

Phase Equilibria Measurement of Binary Mixture for the Propoxylated Neopentyl Glycol Diacrylate in Supercritical Carbon Dioxide

Hun-Soo Byun[†]

Department of Chemical and Biomolecular Engineering, Chonnam National University, 50, Daehak-ro, Yeosu, Jeonnam, 59626, Korea
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Abstract – Experimental data are reported on the phase equilibrium of propoxylated neopentyl glycol diacrylate in supercritical carbon dioxide. Phase equilibria data were measured in static method at a temperature of (313.2, 333.2, 353.2, 373.2 and 393.2) K and at pressures up to 27.82 MPa. At a constant pressure, the solubility of propoxylated neopentyl glycol diacrylate for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system increases as temperature increases. The (carbon dioxide + propoxylated neopentyl glycol diacrylate) system exhibits type-I phase behavior. The experimental result for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system is correlated with Peng-Robinson equation of state using mixing rule. The critical property of propoxylated neopentyl glycol diacrylate is predicted with Joback and Lydersen method.

Key words: Propoxylated Neopentyl Glycol Diacrylate, Carbon Dioxide, Phase Behavior, Bubble-Point, Pressure-Composition

1. Introduction

Propoxylated neopentyl glycol diacrylate, is a low viscosity, highly active, low volatility, low skin irritation monomer for use in free radical polymerization. This monomer is used as a functional monomer for pressure-sensitive adhesives, inks, solder masks, photosensitive resin, PVC floor, wood and optical coatings [1].

Thermodynamic data for binary mixture of the glycol diacrylate group containing supercritical carbon dioxide plays an important role in separation processes, fine chemical industry, polymerization condition and industrial application [2-5]. In our laboratory, experimental data have been reported on the bubble-point, dew-point and critical-point behavior of binary mixtures containing supercritical carbon dioxide [6,7]. Supercritical carbon dioxide has a quadrupole moment, no dipole moment, and low dielectric constant. Carbon dioxide is widely used as an eco-friendly solvent because it is inexpensive, nonflammable, and nontoxic. Also, it is a good solvent with low molecular weight in nonpolar molecules. Therefore, phase behavior information for the carbon dioxide + solute mixtures is required for practical uses.

Phase behavior data for the carbon dioxide + diacrylate system were reported by Cho et al. [8], Jang et al. [9], and Yasmin et al. [10]. Cho et al. [8] reported the high-pressure phase behavior of tri-ethylene glycol dimethacrylate and tetra-ethylene glycol dimethacrylate in supercritical carbon dioxide at temperatures ranging from 303.2 to 363.2 K and pressure up to 27 MPa. Jang et al. [9] presented the phase behavior measurement for the binary mixture of carbon dioxide + neopentyl glycol diacrylate and carbon dioxide + neopentyl glycol dimethacrylate systems at high pressure at temperatures from 313.2 K to 348.2 K and pressures up to 25.28 MPa using a static apparatus. Yasmin et al. [10] determined ultrasonic velocity by interferometric technique and presented a thermodynamical study of alcoholic solutions for binary mixture of poly(ethylene glycol) diacrylate and poly(ethylene glycol) dimethacrylate at temperatures from 293.15 to 313.15 K.

The key point of this work is to obtain high-pressure experimental data for carbon dioxide + propoxylated neopentyl glycol diacrylate mixtures by investigating mixtures of carbon dioxide with a component. The experimental data for the carbon dioxide + propoxylated neopentyl glycol diacrylate system obtained in this work is correlated with the Peng-Robinson equation of state [11] using mixing rule including two adjustable parameters. The critical pressure, critical temperature and acentric factor of propoxylated neopentyl glycol diacrylate were estimated by the Joback and Lydersen method with group contributions [12].

2. Experimental Section

Apparatus and Procedure Fig. 1 shows a schematic diagram of the high pressure experimental apparatus, variable-volume view cell used for the phase equilibria measurement [13,14]. A high-pressure, variable-volume view cell (6.2 cm outer diameter × 1.59 cm inner diameter), a working volume of ~28 cm³, was used to obtain the phase behavior curves, and is capable of operating to pressure of 70.0 MPa. The front part of the cell is fitted with a 1.9 cm thick and 1.9 cm diameter a sapphire window (GT Advanced Technology, USA) which enables observation of the phases inside the cell. The sapphire window is sealed by an O-ring and backup ring placed around the diame-

[†]To whom correspondence should be addressed.

E-mail: hsbyun@jnu.ac.kr

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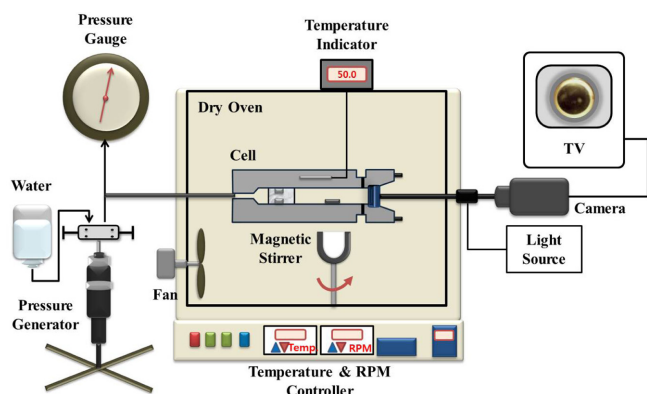


Fig. 1. Schematic diagram of high-pressure apparatus.

ter of window. 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 was measured with a Heise gauge (Dresser Ind., model CM-53920, 0 to 34.0 MPa) accurate to ± 0.02 MPa. The temperature of the cell, which is typically maintained to within ± 0.2 K, is measured using 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 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 ± 0.003 g using a high pressure cylinder. The monomer is loaded into the cell to within ± 0.002 g using 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 of the 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.

2-1. Materials

Propoxylated neopentyl glycol diacrylate (> 0.990 mass fraction purity, CAS RN 84170-74-1, $[H_2C=CHCOO(C_3H_6O)CH_2]_2C(CH_3)_2$) used in this work was obtained from Scientific Polymer Products,

Inc. A component was used without further purification in the experiments. Carbon dioxide (> 0.999 mass fraction purity) was obtained from Daesung Industrial Gases Co. and used as received. The specifications of all chemicals used are summarized in Table 1.

3. Results and Discussion

High pressure phase behavior data for the propoxylated neopentyl glycol diacrylate in supercritical carbon dioxide was measured, and the experimental uncertainty was estimated to be ± 0.02 MPa and ± 0.12 K for a given loading of the cell [15,16]. The combined expanded uncertainties of propoxylated neopentyl glycol diacrylate mole fractions were estimated to be ± 0.0008 [17].

Fig. 2 and Table 2 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 (4.38 to 27.82) MPa for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system. Three phases were not observed at five temperatures. As shown in Fig. 2, the mixture critical pressures are 24.89 MPa (at $T = 373.2$ K). The P - x isotherms shown in Fig. 2 are consistent with those expected for a type-I system [18,19] where a maximum occurs in the critical mixture curve. The solubility of carbon dioxide decreases as temperatures shift higher under a constant pressure.

In this work, the experimental phase behavior data was correlated with the Peng-Robinson equation of state. The Peng-Robinson equations are briefly described here. The Peng-Robinson equation of state [11] is expressed as follows:

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

$$a(T) = 0.457235 \frac{\alpha(T)R^2T_c^2}{P_c} \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

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

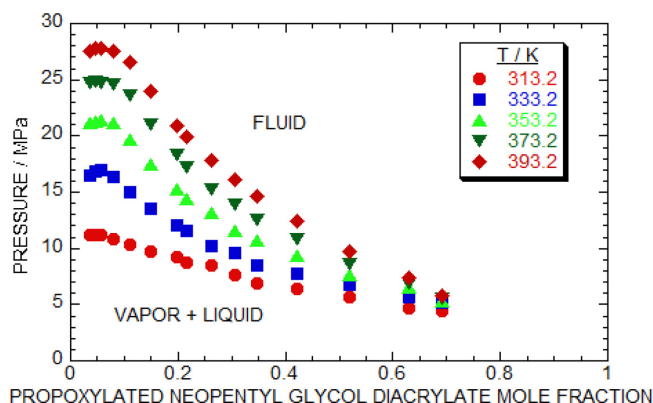


Fig. 2. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system. ●, 313.2 K; ■, 333.2 K; ▲, 353.2 K; ▼, 373.2 K; ◆, 393.2 K.

Table 1. Specifications of the chemicals used

Chemical name	Mass fraction purity	Source	CAS RN
CO ₂	>0.999	Daesung Ind. Gases Co.	124-38-9
Propoxylated Neopentyl Glycol Diacrylate	>0.990	Scientific Polymer Products, Inc.	84170-74-1

Table 2. Experimental Data for the Carbon Dioxide + Propoxylated Neopentyl Glycol Diacrylate System. BP is a bubble-point, CP is a critical-point and DP is a dew-point

Propoxylated Neopentyl Glycol Diacrylate Mole Fraction	p^a/MPa	Transition ^b
$T/\text{K} = 313.2 \text{ K}$		
0.037	11.20	BP
0.046	11.18	BP
0.057	11.15	BP
0.081	10.83	BP
0.110	10.38	BP
0.149	9.76	BP
0.199	9.17	BP
0.217	8.79	BP
0.263	8.45	BP
0.307	7.69	BP
0.347	6.93	BP
0.421	6.44	BP
0.519	5.63	BP
0.629	4.72	BP
0.692	4.38	BP
$T/\text{K} = 333.2 \text{ K}$		
0.036	16.45	DP
0.046	16.86	BP
0.057	17.00	BP
0.081	16.38	BP
0.110	15.07	BP
0.149	13.55	BP
0.199	12.10	BP
0.217	11.62	BP
0.263	10.17	BP
0.307	9.62	BP
0.347	8.52	BP
0.421	7.71	BP
0.519	6.77	BP
0.629	5.63	BP
0.692	5.14	BP
$T/\text{K} = 353.2 \text{ K}$		
0.036	21.14	DP
0.046	21.28	BP
0.057	21.35	BP
0.081	21.14	BP
0.110	19.69	BP
0.149	17.48	BP
0.199	15.21	BP
0.217	14.45	BP
0.263	13.17	BP
0.307	11.62	BP
0.347	10.67	BP
0.421	9.38	BP
0.519	7.66	BP
0.629	6.52	BP
0.692	5.28	BP
$T/\text{K} = 373.2 \text{ K}$		
0.036	24.66	DP
0.046	24.89	CP
0.057	24.76	BP
0.081	24.60	BP

Table 2. (continued)

Propoxylated Neopentyl Glycol Diacrylate Mole Fraction	p^a/MPa	Transition ^b
$T/\text{K} = 373.2 \text{ K}$		
0.110	23.62	BP
0.149	21.00	BP
0.199	18.31	BP
0.217	17.28	BP
0.263	15.24	BP
0.307	13.92	BP
0.347	12.59	BP
0.421	10.82	BP
0.519	8.59	BP
0.629	6.93	BP
0.692	5.55	BP
$T/\text{K} = 393.2 \text{ K}$		
0.036	27.60	DP
0.046	27.82	DP
0.057	27.76	BP
0.081	27.60	BP
0.110	26.59	BP
0.149	23.97	BP
0.199	20.86	BP
0.217	19.90	BP
0.263	17.81	BP
0.307	16.12	BP
0.347	14.60	BP
0.421	12.39	BP
0.519	9.72	BP
0.629	7.41	BP
0.692	5.83	BP

^aStandard uncertainties are $u(T) = T \pm 0.12 \text{ K}$ and $u(p) = p \pm 0.02 \text{ MPa}$ ^bBP: Bubble-point, CP: Critical-point, DP: Dew-point

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

where T_c , p_c , T_r and ω are the critical temperature, critical pressure, reduced temperature (T/T_c) and acentric factor of the pure component, respectively. The Peng-Robinson equation of state was used with the following mixing rules:

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) \quad (7)$$

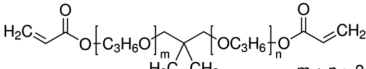
$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij} \quad (8)$$

$$b_{ij} = 0.5(b_{ii} + b_{jj})(1 - \eta_{ij}) \quad (9)$$

where k_{ij} and η_{ij} are binary interaction parameters determined by fitting P-x isotherms curves, and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson [11]. The objection function (OBF) and root mean squared relative deviation (RMSD) percent of this calculation are defined by

$$\text{OBF} = \sum_i^N \left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2 \quad (10)$$

Table 3. The properties of pure component in carbon dioxide and propoxylated neopentyl glycol diacrylate

Compounds	M_w	Chemical Structure ^a	T_b / K	T_c / K	p_c / MPa	ω
Carbon Dioxide	44.01	O=C=O		304.2	7.38	0.225
Propoxylated neopentyl glycol diacrylate	328.0		681.1 ^b	852.2	1.32	0.900

^aSigma-Aldrich Co.^bVast Spring Enterprise Co., Ltd.

$$\text{RMSD}(\%) = \sqrt{\frac{\text{OBF}}{\text{ND}}} \times 100 \quad (11)$$

Marquardt [20] was used to optimize the objective function. Table 3 lists the pure component critical temperatures (T_c), critical pressures (P_c), and the acentric factors (ω) for carbon dioxide [12], propoxylated neopentyl glycol diacrylate [12] used with the Peng-Robinson equation of state. The boiling points were obtained by the Vast Spring Enterprise Co., Ltd. [21]. The property of propoxylated neopentyl glycol diacrylate was calculated by the Joback group-contribution method [12]. The vapor pressures were calculated by the Lee-Kesler method [12].

Fig. 3 shows the comparison between experimental results of carbon dioxide + propoxylated neopentyl glycol diacrylate system and calculated value obtained using Peng-Robinson equation at a temperature of $T = 353.2$ K. The values of optimized parameters of the Peng-Robinson equation of state for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) systems at $T = 353.2$ K are $k_{ij} = 0.032$ and $h_{ij} = -0.025$.

Fig. 3 shows the comparison between the experimental results of the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system and calculated values obtained using the Peng-Robinson equation at 353.2 K. The binary interaction parameters of the Peng-Robinson equation of state were fitted with the experimental data at 353.2 K. The optimized parameter value of the Peng-Robinson equation of state for the (carbon dioxide + propoxylated neopentyl glycol diacrylate)

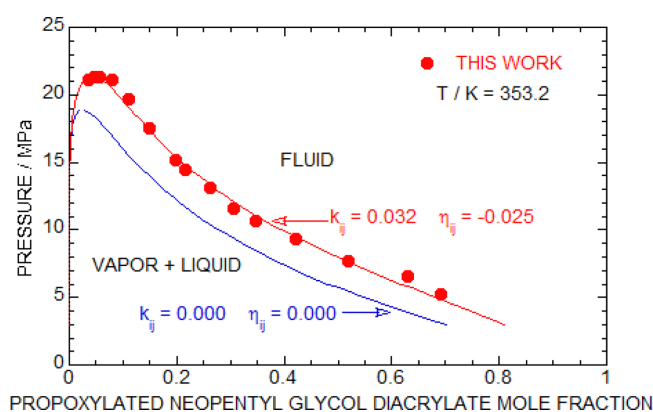


Fig. 3. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system with calculation obtained from the Peng-Robinson equation of state with k_{ij} and h_{ij} set equal to zero (blue solid lines), $k_{ij}=0.032$, $h_{ij}=-0.025$ (carbon dioxide + propoxylated neopentyl glycol diacrylate) (red solid lines) at 353.2 K.

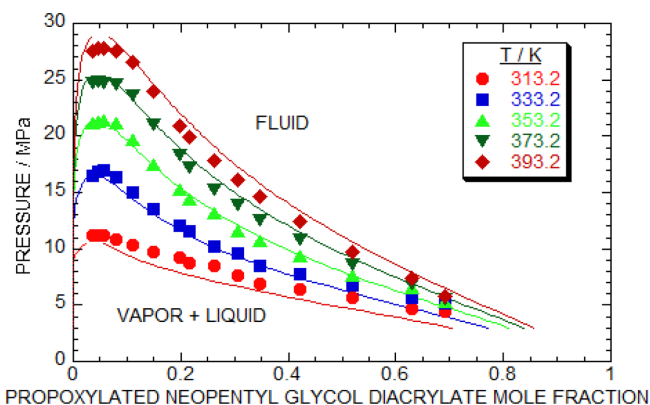


Fig. 4. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system with calculations (solid lines) obtained with the Peng-Robinson equation of state; k_{ij} equal to 0.032 and h_{ij} equal to -0.025 : ●, 313.2 K; ■, 333.2 K; ▲, 353.2 K; ▼, 373.2 K; ◆, 393.2 K.

system was $k_{ij} = 0.032$ and $h_{ij} = -0.025$ (experimental data points: 15; RMSD: 3.95%).

Fig. 4 compares the experimental results with calculated (P - x) isotherms at temperatures of (313.2, 333.2, 353.2, 373.2 and 393.2) K for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system using the optimized k_{ij} and h_{ij} values determined at 353.2 K. As shown in Fig. 4, obtained were well-fitted data with the Peng-Robinson equation using adjustable mixture parameters for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system. RMSD for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system at the five temperatures using two parameters determined at 353.2 K were 9.36% (experimental data points: 75). RMSD for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system became slightly high when the parameters were applied to this system. So it is necessary to obtain the optimized parameters for each temperature to decrease RMSD. The curves calculated by the Peng-Robinson equation of state did not demonstrate three phases at five temperatures.

Fig. 5 plots the pressures against mole fraction to compare the experimental data (symbols) of the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system with calculations (solid lines) obtained with the Peng-Robinson equation of state using optimum parameters (k_{ij} and h_{ij}) at each temperature. As shown in Fig. 5, these curves were calculated using optimized values determined at each temperature. RMSD at five temperatures (313.2, 333.2, 353.2, 373.2

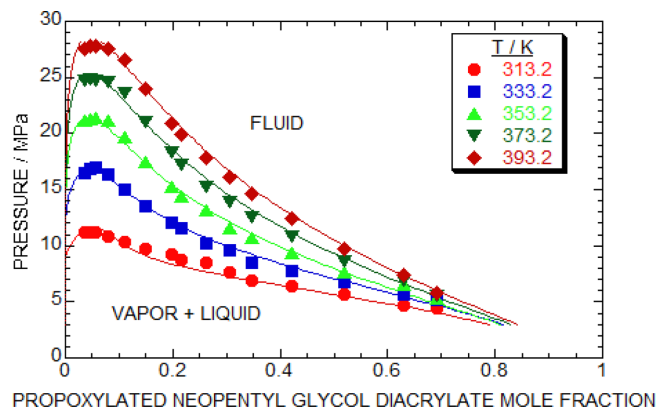


Fig. 5. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system with calculations (solid lines) obtained with the Peng-Robinson equation of state using optimum parameters (k_{ij} and η_{ij}) at each temperature: ●, 313.2 K; ■, 333.2 K; ▲, 353.2 K; ▼, 373.2 K; ◆, 393.2 K.

Table 4. Data of k_{ij} and η_{ij} parameters and the value of RMSD against temperature for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system with the Peng-Robinson equation of state

T / K	k_{ij}	η_{ij}	RMSD (%)
313.2	0.0355	-0.040	3.79
333.2	0.034	-0.036	3.91
353.2	0.032	-0.025	3.95
373.2	0.030	-0.022	4.94
393.2	0.028	-0.019	2.81

and 393.2 K) for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system was 3.79%, 3.91%, 3.95%, 4.94% and 2.81%, respectively (see Table 4). Here, the number for experimental data is 15 at each temperature. In comparison, the experimental data and calculated curve show a good agreement at five temperatures. According to the calculated result, the critical mixture curve showed type-I.

Fig. 6 plots k_{ij} and h_{ij} parameters against temperature for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system with

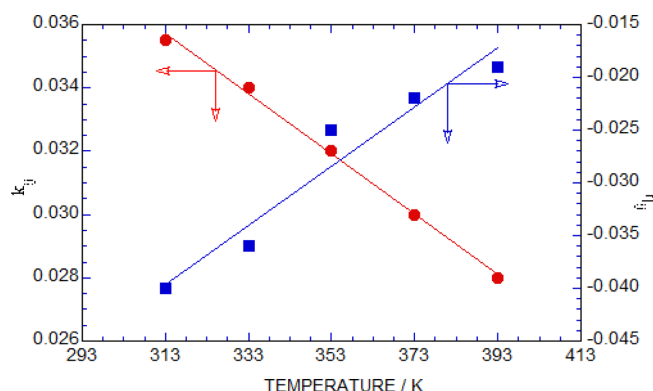


Fig. 6. Plot of k_{ij} and h_{ij} parameters against temperature for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system with the Peng-Robinson equation of state at each temperature.

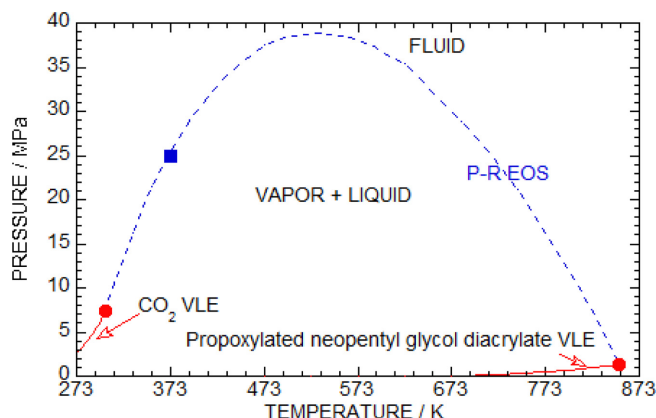


Fig. 7. Plot of pressure against temperature for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) $\{(1-x) \text{CO}_2 + x \text{H}_2\text{C}=\text{CHCOO}(\text{C}_3\text{H}_6\text{O})\text{CH}_2\text{C}(\text{CH}_3)_2\}$ system. Solid lines and circles (red) represent the vapor-liquid lines and critical points for pure CO_2 and propoxylated neopentyl glycol diacrylate. Solid square (blue) is mixture-critical point determined from isotherm measured in this work. Dashed lines (blue) represent calculations obtained using the Peng-Robinson equation of state with $k_{ij}=0.032$, $\eta_{ij}=-0.025$ (carbon dioxide+propoxylated neopentyl glycol diacrylate).

the Peng-Robinson equation of state at each temperature. The parameter equation of the fitting line is $k_{ij} = 0.0395 - 0.00009T$ ($R^2 = 0.998$) and $h_{ij} = -0.0578 + 0.00028T$ ($R^2 = 0.970$) ($313.2 \text{ K} \leq T \leq 393.2 \text{ K}$) determined by Peng-Robinson equation of state.

In Fig. 7, the mixture-critical curve of the experimental data was compared with calculated values by the Peng-Robinson equation of state for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system. The mixture-critical curve for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system exhibits the maximum pressure in pressure-temperature (p , T) space. The calculated mixture-critical curve showed type-I, which is in a reasonable agreement with experimental observations at the one temperature. In Fig. 7, the solid lines mean the vapor pressure for pure carbon dioxide [12] and propoxylated neopentyl glycol diacrylate [12]. The solid lines (red) mean the vapor pressure of pure propoxylated neopentyl glycol diacrylate obtained by the Lee-Kesler method [12]. The solid circles (red) represent the critical point for pure carbon dioxide and propoxylated neopentyl glycol diacrylate. The upper part of the dashed line (blue) is in single phase (fluid), while the lower part is vapor-liquid (two-phases). The dashed lines represent the calculated values obtained by the Peng-Robinson equation of state, with $k_{ij} = 0.032$ and $h_{ij} = -0.025$ (propoxylated neopentyl glycol diacrylate). The solid squares (blue) represent the critical mixture points determined from isotherms measured in this experiment.

4. Conclusions

The P - x isotherm data of (carbon dioxide + propoxylated neopentyl glycol diacrylate) system have been studied using a variable-volume view cell with static-type apparatus. The (carbon dioxide + propox-

ylated neopentyl glycol diacrylate) mixtures do not exhibit three phases at five temperatures. The Peng-Robinson equation of state is capable of properly 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. RMSD for the (carbon dioxide + propoxylated neopentyl glycol diacrylate) system calculated by optimum parameter at each temperature was 3.88%. The linear curves for two binary interaction parameters (k_{ij} and η_{ij}) against the temperatures show reasonably good agreement.

Acknowledgments

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Nomenclatures

- a, b : Parameter in the Peng-Robinson equation of state
 k : Binary interaction parameter in the Peng-Robinson equation of state
 P : Pressure [MPa]
 T : Temperature [K]
 R : Universal gas constant
 x : Mole fraction of liquid
 V : Molar volume [cm³/mol]

Greek letters

- α : Parameter in the Peng-Robinson equation of state
 κ : Parameter in the Peng-Robinson equation of state
 η : Binary interaction parameter in the Peng-Robinson equation of state
 ω : Acentric factor

Subscripts

- i, j : Component identifiers
 c : Critical property
 r : Reduced property
 mix : Mixture
 exp : Experiment
 cal : Calculation

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