1560 *J. Chem. Eng. Data* **2005,** *50,* 1560−1563

High-Pressure Phase Behavior of CO_2 + *N*-Vinyl Caprolactam and CO_2 + *N*-Methyl Caprolactam Systems

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Pressure−composition isotherms for binary mixtures of carbon dioxide (CO_2) + *N*-vinyl caprolactam (NVCL) and carbon dioxide (CO_2) + *N*-methyl caprolactam (NMCL) were measured using a variable volume view cell at temperature from (323.15 to 353.15) K and pressure up to about 21 MPa. Phase behavior of these binary experimental data were correlated with Peng−Robinson equation of state using a van der Waals one-fluid mixing rule including two adjustable parameters. Critical constants were estimated with the Joback method, and the acentric factor was estimated with the Lee−Kesler method.

Introduction

Supercritical carbon dioxide ($scCO_2$) is a useful alternative to toxic or volatile organic solvents for industrial synthesis and processing.[1−3] $scCO_2$ has many advantages, as it has relatively mild critical conditions ($T_c = 304.25$ K, $P_c = 7.38$ MPa), and it is also nontoxic, nonflammable, and inexpensive. As a solvent, $scCO_2$ has no dipole moment and low dielectric constant. As a result, $scCO_2$ is a relatively good solvent for nonpolar molecules with low molecular weight and is not an adequate solvent for polar or nonpolar polymers. But because of $scCO_2$'s strong quadrupole moment, low molecular weight polar compounds such as methanol and ethanol show substantial solubility in $scCO_2$.[1]

$ScCO_2$ also has been widely studied and used as an extraction medium for polymer purification because swelling of common polymer and solubility of nonpolar monomer in $scCO_2$ are substantial.[1] To obtain high-quality polymer for special applications such as electrochemicals, cosmetics, and drug delivery systems, the monomer must be separated from the polymer, and the residual contents of monomer must be very low level.

N-Vinyl caprolactam (NVCL) is a kind of *N*-vinyl amide monomer that is colorless or a yellow solid having a characteristic odor. It is miscible in most organic solvents. Various NVCL copolymers can be made easily with other vinyl monomers.[4] Examples of monomers with which it forms copolymers include acrylic and methacrylic acids; their salts, amides, and esters; vinyl acetate; and styrene. The product can be synthesized by solution, dispersion, and emulsion polymerization techniques. There are several important issues (such as drying, solubility, and polymer plasticization) that are involved when $scCO_2$ is used as a polymerization solvent.[3] The monomer must be dissolved in continuous phase ($scCO_2$) for dispersion polymerization. So phase behavior of CO_2 + NVCL is very important for determining initial polymerization condition because particle size and particle size distribution of the final polymer are directly affected. Also for monomer extraction from polymer, phase behavior data of CO_2 + NVCL are necessary.

N-Methyl caprolactam (NMCL) is a solvent having a good selectivity for the separation of aromatic and saturated hydrocarbons.[5] Also NMCL is one of the most common physical solvents used in gas-treating processes. In the manufacture of hydrogen, ammonia, and synthetic natural gas, very large quantities of carbon dioxide must be removed from gases at high pressure.[6] Absorption into a liquid agent, either by physical absorption or by reaction with a solution of a chemical base, is the most commonly used technique for acid-gas removal. Knowledge of the thermodynamic properties of CO_2 + NMCL mixture in the vicinity of the critical point of CO_2 is required for process design.[6]

In the viewpoint of molecular thermodynamics, NVCL and NMCL have the same functional group (i.e., ϵ-caprolactam). In the case of NVCL, hydrogen of the amide group is substituted with a vinyl group, and for NMCL, hydrogen of the amide group is substituted with a methyl group. So it is interesting to understand the phase behavior of these ϵ-caprolactam derivatives with CO_2.

In this work, we measured pressure−composition isotherms for a binary mixture of CO_2 + NVCL or NMCL at temperatures from (323.15 to 353.15) K and pressures up to 21 MPa. Phase behavior of these binary experimental data was correlated with Peng−Robinson equation of state (PR EOS) with two adjustable parameters.

Experimental Section

Materials. Carbon dioxide (min. 99.99 %) was purchased from Korea Industrial Gases. *N*-Vinyl caprolactam (NVCL: min. 98 % purity) and *N*-methyl caprolactam (NMCL: min. 99 % purity) were obtained from Aldrich and used without further purification.

Apparatus and Experimental Methods. Figure 1 shows a schematic diagram of typical variable volume view cell apparatus to obtain phase behavior data at high pressure. The experimental system has the same equipment as our previous work.[7] Typically CO_2 + NVCL or NMCL systems were studied with the following experimental procedures. Because NVCL is a solid monomer, the measured amount of NVCL is charged first before assembling a cell set. The assembled cell was purged two or three times with N_2 and CO_2 at room temperature to remove traces of air. In the case of NMCL, which is a liquid

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10.1021/je0495334 CCC: $30.25

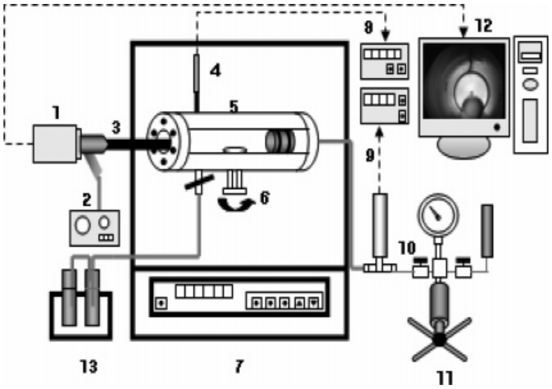

Figure 1. Schematic diagram of the experimental apparatus: (1) camera; (2) light source; (3) borescope; (4) fast response PRT; (5) view cell; (6) magnetic stirrer; (7) air bath; (8) digital thermometer; (9) digital pressure transducer; (10) pressure gauge; (11) hand pump; (12) computer monitor; and (13) trap.

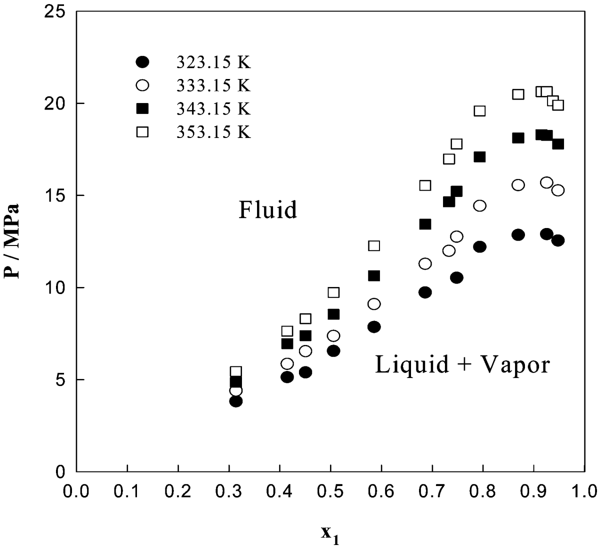

Figure 2. Pressure−composition experimental isotherms of CO_2 + *N*-vinyl caprolactam system: ●, 323.15 K; ○, 333.15 K; ■, 343.15 K; □, 353.15 K.

solvent, a measured amount was loaded in this cell with a syringe within ± 0.001 g. CO_2 was then added to the cell to within ± 0.01 g using a high-pressure bomb. The CO_2 + NVCL or NMCL mixtures could be compressed to the desired operating pressure by moving a piston fitted within the cell using water compressed with a high-pressure generator (High-Pressure Equipment Co., model 62-6-10). A magnetic stirring bar in the cell helped the mixture to reach equilibrium rapidly. The pressure of the solution was obtained by measuring the pressure of the water with a digital pressure transducer (Paroscientific, model 43KR-HHT-101) and pressure indicator (Paroscientific, model 730). Temperature was measured with a PRT-type thermometer (HART, model 5622-32SR, accuracy of ± 0.045 K) fixed to the surface of the cell and displayed by an indicator (HART, model 1502). At a fixed temperature, the mixture in the cell was compressed to a single phase at high pressures. The pressure was then slowly decreased until a second phase (bubble, mixture critical, or dew point) appeared. This was repeated several times until the fluctuation of pressure at phase transition was minimized (± 0.03 MPa). The inside of the cell was projected onto the computer monitor using a camera (Veltek International Inc., model CVC5520) with a borescope (Olympus Corp., model R100-038-000-50).

Table 1. Experimental Data for the CO_2 (1) + *N*-Vinyl Caprolactam (2) System[a]

T/K	x_1	*P*/MPa	transition	*T*/K	x_1	*P*/MPa	transition
323.15	0.314	3.82	BP	323.15	0.748	10.53	BP
	0.415	5.13	BP		0.794	12.20	BP
	0.451	5.39	BP		0.869	12.85	BP
	0.506	6.55	BP		0.925	12.90	BP
	0.586	7.86	BP		0.948	12.54	DP
	0.686	9.74	BP				
333.15	0.314	4.40	BP	333.15	0.733	11.99	BP
	0.415	5.85	BP		0.748	12.76	BP
	0.451	6.54	BP		0.794	14.44	BP
	0.506	7.37	BP		0.869	15.55	BP
	0.586	9.10	BP		0.925	15.69	CP
	0.686	11.28	BP		0.948	15.27	DP
343.15	0.314	4.85	BP	343.15	0.748	15.21	BP
	0.415	6.96	BP		0.794	17.09	BP
	0.451	7.39	BP		0.869	18.12	BP
	0.506	8.55	BP		0.915	18.30	CP
	0.586	10.64	BP		0.925	18.26	DP
	0.686	13.43	BP		0.948	17.79	DP
	0.733	14.64	BP				
353.15	0.314	5.44	BP	353.15	0.748	17.80	BP
	0.415	7.63	BP		0.794	19.58	BP
	0.451	8.31	BP		0.869	20.48	BP
	0.506	9.74	BP		0.915	20.64	CP
	0.586	12.26	BP		0.925	20.64	DP
	0.686	15.54	BP		0.938	20.13	DP
	0.733	16.97	BP		0.948	19.89	DP

[a] BP = bubble point, CP = mixture critical point, DP = dew point.

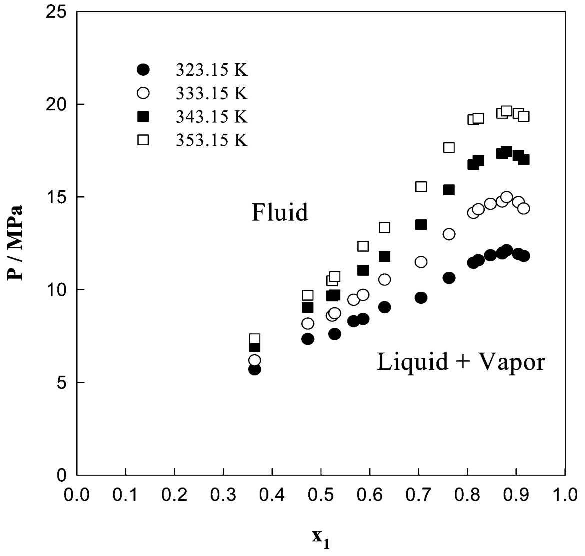

Figure 3. Pressure−composition experimental isotherms of CO_2 + *N*-methyl caprolactam system: ●, 323.15 K; ○, 333.15 K; ■, 343.15 K; □, 353.15 K.

Results and Discussion

Figure 2 and Table 1 show pressure−composition isotherms for the CO_2 + NVCL system at (323.15, 333.15, 343.15, and 353.15) K. The range of pressures is (3.82 to 20.64) MPa. Figure 3 and Table 2 show pressure−composition isotherms for a CO_2 + NMCL system at (323.15, 333.15, 343.15, and 353.15) K. And then the range of pressures is (5.69 to 19.63) MPa. Bubble pressures of CO_2 + NMCL mixture were relatively higher than those of the CO_2 + NVCL mixture at low CO_2 mole fraction region. But the mixture critical point of the CO_2 + NVCL system was higher than that of the CO_2 + NMCL system at all isotherms. Figure 4 shows a comparison of experimental data between the CO_2 + NVCL and the CO_2 + NMCL systems at 323.15 K. Experimental data obtained in this study were modeled with the PR EOS using the van der Waals one-fluid mixing rule[8] including two

Table 2. Experimental Data for the CO_2 (1) + *N*-Methyl Caprolactam (2) System[a]

T/K	x_1	*P*/MPa	transition	*T*/K	x_1	*P*/MPa	transition
323.15	0.364	5.69	BP	323.15	0.812	11.44	BP
	0.473	7.33	BP		0.822	11.58	BP
	0.528	7.59	BP		0.847	11.84	BP
	0.567	8.29	BP		0.871	11.95	BP
	0.586	8.41	BP		0.872	11.99	BP
	0.630	9.04	BP		0.880	12.12	BP
	0.705	9.55	BP		0.904	11.92	DP
	0.762	10.62	BP		0.915	11.81	DP
333.15	0.364	6.18	BP	333.15	0.762	12.98	BP
	0.473	8.16	BP		0.812	14.13	BP
	0.523	8.59	BP		0.822	14.33	BP
	0.528	8.72	BP		0.847	14.62	BP
	0.567	9.45	BP		0.871	14.75	BP
	0.586	9.71	BP		0.880	14.98	BP
	0.630	10.53	BP		0.904	14.71	DP
	0.705	11.48	BP		0.915	14.37	DP
343.15	0.364	6.94	BP	343.15	0.762	15.37	BP
	0.473	9.04	BP		0.812	16.74	BP
	0.523	9.66	BP		0.822	16.95	BP
	0.528	9.71	BP		0.871	17.33	BP
	0.586	11.05	BP		0.880	17.46	BP
	0.630	11.78	BP		0.904	17.23	DP
	0.705	13.50	BP		0.915	17.01	DP
353.15	0.364	7.35	BP	353.15	0.762	17.66	BP
	0.473	9.70	BP		0.812	19.16	BP
	0.523	10.48	BP		0.822	19.24	BP
	0.528	10.71	BP		0.871	19.51	BP
	0.586	12.34	BP		0.880	19.63	BP
	0.630	13.35	BP		0.904	19.50	DP
	0.705	15.55	BP		0.915	19.34	DP

[a] BP = bubble point, CP = mixture critical point, DP = dew point.

binary interaction parameters:

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

$$a(T) = 0.45724\frac{R^2{T_c}^2}{P_c} \tag{2}$$

$$b = 0.07780\frac{RT_c}{P_c} \tag{3}$$

$$a_m = \sum_i\sum_j x_i x_j a_{ij} \tag{4}$$

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1-k_{ij}) \tag{5}$$

$$b_m = \sum_i\sum_j x_i x_j b_{ij} \tag{6}$$

$$b_{ij} = \frac{(b_{ii}+b_{jj})}{2}(1-\eta_{ij}) \tag{7}$$

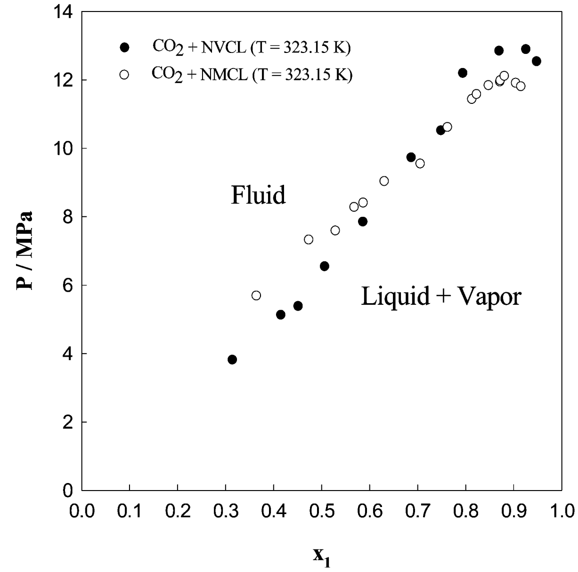

Figure 4. Comparison of experimental data between CO_2 + *N*-vinyl caprolactam (●) and CO_2 + *N*-methyl caprolactam system (○) at T = 323.15 K.

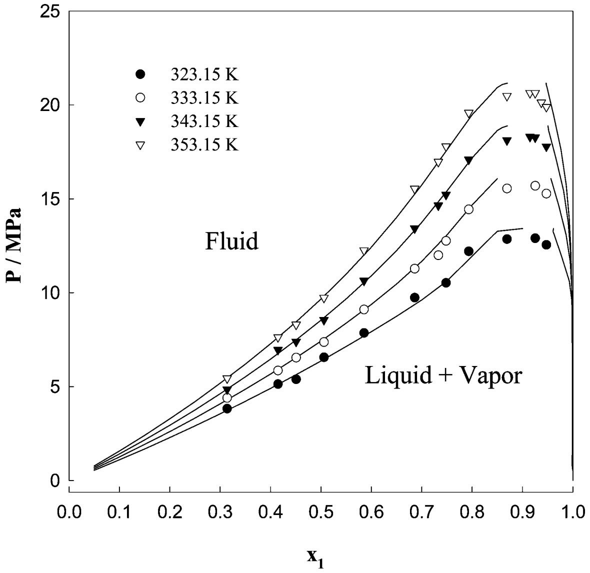

Figure 5. Calculation result for CO_2 + *N*-vinyl caprolactam system using the Peng–Robinson equation of state with k_{ij} = 0.0593 and η_{ij} = −0.0002: ●, 323.15 K; ○, 333.15 K; ▼, 343.15 K; ▽, 353.15 K.

Table 3. Boiling Temperature, Critical Constants, and Acentric Factor[10,11]

component	T_b/K	T_c/K	P_c/MPa	w
CO_2		304.10	7.38	0.225
NVCL	483.60	705.95	3.57	0.437
NMCL	510.20	752.95	3.82	0.412

These two binary interaction parameters were determined by regressing experimental data with the PR EOS. The objective function (OBF) and the root-mean-squared relative deviation (RMSD) of this calculation were defined as follows:

$$\text{OBF} = \sum_i^N\left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}}\right)^2 \tag{8}$$

$$\text{RMSD} = \sqrt{\frac{\text{OBF}}{\text{ND}}} \times 100 \tag{9}$$

ND in eq 9 means the number of data points. We used the Marquardt algorithm to optimize objective function with all isotherms.[9] Critical constants (T_c and P_c) and the acentric factor for PR EOS are listed in Table 3. Critical temperature (T_c) and pressure (P_c) of NVCL and NMCL were estimated with the Joback method. Acentric factor (ω) was estimated with the Lee–Kesler method.[10] Because we could not find experimentally measured boiling temperature (T_b) data of NVCL, which is required to estimate T_c and ω, we estimated T_b of NVCL using the Joback method. In the case of NMCL, a T_b listed in the Aldrich Handbook[11] was used. Figures 5 and 6 represent a comparison of experimental data (symbol) and calculated pressure–composition isotherms (solid line) at (323.15,

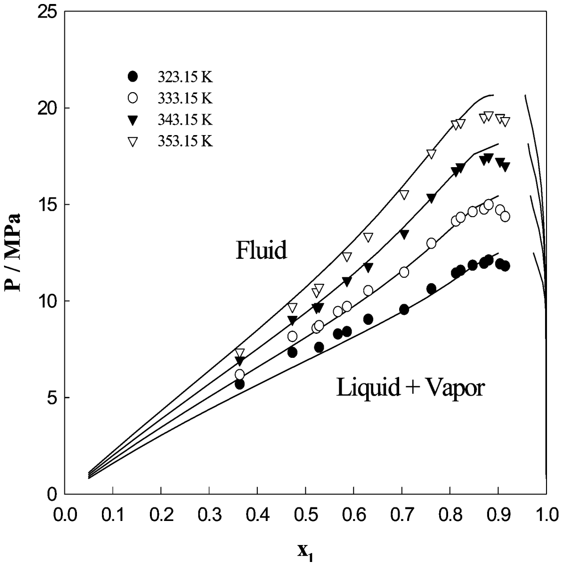

Figure 6. Calculation result for CO_2 + *N*-methyl caprolactam system using the Peng−Robinson equation of state with k_{ij} = 0.0272 and η_{ij} = −0.0357: ●, 323.15 K; ○, 333.15 K; ▼, 343.15 K; ▽, 353.15 K.

333.15, 343.15, and 353.15) K. We obtained $k_{ij} = 0.0595$, $\eta_{ij} = -0.0002$, and RMSD = 1.59 % for the CO_2 + NVCL system and $k_{ij} = 0.0272$, $\eta_{ij} = -0.0357$, and RMSD = 3.28 % for the CO_2 + NMCL system. With two binary interaction parameters, good correlation results were obtained. Correlation results with PR EOS show that the mixture critical points of CO_2 + NVCL system are slightly more overestimated than those of the CO_2 + NMCL system.

Conclusion

We measured pressure−composition isotherms for CO_2 + NVCL or NMCL systems at temperature from (323.15 to 353.15) K and pressures up to 21 MPa. Phase behavior of NVCL or NMCL, which have the same functional group, with CO_2 showed that bubble pressures of the CO_2 + NMCL mixture was relatively higher than those of the CO_2 + NVCL mixture at low mole fraction of CO_2. But the maximum phase transition pressures of the CO_2 + NVCL system were higher than those of the CO_2 + NMCL system for all isotherms. These results were correlated with PR EOS with two adjustable parameters. We obtained good correlation results. RMSD (%) for the CO_2 + NVCL system was 1.59 % and for the CO_2 + NMCL system was 3.28 %.

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Received for review December 30, 2004. Accepted June 25, 2005. This work was supported by the BK21 project of Ministry of Education and the National Research Laboratory (NRL) Program of Korea Institute of Science & Technology Evaluation and Planning.

JE0495334