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# Phase Equilibrium of Binary Mixture for the (Carbon Dioxide + 1-Phenyl-2-Pyrrolidone) System at High Pressure

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**Abstract** – Experimental data of phase equilibria are reported for the binary mixture of 1-phenyl-2-pyrrolidone in supercritical carbon dioxide. Phase behavior data was measured in a synthetic method at a temperature ranging from 333.2 to 393.2 K and at pressures up to 97.14 MPa. The solubility of 1-phenyl-2-pyrrolidone in the carbon dioxide + 1-phenyl-2-pyrrolidone system increased as temperature increased at a constant pressure and it exhibited the type-I phase behavior. The experimental data for the binary mixture were correlated with the Peng-Robinson equation of state using mixing rule and the critical properties of 1-phenyl-2-pyrrolidone were predicted with the Joback and Lyderson method.

Key words: 1-Phenyl-2-pyrrolidone, Carbon dioxide, Phase behavior, P-x isotherm, Phase equilibrium

## 1. Introduction

Among the derivatives of 2-pyrrolidone, 1-phenyl-2-pyrrolidone is an organic compound consisting of a five-membered lactam. It is a colorless liquid used in industrial applications as a high-boiling non-corrosive polar solvent for a wide variety of applications. It is miscible with a wide variety of other solvents including water, ethanol, diethyl ether, ethyl acetate, and carbon disulfide [1].

Understanding two-component and three-component mixtures of the acrylate group containing supercritical solvents plays an important role in the chemical processes, separation technology, polymerization and chemical applications [2-6]. As a matter of fact, we have measured the phase behavior (bubble-point, dew-point and critical-point) for two-component mixtures with supercritical carbon dioxide [7,8]. Carbon dioxide is widely used as a process-friendly solvent because it is cheap, nonflammable, nontoxic and a good solvent with nonpolar molecules. Therefore, a knowledge for the phase equilibria of carbon dioxide and solute binary mixtures is required for practical uses.

Phase behavior data for some of carbon dioxide + solute systems were reported by our group [9-12], Kim et al. [13] and Rebelatto et al. [14]. We [9-12] reported the high-pressure phase behavior for the binary system of 3-phenyl propionitrile, triethylene glycol diacrylate, tetrahydrofurfuryl acrylate and 3-(trimethoxysilyl)propyl methacrylate in supercritical carbon dioxide at temperatures ranging from 313.2 to 393.2 K and several different pressures. Kim et al. [13] presented the carbon dioxide + methyl methoxyacetate and carbon dioxide + methyl *trans*-3-methoxyacrylate systems at pressures from 5 to 20 MPa and at five varying temperatures. Rebelatto et al. [14] measured the experimental phase equilibria data for a pseudo-binary system involving of carbon dioxide + ω-pentadecalactone and for a pseudo-ternary system involving carbon dioxide + ω-pentadecalactone + chloroform at the temperatures from 313 to 343 K, and at pressures between 5.4 MPa and 26.1 MPa.

This work was to measure the high-pressure phase equilibria data for the carbon dioxide + 1-phenyl-2-pyrrolidone system by investigating mixtures of carbon dioxide with a component. The experimental data obtained in this work were correlated with the Peng-Robinson equation of state (P-R EOS) [15] using mixing rule including binary interaction parameters. The critical properties such as critical pressure, critical temperature and acentric factor of 1-phenyl-2-pyrrolidone were estimated by the Joback and Lydersen method with group contributions [16].

## 2. Experimental Section

### 2-1. Apparatus and Procedure

Fig. 1 shows a schematic diagram of the apparatus measuring high-pressure phase behavior view cell used for the phase equilibria measurement [17,18]. A high-pressure view cell of 6.2 cm outer diameter and 1.59 cm inner diameter, an operating volume of ~28 $cm^3$ was used, and it is capable of operating up to pressure of 150.0 MPa. The front part of the cell was fitted with a 1.9 cm thick and 1.9 cm diameter a sapphire window (GT Advanced Technology, USA), which enabled observation of the phases inside the cell. The solution mixture in the cell was compressed to the desired pressure by moving a piston located within the cell. A 2.54 cm long piston was moved using water pressurized by a high pressure generator (HIP, model 37-5.75-60). The pressure of mixture was measured with a Heise gauge (Dresser Ind., model CM-124914, 0 to 136.0 MPa, standard uncertainty: 0.14 MPa). The temperature of the cell, typically maintained

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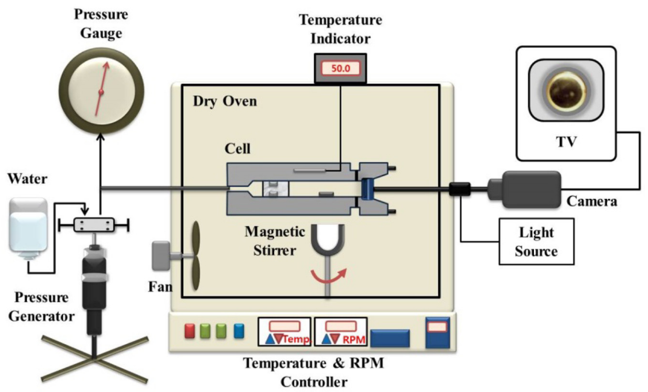


**Fig. 1. Schematic diagram of high-pressure apparatus.**

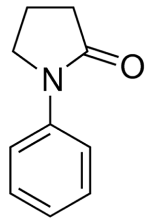


**Fig. 2. Schematic diagram of 1-phenyl-2-pyrrolidone.**

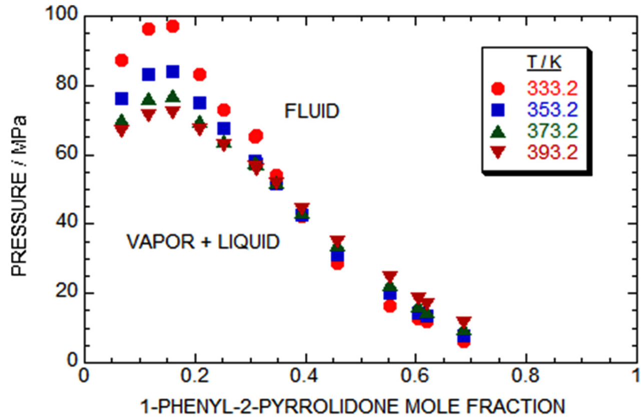


**Fig. 3. Plot of the pressure against the mole fraction, comparing the experimental data (symbols) of the (carbon dioxide + 1-phenyl-2-pyrrolidone) system. ●, 333.2 K; ■, 353.2 K; ▲, 373.2 K; ▼, 393.2 K.**

constant within a narrow range of ±0.12 K, as 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 was 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 very accurately to a target amount within a minimal range of ±0.002 g using a high pressure cylinder. The monomer is loaded into the cell to a target value within a short range of ±0.001 g using a syringe as well.

2-1-1. Materials

1-Phenyl-2-pyrrolidone (> 0.99 mass fraction purity, CAS RN 4641-57-0, $C_{10}H_{11}NO$) used in this work was purchased from Scientific Polymer Products, Inc. A component was used without further purification in the experiments. Carbon dioxide (> 0.999 mass fraction purity) obtained from Daesung Industrial Gases Co. was used as received. The specifications of all the chemicals used in this work are summarized in Table 1 and the chemical structure of 1-phenyl-2-pyrrolidone is represented in Fig. 2.

## 3. Results and discussion

High-pressure phase behavior data for the 1-phenyl-2-pyrrolidone in supercritical carbon dioxide were measured, and the experimental uncertainty was estimated to be 0.20 MPa and 0.2 K for a given loading of the cell [19,20]; the standard uncertainty for the mole fraction of 1-phenyl-2-pyrrolidone was 0.003 [19].

Fig. 3 and Table 2 show the experimental pressure-composition (*P* - *x*) isotherms at $T$ = (333.2, 353.2, 373.2 and 393.2) K, and pressures from (6.26 to 97.14) MPa for the (carbon dioxide + 1-phenyl-2-pyrrolidone) system. First, three phases were not observed at all temperatures, and the *P*-*x* isotherms (see Fig. 3) were consistent with those expected for the type-I system [21,22]. Then, the solubility pressures increased as the temperatures increased at the mole fraction of 1-phenyl-2-pyrrolidone > 0.394, while it decreased with the temperature in increase at the mole fraction < 0.394.

In this work, the experimental phase behavior data were correlated with the P-R EOS. The P-R EOS [15] 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 $T_c$, $p_c$, $T_r$ and $\omega$ are the critical temperature, critical pressure, reduced temperature ($T/T_c$) and acentric factor of the pure component, respectively. The P-R EOS was used for the mixture

**Table 1. Specifications of the chemicals used in this work**

| Chemical name | Mass fraction purity | Source | CAS RN |
|---|---|---|---|
| $CO_2$ | >0.999 | Daesung Ind. Gases Co. | 124-38-9 |
| 1-phenyl-2-pyrrolidone | >0.990 | Scientific Polymer Products, Inc. | 84170-74-1 |

**Table 2. Experimental data for the (carbon dioxide + 1-phenyl-2-pyrrolidone) system. BP is a bubble-point, CP is a critical-point and DP is a dew-point**

| 1-Phenyl-2-Pyrrolidone Mole Fraction | p[a]/MPa | Transition[b] |
|---|---|---|
| | $T^a$ / K = 333.2 K | |
| 0.066 | 87.21 | DP |
| 0.115 | 96.12 | DP |
| 0.161 | 97.14 | BP |
| 0.209 | 83.28 | BP |
| 0.252 | 72.93 | BP |
| 0.308 | 65.34 | BP |
| 0.310 | 65.62 | BP |
| 0.348 | 54.14 | BP |
| 0.394 | 42.31 | BP |
| 0.458 | 28.86 | BP |
| 0.553 | 16.59 | BP |
| 0.604 | 12.66 | BP |
| 0.619 | 11.97 | BP |
| 0.685 | 6.24 | BP |
| | $T$ / K = 353.2 K | |
| 0.066 | 76.24 | DP |
| 0.115 | 83.21 | DP |
| 0.161 | 84.17 | CP |
| 0.209 | 74.93 | BP |
| 0.252 | 67.48 | BP |
| 0.308 | 58.31 | BP |
| 0.310 | 57.48 | BP |
| 0.348 | 51.59 | BP |
| 0.394 | 42.79 | BP |
| 0.458 | 31.00 | BP |
| 0.553 | 20.10 | BP |
| 0.604 | 14.35 | BP |
| 0.619 | 13.62 | BP |
| 0.685 | 7.90 | BP |
| | $T$ / K = 373.2 K | |
| 0.066 | 70.10 | DP |
| 0.115 | 76.17 | DP |
| 0.161 | 77.07 | BP |
| 0.209 | 69.83 | BP |
| 0.252 | 64.17 | BP |
| 0.308 | 57.76 | BP |
| 0.310 | 57.21 | BP |
| 0.348 | 52.03 | BP |
| 0.394 | 43.28 | BP |
| 0.458 | 33.97 | BP |
| 0.553 | 22.66 | BP |
| 0.604 | 16.62 | BP |
| 0.619 | 14.64 | BP |
| 0.685 | 9.69 | BP |
| | $T$ / K = 393.2 K | |
| 0.066 | 66.93 | DP |
| 0.115 | 71.48 | DP |
| 0.161 | 72.10 | BP |
| 0.209 | 67.21 | BP |
| 0.252 | 62.66 | BP |
| 0.308 | 56.66 | BP |
| 0.310 | 55.83 | BP |
| 0.348 | 51.48 | BP |
| 0.394 | 44.24 | BP |
| 0.458 | 34.86 | BP |
| 0.553 | 24.79 | BP |
| 0.604 | 18.55 | BP |
| 0.619 | 16.66 | BP |
| 0.685 | 11.35 | BP |

[a]Standard uncertainties are u(T) = 0.2 K and u(p) = 0.05 MPa
[b]BP: Bubble-point, CP: Critical-point, DP: Dew-point

with the following mixing rules:

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

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

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

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

where $k_{ij}$ and $h_{ij}$ were $i$ and $j$ interaction parameters determined by fitting ($P$-$x$) isotherms curves, and $a_{ii}$ and $b_{ii}$ were pure component parameters as defined by Peng and Robinson [15]. The objective function (OBF) and root mean squared relative deviation (RMSD) percent of this calculation are defined by

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

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

Table 3 lists properties of pure components; critical temperatures ($T_c$), critical pressures ($P_c$), and the acentric factors ($\omega$) for carbon dioxide [16], 1-phenyl-2-pyrrolidone[16] used in the P-R EOS. The boiling points were obtained from the literature [23]. The properties of 1-phenyl-2-pyrrolidone were then calculated by the Joback group-contribution method [16].

Fig. 4 plots the pressure against the mole fraction, comparing the experimental data (symbols) of the carbon dioxide + 1-phenyl-2-pyrrolidone system with calculations obtained from the P-R EOS with $k_{ij}$ and $\eta_{ij}$ set equal to zero (red solid lines), and $k_{ij}$ = 0.020, $\eta_{ij}$ = -0.028 (blue solid lines) at 353.2 K. With the optimized parameters of the P-R EOS for the carbon dioxide + 1-phenyl-2-pyrrolidone system at $T$ = 353.2 K, the comparison shows an error as low as 7.91%.

The experimental data with calculated ($P$-$x$) isotherms at temperatures of 333.2, 353.2, 373.2 and 393.2 K for the carbon dioxide + 1-

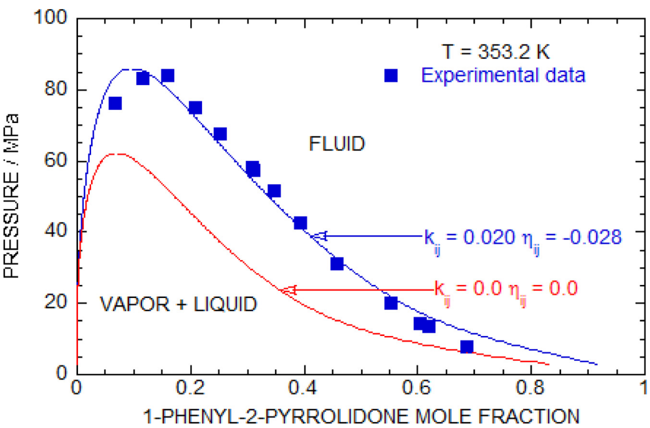


**Fig. 4. Plot of the pressure against the mole fraction, comparing the experimental data (symbols) of the (carbon dioxide + 1-phenyl-2-pyrrolidone) system with calculations obtained from the Peng-Robinson equation of state with $k_{ij}$ and $\eta_{ij}$ set equal to zero (red solid lines), and $k_{ij}$ = 0.020, $\eta_{ij}$ = -0.028 (carbon dioxide + 1-phenyl-2-pyrrolidone) (blue solid lines) at 353.2 K.**

**Table 3. The properties of pure components of carbon dioxide and 1-phenyl-2-pyrrolidone**

| 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 |
| 1-Phenyl-2-Pyrrolidone | 161.2 | $C_{10}H_{11}NO$ | 694.5[a] | 992.7 | 3.80 | 0.571 |

[a]ChemSpider.

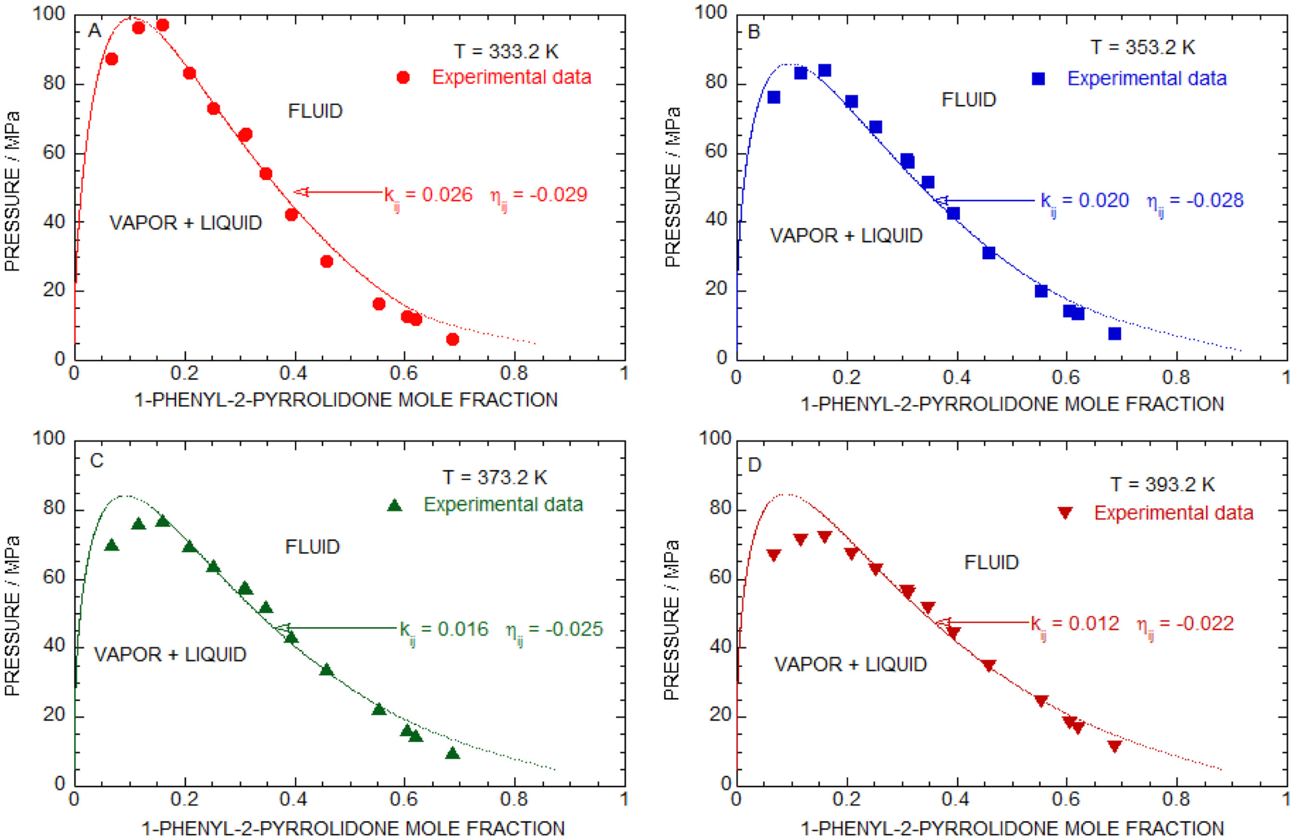


**Fig. 5. Plot of the pressure against the mole fraction, comparing the experimental data (symbols) of the (carbon dioxide + 1-phenyl-2-pyrrolidone) system with calculations (solid lines) obtained with the Peng-Robinson equation of state using optimized $k_{ij}$ and $\eta_{ij}$ at each temperature: ●, 333.2 K; ■, 353.2 K; ▲ 373.2 K; ▼, 393.2 K.**

phenyl-2-pyrrolidone system using the optimized $k_{ij}$ and $h_{ij}$ values determined at the each temperature were compared Fig. 5(a~d). RMSD

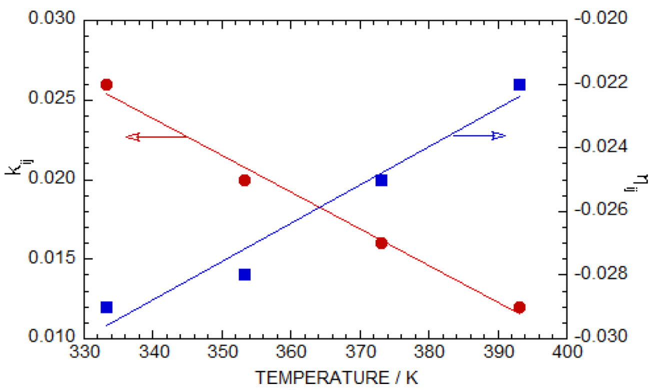


**Fig. 6. Plot of $k_{ij}$ and $h_{ij}$ parameters against the temperature for the (carbon dioxide + 1-phenyl-2-pyrrolidone) {(1 - $x$) $CO_2$ + $x$ $C_{10}H_{11}NO$} system with the Peng-Robinson equation of state. The equations of the fitting line for the (carbon dioxide + 1-phenyl-2-pyrrolidone) are $k_{ij}$ = -0.00023$T$ + 0.10204 and $h_{ij}$ = 0.00012$T$ - 0.06958 (333.2 K ≤ T ≤ 393.2 K).**

for the system at temperatures of 333.2, 353.2, 373.2 and 393.2 K was 13.1%, 7.91%, 7.88% and 9.66%, respectively, and experimental data point at each temperature was 14. In comparison of Fig. 5(a~d), the experimental data and calculated curve show a good agreement at four temperatures for high pressures.

Fig. 6 plots $k_{ij}$ and $h_{ij}$ parameters against the temperature for the (carbon dioxide + 1-phenyl-2-pyrrolidone) system with the P-R EOS. The parameter equations of the fitting line were $k_{ij}$ = -0.00023$T$ + 0.10204 and $\eta_{ij}$ = 0.00012$T$ - 0.06958 (333.2 K ≤ T ≤ 393.2 K) determined by the P-R EOS.

## 4. Conclusions

The $P$-$x$ isotherm for the (carbon dioxide + 1-phenyl-2-pyrrolidone) system was studied using a variable-volume view cell with a static-type apparatus. The (carbon dioxide + 1-phenyl-2-pyrrolidone) mixtures did not exhibit three phases at all four selected temperatures. The Peng-Robinson equation of state is properly capable of predicting the phase behavior of mixtures using two temperature-independent mixture interaction parameters. The agreement between calculated and experimental mixture curves was reasonably good by using two optimized parameters obtained at each temperature with the Peng-Robinson equation of state. RMSD for the (carbon dioxide + 1-phenyl-2-pyrrolidone) system was calculated by 8.82%, a mean for four selected temperatures.

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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

### Subscrpits

i, j : Component identifiers
c : Critical property
r : Reduced property
mix : Mixture
exp : Experiment
cal : Calculation

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