

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

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(Received 13 August 2018; Received in revised form 1 September 2018; accepted 7 September)

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 Lydersen 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 cm³ 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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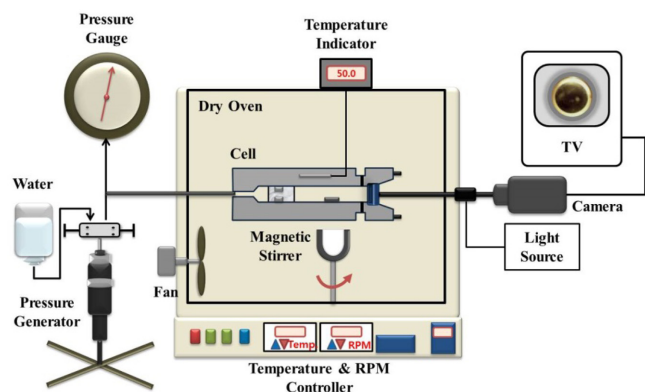


Fig. 1. Schematic diagram of high-pressure apparatus.

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

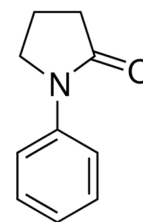


Fig. 2. Schematic diagram of 1-phenyl-2-pyrrolidone.

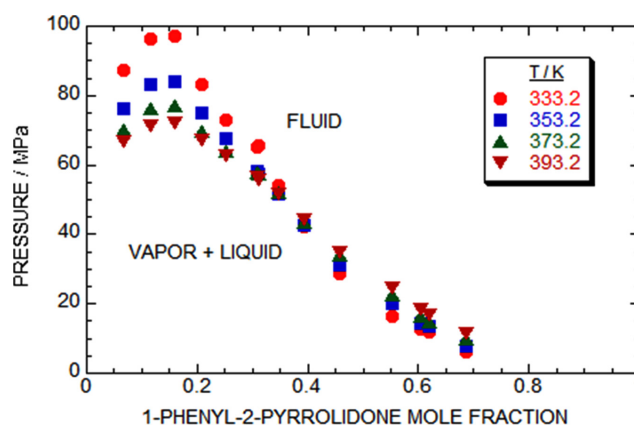


Fig. 3. Plot of the pressure against the mole fraction, comparing the experimental data (symbols) of the (carbon dioxide + 1-phenyl-2-pyrrolidone) system. ●, 333.2 K; ■, 353.2 K; ▲, 373.2 K; ▼, 393.2 K.

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:

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

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

$$b = 0.077796 \frac{RT_c}{p_c} \quad (3)$$

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

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

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 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
$T/K = 333.2$ 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

^aStandard uncertainties are $u(T) = 0.2$ K and $u(p) = 0.05$ MPa

^bBP: Bubble-point, CP: Critical-point, DP: Dew-point

with the following mixing rules:

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

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

$$b_{mix} = \sum_i \sum_j x_i x_j b_{ij} \quad (8)$$

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

where k_{ij} and η_{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

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

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

Table 3 lists properties of pure components; critical temperatures (T_c), critical pressures (P_c), and the acentric factors (ω) 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 η_{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-

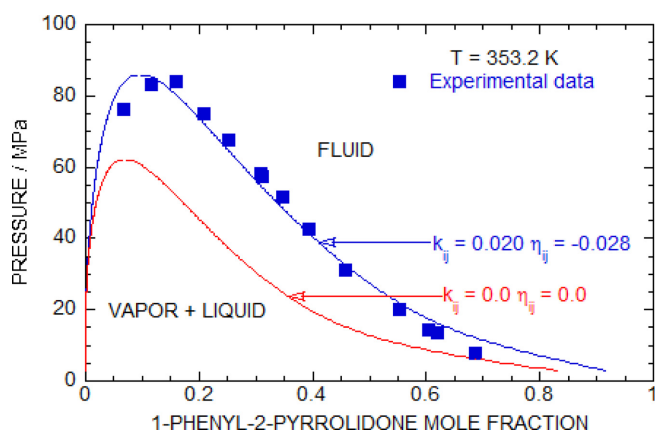


Fig. 4. Plot of the pressure against the mole fraction, comparing the experimental data (symbols) of the (carbon dioxide + 1-phenyl-2-pyrrolidone) system with calculations obtained from the Peng-Robinson equation of state with k_{ij} and η_{ij} set equal to zero (red solid lines), and $k_{ij} = 0.020$,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

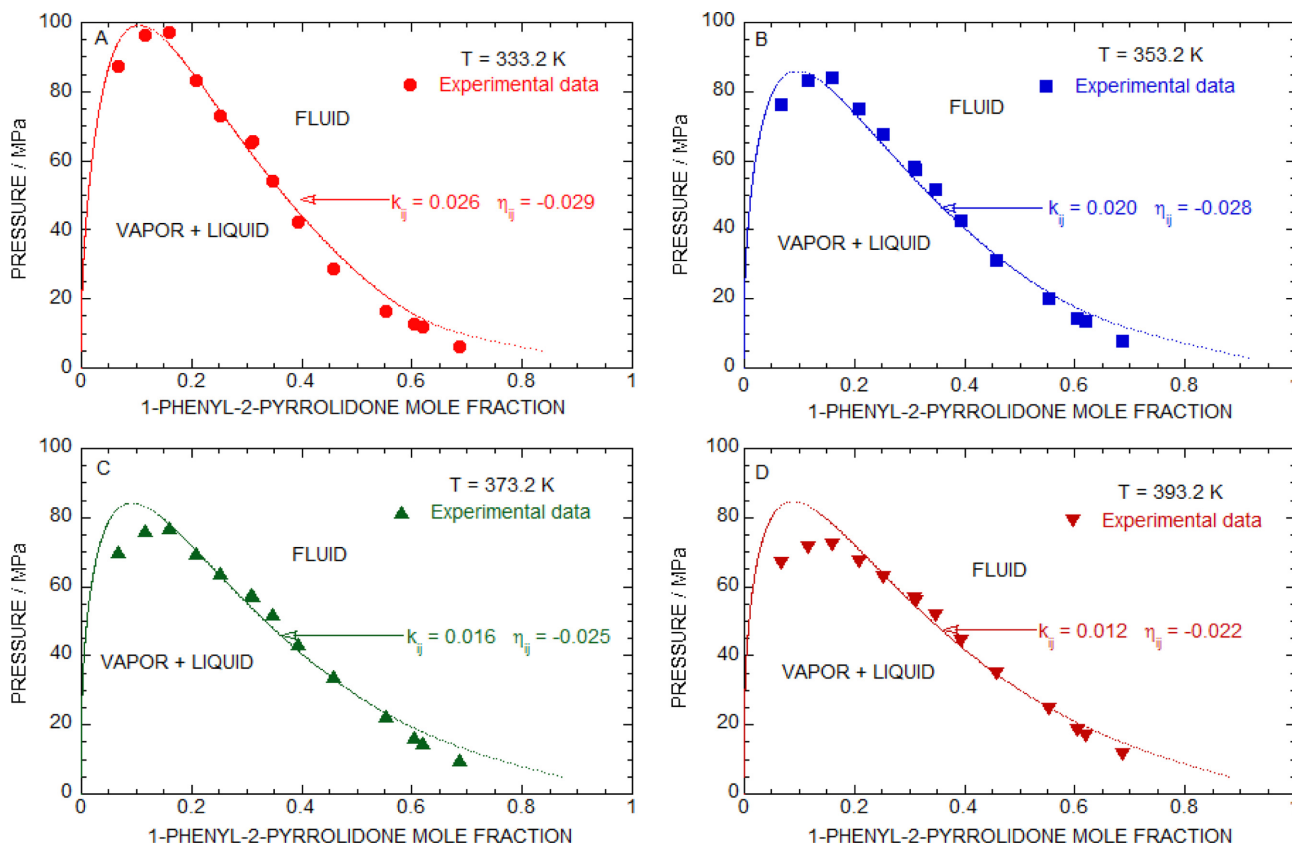
^aChemSpider.

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 η_{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

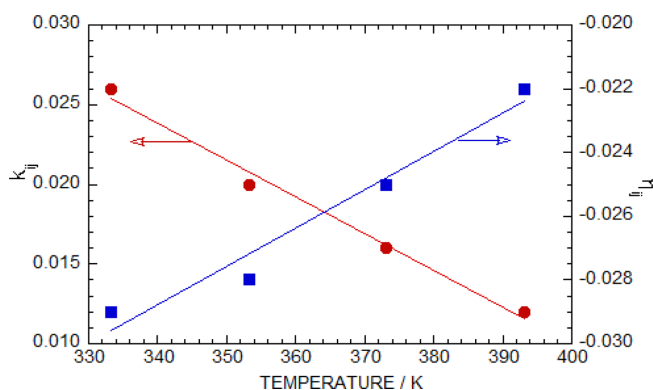


Fig. 6. Plot of k_{ij} and h_{ij} parameters against the temperature for the (carbon dioxide + 1-phenyl-2-pyrrolidone) $\{(1-x) \text{CO}_2 + x \text{C}_{10}\text{H}_{11}\text{NO}\}$ system with the Peng-Robinson equation of state. The equations of the fitting line for the (carbon dioxide + 1-phenyl-2-pyrrolidone) are $k_{ij} = -0.00023T + 0.10204$ and $h_{ij} = 0.00012T - 0.06958$ ($333.2 \text{ K} \leq T \leq 393.2 \text{ K}$).

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 $k_{ij} = -0.00023T + 0.10204$ and $h_{ij} = 0.00012T - 0.06958$ ($333.2 \text{ K} \leq T \leq 393.2 \text{ K}$) 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.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (Grant No. NRF-2016R1D1A1B04931921).

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, cm³/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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