Korean J. Chem. Eng., 34(4), 1170-1176 (2017)
DOI: 10.1007/s11814-016-0332-y

pISSN: 0256-1115
eISSN: 1975-7220

Phase equilibria measurement of binary mixtures for triethylene glycol dimethacrylate and triethylene glycol diacrylate in supercritical CO_2

Hun-Soo Byun*,† and Seung Yeop Rhee**

*Department of Chemical and Biomolecular Engineering, Chonnam National University, Yeosu, Jeonnam 59626, Korea
**Department of Electronic Communication Engineering, Chonnam National University, Yeosu, Jeonnam 59626, Korea

(*Received 13 October 2016 • accepted 20 November 2016*)

Abstract−The phase equilibrium curves for the (CO_2+triethylene glycol dimethacrylate) and (CO_2+triethylene glycol diacrylate) systems at five temperatures (313.2, 333.2, 353.2, 373.2 and 393.2) K and pressures up to 30.34 MPa were measured by synthetic apparatus. The solubility of triethylene glycol di(meth)acrylate in the (CO_2+triethylene glycol dimethacrylate) and (CO_2+triethylene glycol diacrylate) systems increased as the temperature increased at a fixed pressure. The (CO_2+triethylene glycol dimethacrylate) and (CO_2+triethylene glycol diacrylate) systems exhibited type-I phase equilibria. The experimental results for the (CO_2+triethylene glycol dimethacrylate) and (CO_2+triethylene glycol diacrylate) mixtures were correlated with the Peng-Robinson equation of state using a mixing rule including two adjustable parameters. The properties for the critical pressure, critical temperature and acentric factor of triethylene glycol dimethacrylate and triethylene glycol diacrylate were predicted with the Joback and Lyderson group contribution method.

Keywords: Carbon Dioxide, Triethylene Glycol Diacrylate, Triethylene Glycol Dimethacrylate, High Pressure Phase Behavior

INTRODUCTION

Methacrylate and acrylate esters have been applied to a wide variety of industrial, laboratory and consumer products. These useful chemicals are the main components of textiles, plastics, and surface coatings; they are often associated with other several polymers and resins [1,2]. Triethylene glycol di(meth)acrylate has been used as an intermediate for the production of polymers in the chemical industry [3,4]. Triethylene glycol di(meth)acrylate is used for the cross-linking agent, plastisol, acrylic sheet, ion exchange resin, dental composite materials, functional monomer for polymers and rubbers, and other industrial applications [5-7]. Also, associated activity of the chemical structure revealed that acrylate esters were more potent mutagens than corresponding methacrylates, and multifunctional acrylate esters were more active than difunctional and monofunctional compounds. It was also found that as the functionality increased by one unit, the concentrations required to cause maximal toxic and mutagenic responses decreased by one order of magnitude [8].

The knowledge of phase behavior in binary mixtures containing supercritical fluids is required for practical application of chemical separation processes, polymerization processes, supercritical extraction and related industry [9-12]. However, phase equilibria data in binary systems containing supercritical fluids is available to a wide range of applications. CO_2 has been particularly recommended as a solvent for many industrial applications because it is not only an eco-friendly, non-hazardous, affordable, and non-poison solvent with a nonpolar molecule [13] but also a solvent with a quadrupole moment and no dipole moment [14].

Recently, phase equilibria experiments have been reported on the bubble-point, dew-point and critical-point behaviors of mixtures containing CO_2 [15,16]. Miscibility of the supercritical carbon dioxide+di(meth)acrylate systems is an important condition needed for polymer synthesis and polymerization processes. However, phase equilibria data for the CO_2+di(meth) acrylate systems were reported by several researchers. Phase behavior for the CO_2+1,3-butanediol diacrylate and CO_2+1,3-butanediol dimethacrylate systems at elevated pressures and temperatures using variable volume view cell apparatus was reported by Yoon and Byun [17]. Cho et al. [18] used variable volume view cell apparatus to present the high-pressure phase behavior for the CO_2+diethylene glycol di(meth)acrylate systems at various temperatures. Kim et al. [19] measured the bubble-, dew-, and critical-point curves for the CO_2+ethylene glycol dimethacrylate systems at several temperatures and pressures up to 22 MPa. Jang et al. [20] presented the phase equilibria data for the CO_2+neopentyl glycol di(meth)acrylate at temperatures from (313.2 K to 393.2 K) using static method.

Our major purpose was to obtain the phase equilibrium data for the CO_2+triethylene glycol dimethacrylate and CO_2+triethylene glycol diacrylate mixtures at high pressure. The experimental phase equilibria data for the CO_2+triethylene glycol dimethacrylate and CO_2+triethylene glycol diacrylate systems obtained in this work were correlated with the Peng-Robinson equation of state [21] using a van der Waals one-fluid mixing rule that includes two (k_{ij} and η_{ij}) parameters. The critical properties of triethylene glycol dimethacrylate and triethylene glycol diacrylate were estimated by the Joback

---

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

Table 1. Specifications of the chemical used

Chemical name	Source	Mass fraction purity[a]	Purification method	Analysis method[a]
CO_2	Deok Yang Co.	>0.999	None	-
Triethylene glycol diacrylate	Scientific Polymer Product, Ltd.	>0.900	None	GC[b]
Triethylene glycol dimethacrylate	Scientific Polymer Product, Ltd.	>0.950	None	GC[b]

[a] Both the analysis method and the mass fraction purity were provided by the suppliers

[b] Gas-liquid chromatography

and Lydersen method with group contributions [22].

EXPERIMENTAL SECTION

1. Apparatus and Procedure

The experimental apparatus and techniques used to measure the phase behavior of triethylene glycol diacrylate and triethylene glycol dimethacrylate in supercritical carbon dioxide are already described in detail elsewhere [23,24]. To measure the phase behavior data, a variable-volume view cell in air bath was used and operated up to pressures of 68.0 MPa. Typically, supercritical carbon dioxide was added to the cell to within 0.002 g by using a high pressure bomb. The monomer was loaded into the cell to within ±0.0008 g using a syringe. The piston was moved by using water pressurized by a high pressure generator (HIP, model 37-5.75-60). Pressure of the mixture was measured with a Heise gauge (Dresser Ind., model CM-142719, 0 to 68.0 MPa) accurate to within ±0.068 MPa. The temperature of the cell, typically maintained to within ±0.2 K, 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 could 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.

The solution in the view cell was maintained in the single phase region at the desired temperature for at least 30-40 min to allow the cell to reach phase equilibrium. The pressure was then slowly decreased until a two phase (vapor+liquid) appeared. When dropping pressure from one phase to two phases, we dropped the pressure very slowly near the two phases. The stability time was around 5-10 min. during drop pressure. The real drop pressure was operated by the pressure generator. As mentioned in the experimental section, the measurement instrument was a Heise gauge. To determine the bubble point, dew point and mixture-critical point, a bubble point pressure was obtained when small vapor bubbles appeared in the cell, while a dew point was obtained after appearance of a fine mist. Mixture-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

CO_2 (>0.999 mass fraction purity, CAS RN 124-38-9) was purchased from Deokyang Co. and used as received. Triethylene glycol dimethacrylate (>0.950 mass fraction purity, $C_{14}H_{22}O_6$, CAS RN 109-16-0) and triethylene glycol diacrylate (>0.900 mass fraction purity, $C_{12}H_{18}O_6$, CAS RN 1680-21-3) used in this work were obtained from Scientific Polymer Products, Inc. Both components were used without further purification in the experiments. The specifications of all chemicals used are summarized in Table 1.

RESULTS AND DISCUSSION

Reported were phase equilibria data for binary mixtures on the triethylyene glycol dimethacrylate and triethylene glycol diacrylate in supercritical CO_2. The standard uncertainties were estimated to be u(P)=0.2 MPa at pressure and u(T)=0.12 K [17,25] at temperature. The standard uncertainties of triethylene glycol dimethacrylate and triethylene glycol diacrylate mole fractions were estimated

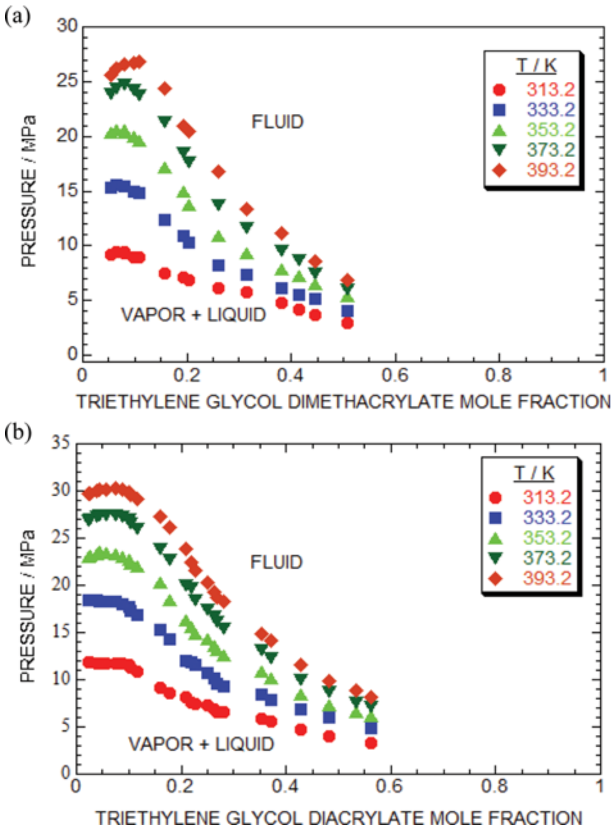


Fig. 1. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (CO_2+triethylene glycol dimethacrylate) {(1–x) CO_2+x $CH_2{=}C(CH_3)COO(CH_2CH_2O)_3COC(CH_3){=}CH_2$} system (a) and ($CO_2$+triethylene glycol diacrylate) {(1–x) CO_2+x $CH_2{=}CHCOO(CH_2CH_2O)_3COCH{=}CH_2$} system (b). ●, 313.2 K; ■, 333.2 K; ▲, 353.2 K; ▼, 373.2 K; ◆, 393.2 K.

Table 2. Experimental data for the CO_2+triethylene glycol dimethacrylate (TEGDMA) system measured in this work

TEGDMA mole fraction	p^a/MPa	Transition^b
T^a/K=313.2		
0.055	9.24	DP
0.065	9.47	BP
0.080	9.39	BP
0.081	9.31	BP
0.099	8.97	BP
0.107	8.97	BP
0.158	7.52	BP
0.195	7.17	BP
0.205	6.83	BP
0.261	6.10	BP
0.315	5.79	BP
0.382	4.76	BP
0.416	4.15	BP
0.446	3.72	BP
0.507	2.98	BP
T/K=333.2		
0.055	15.31	DP
0.065	15.59	CP
0.080	15.45	BP
0.081	15.38	BP
0.099	14.93	BP
0.107	14.79	BP
0.158	12.35	BP
0.195	10.97	BP
0.205	10.28	BP
0.261	8.21	BP
0.315	7.38	BP
0.382	6.14	BP
0.416	5.56	BP
0.446	5.10	BP
0.507	4.08	BP
T/K=353.2		
0.055	20.28	DP
0.065	20.62	DP
0.080	20.52	BP
0.081	20.28	BP
0.099	19.98	BP
0.107	19.55	BP
0.158	17.17	BP
0.195	14.93	BP
0.205	13.72	BP
0.261	10.97	BP
0.315	9.28	BP
0.382	7.79	BP
0.416	7.18	BP
0.446	6.48	BP
0.507	5.36	BP
T/K=373.2		
0.055	23.87	DP
0.065	24.35	DP
0.080	24.76	CP
0.081	24.72	BP
0.099	24.31	BP
0.107	23.72	BP
0.158	21.31	BP
0.195	18.55	BP
0.205	17.62	BP
0.261	13.72	BP
0.315	11.66	BP
0.382	9.59	BP
0.416	8.69	BP
0.446	7.52	BP
0.507	5.98	BP
T/K=393.2		
0.055	25.66	DP
0.065	26.26	DP
0.081	26.53	DP
0.099	26.73	DP
0.107	26.79	CP
0.158	24.41	BP
0.195	20.97	BP
0.205	20.43	BP
0.261	16.74	BP
0.315	13.38	BP
0.382	11.10	BP
0.446	8.55	BP
0.507	6.81	BP

[a] Standard uncertainties are u(T)=0.12 K, u(p)=0.2 MPa and u(x)=0.0008

[b] BP is a bubble-point, CP is a critical point, and DP is a dew point

to be u(x)=0.0008 [17].

Fig. 1(a) 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 ranging from (4.08 to 26.79) MPa for the (CO_2+triethylene glycol dimethacrylate) system. As shown in Fig. 1(a), three phases were not observed in the five temperatures. The mixture-critical pressures were 15.59 MPa at T=333.2 K, 24.76 MPa at T=373.2 K and 26.79 MPa at T=393.2 K. The (p, x) isotherms shown in Fig. 1(a) are consistent with those anticipated for a type-I region [26,27], where a maximum takes place in the mixture-critical curve. The type-I phase diagram for a binary mixture is the simplest behavior. The apparent characteristics of type-I curve are that only one phase exists throughout the phase diagram and that the mixture-critical curve runs continuously from the critical-point of the CO_2 component to that of the triethylene glycol dimethacrylate and triethylene glycol diacrylate components. The solubility curve of CO_2 decreases as the temperatures shift higher under a fixed pressure.

Fig. 1(b) and Table 3 show the experimental equilibria data at T=(313.2, 333.2, 353.2, 373.2 and 393.2) K, and at pressures from (3.35 to 30.34) MPa for the (CO_2+triethylene glycol diacrylate) mix-

Table 3. Experimental data for the CO_2+triethylene glycol diacrylate (TEGDA) system measured in this work

TEGDA mole fraction	p^a/MPa	Transition^b
T^a/K=313.2		
0.023	11.93	BP
0.027	11.82	BP
0.039	11.76	BP
0.044	11.76	BP
0.057	11.77	BP
0.074	11.77	BP
0.089	11.69	BP
0.100	11.60	BP
0.104	11.27	BP
0.115	10.90	BP
0.159	9.14	BP
0.179	8.55	BP
0.208	8.21	BP
0.219	7.62	BP
0.228	7.46	BP
0.249	7.28	BP
0.263	6.90	BP
0.268	6.62	BP
0.280	6.55	BP
0.352	5.94	BP
0.371	5.64	BP
0.427	4.76	BP
0.483	3.97	BP
0.563	3.35	BP
T/K=333.2		
0.023	18.42	DP
0.027	18.48	CP
0.039	18.41	BP
0.044	18.32	DP
0.057	18.35	BP
0.074	18.25	BP
0.089	18.08	BP
0.100	17.69	BP
0.104	17.32	BP
0.115	16.83	BP
0.159	15.35	BP
0.179	14.31	BP
0.208	12.00	BP
0.219	11.87	BP
0.228	11.56	BP
0.249	10.69	BP
0.263	10.14	BP
0.268	9.52	BP
0.280	9.24	BP
0.352	8.43	BP
0.371	7.90	BP
0.427	6.90	BP
0.483	6.07	BP
0.563	4.85	BP
T/K=353.2		
0.023	23.07	DP
0.027	23.10	DP
0.039	23.31	DP
0.044	23.52	CP
0.057	23.44	BP
0.074	23.31	BP
0.089	23.04	BP
0.100	22.79	BP
0.104	22.35	BP
0.115	22.07	BP
0.159	20.24	BP
0.179	18.45	BP
0.208	16.34	BP
0.219	15.58	BP
0.228	14.90	BP
0.249	14.362	BP
0.263	13.52	BP
0.268	13.10	BP
0.280	12.62	BP
0.352	10.87	BP
0.371	10.14	BP
0.427	8.41	BP
0.483	7.35	BP
0.532	6.60	BP
0.563	6.11	BP
T/K=373.2		
0.023	26.93	DP
0.027	27.00	DP
0.039	27.31	DP
0.044	27.46	DP
0.057	27.47	CP
0.074	27.44	BP
0.089	27.31	BP
0.100	26.96	BP
0.104	26.62	BP
0.115	26.00	BP
0.159	23.90	BP
0.179	22.72	BP
0.208	20.07	BP
0.219	19.69	BP
0.228	18.51	BP
0.249	17.43	BP
0.263	16.76	BP
0.268	16.14	BP
0.280	15.45	BP
0.352	13.17	BP
0.371	12.35	BP
0.427	10.07	BP
0.483	8.76	BP
0.532	7.64	BP
0.563	7.15	BP

Table 3. Continued

TEGDA mole fraction	p^a/MPa	Transition^b
T/K=393.2		
0.023	29.72	DP
0.027	29.72	DP
0.039	30.07	DP
0.044	30.21	DP
0.057	30.21	DP
0.074	30.34	CP
0.089	30.14	BP
0.100	29.92	BP
0.104	29.55	BP
0.115	29.10	BP
0.159	27.24	BP
0.179	26.4	BP
0.208	23.93	BP
0.219	22.48	BP
0.228	21.57	BP
0.249	20.28	BP
0.263	19.24	BP
0.268	18.69	BP
0.280	18.31	BP
0.352	14.90	BP
0.371	14.20	BP
0.427	11.52	BP
0.483	9.90	BP
0.532	8.80	BP
0.563	8.21	BP

[a] Standard uncertainties are u(T)=0.12 K, u(p)=0.2 MPa and u(x)=0.0008

[b] BP is a bubble-point, CP is a critical point, and DP is a dew point

ture. As shown in Fig. 1(b), the critical mixture pressures are 18.48 MPa (at T=333.2 K), 23.52 MPa (at T=353.2 K), 27.47 MPa (at T=373.2 K) and 30.34 MPa (at T=393.2 K). The (CO_2+triethylene glycol diacrylate) system does not display three phases at various temperatures investigated. The critical mixture curve for the (CO_2+triethylene glycol diacrylate) system exhibits maximum pressure in (p, T) space.

In this research, the experimental result was correlated with the Peng-Robinson equation of state. At this point, the Peng-Robinson equations of state are briefly described. The Peng-Robinson equation of state [21] is expressed as follows:

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

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

$$b=0.077796\frac{RT_c}{p_c} \tag{3}$$

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

$$\kappa=0.37464+1.54226\omega-0.26992\omega^2 \tag{5}$$

where T_c, p_c and ω are the critical temperature, critical pressure and acentric factor of the pure component, respectively. The Peng-Robinson equation of state used with a van der Waals one-fluid mixing rule is as follows:

$$a_{mix}=\sum_i\sum_j x_i x_j a_{ij} \tag{6}$$

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

$$b_{mix}=\sum_i\sum_j x_i x_j b_{ij} \tag{8}$$

$$b_{ij}=\frac{1}{2}(b_{ii}+b_{jj})(1-\eta_{ij}) \tag{9}$$

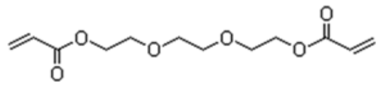
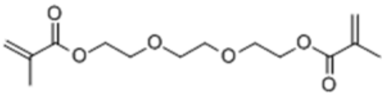
where a_{ii}, a_{jj}, b_{ii} and b_{jj} are pure component parameters as defined by Peng-Robinson equation [21], and k_{ij} and η_{ij} are two component (i and j) interaction parameters determined by fitting (p, x) isotherms curves. The OBF (objection function) [28] and RMSD (root mean squared relative deviation) percent of this calculation are defined by

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

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

The pure component molecular weight (M_w), critical temperatures (T_c), critical pressures (p_c) and acentric factors (ω) for CO_2 [22], triethylene glycol dimethacrylate [22] and triethylene glycol diacrylate [22] are described in Table 4, and all of them were used with the Peng-Robinson equation of state. The boiling points of two

Table 4. Pure component properties used in this work

Compound	M_w	Structure	T_b/K	T_c/K	p_c/MPa	ω
Carbon dioxide	44.01	O=C=O		304.2	7.38	0.225
Triethylene glycol diacrylate	258.27		612.1^a	781.8	1.94	0.982
Triethylene glycol dimethacrylate	286.32		608.7^b	768.8	1.66	0.980

[a] ChemSpider

[b] BASF

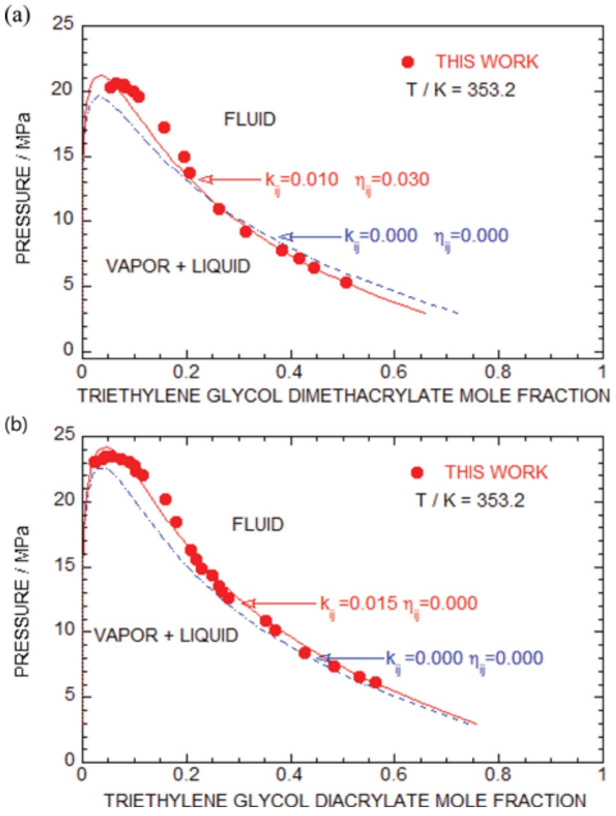


Fig. 2. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (CO_2+triethylene glycol dimethacrylate) {(1–x) CO_2+x CH_2=C(CH_3)COO(CH_2CH_2O)$_3$COC(CH_3)=CH_2} system (a) and (CO_2+triethylene glycol diacrylate) {(1–x) CO_2+x CH_2=CHCOO(CH_2CH_2O)$_3$COCH=CH_2} system (b) systems with calculation obtained from the Peng-Robinson equation of state with k_{ij} and η_{ij} set equal to zero (blue dashed lines), k_{ij}=0.010, η_{ij}=0.030 (CO_2+triethylene glycol dimethacrylate) and k_{ij}=0.015, η_{ij}=0.000 (CO_2+triethylene glycol diacrylate) (red solid lines) at 353.2 K.

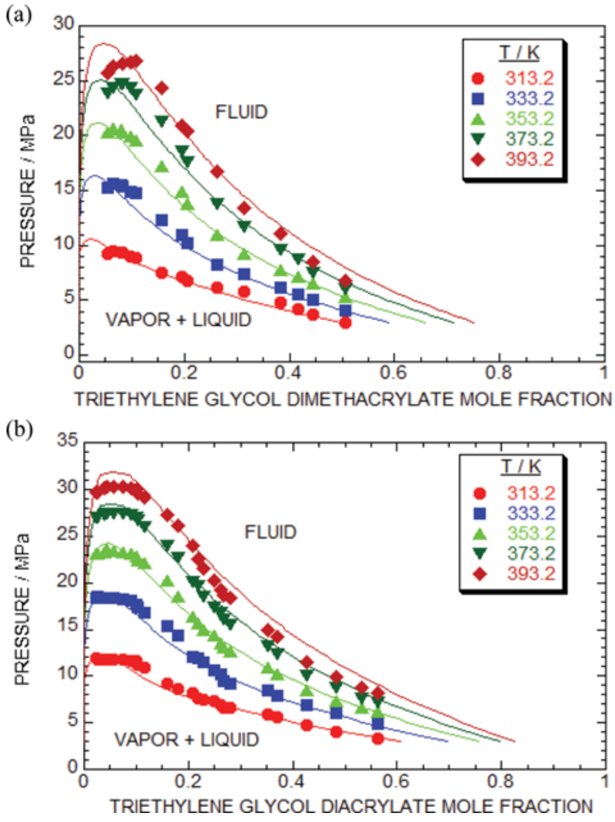


Fig. 3. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (CO_2+triethylene glycol dimethacrylate) {(1–x) CO_2+x CH_2=C(CH_3)COO(CH_2CH_2O)$_3$COC(CH_3)=CH_2} system (a) and (CO_2+triethylene glycol diacrylate) {(1–x) CO_2+x CH_2=CHCOO(CH_2CH_2O)$_3$COCH=CH_2} system (b) with calculations (solid lines) obtained with the Peng-Robinson equation of state; k_{ij}=0.010, η_{ij}=0.030 (CO_2+triethylene glycol dimethacrylate) and k_{ij}=0.015, η_{ij}=0.000 (CO_2+triethylene glycol diacrylate). ●, 313.2 K; ■, 333.2 K; ▲, 353.2 K; ▼, 373.2 K; ◆, 393.2 K.

chemicals were found from the literature [29,30].

Fig. 2 shows the comparison of experimental values for the (CO_2+triethylene glycol dimethacrylate) (a) and (CO_2+triethylene glycol diacrylate) (b) systems and estimated values obtained using the Peng-Robinson equation of state at 353.2 K. The interaction parameters (k_{ij} and η_{ij}) for the binary system of the Peng-Robinson equation were fitted with the experimental results at 353.2 K. The optimized parameters of the Peng-Robinson equation for the (CO_2+triethylene glycol dimethacrylate) (a) and (CO_2+triethylene glycol diacrylate) (b) systems were k_{ij}=0.010 and η_{ij}=0.030 (number of experimental data=15, RMSD=4.56%), and k_{ij}=0.015 and η_{ij}=0.000 (number of experimental data=25, RMSD=2.71%), respectively.

Fig. 3(a) compares the experimental results with calculated (p, x) isotherms at the temperatures of T=(313.2, 333.2, 353.2, 373.2 and 393.2) K for the (CO_2+triethylene glycol dimethacrylate) system using the optimized k_{ij} and η_{ij} values (number of experimental data=15, RMSD=4.56%) determined at 353.2 K. As shown in Fig. 3(a), obtained data were reasonably fitted with the Peng-Robinson equation using optimized parameters for the (CO_2+triethylene glycol dimethacrylate) system (number of experimental data=73, RMSD=5.74%). RMSD at various temperatures (313.2, 333.2, 373.2 and 393.2 K) for the (CO_2+triethylene glycol dimethacrylate) (a) system was 5.90% (at 313.2 K, data point no.=15), 5.27% (at 333.2 K, data point no.=15), 5.25% (at 373.2 K, data point no.=15) and 7.56% (at 393.2 K, data point no.=13), respectively.

Fig. 3(b) compares the experimental values with predicted (p, x) isotherms at temperatures of T=(313.2, 333.2, 353.2, 373.2 and 393.2) K for the (CO_2+triethylene glycol diacrylate) system. In the same manner as above, these isotherms were predicted using the optimized values of k_{ij}=0.015 and η_{ij}=0.000 (number of experimental data=25, RMSD=2.71%) decided at 353.2 K. RMSD for the (CO_2+triethylene glycol diacrylate) system using two parameters determined at five temperatures were 5.02%. Here, the number of experimental data at five temperatures is 123 points. RMSD at five temperatures for the (CO_2+triethylene glycol diacrylate) (b) system was 4.94% (at 313.2 K), 3.97% (at 333.2 K), 4.65% (at 373.2 K) and 7.42% (at 393.2 K), respectively. And the number of experimental data is 25 at each temperature except at 313.2 K and 333.2 K. The comparison between the experimental results and predicted curve shows a good agreement at various temperatures. The curves predicted by the Peng-Robinson equation of state did not display vapor-liquid-liquid (three) phases at the five temperatures. This accorded with the predicted results.

CONCLUSIONS

High pressure phase behavior data of (p, x) isotherm for the binary (CO_2+triethylene glycol dimethacrylate) and (CO_2+triethylene glycol diacrylate) systems were studied by using a synthetic apparatus of a variable-volume view cell at pressure up to 30.34 MPa and temperatures ranging from (313.2 to 393.2) K. The (CO_2+triethylene glycol dimethacrylate) and (CO_2+triethylene glycol diacrylate) mixtures do not exhibit three phases at the several temperatures. The Peng-Robinson equation of state moderately predicted the phase behavior for the (CO_2+triethylene glycol dimethacrylate) and (CO_2+triethylene glycol diacrylate) systems using two temperature-independent mixture interaction parameters. RMSD for the (CO_2+triethylene glycol dimethacrylate) and (CO_2+triethylene glycol diacrylate) systems calculated by adjustable parameter at each temperature were 5.74% and 5.02% (mean error of five temperatures), respectively.

ACKNOWLEDGEMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (Grant No. NRF-2016R1D1A1B04931921).

REFERENCES

1. H. Schweikl, G. Schmalz and K. Rackebrandt, *Mutat. Res.*, **415**, 119 (1998).
2. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 19, International Agency for Research on Cancer, Lyon (1979).
3. Evonik Industries AG, GPS Safety Summary, Version 1, pp. 1-6 (2013).
4. A. Peutzfeldt, *Eur. J. Oral. Sci.*, **105**, 97 (1997).
5. D. Djozan, S. Jozan, R. Aminian and T. Baheri, *J. Chromatographic Sci.*, **48**, 130 (2010).
6. J. M. Meyer, *Autredent*, **56**, 81 (2010).
7. G. Batarseh, L. J. Windsor, N. Y. Labban, Y. Liu and K. Gregson, *Operative Dentistry*, 39-1, E1 (2014).
8. L. S. Andrews and J. J. Clary, *J. Toxicol. Environ. Health*, **19**, 149 (1986).
9. F. Rindfleisch, T. P. DiNoia and M. A. McHugh, *J. Phys. Chem.*, **100**, 15581 (1996).
10. I. Wichterle, *Pure Appl. Chem.*, **65**, 1003 (1993).
11. E. Kiran, *J. Supercritical Fluids*, **47**, 466 (2009).
12. H. S. Byun, B. M. Hasch, M. A. McHugh, F. O. Mahling, M. Busch and M. Buback, *Macromolecules*, **29**, 1625 (1996).
13. M. A. McHugh and V. J. Krukonis, Supercritical Fluid Extraction; 2nd Ed., Butterworth-Heinemann: Stoneham (1994).
14. J. M. Prausnitz, R. N. Lichtenthaler and E. Gomes de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria; 3rd Ed., Prentice-Hall, Inc.: Englewood Cliffs, NJ (1998).
15. Y. S. Jang, D. S. Yang and H. S. Byun, *J. Chem. Eng. Data*, **56**, 4116 (2011).
16. S. H. Kim, Y. S. Jang, S. D. Yoon and H. S. Byun, *Fluid Phase Equilib.*, **312**, 93 (2011).
17. S. D. Yoon and H. S. Byun, *J. Chem. Thermodyns.*, **71**, 91 (2014).
18. S. H. Cho, S. D. Yoon and H. S. Byun, *Korean J. Chem. Eng.*, **30**, 739 (2013).
19. S. H. Kim, Y. S. Jang and H. S. Byun, *Korean J. Chem. Eng.*, **27**, 1291 (2010).
20. Y. S. Jang, S. H. Kim, K. P. Yoo and H. S. Byun, *Fluid Phase Equilib.*, **302**, 234 (2011).
21. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).
22. B. E. Poling, J. M. Prausnitz and J. P. O'Connell, The Properties of Liquids and Gases, 5th Ed., McGraw-Hill, New York (2001).
23. Y. S. Jang, Y. S. Choi and H. S. Byun, *Korean J. Chem. Eng.*, **32**, 958 (2015).
24. S. D. Yoon and H. S. Byun, *Korean J. Chem. Eng.*, **31**, 522 (2014).
25. R. D. Chirico, M. Frenkel, V. V. Diky, K. N. Marsh and R. C. Wilhoit, *J. Chem. Eng. Data*, **48**, 1344 (2003).
26. R. L. Scott and P. B. van Konynenburg, *Discuss. Faraday Soc.*, **49**, 87 (1970).
27. J. S. Rowlinson and F. L. Swinton, Liquid and Liquid Mixtures, 3rd Ed., Butterworth, Boston (1982).
28. J. L. Kuester and J. H. Mize, Optimization Techniques with Fortran, McGraw-Hill, New York (1973).
29. http://www.specialty-monomers.basf.com/portal/streamer?fid=235707.
30. http://www.chemspider.com/Chemical-structure.7691.htm.