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Bubble-Point Measurement of Binary Mixture for the CO_2 + Caprolactone Acrylate System in High Pressure

Jong-Dae Jeong and Hun-Soo Byun†

Department of Chemical and Biomolecular Engineering, Chonnam National University, Yeosu, Jeonnam 59626, Korea
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Abstract – Experimental data of phase equilibrium is reported for caprolactone acrylate in supercritical carbon dioxide. Bubble-point data was measured by synthetic method at temperatures ranging from (313.2 to 393.2) K and pressures up to 55.93 MPa. In this research, the solubility of carbon dioxide for the (carbon dioxide + caprolactone acrylate) system decreases as temperature increases at a constant pressure. The (carbon dioxide + caprolactone acrylate) system exhibits type-I phase behavior. The experimental result for the (carbon dioxide + caprolactone acrylate) system was correlated with Peng-Robinson equation of state using mixing rule. The critical property of caprolactone acrylate was predicted with the Joback and Lyderson method.

Key words: Caprolactone acrylate, Carbon dioxide, Phase behavior, Bubble-point, Pressure-composition

1. Introduction

Caprolactone acrylate is a low viscosity, high active, low volatility, low skin irritation monomer for use in free radical polymerization. This monomer is used for the performance properties as a good adhesion, good chemical resistance, good weatherability, high flexibility, high impact strength and low shrinkage, and applications as pressure sensitive adhesives, chemical intermediates and coatings [1]. Especially, phase equilibrium data on caprolactone acrylate plays an essential role in polymer and polymerization processes.

Thermodynamic data for binary mixture of the acrylate group containing supercritical carbon dioxide plays an important role in the separation processes, fine chemical industry, polymerization condition and industrial application [2-5]. So far, our laboratory has reported various experimental data 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 has been 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 + acrylate system were reported by Yoon and Byun [8], Cho et al. [9] and Jang et al. [10]. Yoon and Byun [8] presented the experimental data of phase behavior for the binary systems of heptafluorobutyl acrylate and heptafluorobutyl methacrylate under carbon dioxide at high pressure. Cho et al. [9] reported 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. [10] presented phase behavior measurements 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.

The major point of this work was to obtain high-pressure experimental data for (carbon dioxide + caprolactone acrylate) mixture by investigating mixtures of carbon dioxide with a component. The experimental data for the carbon dioxide + caprolactone acrylate system obtained in this work was 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 caprolactone acrylate were estimated by the Joback and Lydersen method with group contributions [12].

2. Experimental Section

Apparatus and Procedure Fig. 1 shows a schematic 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 cm^3, was used to obtain the phase behavior curves; it is capable of operating up to a pressure of 70.0 MPa. The front cap section of the cell is fitted with a (1.9 cm thick × 1.9 cm diameter) a sapphire window (GT Advanced Technology, USA) which enabled us to observe the phases inside the cell. The sapphire window is sealed by an O-ring and backup ring placed around the diameter of window. The mixture in the cell was compressed to the desired

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

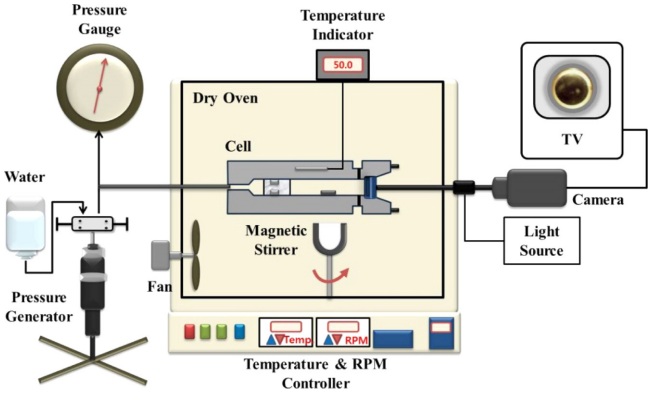

Fig. 1. Schematic of high-pressure apparatus.

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 the 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, was measured using 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 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 (0.7~5.0) ±0.003 g using a high pressure cylinder. The monomer is loaded into the cell to within (4.4~11.1) ±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.

2-1. Materials

Caprolactone acrylate (> 0.90 mass fraction purity, CAS RN 110489-05-9, $C_9H_{14}O_4$) used in this work was obtained from Scientific Polymer Products, Inc. (Ontario, NY 14519, USA). A component was used without further purification in the experiments. Carbon dioxide (> 0.999 mass fraction purity) was obtained from Deokyang Gases Co. and used as received. The specifications of all chemicals used in the experiment are summarized in Table 1.

3. Results and Discussion

High pressure phase behavior data for the caprolactone acrylate in supercritical carbon dioxide was measured, and the experimental uncertainty was estimated to be ±0.02 MPa and ±0.24 K for a given loading of the cell [15,16]. The standard uncertainties of caprolactone acrylate mole fractions were estimated to be ±0.0025 [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 (4.21 to 55.93) MPa for the (carbon dioxide + caprolactone acrylate) system. Three phases were not observed at five temperatures. As shown in Fig. 2, the P-x isotherms are consistent with those expected for a type-I behavior [18,19]. The solubility of carbon dioxide decreases as temperatures shift higher under a constant pressure. Then, the solubility pressure increases as the temperature increases at the mole fraction of caprolactone acrylate ≥ 0.097.

In this research, the experimental result was correlated with the Peng-Robinson equation of state. The Peng-Robinson equation of state [11] is as follows:

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

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

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

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

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

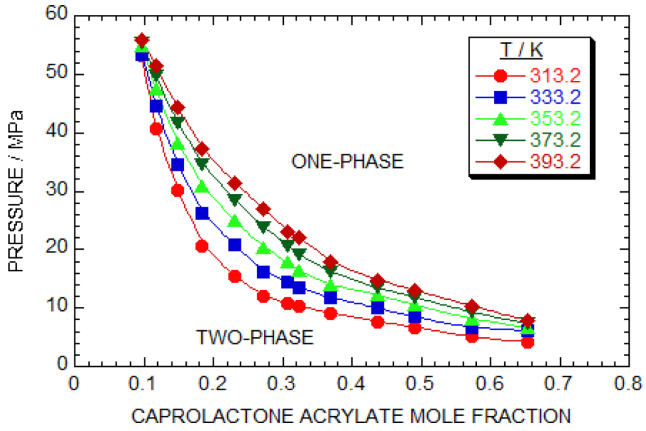

Fig. 2. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (carbon dioxide + caprolactone acrylate) system. ●, 313.2 K; ■, 333.2 K; ▲, 353.2 K; ▼, 373.2 K; ◆, 393.2 K.

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
Caprolactone acrylate	>0.900	Scientific Polymer Products, Inc.	110489-05-9

Table 2. Experimental Data for the Carbon Dioxide + Caprolactone Acrylate System. BP is a bubble-point

Caprolactone Acrylate Mole Fraction	p^a/ MPa	Transition[b]
T^a / K = 313.2 K		
0.097	53.21	BP
0.118	40.59	BP
0.148	30.10	BP
0.184	20.69	BP
0.231	15.38	BP
0.273	12.10	BP
0.308	10.76	BP
0.324	10.32	BP
0.370	9.17	BP
0.437	7.70	BP
0.491	6.72	BP
0.574	5.07	BP
0.653	4.21	BP
T / K = 333.2 K		
0.097	53.41	BP
0.118	44.69	BP
0.148	34.52	BP
0.184	26.24	BP
0.231	20.72	BP
0.273	16.17	BP
0.308	14.45	BP
0.324	13.45	BP
0.370	11.79	BP
0.437	10.00	BP
0.491	8.48	BP
0.574	6.72	BP
0.653	6.14	BP
T / K = 353.2 K		
0.097	54.90	BP
0.118	47.52	BP
0.148	38.24	BP
0.184	30.90	BP
0.231	24.90	BP
0.273	20.38	BP
0.308	17.83	BP
0.324	16.31	BP
0.370	13.97	BP
0.437	12.31	BP
0.491	10.52	BP
0.574	8.21	BP
0.653	6.66	BP
T / K = 373.2 K		
0.097	55.35	BP
0.118	49.66	BP
0.148	41.69	BP
0.184	34.66	BP
0.231	28.52	BP
0.273	23.83	BP
0.308	20.66	BP
0.324	19.21	BP
0.370	16.10	BP
0.437	13.52	BP
0.491	11.86	BP
0.574	9.28	BP
0.653	7.41	BP

Table 2. Continued

Caprolactone Acrylate Mole Fraction	p^a/ MPa	Transition[b]
T / K = 393.2 K		
0.097	55.93	BP
0.118	51.35	BP
0.148	44.31	BP
0.184	37.24	BP
0.231	31.41	BP
0.273	27.07	BP
0.308	22.93	BP
0.324	22.17	BP
0.370	17.93	BP
0.437	14.83	BP
0.491	13.03	BP
0.574	10.38	BP
0.653	7.90	BP

[a]Standard uncertainties are $u(T)$ = 0.2 K, $u(p)$ = 0.04 MPa and $u(x)$ = 0.0025
[b]BP: Bubble-point

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:

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

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

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

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

In the rule, k_{ij} and h_{ij} are binary interaction parameters and a_{ii} and b_{ii} are pure component parameters [11]. Objective function (OBF) and root mean squared relative deviation (RMSD) percent of this calculation are defined by

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

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

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], caprolactone acrylate [12] used with the Peng-Robinson equation of state. The boiling points were obtained by the Scientific Polymer Products Co., Ltd. [21]. The property of caprolactone acrylate was calculated by the Joback group-contribution method [12].

Fig. 3 shows the comparison between the experimental results of the (carbon dioxide + caprolactone acrylate) 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

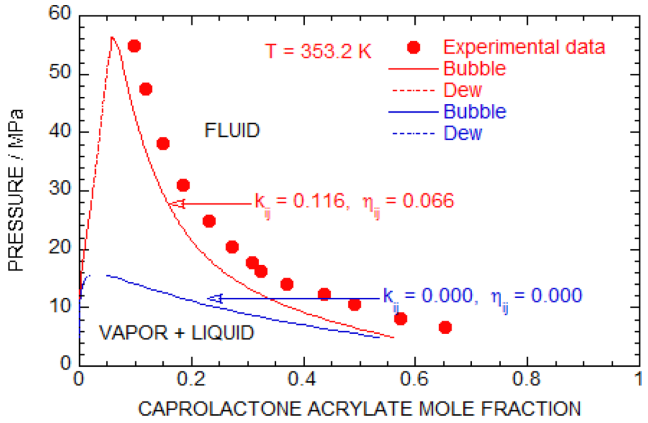

Fig. 3. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (carbon dioxide + caprolactone acrylate) system with calculation obtained from the Peng-Robinson equation of state with k_{ij} and η_{ij} set equal to zero (blue solid lines), k_{ij} = 0.065, η_{ij} = 0.045 (carbon dioxide + caprolactone acrylate) (red solid lines) at 353.2 K.

parameter value of the Peng-Robinson equation of state for the (carbon dioxide + caprolactone acrylate) system was k_{ij} = 0.116 and h_{ij} = 0.066 (experimental data points: 13; RMSD: 23.9%).

Fig. 4 compares the experimental results with calculated (*P*-*x*) isotherms at temperatures of (313.2, 333.2, 373.2 and 393.2) K for the (carbon dioxide + caprolactone acrylate) system using the optimized k_{ij} and h_{ij} values determined at each temperatures. As shown in Fig. 4, obtained were well-fitted data with the Peng-Robinson equation using adjustable mixture parameters for the (carbon dioxide + caprolactone acrylate) system. The five temperatures using two parameters determined at 353.2 K, RMSD for the (carbon dioxide + caprolactone acrylate) system became too high when the parameters were applied to this system. So it is necessary to obtain the optimized parameters for each temperature to decrease RMSD (see Table 4). The curves calculated by the Peng-Robinson equation of state did not demonstrate three phases at five temperatures. As shown in Fig. 4, it is plotted the pressures against mole fraction in order to compare the experimental data (symbols) of the (carbon dioxide + caprolactone acrylate) system with calculations (solid lines) obtained with the Peng-Robinson equation of state using optimum parameters (k_{ij} and η_{ij}) at each temperature. Here, the number for experimental data is 13 at each temperature. In comparison, the experimental data and calculated curve show poor agreement at four

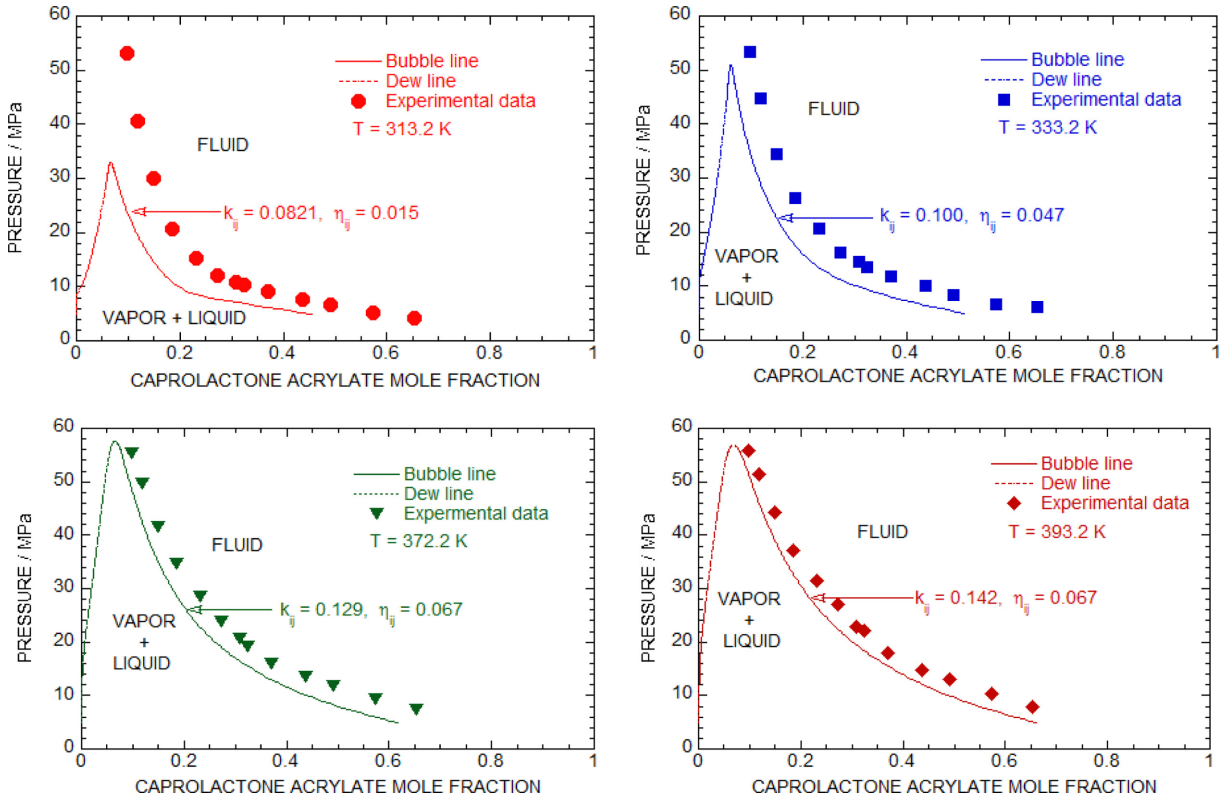

Fig. 4. Plot of the pressure against the mole fraction, comparing the experimental data (symbols) of the (carbon dioxide + caprolactone acrylate) system with calculations (solid lines) obtained with the Peng-Robinson equation of state using optimized k_{ij} and η_{ij} at each temperature: ●, 313.2 K; ■, 333.2 K; ▼, 373.2 K; ◆, 393.2 K.

Table 3. The properties of pure component in carbon dioxide and caprolactone acrylate

Compounds	M_w	Chemical Structure	T_b / K	T_c / K	p_c / MPa	ω
Carbon Dioxide	44.01	O=C=O		304.2	7.38	0.225
Caprolactone Acrylate	345.41	$C_{17}H_{28}O_7$	539.2[a]	663.4	1.45	1.149

[a]Scientific Polymer Products Co., Ltd.

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

T / K	k_{ij}	η_{ij}	RMSD (%)
313.2	0.0821	0.015	-
333.2	0.100	0.047	-
353.2	0.116	0.066	29.8
373.2	0.129	0.067	25.7
393.2	0.142	0.067	18.7

temperatures. This poor agreement is due to error of boiling point and critical properties. According to the calculated result, the critical mixture curve showed type-I.

4. Conclusions

The *P-x* isotherm data of (carbon dioxide + caprolactone acrylate) system was studied using a variable-volume view cell with static-type apparatus. Phase equilibrium data was measured in synthetic method in a temperatures of ($313.2 \le T \le 393.2$) K and pressures of ($4 < P < 56$) MPa. The (carbon dioxide + caprolactone acrylate) mixtures did 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 curves was poor for using two optimized parameters obtained with the Peng-Robinson equation of state at each temperature. The linear curves for two binary interaction parameters (k_{ij} and η_{ij}) against the temperatures show reasonable tendency.

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 [cm^3/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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