Korean J. Chem. Eng., **19**(6), 1007-1013 (2002)

High Pressure Phase Behavior for Carbon Dioxide-1-Butanol and Carbon Dioxide-1-Octanol Systems

Hun-Soo Byun† **and Chul Kwak***

Department of Chemical Engineering, Yosu National University, Yosu, Chonnam 550-749, South Korea
*School of Chemical Engineering, Kyungnam University, Masan, Kyungnam 550-701, South Korea

(*Received 13 June 2002 • accepted 31 July 2002*)

Abstract−Pressure-composition isotherms are obtained for binary mixtures of carbon dioxide-1-butanol and carbon dioxide-1-octanol systems at 40, 60, 80, 100, and 120 °C and pressures up to 220 bar. The accuracy of the experimental apparatus was tested by comparing the measured phase equilibria data of the carbon dioxide-1-butanol system at 40 °C with those of Ishihara et al. [1996]. The solubility of 1-butanol and 1-octanol for the carbon dioxide-1-butanol and carbon dioxide-1-octanol systems increases as the temperature increases at constant pressure. The carbon dioxide-1-butanol and carbon dioxide-1-octanol systems have continuous critical mixture curves that exhibit maximums in pressure at temperatures between the critical temperatures of carbon dioxide- and 1-butanol or 1-octanol. The carbon dioxide-1-butanol system exhibits type-I phase behavior, characterized by a continuous critical line from pure carbon dioxide, to the second component with a maximum in pressure. Also, the carbon dioxide-1-octanol system exhibits type-I curve at 60-120 °C, and shows liquid-liquid-vapor phase behavior at 40 °C. The experimental results for the carbon dioxide-1-butanol and carbon dioxide-1-octanol systems have been modeled by the Peng-Robinson equation of state. A good fit of the data is obtained with the Peng-Robinson equation by using two adjustable interaction parameters for the carbon dioxide-1-butanol system and a poor fit using two adjustable parameters for the carbon dioxide-1-octanol mixture.

Key words: Phase Behavior, Carbon Dioxide-1-Butanol System, Carbon Dioxide-1-Octanol System, Peng-Robinson Equation of State

INTRODUCTION

Phase behavior experiments for mixtures containing supercritical fluids are required for practical uses such as in plant design and operation of separation process in the petroleum, natural gas and related application fields. The bubble-, critical- and dew-point behavior of mixtures containing supercritical carbon dioxide is important for industrial application [Lee and Kim, 2002], supercritical fluid extraction [Hwang et al., 1995] and process design [McHugh and Krukonis, 1993]. Phase behavior experiments for mixtures containing supercritical carbon dioxide have recently been performed for bubble-, dew- and critical-point behavior [Byun, 1999, 2002; Byun and Kwak, 2000; Byun et al., 2000; Byun and Jeon, 2000]. The advance of supercritical fluid extraction development is often dependent on new thermodynamics data on vapor-liquid, liquid-liquid-vapor, and liquid-liquid equilibria. However, it is important to determine three-phase equilibria in the binary system.

Phase behavior relations with the carbon dioxide-1-butanol system were reported by Ishihara et al. [1996] at 40 °C, King et al. [1983] at 40 °C and Jennings et al. [1991] at 41.65 °C. Ishihara et al. [1996] used a static-circulation apparatus, and reported no three-phase separation. King et al. [1983] used a recirculation type and presented the liquid-liquid-vapor curves in the vicinity of the critical region. Jennings et al. [1991] used a flow apparatus and reported no three (liquid-liquid-vapor) phase behavior.

The first part of this work is a high-pressure experiment for carbon dioxide-1-butanol and carbon dioxide-1-octanol mixtures by investigating mixtures of carbon dioxide with two polar components: 1-butanol, which has a dipole moment of 1.8 D [Reid et al., 1987] and 1-octanol, which is expected to have a large dipole moment of 2.0 D [Daubert et al., 1992]. Also presented is a portion of the pressure-temperature (P-T) trace of the mixture critical curve for the carbon dioxide-1-butanol and carbon dioxide-1-octanol systems measured in the vicinity of the critical point of pure carbon dioxide. Recently, Byun et al. [2000, 2002] performed phase behavior experiments for mixtures containing carbon dioxide and polar solutes.

It has long been known that three-phase, liquid-liquid-vapor regions occur with carbon dioxide - alcohol systems and with low-molecular-weight hydrocarbon solvent - alcohol mixtures near the critical of the solvent [Rowlinson and Swinton, 1982; Mallett et al., 1983; Diguet et al., 1987; Brunner and Hultenschmidt, 1990; Hasch et al., 1994]. A detailed description of the characteristics of this type of phase behavior can be found in Scott and Konynenburg [1970] and McHugh and Krukonis [1993]. Also, to provide phase behavior information for high pressure process design purposes, the measured bubble-, critical- and dew-point data of binary systems is modeled by using the Peng-Robinson equation of state. These results can provide valuable information for rational design and operation of the supercritical region.

EXPERIMENTAL SECTION

1. Apparatus and Procedure

Fig. 1 shows a schematic diagram of the experimental apparatus [Byun et al., 1996; Byun and McHugh, 2000]. The main compo-

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†To whom correspondence should be addressed.
E-mail: hsbyun@yosu.ac.kr

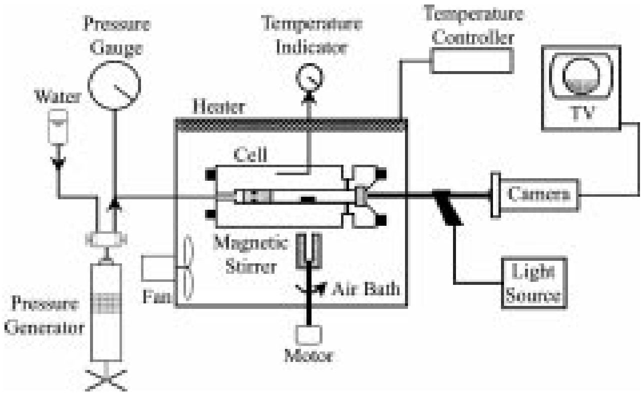

Fig. 1. Schematic diagram of the high-pressure experimental apparatus used in this study.

nent of the experimental apparatus is a high pressure, variable-volume cell which is constructed of a high-nickel-content austenitic steel (Nitronic 50®, 5.7 cm O.D., 1.59 cm I.D., a working volume of ~28 cm^3) and is capable of operating up to pressure of 2,000 bar. A 1.9 cm thick sapphire window is fitted in the front part of the cell to allow observation of the phases. Typically, liquid 1-butanol or 1-octanol is loaded into the cell to within ±0.002 g by using a syringe after the empty cell is purged several times with carbon dioxide to remove air. Carbon dioxide is then added to the cell to within ±0.004 g by using a high pressure bomb.

The solution in the cell was compressed to the desired pressure by moving a piston located within the cell. The piston was moved by using water pressurized by a high pressure generator (HIP, Model 37-5.75-60) The pressure of the mixture was measured with a Heise gauge (Dresser Ind., model CM-53920, 0 to 340 bar) accurate to ±0.3 bar. The temperature of the cell, which was typically maintained to within ±0.2 °C, was measured with a platinum-resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (Yokogawa, model 7563, accurate to ±0.005%). The mixture inside the cell can be viewed on a video monitor by using a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window. A fiber optic cable connected to a high density illuminator (Dolan-Jenner Industries, Inc., model 180) and to the borescope was used for transmitting light into the cell. The solution in the cell was well mixed by using a magnetic stir bar activated by an external motor beneath the cell.

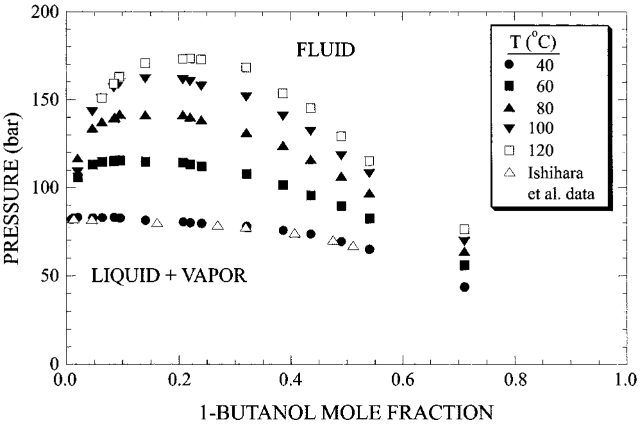

Fig. 2. Experimental isotherms for the carbon dioxide-1-butanol system obtained at 40, 60, 80, 100, and 120 °C.

At a fixed temperature, the solution in the cell was compressed to a single phase. The solution was maintained in the single phase region at the desired temperature for at least 30 min for the cell to reach phase equilibrium. The pressure was then slowly decreased until the second phase appeared. A bubble point pressure was obtained when small bubbles appeared in the cell, and a dew point was obtained if a fine mist appeared in the cell. In either case, the composition of the predominant phase present in the cell was equal to

Table 1. The pressure-composition isotherms data for the carbon dioxide-1-butanol system. BP: Bubble Point, CP: Critical Point, DP: Dew Point

1-Butanol mole fraction	Pressure (bar)	Transition
T=40 °C		
0.710	43.8	BP
0.540	64.8	BP
0.490	69.3	BP
0.435	75.5	BP
0.386	77.6	BP
0.320	79.7	BP
0.240	80.7	BP
0.220	81.5	BP
0.207	82.0	BP
0.140	82.5	BP
0.095	82.8	BP
0.094	82.7	BP
0.086	82.9	BP
0.085	83.0	BP
0.063	82.9	BP
0.047	82.9	BP
0.020	83.1	BP
0.013	83.8	BP
0.009	83.1	DP
T=60 °C		
0.710	55.9	BP
0.540	82.4	BP
0.490	89.7	BP
0.435	95.2	BP
0.386	101.7	BP
0.320	107.9	BP
0.240	112.3	BP
0.220	113.5	BP
0.207	114.3	BP
0.140	115.0	BP
0.095	115.5	BP
0.094	115.7	BP
0.086	115.8	BP
0.085	115.1	BP
0.063	114.8	BP
0.047	113.4	DP
0.020	105.9	DP

Table 1. Continued

1-Butanol mole fraction	Pressure (bar)	Transition
T=80 °C		
0.710	63.8	BP
0.540	96.9	BP
0.490	106.6	BP
0.435	116.2	BP
0.386	124.1	BP
0.320	131.4	BP
0.240	138.6	BP
0.220	140.3	BP
0.207	141.4	BP
0.140	141.5	BP
0.095	141.6	BP
0.094	141.7	CP
0.086	140.3	DP
0.085	139.7	DP
0.063	137.6	DP
0.047	134.1	DP
0.020	116.9	DP
T=100 °C		
0.710	69.3	BP
0.540	107.9	BP
0.490	118.3	BP
0.435	132.1	BP
0.386	140.7	BP
0.320	151.4	BP
0.240	157.6	BP
0.220	160.3	BP
0.207	161.3	BP
0.140	161.9	CP
0.095	159.6	DP
0.094	159.3	DP
0.086	157.1	DP
0.085	156.8	DP
0.063	150.7	DP
0.047	143.1	DP
0.020	109.0	DP
T=120 °C		
0.710	76.2	BP
0.540	115.2	BP
0.490	129.3	BP
0.435	145.2	BP
0.386	153.5	BP
0.320	168.3	BP
0.240	172.7	BP
0.220	173.3	BP
0.207	173.0	CP
0.140	170.7	DP
0.095	163.0	DP
0.093	162.8	DP
0.086	159.0	DP
0.085	159.0	DP
0.063	151.0	DP

the overall solution composition as the amount of mass present in the second phase was considered negligible. Critical points were obtained by adjusting the temperature and pressure of the mixture until critical opalescence was observed along with equal liquid and vapor volume upon the formation of the second phase.

2. Materials

Carbon dioxide was obtained from Daesung Oxygen Co. (99.9% minimum purity) and used as received. The 1-butanol (99% purity) and 1-octanol (99% purity) used in this work were obtained from Junsei Chemical Co. and Aldrich Co., respectively. Both components were used without further purification in the experiments.

EXPERIMENTAL RESULTS AND DISCUSSION

Bubble, critical, and dew point data for both the carbon dioxide-1-butanol and carbon dioxide-1-octanol systems are measured and reproduced at least twice to within ±0.3 bar and 0.2 °C for a given loading of the cell. The mole fractions are accurate to ±0.002.

The carbon dioxide-1-butanol and carbon dioxide-1-octanol mole fraction for the solubility isotherms at 40-125 °C are arranged according to the value of at least two independent data points that have an estimated accumulated error of less than ±1.0%.

Fig. 2 and Table 1 show the experimental pressure-composition (P-x) isotherms at 40, 60, 80, 100 and 120 °C, and the range of pressures of 19-132 bar for the carbon dioxide-1-butanol system. In order to check the accuracy and reproducibility of the experimental apparatus, we measured phase behavior data for binary carbon dioxide-1-butanol mixture which was measured by Ishihara et al. [1996] at 40 °C.

As shown in Fig. 2, the experimental data presented are in good agreement with those of Ishihara et al. [1996]. In Fig. 2, three phases were not observed at any of the five temperatures studied. Although the characteristics of the P-x isotherms appear to be consistent with those expected for a type-I system, the lowest temperature isotherm is too far away from the critical point of pure carbon dioxide for us to make any definitive statement concerning whether this mixture indeed exhibits type-I behavior [McHugh and Krukonis, 1993; Scott and Konynenburg, 1970].

Fig. 3 and Table 2 show the experimental phase behavior of P-x isotherms at 40, 60, 80, 100, and 120 °C for the carbon dioxide-1-

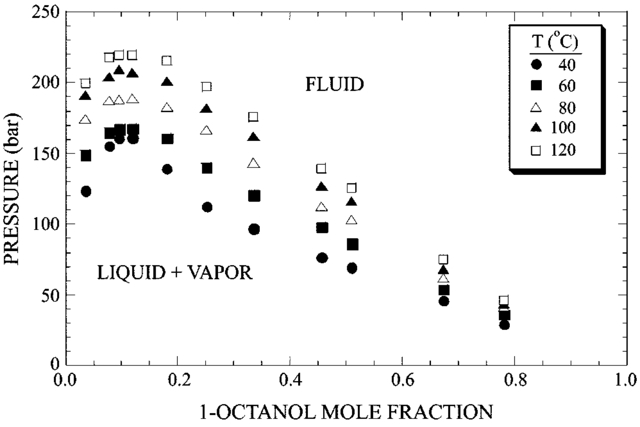

Fig. 3. Experimental isotherms for the carbon dioxide-1-octanol system obtained at 40, 60, 80, 100, and 120 °C.

octanol system. The P-x isotherms shown in Fig. 3 are consistent with the characteristics expected for a type-I system where a maximum occurs in the critical mixture curve at 40, 60, 80, 100 and 120 °C. As shown in Fig. 3, this system is observed for three-phase behavior at 40 °C. The solubility of carbon dioxide for carbon dioxide-1-octanol system decreases as the temperature increases at constant pressure. Also, the mixture-critical points for the carbon dioxide-

Table 2. The pressure-composition data for the carbon dioxide-1-octanol system. BP: Bubble Point, CP: Critical Point, DP: Dew Point

1-Octanol mole fraction	Pressure (bar)	Transition
T=40 °C		
0.780	29.3	BP
0.673	46.6	BP
0.509	69.3	BP
0.456	76.6	BP
0.335	96.9	BP
0.251	124.5	BP
0.181	139.7	BP
0.119	161.0	BP
0.095	160.3	BP
0.077	154.8	BP
0.035	123.8	BP
T=60 °C		
0.780	36.2	BP
0.673	54.1	BP
0.509	86.2	BP
0.456	98.3	BP
0.335	121.0	BP
0.251	140.3	BP
0.181	160.7	BP
0.119	167.6	BP
0.095	167.2	BP
0.077	165.2	BP
0.035	149.3	BP
T=80 °C		
0.780	41.7	BP
0.673	62.4	BP
0.509	103.1	BP
0.456	112.2	BP
0.335	143.5	BP
0.251	166.6	BP
0.181	182.4	BP
0.119	188.6	BP
0.095	187.9	BP
0.077	187.2	CP
0.035	174.5	DP
T=80 °C		
0.780	41.7	BP
0.673	62.4	BP
0.509	103.1	BP
0.456	112.2	BP
0.335	143.5	BP
0.251	166.6	BP
0.181	182.4	BP
0.119	188.6	BP
0.095	187.9	BP
0.077	187.2	CP
0.035	174.5	DP
T=100 °C		
0.780	44.1	BP
0.673	68.3	BP
0.509	116.2	BP
0.456	127.2	BP
0.335	162.1	BP
0.251	181.7	BP
0.181	201.4	BP
0.119	207.2	BP
0.095	209.3	CP
0.077	203.8	DP
0.035	191.4	DP
T=120 °C		
0.780	46.6	BP
0.673	75.2	BP
0.509	125.9	BP
0.456	139.7	BP
0.335	175.2	BP
0.251	196.9	BP
0.181	215.5	BP
0.119	219.7	CP
0.095	219.7	CP
0.077	218.3	DP
0.035	199.7	DP

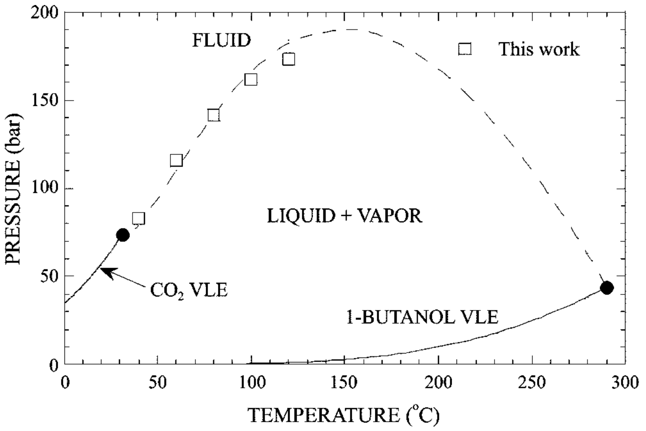

Fig. 4. Pressure-temperature diagram for the carbon dioxide-1-butanol system. The solid line and the solid circles represent the vapor-liquid line and the critical point for pure carbon dioxide and 1-butanol. The open squares are critical points determined from isotherms measured in this study. The dashed line represents calculated values obtained by using the Peng-Robinson equation of state with k_{ij} equal to 0.068 and η_{ij} equal to −0.045.

1-octanol system increases as the temperature increases.

Fig. 4 presents the experimentally determined pressure-temperature (P-T) trace of the mixture critical curve in the vicinity of the critical point of carbon dioxide [Reid et al., 1987; Daubert and Danner, 1985-1992; Vargaftik, 1983]. The 1-butanol is a very polar, and 1-butanol can form linear, hydrogen-bonded multimers [Prausnitz et al., 1986]. The mixture critical curves of the dashed lines in the Fig. 4 represent calculation obtained by using the Peng-Robinson equation of state which is discussed later. There were no three-phase regions observed during the gathering of either P-x or P-T data for the carbon dioxide-1-butanol system. Also, the calculated mixture critical curve of carbon dioxide-1-butanol system is type-I behavior, in agreement with the experimental observation.

The experimental data obtained in this work is modeled by using the Peng-Robinson equation of state. This equation is briefly described here. The Peng-Robinson equation [1976] of state is used with the following mixing rules:

$$a_{mix}=\sum_i\sum_j x_i x_j a_{ij}$$

$$a_{ij}=(a_{ii}a_{jj})^{1/2}(1-k_{ij})$$

$$b_{mix}=\sum_i\sum_j x_i x_j b_{ij}$$

$$b_{ij}=0.5\lfloor(b_{ii}+b_{jj})\rfloor(1-\eta_{ij})$$

where k_{ij} and η_{ij} are interaction mixture parameters that are determined by fitting pressure-composition data and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson [1976]. The expression for the fugacity coefficient using these mixing rules is given by McHugh and Krukonis [1993] and is not reproduced here. Table 3 lists the pure component critical temperatures, critical pressures, and the acentric factors for carbon dioxide, 1-butanol and 1-octanol that are used with the Peng-Robinson equation of state [Reid et al., 1987; Daubert and Danner, 1985-1992].

Fig. 5 shows a comparison of experimental results of carbon dioxide-1-octanol with calculations of that obtained by using Peng-Robinson equation at a temperature of 80 °C. A reasonable fit of the data is obtained over most of the composition range even if no mixture parameters are used. But if two mixture parameters, k_{ij}= 0.08 and η_{ij}=−0.03, are used the fit of the experimental results is significantly better. We compared experimental results with calculated P-x isotherms at temperatures of 40, 60, 100, and 120 °C for the carbon dioxide-1-octanol system using the adjusted values of k_{ij} and η_{ij} determined at 80 °C. As shown in Fig. 6, a poor fit of the data is obtained with the Peng-Robinson equation by using an adjustable mixture parameter for the carbon dioxide-1-octanol system. This system is a poor fit at four temperatures (40, 60, 100, and 120 °C), except for 80 °C because the 1-octanol component is very large polar and hydrogen-bonding multimer.

Fig. 7 shows a comparison of experimental with calculated P-x

Table 3. Pure component parameters for the Peng-Robinson equation of state[12,13]

Compound	M_w	T_c, K	P_c, bar	ω
Carbon dioxide	44.01	304.3	7.39	0.225
1-Butanol	74.12	563.1	4.42	0.593
1-Octanol	130.23	652.5	2.86	0.587

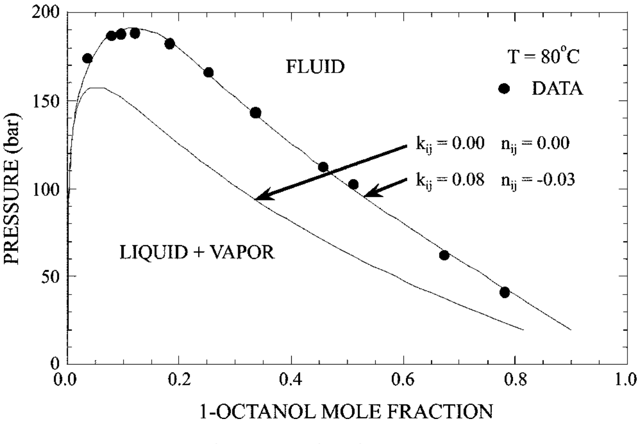

Fig. 5. Comparison of the best fit of Peng-Robinson equation of state to carbon dioxide-1-octanol system obtained in this work.

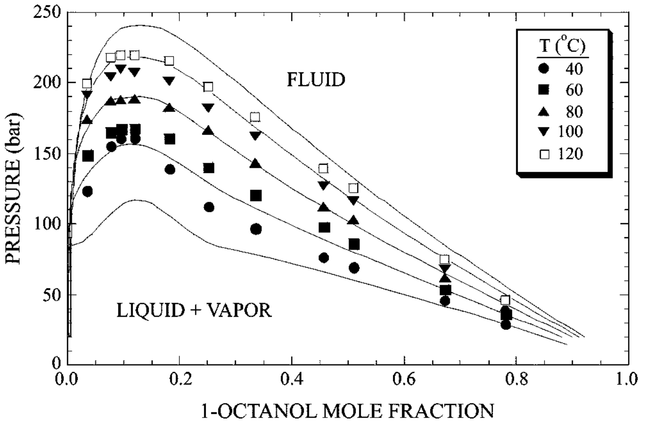

Fig. 6. A comparison of the experimental data (symbols) for the carbon dioxide-1-octanol system with calculations (solid lines) obtained by using the Peng-Robinson equation of state with k_{ij} equal to 0.08 and η_{ij} equal to −0.03.

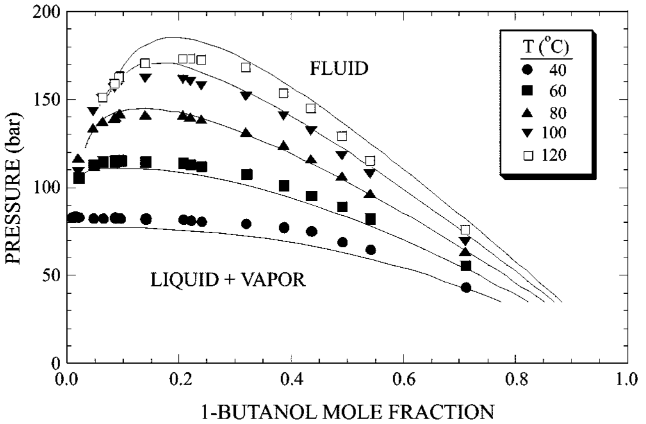

Fig. 7. A comparison of the experimental data (symbols) for the carbon dioxide-1-butanol system with calculations (solid lines) obtained by using the Peng-Robinson equation of state with k_{ij} equal to 0.068 and η_{ij} equal to −0.045.

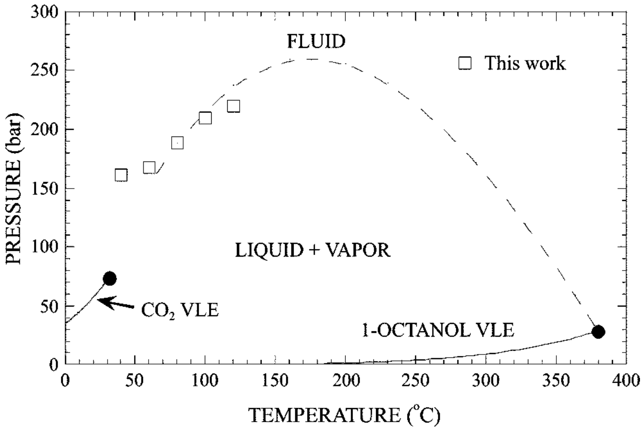

Fig. 8. Pressure-temperature diagram for the carbon dioxide-1-octanol system. The solid line and the solid circles represent the vapor-liquid line and the critical point for pure carbon dioxide and 1-octanol. The open squares are critical points determined from isotherms measured in this study. The dashed line represents calculated values obtained by using the Peng-Robinson equation of state with k_{ij} equal to 0.08 and η_{ij} equal to −0.03.

isotherms at temperatures of 40, 60, 80, 100, and 120 °C for the carbon dioxide-1-butanol system. These isotherms are calculated by using the adjusted values of k_{ij} equal to 0.068 and η_{ij} equal to −0.045 determined at 80 °C in the same way as above.

Fig. 8 shows the mixture-critical curve for the carbon dioxide-1-octanol system predicted by the Peng-Robinson equation of state. The calculated mixture-critical curve is type-I, in agreement with experimental observations at 80 and 100 °C. The carbon dioxide-1-octanol system is observed to have three-phase behavior at 40 °C. As shown in Fig. 8, the solid lines represent the vapor pressure for pure carbon dioxide [Reid et al., 1983; Daubert and Danner, 1985-1992] and 1-octanol [Daubert and Danner, 1985-1992]. The solid circles represent the critical point for pure carbon dioxide and 1-octanol. The upper part of the dashed line is single phase, the lower part is vapor-liquid. The open squares are for the mixture-critical points determined from isotherms measured in this experiment. The dashed lines represent the calculated value obtained by using the Peng-Robinson equation of state. The mixture parameters are then obtained from the case Peng-Robinson equation, with k_{ij} equal to 0.068 and η_{ij} equal to −0.045.

CONCLUSIONS

Pressure-component isotherm data of carbon dioxide-1-butanol and carbon dioxide-1-octanol systems are obtained at 40-125 °C and pressure range of 17-136 bar for binary mixtures. The carbon dioxide-1-butanol systems exhibit type-I phase behavior, which is characterized by an uninterrupted critical-mixture curve. The carbon dioxide-1-octanol system was observed for three-phase behavior at 40 °C. Besides, the carbon dioxide-1-octanol system exhibited type-I phase behavior at 60, 80, 100, and 120 °C for the system studied. The solubility of 1-butanol and 1-octanol for the carbon dioxide-1-butanol and carbon dioxide-1-octanol systems increases as the temperature increases at constant pressure.

The Peng-Robinson equation of state models the pressure-composition isotherms for two carbon dioxide-1-butanol and carbon dioxide-1-octanol systems reasonably well by using independent temperature mixture parameters.

ACKNOWLEDGMENT

This work was supported by the RRC program of MOST and KOSEF through the Research and Development Center for Facility Automation and Information System (FAIS) at Yosu National University. Also, this work is supported by the Kyungnam University Research Fund (2001).

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