High Pressure Phase Behavior of CO_2 + *N*-vinyl caprolactam and CO_2 + *N*-methyl caprolactam systems

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ABSTRACT

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 K to 353 K and pressure up to 21 MPa. Phase behavior of these binary experimental data was modeled with Peng-Robinson equation of state with two adjustable parameters. Critical constants were estimated with Joback method and acentric factor was estimated with Lee-Kesler method. Good correlation results were obtained.

KEY WORDS

N-vinyl caprolactam, *N*-methyl caprolactam, carbon dioxide, high pressure phase behavior

INTRODUCTION

Recently, supercritical carbon dioxide ($scCO_2$) is considered as a useful alternative of toxic or volatile organic solvents for industrial synthesis and processing. $ScCO_2$ has many advantages, as it has relatively mild critical conditions (T_c = 304.25 K, P_c = 7.38 MPa) and it is also non-toxic, nonflammable and inexpensive. As a solvent, $scCO_2$ has no dipole moment and has low dielectric constant. So, $scCO_2$ is a good solvent for non-polar molecules with low molecular weight and slightly polar molecules (Beckman, 2004). $ScCO_2$ also has been widely studied and used as an extraction medium for polymer purification because degree of swelling of common polymer and solubility of non-polar monomer in supercritical carbon dioxide is substantial. And to obtain high quality polymer for special applications such as electro chemicals, cosmetics and drug delivery system, monomer must be separated from polymer and residual contents of monomer must be very low level.

N-vinyl caprolactam (NVCL) is a monomer that is colorless to yellow solid having a characteristic odor. It is miscible in all proportions with most organic solvents. As a vinyl compound, vinyl caprolactam is ideal for manufacturing copolymers (BASF, 2004). 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 polymerized by solution, dispersion and emulsion techniques. Then it is possible to use $scCO_2$ as a polymerization medium (Kendall, 1999). Because monomer (NVCL) must be dissolved in $scCO_2$ (continuous phase), phase behavior of CO_2 + NVCL is very important for determining initial polymerization condition in these polymerization steps.

N-methyl caprolactam (NMCL) is a solvent having a good selectivity for the separation of aromatic and saturated hydrocarbons (Bittrich, 1989). NMCL is among the most common physical solvents used in gas-treating process. In the manufacture of hydrogen, ammonia, and synthetic natural gas, very large quantities of carbon dioxide must be removed from gases at high pressure (Zhao, 1995). 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. Operating conditions including the critical temperature and pressure of carbon dioxide and a 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.

There are differences in applications of high-pressure phase behavior between CO_2 and NVCL, or NMCL. But it is important to obtain information about binary phase behaviors of NVCL or NMCL with similar structure and molecules. NVCL and NMCL have same aliphatic ring containing amide group, but NVCL has a vinyl group and NMCL has a methyl group in its backbone. In this work we measured pressure – composition isotherms for binary mixture of carbon dioxide + *N*-vinyl caprolactam (NVCL) or *N*-methyl caprolactam (NMCL) at temperature from 323 K to 353 K and pressure up to 21 MPa. Phase behavior of these binary experimental data was modeled with Peng-Robinson equation of state with two adjustable parameters.

EXPERIMENTAL

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

Figure 1 shows a schematic diagram of typical variable volume view cell apparatus to obtain phase behavior data at high pressure. The key components of experimental system are variable volume view cell, high-pressure generator and visual apparatus, etc.

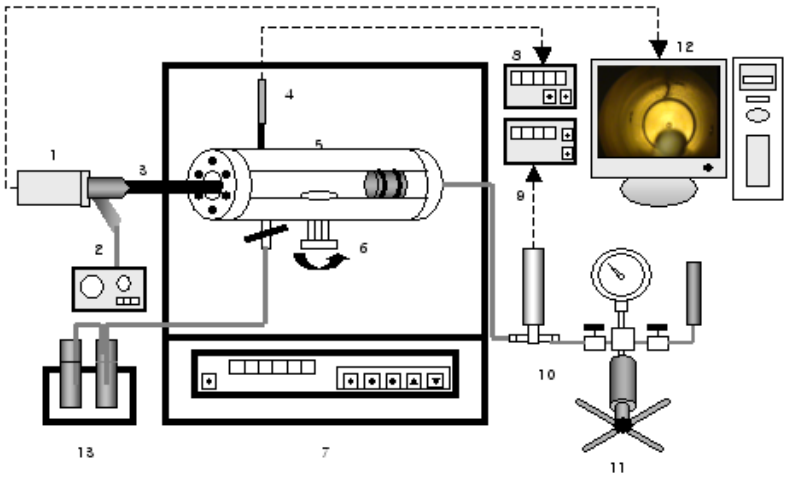

Figure 1. Schematic Diagram of the experimental apparatus
(1.Camera 2. Light source 3. Borescope 4. Thermocouple 5. View cell 6. Magnetic stirrer 7. Air bath 8. Digital thermometer 9. Digital pressure transducer 10. Pressure gauge 11. Hand pump 12. Computer monitor 13. Trap).

This view cell is constructed of high nickel-content austenitic steel (5.7 cm OD, 1.59 cm ID, ~25 cm^3 working volume, fitted with a 1.9 cm OD, 1.3 cm thick sapphire window). Typically CO_2 + NVCL or NMCL systems were studied with following experimental procedures. The cell was initially purged two or three times with inert gas and CO_2 at room temperature to remove the trace of air. And a measured amount of monomer 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 replacing a piston fitted within the cell using water pressed with a high-pressure generator (High pressure Equipment Co., model 62-6-10). Magnetic stir bar in the cell helped mixture to reach at equilibrium rapidly. The pressure of the solution was fitted with measuring the pressure of the water with a digital pressure transducer (Paroscientific INC., model 43KR-HHT-101) and pressure indicator (paroscientific INC., model NO.730). Temperature was measured with PRT type thermometer (HART SCIENTIFIC INC., model 5622-32SR, accuracy of ± 0.045K) fixed to surface of the cell and displayed by indicator (HART SCIENTIFIC INC., 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 fluctuation of pressure to mean phase transition was minimum (± 0.03 MPa). The status of the inside was projected onto the computer monitor using a camera (Veltek international INC., model CVC5520) with a borescope (Olympus Corp., model R100-038-000-50).

RESULTS AND DISCUSSION

Figure 2 and 3 show pressure-composition isotherm for CO_2 + NVCL or NMCL systems at 323.15, 333.15, 343.15 and 353.15 K.

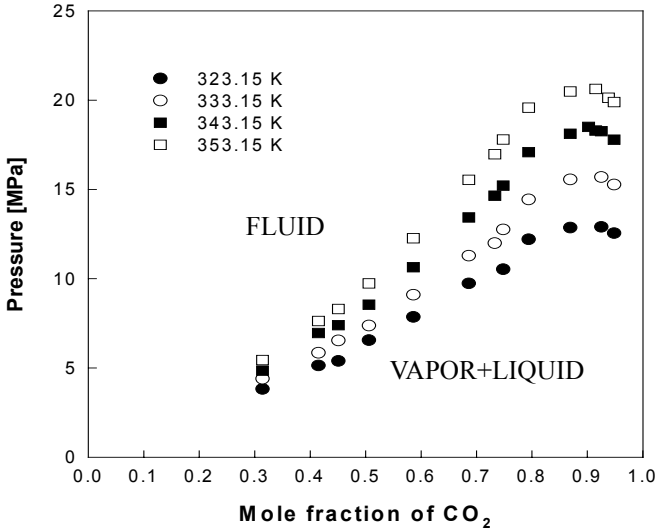

Fig 2. Pressure-composition isotherms of CO_2 + *N*-vinyl caprolactam system.

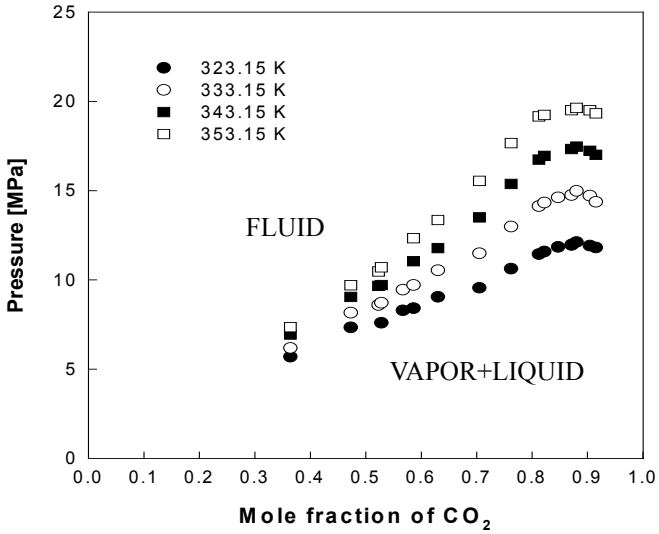

Fig 3. Pressure-composition isotherms of CO_2 + *N*-methyl caprolactam system.

Experimental data obtained in the present study were correlated with Peng-Robinson equation of state using van der Waals one fluid mixing rule (Peng and Robinson, 1976) including two binary interaction parameters.

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

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

$$b = 0.07780 \frac{RT_c}{P_c} \quad (3)$$

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (4)$$

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

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \quad (6)$$

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

These two binary interaction parameters were determined by regression experimental data with Peng-Robinson equation of state (PR EOS). Object function (OBF) and root mean squared relative deviation (RMSD) percent of this calculation were defined as follows.

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

$$RMSD(\%) = \sqrt{\frac{OBF}{ND}} * 100 \quad (9)$$

ND in equation (9) means the number of data points. We used Marquardt algorithm to optimize object function (Kuester and Mize, 1973). All isotherms were included for calculation.

Critical constants (T_c, P_c) and acentric factor for PR EOS are listed in Table 1.

Table 1. Critical constants and acentric factor (Reid, et al., 1987).

Component	T_b [K]	T_c [K]	P_c [MPa]	ω
CO_2	-	304.10	7.38	0.239
NVCL	483.60	705.95	3.57	0.455
NMCL	510.20	752.95	3.82	0.412

Critical temperature (T_c) and pressure (P_c) of NVCL and NMCL were estimated with Joback method.

Acentric factor (ω) was estimated with Lee-Kesler method (Reid, et al., 1987). Because we didn't 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 Joback method. In the case of NMCL, T_b data in Aldrich (1990) was used.

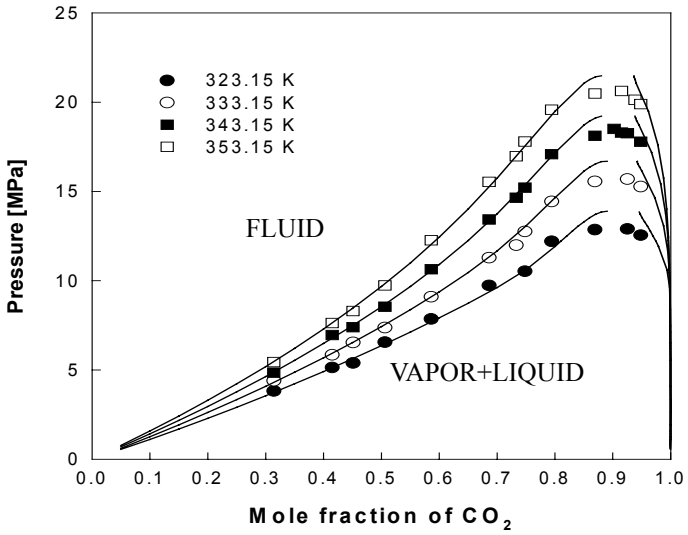

Fig 4. Calculation result for CO_2 + *N*-vinyl caprolactam system (k_{ij} = 0.0556, η_{ij} = -0.0014).

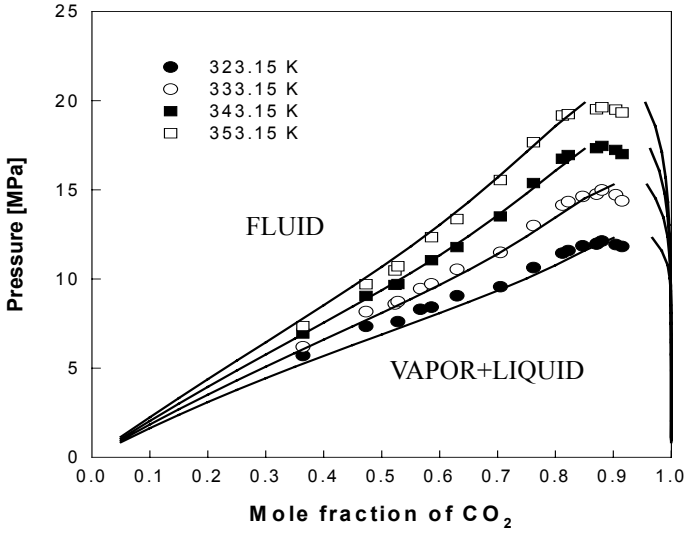

Fig 5. Calculation result for CO_2 + *N*-methyl caprolactam system (k_{ij} = 0.0247, η_{ij} = -0.0383).

Figure 4 and 5 represent a comparison of experimental data (symbol) and calculated pressure - composition isotherms (solid line) at 323.15, 333.15, 343.15 and 353.15 K. We obtained k_{ij} = 0.0556, η_{ij} = -0.0014 and RMSD = 1.64% in calculation of CO_2 + NVCL system and k_{ij} = 0.0247, η_{ij} = -0.0383 and RMSD = 2.93% in calculation of CO_2 + NMCL system. With two binary interaction parameters, good

correlation result was obtained.

Bubble pressures of CO_2 + NMCL mixture was relatively higher than those of CO_2 + NVCL mixture until mole fraction of CO_2 was near 0.7. But the highest mixture bubble pressure of CO_2 + NVCL system was about 1 MPa more elevated than that of CO_2 + NMCL system at the similar temperature (about 353.15 K). The result of calculation shows that mixture critical points of CO_2+ NVCL system are more overestimated.

ACKNOWLEDGMENTS

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LIST OF SYMBOLS

a = attraction parameter
b = van der Waals covolume
k = binary interaction parameter
P = pressure
R = gas constant
T = temperature
V = volume
x = mole fraction

Greek letters

η = secondary binary interaction parameter
ω = acentric factor

Subscripts

c = critical property
cal = calculated
exp = experimental
m = mixture

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