is a flow type for C_2H_5OH (1) + $CH_3COC_2H_5$ (3) system. The principle and the experimental procedures have been already described [2,3]. Figure 1 shows the schematic diagram of a circulation type apparatus. The apparatus was mainly designed by AKICO Co., Tokyo, and some assemblies were improved in our laboratory [2]. The equilibrium cell was made of stainless steal, and the inner volume was about 500cm^3. The cell was held in the air chamber, and the temperature was maintained to be 313.2K within the precision of 0.1K. The three windows were assembled with the cell to observe phase equilibrium. In the measurement, the liquid sample was fed into the cell, and successively liquidated CO_2 (1) was loaded up to the desired pressure. In case of the ternary system, the mole ratio of C_2H_5OH (2): $CH_3COC_2H_5$ (3) in the feed solution was set to be about 50:50 and 25:75. Two magnetic driven pumps were equipped with the cell to agitate the vapor and liquid phase. The pressure was measured by a precise Burdon tube gauge (Nagano Keiki Co. GP35-141, Tokyo) with the precision of 0.05MPa. Temperature was measured with a platinum resistance thermometer with the precision of 0.1K. After ensuring the constant temperature and pressure, a portion of the samples, the volume from 1 to 10 cm^3, were individually picked up from the vapor and liquid phase by the sampling valve. The samples were heated and expanded to vaporize, and the compositions were determined by a gaschromatograph with a thermal conductivity detector. The gaschromatograph used was GL Science GC-323TCD, and the packing in the column (stainless tube, i.d.2.20 mm x 5.0m long) was Porapak Q 80/100 mesh.



1:Precise Bourdon Tube Gauge **2:**Heater **3:**Sample Loader **4:**Pt Resistance Thermometer **5:**CO_2 Cylinder **6:**Agitator **7:**Safety Valve **8:**Eqilibrium Cell **9:**Circulation Pump **10:**Sampling Valve **11:**Air Chamber **12:**Bourdon Tube Gauge **13:**Surge Tank **14:**Calibration Cell **15:**Six-way Valve **16:**Gaschromatograph **17:**He Cylinder

Figure 1. Schematic diagram of a circulation type apparatus

Figure 2 shows the schematic diagram of a flow type apparatus. The apparatus was completely designed and

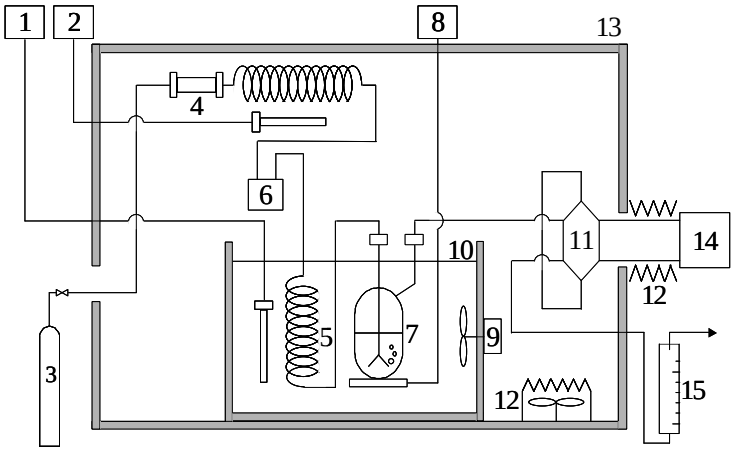
constructed in our laboratory [3]. The flow cell was made of Pyrex? grass, and the inner volume is about 200cm^3. In the measurement, the sample solution was loaded into a sample cell. A stirrer tip, driven by the magnetic stirrer with the water proofing assemblies, was in the cell to agitate the solution. The cell was held in a water bath maintained to be a desired temperature. The temperature was measured by thermistor thermometer (Technoseven D641, SXA-33, Yokohama, Japan) within the precision of 0.01K. The helium, with a constant flow rate, was slowly passed through the cell. The helium, saturated with the solvent vapor, was introduced into a gas chromatograph with a thermal conductivity detector. The gaschromatograph used was GL Science GC-380TCD, and the packing in the column (grass tube, i.d.2.0 mm x 12ft. long) was Gasukuropak 54 80/100 mesh.

In this study, the composition in the liquid phase was regarded as that at the preparation, and that in the vapor phase was evaluated by the partial pressure. The partial pressure can be estimated from the peak height in the gaschromatogram. When the peak height of the pure solvent at some temperature was the same as that of the mixture at the experimental temperature, the vapor pressure of the pure solvent was assumed to be the partial pressure of the mixture.

RESULT AND DISCUSSION

Ensuring the reliability of the experimental data, we first measured VLE for CO_2 (1) + C_2H_5OH (2) system. Figure 3 shows the experimental VLE for CO_2 (1) + C_2H_5OH (2) at 313.2K. In the figure, the data of Yoon et al. [4], Suzuki et al. [5], and Jennings et al.[6] were also illustrated. As shown in the figure, some researcher reported the VLE around the experimental temperature. Though Yoon et al. [4] have measured the VLE at the same temperature, the experimental data did not agreed in the liquid composition. However, the experimental data showed the same tendency with those of Suzuki et al. [5] and Jennings et al. [6]. Comparing with the data of literature, those of Yoon et al. [4] seem to be have some discrepancies with other data.

In the figure, the mole fraction of CO_2 in the liquid phase was drastically



1:Thermistor Thermometer **2:**Pt Resistance Thermometer **3:**He cylinder **4:**Gas Dryer **5:**Heat Exchanger **6:**Mass Flow Controller **7:**Flow Cell **8:**Magnetic Stirrer **9:**Agitator **10:**Water Bath **11:**Six-way Valve **12:**Heater **13:**Air Chamber **14:**Gaschromatograph **15:**Flowmeter

Figure 2. Schematic diagram of a flow type apparatus

changed at the pressure higher than 6.89 MPa. Otherwise, that in the vapor phase had a maximum at 5.10 MPa. The critical point of CO_2 (1) + C_2H_5OH (2) system seems to exist around x_1=0.965, and P=8.2MPa at 313.2K.

Figure 4 shows the experimental VLE for CO_2 (1)+ $CH_3COC_2H_5$ (3) system at 313.2K. The data were not available in the literature. As shown in the figure, the mole fraction of CO_2 was monotonously increased with the pressure, and reached the critical point. Thus, the solubility of CO_2 in liquid phase tended to be proportional to the pressure. Otherwise, the mole fraction of CO_2 in the vapor phase had a maximum at 6.04MPa. The critical point of CO_2 (1) + $CH_3COC_2H_5$ (3) system seems to exist around x_1= 0.983, and P= 8.2MPa at 313.2K. Comparing with CO_2 (1) + C_2H_5OH(2) system, CO_2 is well dissolved in $CH_3COC_2H_5$ in the lower pressure range. However, the solubility of CO_2 for C_2H_5OH became larger near the critical point.

Figure 5 shows the VLE for C_2H_5OH (2) + $CH_3COC_2H_5$ (3) system at 313.15K. For the system, Garriga et al. [7] reported just the bubble point pressure at the same temperature. In the figure, the data of Garriga et al. [7] were also illustrated. As shown in the figure, the experimental bubble point pressures were higher than those of Garriga et al. [7]. So, the thermodynamic consistency test was adopted for the experimental data. The test employed was Herington's area test by use of activity coefficients [8]. The test indicates that the experimental VLE was consistent.

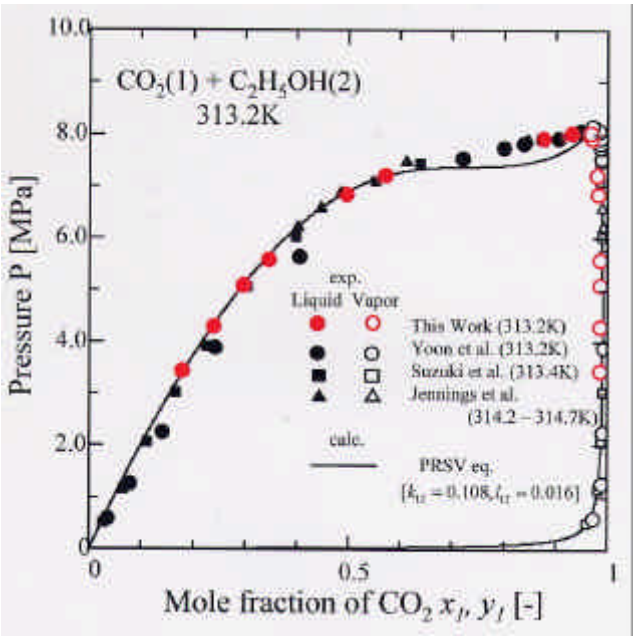


Figure 3. VLE for the CO_2 (1) + C_2H_5OH (2) system at 313.2K

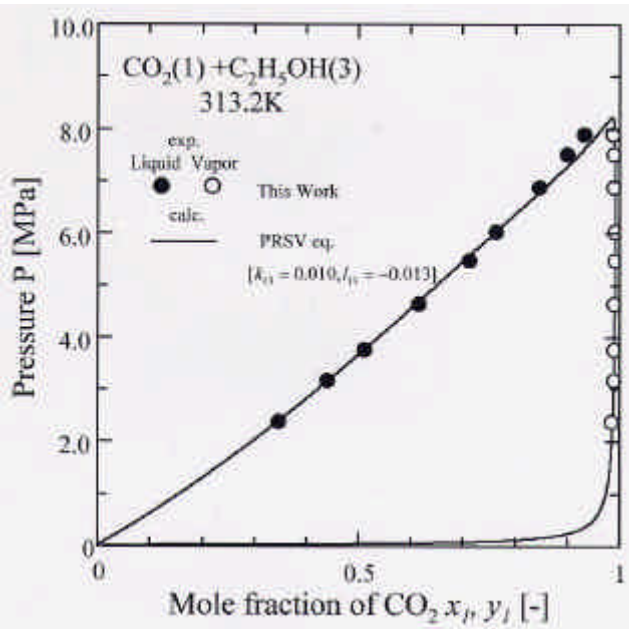


Figure 4. VLE for the CO_2 (1) + $CH_3COC_2H_5$ (3) system at 313.15K

In the figure, the normal boiling point of C_2H_5OH (2) is higher than that of $CH_3COC_2H_5$ (3). However, the vapor pressure of $CH_3COC_2H_5$ (3) was larger than that of C_2H_5OH (2) at the experimental temperature. As shown in the figure, the azeotropic point can be seen around x_2=0.41, P=0.0265MPa.

Figure 6 shows the VLE for CO_2(1)+ C_2H_5OH (2) + $CH_3COC_2H_5$ (3) system at 313.15K. In the figure, the feed planes at the preparation were also illustrated. In the ternary systems, the pressure dependence of the liquid composition was similar to that of CO_2 (1) + $CH_3COC_2H_5$ (2) system. To make clear the distribution of C_2H_5OH for the vapor and liquid phase, Figure 7 shows the pressure dependence of CO_2 free mol fraction of C_2H_5OH. In case of C_2H_5OH (2) : $CH_3COC_2H_5$ (3) =25:75 at the preparation, C_2H_5OH was distributed in the vapor phase in the whole range of pressure. In case of C_2H_5OH (2): $CH_3COC_2H_5$ (3) =25:75 at the preparation, C_2H_5OH was distributed to the liquid phase at the pressure lower than 6.51MPa. Otherwise, C_2H_5OH was distributed to the vapor phase at the pressure higher than 6.51MPa. Thus, a singular point, showing no selectivity, was existed except for the azeotropic point and the critical point.

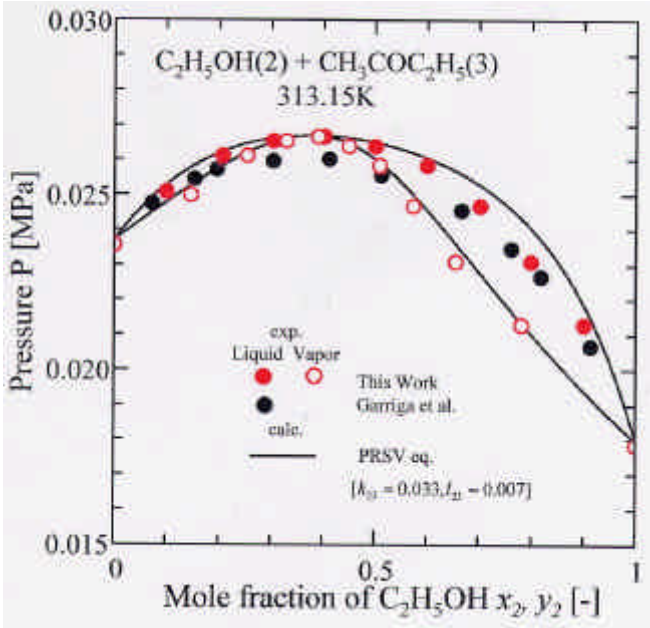


Figure 5. VLE for the C_2H_5OH (1) + $CH_3COC_2H_5$ (3) system at 313.15K

The experimental data were correlated with improved version of Peng-Robinson equation of state proposed by Stryjek et al. (PRSV eq.) [9].

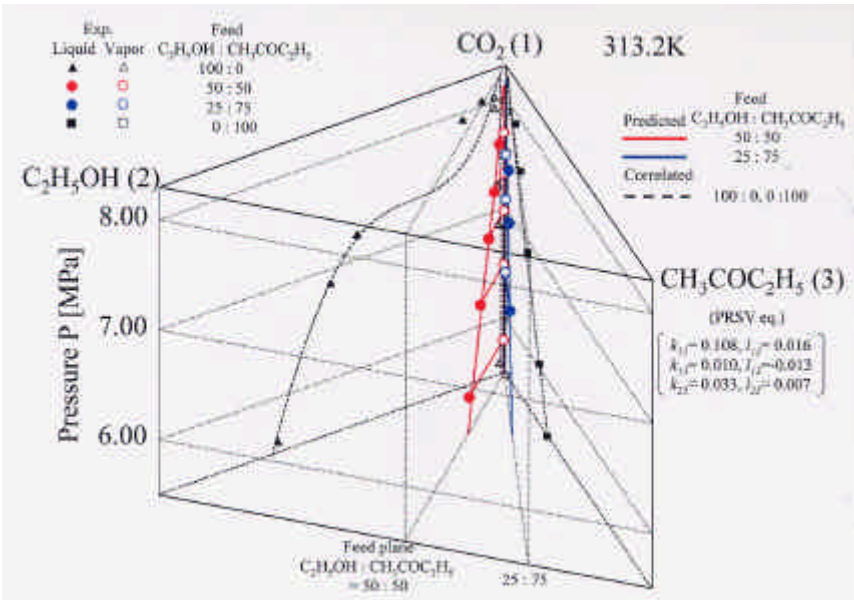


Figure 6. VLE for the CO_2 (1) + C_2H_5OH (2) + $CH_3COC_2H_5$ (3) system at 313.15K

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

The mixing rules employed were Adachi-Sugie type ones [10].

$$a = \sum_i \sum_j x_i x_j [1 - k_{ij} + l_{ij}(x_i - x_j)](a_i a_j)^{0.5} \quad (2) \quad b = \sum_i \sum_j x_i x_j \frac{b_i + b_j}{2} \qquad (3)$$

where the binary parameters, k_{ij}, and l_{ij} , were optimized by using the experimental binary data. The calculation results are shown in Figures 3, 4, and 5. The calculation agreed well with the experimental binary data.

Using the optimized parameters, the VLE was calculated for the ternary system. Figures 6, and 7 show the calculation for the ternary system. Though some degree of discrepancy can be seen in the figures, the calculation shows the same tendency with the experimental data.

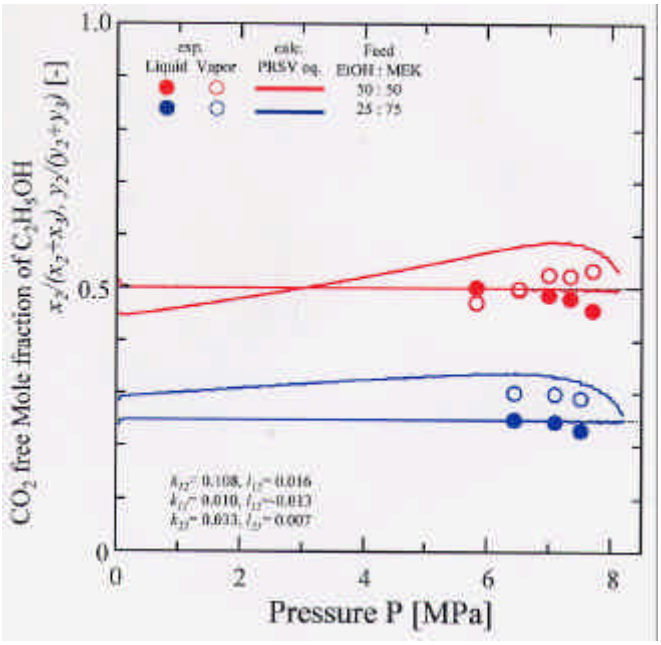


Figure 7. Distribution of C_2H_5OH (2) for the vapor and liquid phase

REFFERNCES

[1]Arai, Y., Sako, T., Takebayashi, Y., “Supercritical Fluids –Molecular Interactions, Physical Properties, and New Applications-”, Springer, Berlin, **2002** [2]Hiaki, T, Miyagi, H., Tsuji, T., and Hongo, M., J. Supercritical Fluids, Vol. 13, **1998**, p.23 [3] Tsuji, T., Hiaki, T., Hongo, M., Ind. Eng. Chem. Res., Vol. 37, **1998**, p. 1685 [4] Yoon J. H., Lee, H. S., Huen, L., J. Chem. Eng. Data, Vol. 38, **1993**, p. 53 [5] Suzuki, K., Sue, H., Itou, M. Smith, R. L., Inomata, H., Arai, K., Saito, S., J. Chem. Eng. Data, Vol. 35, **1990**, p.63 [6] Jennings, D. W., Lee, R. J., Teja, A. S., J. Chem. Eng. Data, Vol. 36, **1991**, p. 303 [7] Garriga, R., Sanchez, F., Perez, P., Gracia, M., J. Chem. Thermodyn., Vol. 28, 1996, p. 567 [8]Herington E. F. G., J. Inst. Petrol., Vol. 37, **1951**, p.457 [9]Stryjek, R., Vera, J. H., Can. J. Chem. Eng. Vol. 64, **1986**, p. 323 [10]Adachi, Y., Sugie, H., Fluid Phase Equilibria, Vol. 28, **1986**, p.103