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디메틸카보네이트와 이산화탄소 혼합물의 기포점 측정

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Measurement of Bubble Points of Dimethyl Carbonate and Carbon Dioxide Mixtures

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본 연구에서는 가변부피 투시창이 설치되어 있는 고압 상평형 측정 장치를 사용하여 이산화탄소의 임계온도 이상과 디메틸카보네이트의 임계온도 이하의 온도 범위에서 혼합물의 조성을 변화시키면서 디메틸카보네이트와 이산화탄소 혼합물의 기포점을 압력을 측정하였다. 실험적으로 측정된 기포점 압력 데이터를 Peng-Robinson 상태방정식에 상관시킴으로써 기포점 조성과 평형을 이루는 이슬점 조성을 추정하였다. 실험적으로 측정된 기포점 압력은 Peng-Robinson 상태방정식으로 계산한 결과와 매우 잘 일치하였다. 가변부피 투시창이 설치되어 있는 고압 상평형 실험장치는 고압의 압축유체 혼합물의 기포점을 매우 쉽고 빠르게 측정할 수 있는 방법이라고 할 수 있다.

The bubble point pressures of dimethyl carbonate and carbon dioxide mixtures were measured by using a high-pressure experimental apparatus equipped with a variable-volume view cell, at various CO_2 compositions in the range of temperatures above the critical temperature of CO_2 and below the critical temperature of dimethyl carbonate. The experimental bubble point pressure data were correlated with the Peng-Robinson equation of state (PR-EOS) to estimate the corresponding dew point compositions at equilibrium with the bubble point compositions. The experimentally measured bubble point pressures gave good agreement with those calculated by the PR-EOS. The variable-volume view cell equipment was verified to be an easy and quick way to measure the bubble point pressures of high-pressure compressible fluid mixtures.

***Keywords**: bubble point pressure, carbon dioxide, dimethyl carbonate, variable-volume view cell, Peng-Robinson equation of state*

1. Introduction

To experimentally measure the vapor-liquid equilibrium (VLE) data of high-pressure compressible fluid mixtures, it is common to use a circulation-type apparatus equipped with a constant-volume cell. However, this conventional equipment has a disadvantage in that it requires a time sufficient to ensure equilibrium during the circulation of the vapor and liquid mixtures. It also requires obtaining samples from the liquid and vapor phases simultaneously and accurately and then analyzing their compositions. On the other hand, a variable-volume view cell apparatus is well-known as a simple and quick way capable of measuring the phase equilibrium behavior of high-pressure compressible fluid mixtures[1,2]. The phase equilibrium can be easily measured by changing the volume of the view cell containing the fluid mixture of a known composition and by observing the phase change through the window of the cell. The advantage of using the variable-volume cell is that the concentration of the system is kept constant during the experiment.

In this work, the bubble point pressures of mixtures of carbon dioxide (CO_2) and dimethyl carbonate (DMC) were measured using the variable-volume view cell apparatus in the range of temperatures above the critical temperature of CO_2 and below the critical temperature of DMC. The experimentally measured bubble point data were correlated with the popular Peng-Robinson equation of state (PR-EOS)[3]. The vapor phase compositions, i.e., the dew point compositions corresponding to the bubble points, were calculated with the optimum values of the PR-EOS binary interaction parameters.

2. Experimental

CO_2 of 99.99 % purity and DMC of 99.5 % purity were purchased from Myung Sin General Gas Co. (Korea) and Sigma-Aldrich Co. (USA), respectively. They were used without further purification. The phase behavior of the mixtures of CO_2 and DMC was measured using a high-pressure apparatus equipped with a variable-volume view cell.

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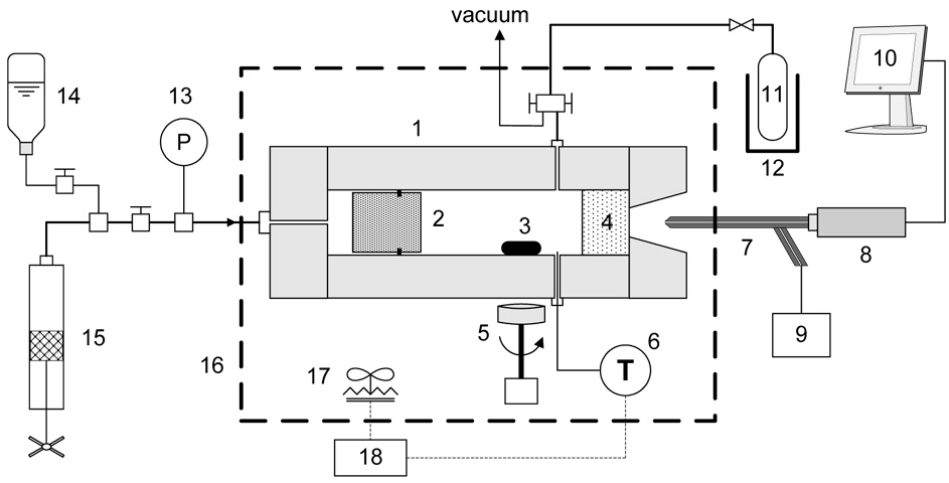

Figure 1. A schematic diagram of the experimental apparatus: (1) variable-volume view cell; (2) piston; (3) spin bar; (4) sapphire window; (5) magnetic stirrer; (6) temperature indicator; (7) borescope; (8) CCD camera; (9) light source; (10) monitor; (11) CO_2 sample cylinder; (12) Dewar flask; (13) Heise pressure gauge; (14) water; (15) pressure generator; (16) air bath; (17) heater and fan; (18) temperature controller.

Figure 1 shows a schematic diagram of the experimental apparatus used in this work. A detailed description of the experimental apparatus and procedure can be obtained from our previous publications[2,4,5]. The apparatus consists of a view cell equipped with a sapphire window and a movable piston, a pressure generator, a borescope, a video monitor, a magnetic stirring system, and an air bath. The cell has dimensions of 16 mm i.d. by 70 mm o.d. Pressure is measured using a high-precision pressure gauge (Dresser Heise model CC-12-G-A-02B, ± 0.5 bar accuracy). Temperature is measured to within ± 0.1 K by an RTD inserted into the interior of the cell. A movable piston is placed inside the cell to change the cell volume. Water pressurezed by the pressure generator displaces the piston in the cell. A change in the cell volume causes a change of the system pressure. The interior of the cell is visually observed though a sapphire window by a borescope and a CCD camera connected to a monitor.

The experiment for measuring the bubble point pressures of the CO_2 + DMC mixtures was performed by the following procedure. DMC was taken using a gas-tight syringe and then injected into the cell. After immediately assembling a piston, o-rings and a sapphire window in the view cell, the cell was then placed inside the air bath. The amount of DMC loaded was determined by using a sensitive balance (AND model HM-30) measurable to ± 0.1 mg. A known mass of CO_2 was charged into the cell through a feed line. The exact amount of CO_2 introduced into the cell was determined by weighing the CO_2 sample cylinder before and after loading using a balance (Precisa model 1212 M) with an accuracy of ± 1 mg. To prevent any loss of CO_2 gas in the feed line during loading, the CO_2 gas in the feed line was recovered back into the CO_2 sample cylinder by dipping the cylinder into a Dewar flask filled with liquid nitrogen.

The pressure was varied until a phase change was visually observed for a mixture with a constant overall composition. To mix the CO_2 and DMC in the cell, the fluid in the cell was compressed by moving the piston located within the cell using the pressure generator. The liquid was well agitated by a magnetic stirrer. At the same time, the system was heated to a desired temperature. The temperature was controlled with an uncertainty of ± 0.1 K. As the pressure increased, the CO_2 and DMC was mixed together and finally the fluid became a single homogeneous phase. Once the system reached thermal equilibrium and the solution was maintained at a homogeneous single phase, the pressure was then slowly reduced at about 0.5 MPa/min until tiny vapor bubbles started to form from the single phase solution. The initial pressure at which the first bubbles are observed is the bubble pressure of the solution at a given composition and temperature. For reproducing consistent measurements, every measurement was repeated at least twice at each temperature. The uncertainty in the bubble point pressure was 0.02 MPa. The bubble point pressures at different temperatures and compositions were measured by the same procedure, thus creating pressure-temperature (*P-T*) iospleths.

3. Results and Discussion

The bubble point pressures for the CO_2 + DMC mixtures of different compositions were measured in the temperature range from a room temperature to 71.8 ℃. The experimental data are given in Table 1, and their *P-T* isopleths are shown in Figure 2. The bubble point pressure increased with increasing the system temperature at a fixed CO_2 mole fraction. As shown in Figure 2, the slope of the bubble point pressure with respect to temperature increased as the CO_2 mole fraction increased.

When the CO_2 mole fraction increased isothermally, the bubble point pressure increased significantly. This can be more easily seen from a P-x_1 diagram in which the bubble point pressure is plotted against the CO_2 mole fraction at various temperatures. This plot was obtained by fitting the *P-T* curves of Figure 2 at different CO_2 mole fractions with polynomial equations and then by determining the pressures corresponding to desired temperatures from the curve fits. Figure 3 shows

Table 1. Experimental Bubble Point Data for Various CO_2 Mole Fractions (x_1) in the CO_2(1) + DMC(2) System

x_1	T/℃	P/MPa	x_1	T/℃	P/MPa	x_1	T/℃	P/MPa
0.1730	23.7	1.48	0.6026	23.9	3.25	0.7900	24.6	4.32
	31.0	1.49		30.0	3.67		31.1	4.99
	40.2	1.64		41.6	4.55		41.6	5.94
	50.7	1.86		50.5	5.27		50.4	6.93
	59.9	2.03		52.3	5.50		63.0	8.40
	70.3	2.22		62.2	6.32		71.1	9.40
0.2984	23.5	1.85		71.8	7.13	0.8168	24.3	4.50
	31.6	2.08	0.7042	20.5	3.48		34.9	5.53
	40.8	2.36		36.8	4.74		40.7	6.18
	50.0	2.70		47.8	5.77		46.0	6.81
	61.4	3.08		51.6	6.12		50.9	7.37
	72.9	3.52		60.0	6.95		57.6	8.14
0.3740	23.3	2.22		70.0	8.05		66.6	9.27
	30.0	2.35	0.7530	20.7	3.66		71.1	9.81
	41.0	2.73		29.7	4.41	0.8725	23.8	4.82
	50.2	3.14		37.0	5.10		30.3	5.50
	60.4	3.62		44.6	5.85		40.2	6.67
	70.2	4.07		53.1	6.75		50.2	7.91
0.4841	29.4	2.92		59.9	7.49		59.9	9.17
	41.0	3.54		69.8	8.68		70.1	10.48
	50.1	4.05						
	60.7	4.77						
	71.2	5.48						

the P-x_1 diagrams at several temperatures from 30 ℃ to 70 ℃ for the CO_2 + DMC systems. Second-order polynomial equations were used, and the correlation coefficients of the curve fits, which expressed the goodness of the fits, were greater than 0.995 for all cases. As described above, the bubble point pressure increased as the CO_2 composition and temperature increased.

The dew point compositions were not measured experimentally in this work, and therefore they should be estimated by a thermodynamic model. We used the well-known Peng-Robinson equation of state (PR-EOS) with the quadratic mixing rules to calculate the dew point compositions corresponding to the bubble points. The PR-EOS[3] is expressed as:

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

The mixing rules for calculating the a and b parameters in a mixture are as follows:

$$a=\sum_i\sum_j z_i z_j a_{ij} \tag{2}$$

$$a_{ij}=(a_{ii}a_{jj})^{1/2}(1-k_{ij}) \tag{3}$$

$$b=\sum_i\sum_j z_i z_j b_{ij} \tag{4}$$

$$b_{ij}=\left(\frac{b_i+b_j}{2}\right)(1-l_{ij}) \tag{5}$$

In Eqs. (2) and (4), z_i is the liquid or vapor phase mole fraction (x_i or y_i). In Eq. (4), $b_{ii}=b_i$ and $b_{jj}=b_j$. Two adjustable binary interaction parameters (k_{ij} and l_{ij}) in Eqs. (3) and (5) should be determined by the correlation with the experimental data. The expressions for the a_{ii} and b_i parameters of a pure component are the same as shown in all the textbooks of classical thermodynamics[3,7]. The expressions for the fugacity coefficients of a component in a mixture required for the VLE calculation of the mixture are available from the textbooks[3,7]. The characteristic properties of CO_2 and DMC required to calculate the a_{ii} and b_i parameters were obtained from the literature[6] and are shown

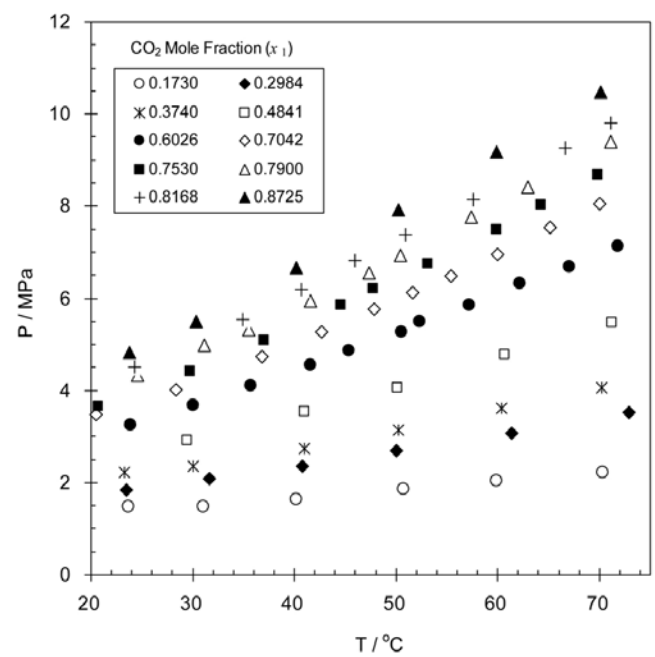

Figure 2. Experimental bubble point pressures of CO_2 + DMC mixtures at different CO_2 mole fractions.

Table 2. Characteristic Properties of CO_2 and DMC

Compound	T_c/K	P_c/MPa	ω
CO_2	30.95	73.8	0.239
DMC	283.85	48.0	0.336

Table 3. Binary Interaction Parameters of the PR-EoS for the CO_2 + DMC System

Binary interaction parameters	30 ℃	40 ℃	50 ℃	60 ℃	70 ℃
k_{12}	-0.0702	-0.0661	-0.0665	-0.0638	-0.0576
l_{12}	-0.1096	-0.0950	-0.0916	-0.0860	-0.0772

in Table 2.

To describe the vapor-liquid equilibrium with the PR-EOS, the adjustable binary interaction parameters (k_{ij} and l_{ij}) should be determined first. In this work the experimental bubble point data were correlated with the PR-EOS[7], and then a set of optimum values of the k_{ij} and l_{ij} parameters were found by minimizing the following objective function:

$$F=\sum_{i=1}^{N}\frac{\left|P_i^{calc}-P_i^{\exp}\right|}{P_i^{\exp}} \tag{6}$$

where $P_i^{\exp}$ is the experimental value of pressure and P_i^{calc} is the pressure calculated by the PR-EOS at the experimental value of CO_2 mole fraction, and N is the number of data points. An optimization routine, UNLSF in IMSL/Math Library, which solved a nonlinear least-squares problem, was used. Table 3 summarizes the optimum values of the binary interaction parameters at five different temperatures for the CO_2 + DMC system.

Using the optimum values of the binary interaction parameters, the vapor-liquid equilibrium (*P-xy*) was calculated by simultaneously solving the following equilibrium relations:

$$y_i\hat{\phi}_i^v = x_i\hat{\phi}_i^l \quad (i = 1,2) \tag{7}$$

where $\hat{\phi}_i^v$ and $\hat{\phi}_i^l$ are the fugacity coefficients of component i in the mixture in vapor and liquid phases, respectively. At an arbitrarily fixed liquid phase mole fraction (x_i) and temperature, the system pressure and the vapor phase mole fraction (y_i), which satisfied Eq. (7), were calculated. The same calculations were repeated at different liquid phase mole fractions from 0 to 1 with a small interval, and finally a pressure-composition (*P-xy*) diagram was completed. In these calculations we used the NEQNF subroutine in the IMSL/Math library.

Figure 3 shows the *P-xy* diagram calculated by the PR-EOS at several temperatures for the CO_2(1) + DMC(2) system along with the experimental points. The bubble point pressure curves (solid lines) and the dew point pressure curves (dashed lines) at temperatures of 30 ℃ to 70 ℃ started from the vapor pressure of pure DMC and finally met at the critical points of the mixture. The bubble points calculated by the PR-EOS gave good agreement with those measured experimentally

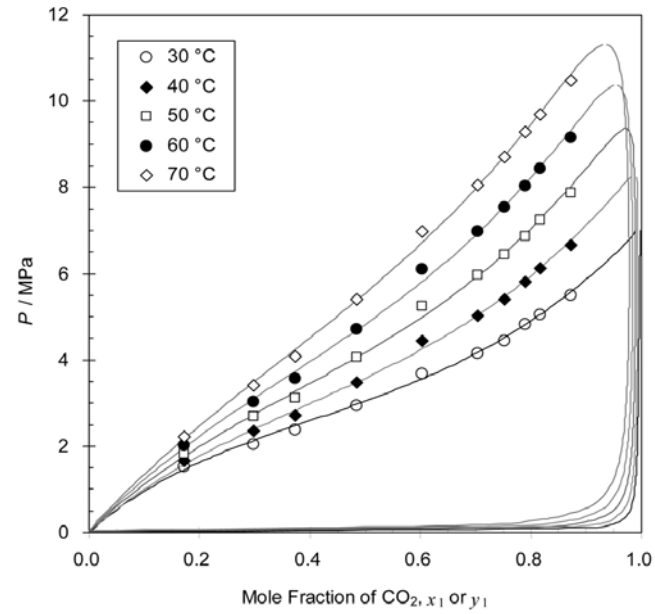

Figure 3. *P-xy* diagram at different temperatures for CO_2(1) + DMC(2) system. The symbols are experimental bubble points, and the lines are the bubble point and dew point curves correlated by the PR-EOS.

for all temperatures. However, although the results of the bubble and critical points calculated by the PR-EOS showed good agreement with their experimental values, the dew points estimated by the PR-EOS are not guaranteed to be accurate values. Thus, there may exist a difference between the calculated and actual values of the mixture dew points.

4. Conclusions

The bubble point pressures of CO_2 + DMC mixtures were measured by using a high-pressure experimental apparatus equipped with a variable-volume view cell. The experimental bubble point pressure data at different temperatures were correlated with the Peng-Robinson equation of state to obtain the dew point pressures and compositions in equilibrium with the bubble points. The experimentally measured bubble point pressures gave good agreement with those calculated by the PR-EOS.

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