

## Phase behavior measurement for the ethylene glycol dimethacrylate in supercritical carbon dioxide at temperatures between (313.2 and 393.2) K and pressures from (5.8 to 22) MPa

Sung-Hyun Kim, Yoon-Seok Jang, and Hun-Soo Byun<sup>†</sup>

School of Biotechnology and Chemical Engineering, Chonnam National University, Yeosu, Jeonnam 550-749, Korea  
(Received 11 March 2010 • accepted 3 May 2010)

**Abstract**—High pressure experimental data are presented on the phase equilibrium of ethylene glycol dimethacrylate in supercritical carbon dioxide. Pressure-composition (P-x) isotherms were measured in static method at five temperatures of (313.2, 333.2, 353.2, 373.2 and 393.2) K and at pressures up to 22.0 MPa. This (carbon dioxide+ethylene glycol dimethacrylate) system has continuous critical mixture curves that exhibit maximums in pressure at temperatures between the critical temperatures of carbon dioxide and ethylene glycol dimethacrylate. At a fixed pressure, the solubility of ethylene glycol dimethacrylate for the (carbon dioxide+ethylene glycol dimethacrylate) system increases with increasing temperature. The (carbon dioxide+ethylene glycol dimethacrylate) system exhibits type-I phase behavior. The experimental result for the (carbon dioxide+ethylene glycol dimethacrylate) system is correlated with Peng-Robinson equation of state using mixing rule including two adjustable parameters. The critical property of ethylene glycol dimethacrylate is predicted with Joback and Lee-Kesler method.

Key words: Carbon Dioxide, Ethylene Glycol Dimethacrylate, Phase Behavior

### INTRODUCTION

Ethylene glycol dimethacrylate is used as a functional monomer for polymers and as a crosslinking agent between the molecular chains of polymers and elastomers. Polymers based on ethylene glycol dimethacrylate monomers is an important use as chromatographic packings in both gas and liquid chromatography. [1] The crosslinked macroporous packings based on ethylene glycol dimethacrylate have a special advantage to the morphological aspects and the macroporous structure [2-4].

The phase behavior for binary mixture of the hydrocarbon with supercritical carbon dioxide plays an important role in the chemical separation process, supercritical fluid extraction, polymerization condition and industrial application [5-7]. Recently, experimental data of phase equilibria have been reported on the bubble-point, dew-point and critical-point behavior of mixtures containing supercritical carbon dioxide [8,9]. The carbon dioxide used in this work is widely used as an environmentally benign solvent which is inexpensive, nonflammable, and nontoxic. Also, supercritical carbon dioxide has a quadrupole moment, no dipole moment, and low dielectric constant. Carbon dioxide is a good solvent with low molecular weight in nonpolar molecules. Therefore, phase behavior information for mixtures containing carbon dioxide is required for practical uses.

Phase behavior data for the carbon dioxide+alkyl methacrylate system were reported by Franceschi et al. [10], Lora and McHugh [11], Zainul Husain et al. [12], and Soares da Silva et al. [13]. Franceschi et al. [10] reported the phase behavior curves for the carbon dioxide+glycidyl methacrylate system at temperature from 303 to

343 K and pressure up to 13 MPa. Lora and McHugh [11] presented the phase behavior for carbon dioxide+methyl methacrylate system at 308.2 K and 348.2 K using a static apparatus. Zainul Husain et al. [12] used a volumetric expansion apparatus and presented the liquid-vapor equilibria curves for carbon dioxide+butyl methacrylate mixture at (323 and 333) K and pressures up to 10 MPa. Soares da Silva et al. [13] reported the phase equilibrium data of a binary system for carbon dioxide+methyl methacrylate and carbon dioxide+2-hydroxyethyl methacrylate systems at (313.15, 323.15 and 338.15) K and pressure up to 21.1 MPa.

The purpose of this work is to obtain the high-pressure experimental data for carbon dioxide+ethylene glycol dimethacrylate mixtures by investigating mixtures of carbon dioxide with a component. Also, the pressure-temperature (P-T) diagram of the mixture critical curve is presented for the carbon dioxide+ethylene glycol dimethacrylate system in the vicinity of the critical point of pure carbon dioxide. The experimental data for the carbon dioxide+ethylene glycol dimethacrylate system obtained in this work are correlated with the Peng-Robinson equation of state [14] using mixing rule including two adjustable parameters. The critical pressure, critical temperature, and acentric factor of ethylene glycol dimethacrylate is estimated by the Joback and Lydersen method with group contributions, while the vapor pressure is estimated by the Lee-Kesler method [15].

### EXPERIMENTAL SECTION

#### 1. Apparatus and Procedure

Fig. 1 shows a schematic diagram of the experimental high pressure, variable-volume view cell used for the phase equilibria measurement. [16] A high-pressure, variable volume view cell (6.2 cm O.D×1.59 cm I.D), a working volume of ~28 cm<sup>3</sup>, is used to obtain

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: hsbyun@chonnam.ac.kr

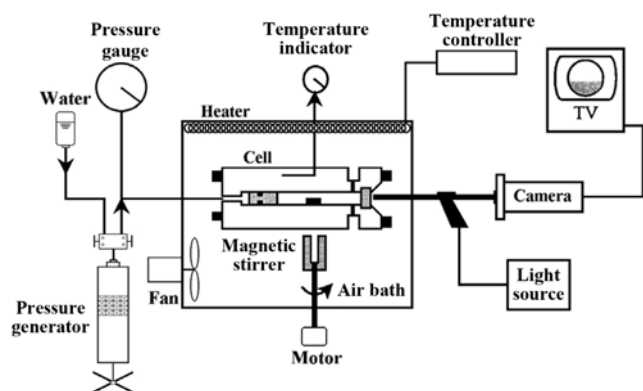


Fig. 1. Schematic diagram of the experimental setup for high pressure phase equilibria measurements.

the bubble-, dew- and critical-point curves, and is capable of operating to pressure of 70.0 MPa. A sapphire window (1.9 cm thick  $\times$  1.9 cm diameter) is fitted in the front part of the cell to allow observation of the phases. The mixture in the cell was compressed to the desired pressure by moving a piston located within the cell. The piston (2.54 cm length) was moved using water pressurized by a high pressure generator (HIP, model 37-5.75-60). The pressure of mixture is measured with a Heise gauge (Dresser Ind., model CM-53920, 0 to 34.0 MPa) accurate to  $\pm 0.02$  MPa. The temperature of the cell, which is typically maintained to within  $\pm 0.2$  K, is measured with a platinum-resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (Yokogawa, model 7563, accurate to  $\pm 0.005\%$ ). 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. Typically, supercritical carbon dioxide is added to the cell to within  $\pm 0.002$  g by using a high pressure cylinder. The monomer is loaded into the cell to within  $\pm 0.001$  g with a syringe after the empty cell is purged several times with carbon dioxide and nitrogen to remove traces of air and organic matter.

At a fixed temperature, the solution in the cell is compressed to a single phase. The inside solution is maintained in the single phase region at the desired temperature for at least 30–40 min for the cell to reach phase equilibrium. The pressure is then slowly decreased until a second phase appears. A bubble point pressure is obtained when small vapor bubbles appear first in the cell, while a dew point is obtained if a fine mist appears in the cell. Critical points are obtained by adjusting the temperature and pressure of the mixture until critical opalescence is observed along with equal liquid and vapor volume upon the formation of the second phase. The vicinity region of mixture-critical point is sensitive for a slight change in either pressure or temperature. A slight change in pressure (or temperature) for the mixture-critical point causes a dramatic change in the amount of one phase or two phases present in the cell [17].

## 2. Materials

Ethylene glycol dimethacrylate (>98 wt% purity, CAS RN 97-90-5,  $C_{10}H_{14}O_4/CH_2=C(CH_3)C(O)OCH_2CH_2OC(O)C(CH_3)=CH_2$ ) used in this work was obtained from Scientific Polymer Products, Inc. A component was used without further purification in the experiments. Carbon dioxide (99.8 wt% purity) was obtained from Daesung Industrial Gases Co. and used as received.

## RESULTS AND DISCUSSION

High pressure phase behavior data for the ethylene glycol dimethacrylate in supercritical carbon dioxide are measured and reproduced at least twice to within  $\pm 0.02$  MPa and  $\pm 0.2$  K for a given loading of the cell. The mole fractions are accurate to within  $\pm 0.002$ .

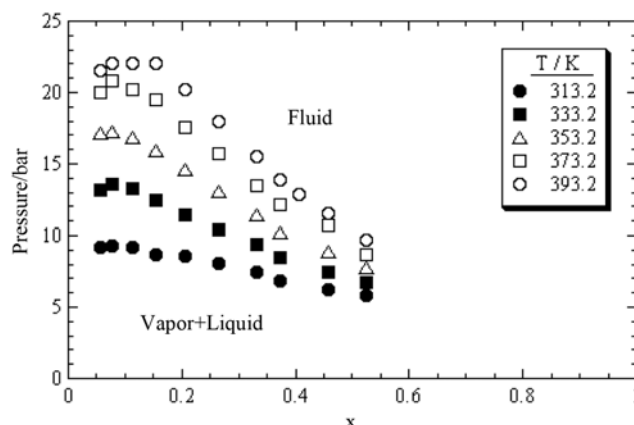


Fig. 2. Plot of pressure against mole fraction to illustrate the experimental data (symbols) for the (carbon dioxide+ethylene glycol dimethacrylate)  $\{(1-x) CO_2 + x CH_2=C(CH_3)C(O)OCH_2CH_2OC(O)C(CH_3)=CH_2\}$  system.  $\bullet$ , 313.2 K;  $\blacksquare$ , 333.2 K;  $\triangle$ , 353.2 K;  $\square$ , 373.2 K;  $\circ$ , 393.2 K.

Table 1. Experimental data of pressure-composition isotherms for (carbon dioxide+ethylene glycol dimethacrylate)  $\{(1-x) CO_2 + x CH_2=C(CH_3)C(O)OCH_2CH_2OC(O)C(CH_3)=CH_2\}$  system. BP is bubble point, DP is dew point and CP is critical point

x	p/MPa	Transition
T=313.2 K		
0.525	5.83	BP
0.457	6.22	BP
0.373	6.79	BP
0.332	7.48	BP
0.264	8.10	BP
0.206	8.55	BP
0.155	8.69	BP
0.113	9.21	BP
0.079	9.31	BP
0.058	9.17	BP
T=333.2 K		
0.525	6.72	BP
0.457	7.46	BP
0.373	8.52	BP
0.332	9.35	BP
0.264	10.38	BP
0.206	11.41	BP
0.155	12.41	BP
0.113	13.28	BP
0.079	13.59	BP
0.058	13.21	DP

Table 1. Continued

x	p/MPa	Transition
T=353.2 K		
0.525	7.72	BP
0.457	8.88	BP
0.373	10.24	BP
0.332	11.41	BP
0.264	13.03	BP
0.206	14.62	BP
0.155	15.97	BP
0.113	16.86	BP
0.079	17.28	BP
0.058	17.14	DP
T=373.2 K		
0.525	8.66	BP
0.457	10.72	BP
0.373	12.17	BP
0.332	13.48	BP
0.264	15.69	BP
0.206	17.59	BP
0.155	19.45	BP
0.113	20.17	BP
0.079	20.86	CP
0.058	20.03	DP
T=393.2 K		
0.525	9.66	BP
0.457	11.57	BP
0.407	12.81	BP
0.373	13.93	BP
0.332	15.48	BP
0.264	17.97	BP
0.206	20.17	BP
0.155	22.03	BP
0.113	22.00	CP
0.079	22.03	DP
0.058	21.55	DP

Fig. 2 and Table 1 show the experimental pressure-composition P, x isotherms at T=(313.2, 333.2, 353.2, 373.2 and 393.2) K, and pressures from (5.83 to 22.03) MPa for the (carbon dioxide+ethylene glycol dimethacrylate) system. Three phases were not observed at five temperatures. As shown in Fig. 1, the mixture critical pressures are 20.86 MPa (at T=373.2 K), and 22.00 MPa (at T=393.2 K). The (P-x) isotherms shown in Fig. 2 are consistent with those expected for a type-I system [17,18] where a maximum occurs in

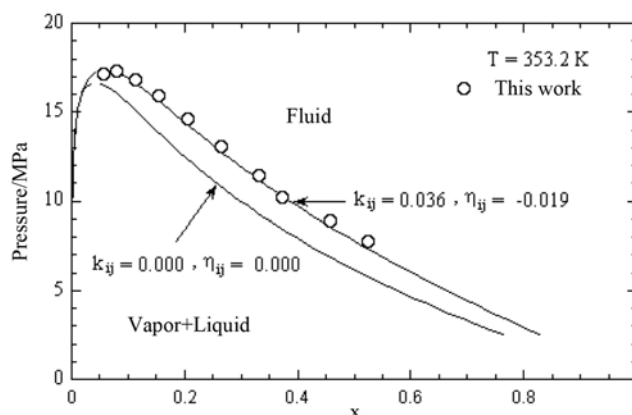


Fig. 3. Plot of pressure against mole fraction to illustrate the comparison of experimental data (symbols) for the (carbon dioxide+ethylene glycol dimethacrylate)  $\{(1-x) \text{ CO}_2 + x \text{ CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2\}$  with calculation obtained from the Peng-Robinson equation of state by  $k_{ij}$  and  $\eta_{ij}$  set equal to zero (dashed lines), and  $k_{ij}=0.036$ ,  $\eta_{ij}=-0.019$  (carbon dioxide+ethylene glycol dimethacrylate) at 353.2 K.

the critical mixture curve. The solubility of carbon dioxide decreases as temperatures shift higher under the constant pressure.

In this work, the experimental phase behavior data are correlated with the Peng-Robinson equation of state. The Peng-Robinson equation of state [14] is used with the following mixing rules:

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

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij})$$

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

$$b_{ij} = 0.5[(b_i + b_j)](1 - \eta_{ij})$$

where  $k_{ij}$  and  $\eta_{ij}$  are binary interaction parameters that are determined by fitting (P-x) isotherms curves and  $a_i$  and  $b_i$  are pure component parameters as defined by Peng and Robinson [11]. Objective function (OBF) and root mean squared relative deviation (RMSD) percent of this calculation were defined by,

$$\text{OBF} = \sum_i^N \left( \frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2$$

$$\text{RMSD} (\%) = \sqrt{\frac{\text{OBF}}{\text{ND}}} \times 100$$

ND means the number of experimental data points and  $P_{\text{exp}}$  and  $P_{\text{cal}}$  are the experimental and calculated pressures, respectively. We used

Table 2. The properties of pure component

Components	Molecular weight	Molecular structure	Boiling point/K	T <sub>c</sub> /K	P <sub>c</sub> /MPa	$\omega$
Carbon dioxide	44.01	O=C=O	304.2	313.2	7.38	0.225
Ethylene glycol dimethacrylate	198.22		513.2	692.0	2.32	0.679

Marquardt [19] to optimize the objective function. Table 2 lists the pure component critical temperatures ( $T_c$ ), critical pressures ( $P_c$ ), and the acentric factors ( $\omega$ ) for carbon dioxide, [15] ethylene glycol dimethacrylate [15] that are used with the Peng-Robinson equation of state. The boiling points are obtained by the Scientific Polymer Products, Inc. The properties of ethylene glycol dimethacrylate were calculated by the Joback group-contribution method [15]. Also, the vapor pressures were calculated by the Lee-Kesler method [15].

Fig. 3 shows the comparison between experimental results of carbon dioxide+ethylene glycol dimethacrylate system and calculated value obtained using Peng-Robinson equation at a temperature of  $T=353.2$  K. The binary interaction parameters of the Peng-

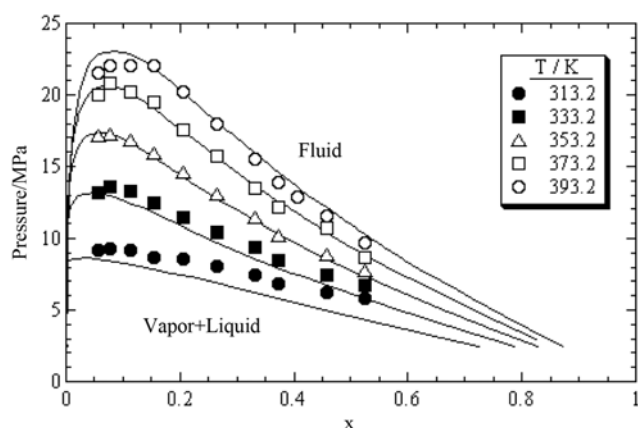


Fig. 4. Plot of pressure against mole fraction to illustrate the comparison of the experimental data (symbols) for the (carbon dioxide+ethylene glycol dimethacrylate)  $\{(1-x) \text{CO}_2 + x \text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2\}$  system with calculations (solid lines) obtained with the Peng-Robinson equation of state  $k_{ij}$  equal to 0.036 and  $\eta_{ij}$  equal to -0.019. ●, 313.2 K; ■, 333.2 K; △, 353.2 K; □, 373.2 K; ○, 393.2 K.

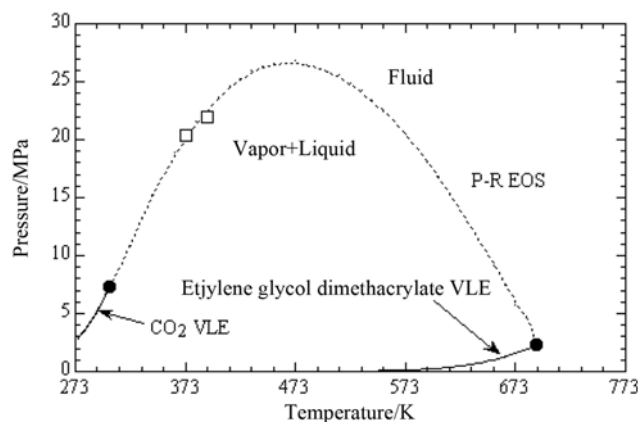


Fig. 5. Plot of pressure against temperature for the (carbon dioxide+ethylene glycol dimethacrylate) system. The solid lines and the solid circles represent the vapor-liquid lines and the critical points for pure carbon dioxide and ethylene glycol dimethacrylate. The open squares are critical points determined from isotherms measured in this work. The dashed lines represent calculations obtained using Peng-Robinson equation of state with  $k_{ij}$  equal to 0.036 and  $\eta_{ij}$  equal to -0.019.

Robinson equation of state are fitted by the experimental data at  $T=353.2$  K. The values of optimized parameters of the Peng-Robinson equation of state for the (carbon dioxide+ethylene glycol dimethacrylate) systems are  $k_{ij}=0.036$  and  $\eta_{ij}=-0.019$  (RMSD=2.43%, data point no.=10).

Fig. 4 compares experimental results with calculated  $P, x$  isotherms at temperatures of  $T=(313.2, 333.2, 353.2, 373.2$  and  $393.2)$  K for the (carbon dioxide+ethylene glycol dimethacrylate) system using the optimized values of  $k_{ij}=0.036$  and  $\eta_{ij}=-0.019$  determined at  $T=353.2$  K. As shown in Fig. 3, a reasonable fit of the data is obtained with Peng-Robinson equation using an adjustable mixture parameter for the (carbon dioxide+ethylene glycol dimethacrylate) system. The calculated curves by Peng-Robinson equation of state were not observed of three phases at five temperatures.

Fig. 5 compares the mixture-critical curves of the experimental data with calculated values by the Peng-Robinson equation of state for the (carbon dioxide+ethylene glycol dimethacrylate) system. The calculated mixture-critical curve is type-I, in good agreement with experimental observations at five temperatures. In Fig. 5, the solid lines represent the vapor pressure for pure carbon dioxide [15] and ethylene glycol dimethacrylate [15]. The solid lines representing the vapor pressure of pure ethylene glycol dimethacrylate were obtained by Lee-Kesler method [15]. The solid circles represent the critical point for pure carbon dioxide and ethylene glycol dimethacrylate. The upper part of the dashed line is single phase (fluid), the lower part vapor-liquid (two-phases). The dashed lines represent the calculated value obtained using the Peng-Robinson equation of state, with  $k_{ij}=0.036$  and  $\eta_{ij}=-0.019$  (ethylene glycol dimethacrylate). The open squares are for the mixture-critical points determined from isotherms measured in this experiment.

Fig. 6 plots pressures against mole fraction to illustrate the comparison of the experimental data (symbols) for the (carbon dioxide+ethylene glycol dimethacrylate) system with calculations (solid lines) obtained with the Peng-Robinson equation of state at each temper-

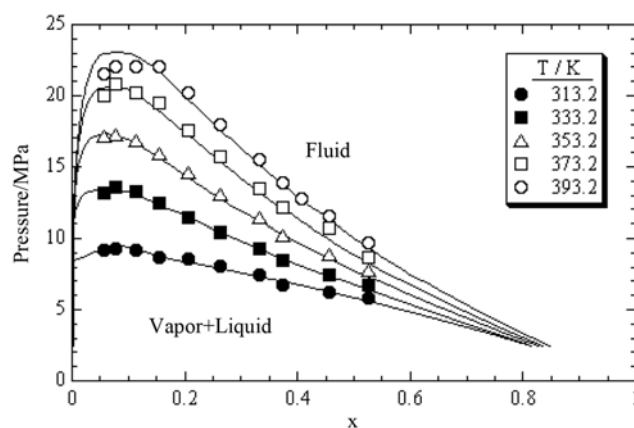


Fig. 6. Plot of pressure against mole fraction to illustrate the comparison of the experimental data (symbols) for the (carbon dioxide+ethylene glycol dimethacrylate)  $\{(1-x) \text{CO}_2 + x \text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2\}$  system with calculations (solid lines) obtained with the Peng-Robinson equation of state using optimum parameters ( $k_{ij}$  and  $\eta_{ij}$ ) at each temperatures: ●, 313.2 K; ■, 333.2 K; △, 353.2 K; □, 373.2 K; ○, 393.2 K.

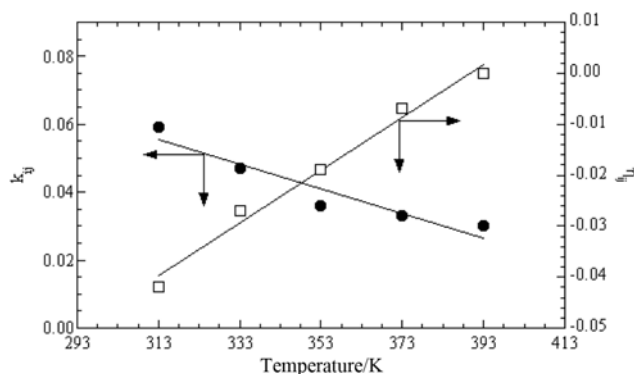


Fig. 7. Plot of  $k_{ij}$  and  $\eta_{ij}$  parameters against temperature for the (carbon dioxide+ethylene glycol dimethacrylate)  $\{(1-x) \text{CO}_2 + x \text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2\}$  system with the Peng-Robinson equation of state. The equation of the fitting line is  $k_{ij}=0.0698-0.00036T$  and  $\eta_{ij}=-0.0606+0.00052T$  ( $313.2 \text{ K} \leq T \leq 393.2 \text{ K}$ ).

ature. As shown in Fig. 6, these curves are calculated using optimized values determined at each temperature. The comparison between experimental data and calculated curve shows good agreement at five temperatures. According to calculated results, the mixture-critical curve is type-I.

Fig. 7 plots  $k_{ij}$  and  $\eta_{ij}$  parameters against temperature for the (carbon dioxide+ethylene glycol dimethacrylate) system with the Peng-Robinson equation of state at each temperature. The parameter equation of the fitting line is  $k_{ij}=0.0698-0.00036T$  and  $\eta_{ij}=-0.0606+0.00052T$  ( $313.2 \text{ K} \leq T \leq 393.2 \text{ K}$ ) determined by Peng-Robinson equation of state.

## CONCLUSIONS

The P-x isotherm data of (carbon dioxide+ethylene glycol dimethacrylate) system have been studied using a variable-volume view cell. The (carbon dioxide+ethylene glycol dimethacrylate) mixtures do not exhibit three phases at any five temperatures. The Peng-Robinson equation of state is capable of accurately predicting the phase behavior for the system using two temperature-independent mixture interaction parameters. The agreement between calculated and experimental mixture-critical curves is reasonably good for using two optimized parameters obtained at each temperature with Peng-Robinson equation of state.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the Korea Ministry of Commerce, Industry & Energy and the Korea Energy Management Corporation.

## REFERENCES

1. C. N. Cascaval, N. Hurduc and Ig. C. Poinescu, *J. Thermal Analysis*, **34**, 311 (1988).
2. D. Horak, Z. Peltzboer, Fr. Svec and J. Kalal, *J. Appl. Polym. Sci.*, **26**, 3205 (1981).
3. J. Kopacek and D. Lim, *J. Polym. Sci., A-1*, **9**, 147 (1971).
4. J. Hradil, *J. Chromatog.*, **144**, 6 (1977).
5. S. D. Yeo and E. Kiran, *Macromolecules*, **37**, 8239 (2004).
6. F. Rindfleisch, T. P. DiNoia and M. A. McHugh, *J. Phys. Chem.*, **100**, 15581 (1996).
7. J. L. Kendall, D. A. Canelas, J. L. Young and J. M. DeSimone, *Chem. Rev.*, **99**, 543 (1999).
8. M. A. McHugh, F. Rindfleisch, T. Kuntz, C. Schmaltz and M. Buback, *Polymer*, **39**, 6049 (1998).
9. D. H. Lee and H. S. Byun, *Polymer*, **48**, 805 (2007).
10. E. Franceschi, M. H. Kunita, A. F. Rubira, E. C. Muniz and M. L. Corazza, *J. Chem. Eng. Data*, **51**, 686 (2006).
11. M. Lora and M. A. McHugh, *Fluid Phase Equil.*, **157**, 285 (1999).
12. A. Zainul Husain, G. Zwolak and F. P. Lucien, *J. Chem. Eng. Data*, **51**, 718 (2006).
13. M. Soares da Silva, M. Temtem, S. Henriques, T. Casimiro and A. Aguiar-Ricardo, *J. Chem. Eng. Data*, **52**, 1970 (2007).
14. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).
15. B. E. Poling, J. M. Prausnitz, J. P. O'Connell, *The properties of liquids and gases*, 5th Ed., McGraw-Hill, New York (2001).
16. H. S. Byun and M. Y. Choi, *J. Chem. Thermodynamics*, **39**, 855 (2007).
17. M. A. McHugh and V. J. Krukonis, *Supercritical fluid extraction*, second Ed., Butterworth-Heinemann, Stoneham (1994).
18. R. L. Scott and P. B. van Konynenburg, *Discuss. Faraday Soc.*, **49**, 87 (1970).
19. J. L. Kuester and J. H. Mize, *Optimization techniques with fortran*, McGraw-Hill, New York (1973).