

HIGH PRESSURE PHASE BEHAVIOR FOR THE BINARY MIXTURE OF VALERONITRILE, CAPRONITRILE AND LAURONITRILE IN SUPERCRITICAL CARBON DIOXIDE AT TEMPERATURES FROM (313.2 TO 393.2) K AND PRESSURES FROM (3.9 TO 25.7) MPa

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High pressure phase equilibria for the (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) systems are measured in static apparatus at five temperatures of (313.2, 333.2, 353.2, 373.2 and 393.2) K and pressures up to 25.7 MPa. These three carbon dioxide + nitriles systems have continuous critical mixture curves that exhibit maximums in pressure at temperatures between the critical temperatures of carbon dioxide and nitriles. The solubility of valeronitrile, capronitrile and lauronitrile for the (carbon dioxide + nitriles) systems increases as the temperature increases at a fixed pressure. The (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) systems exhibit type-I phase behavior. The experimental results for (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) systems are correlated with Peng-Robinson equation of state using a mixing rule including two adjustable parameters.

INTRODUCTION

Nitriles are an important laboratory and industrial solvents because of their unusual physical properties. For example, nitriles boil much higher than the corresponding hydrocarbon of similar molecular weight; valeronitrile ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$, MW 83.13) boils at 414.5 K whereas n-hexane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, MW 86.2) boils at 342.2 K. This increase can be ascribed to the polar nature (uneven distribution of electron density) of nitriles; the $\text{C}\equiv\text{N}$ bond is polarized and intermolecular alignment of these dipoles increases the intermolecular attraction between the solvent molecules. Its high dielectric constant and dipole moment make nitrile ideal for promoting chemical reactions where ionization is involved, as a solvent for inorganic salts (electrolytes), and as a medium for electrochemical studies. [1,2]

The phase behavior for binary mixture of the hydrocarbon with supercritical carbon dioxide plays an important role in the chemical separation process, supercritical fluid extraction, polymerization condition and industrial application. [3,4] Recently, phase behavior experiments have been reported on the bubble-point, dew-point and critical-point behavior of mixtures containing supercritical carbon dioxide. [5,6] Supercritical carbon dioxide used in this work is widely used as an environmentally benign solvent which is inexpensive, nonflammable, and nontoxic. Also, supercritical carbon dioxide has a quadrupole moment, no

dipole moment, and low dielectric constant. Supercritical carbon dioxide is a good solvent with low molecular weight in nonpolar molecules. Therefore, phase behavior information for mixtures containing supercritical carbon dioxide is required for practical uses. The valeronitrile, carpronitrile and lauronitrile monomers are used mainly for a variety of applications such as insecticides manufacture, forming agent, pharmaceutical, elastomers, and polymerization initiators. Phase behavior data for the carbon dioxide + acetonitrile and carbon dioxide + acrylonitrile systems were reported by Byun et al. [7,8]. The miscibility for supercritical carbon dioxide + monomer system is an important condition needed for polymer synthesis and polymerization process. Byun et al. [7] used a static apparatus and presented the liquid-vapor equilibria curves for carbon dioxide + acetonitrile mixture at (308, 328 and 348) K and pressures up to 12 MPa. Byun et al. [8] reported the phase behavior curves for the carbon dioxide + acrylonitrile system at temperature from 318 to 378 K and pressure up to 14 MPa using a static apparatus.

The purpose of this work is to obtain the high-pressure experimental data for (carbon dioxide + carpronitrile), (carbon dioxide + valeronitrile) and (carbon dioxide + lauronitrile) mixtures by investigating mixtures of carbon dioxide with three components. Also, the pressure-temperature ($P - T$) diagrams of the mixture critical curve are presented for the (carbon dioxide + carpronitrile), (carbon dioxide + valeronitrile) and (carbon dioxide + lauronitrile) systems in the vicinity of the critical point of pure carbon dioxide. The experimental data for (carbon dioxide + carpronitrile), (carbon dioxide + valeronitrile) and (carbon dioxide + lauronitrile) systems obtained in this work are correlated with the Peng-Robinson equation of state [9] using a van der Waals one-fluid mixing rule including two adjustable parameters. The critical pressure, critical temperature, and acentric factor of carpronitrile, valeronitrile and lauronitrile are reported a literature, while the vapor pressure is estimated by the Lee-Kesler method. [10]

EXPERIMENTAL SECTION

Apparatus and Procedure Described in detail elsewhere are the experimental apparatus and techniques used to measure the phase behavior of monomers in supercritical carbon dioxide. [11] A high-pressure, variable volume view cell (6.4 cm O.D x 1.59 cm I.D), a working volume of $\sim 28 \text{ cm}^3$, is used to obtain the bubble-, dew- and critical-point curves, and is capable of operating to pressure of 70.0 MPa. A sapphire window (1.2 cm thick \times 1.9 cm diameter) is fitted in the front part of the cell to allow observation of the phases. Typically, supercritical carbon dioxide is added to the cell to within $\pm 0.004 \text{ g}$ using a high pressure bomb. The monomer is loaded into the cell to within $\pm 0.002 \text{ g}$ using a syringe after the empty cell is purged several times with carbon dioxide and nitrogen to remove traces of air and organic matter. The mixture in the cell was compressed to the desired pressure by moving a piston located within the cell. The piston (2.54 cm) was moved using water pressurized by a high pressure generator (HIP, model 37-5.75-60). The pressure of mixture is measured with a Heise gauge (Dresser Ind., model CM-53920, 0 to 34.0 MPa) accurate to $\pm 0.02 \text{ MPa}$. The temperature of the cell, which is typically maintained to within $\pm 0.2 \text{ K}$, is measured using a platinum-resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (Yokogawa, model 7563, accurate to $\pm 0.005 \%$). The mixture inside the cell can be 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.

First, the solution in the cell is compressed to a single phase at a fixed temperature. The inside solution is maintained in the single phase region at the desired temperature for at least 30 ~ 40 min for the cell to reach phase equilibrium. The pressure is then slowly decreased until a second phase appears. A bubble point pressure is obtained when small vapor bubbles appear first in the cell, while a dew point is obtained if a fine mist appears in the cell. Critical points are obtained by adjusting the temperature and pressure of the mixture until critical opalescence is observed along with equal liquid and vapor volume upon the formation of the second phase.

Materials Carbon dioxide (99.8 % purity) is obtained from Daesung Industrial Gases Co. (Yeosu, Korea) and used as received. Capronitrile (> 96 % purity, CAS RN 628-73-9) and lauronitrile (> 98 % purity; CAS RN 2437-25-4) used in this work are obtained from Tokyo Chemical Industry, and Valeronitrile (> 99.5 % purity, CAS RN 110-59-8) are obtained from Aldrich Co. Three components are used without further purification in the experiments.

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental phase equilibria data of binary mixture for the capronitrile, valeronitrile and lauronitrile in supercritical carbon dioxide are measured and reproduced at least twice to within ± 0.02 MPa and ± 0.1 K for a given loading of the cell. The mole fractions are accurate to within ± 0.002 .

Figure 1(a) ~ 1(c) show the experimental pressure-composition ($P - x$) isotherms at $T = (313.2, 333.2, 353.2, 373.2 \text{ and } 393.2)$ K, and pressures from (3.90 to 25.69) MPa for the (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) systems. The solubility of carbon dioxide decreases as temperatures shift higher under the constant pressure. Three phases were not observed at five temperatures for the three systems. As shown in Figure 1(a) ~ 1(c), the mixture critical pressures are ca. 14.38 MPa (at $T = 353.2$ K), ca. 16.03 MPa (at $T = 373.2$ K) and ca. 17.28 MPa (at $T = 393.2$ K) for the (carbon dioxide + valeronitrile) system, the mixture critical pressures at ca. 14.66 MPa (at $T = 353.2$ K) and ca. 18.52 MPa (at $T = 393.2$ K) for the (carbon dioxide + capronitrile) system and the mixture critical pressures at ca. 19.90 MPa (at $T = 353.2$ K), ca. 23.21 MPa (at $T = 373.2$ K) and ca. 25.69 MPa (at $T = 393.2$ K) for the (carbon dioxide + lauronitrile) system. Also, the pressure of each mixture-critical point continually increases as the temperature increases for the three systems. The (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) systems does not exhibit three phases at five temperatures investigated. The mixture-critical curve for the (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) systems exhibit the maximum pressure in $P - T$ space.

In this work, the experimental phase equilibria data are correlated with the Peng-Robinson equation of state (EOS). The Peng-Robinson EOS are briefly described here. The Peng-Robinson EOS [10] is used with the following mixing rules:

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

$$a_{ij} = \left(\frac{a_{ii} a_{jj}}{z} \right)^{1/2} (1 - k_{ij})$$

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

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

Where, k_{ij} and η_{ij} are binary interaction parameters that are determined by fitting $P - x$ isotherms curves and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson [10]. Objection function (OBF) of this calculation was defined by,

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

$$RMSD(\%) = \sqrt{\left(\frac{OBF}{ND} \right)} \times 100$$

ND means the number of data points. We used Marquardt [12] to optimize the objection function. Table 1 lists the pure component critical temperatures (T_c), critical pressures (P_c), and the acentric factors (ω) for carbon dioxide, [11] valeronitrile, capronitrile and lauronitrile [11] that are used with the Peng-Robinson EOS. The properties of capronitrile and valeronitrile were reported of literature.[13] The properties of lauronitrile were calculated by the Joback group-contribution method.[11] Also, the vapor pressures were calculated by the Lee-Kesler method. [11]

Table 1. Properties of Pure Component.

Components	Molecular Weight	Molecular Structure	Boiling Point T_b / K	Critical Temp. T_c / K	Critical Press. p_c / MPa	Acentric Factor ω
Carbon Dioxide	44.01	O=C=O		304.2	7.38	0.225
Valeronitrile	83.13	C ₄ H ₉ -C≡N	414.45	603.0	3.26	0.415
Capronitrile	97.16	C ₅ H ₁₁ -C≡N	436.75	622.1	2.92	0.474
Lauronitrile	181.32	C ₁₁ H ₂₃ -C≡N	549.15	718.9	1.74	0.714

Figure 2a ~ 2c shows the comparison between experimental results of (carbon dioxide + valeronitrile) (a), (carbon dioxide + capronitrile) (b) and (carbon dioxide + lauronitrile) (c) systems and calculated value obtained using Peng-Robinson EOS at a temperature of $T = 353.2$ K. The binary interaction parameters of Peng-Robinson EOS are fitted by the experimental data at $T = 353.2$ K. The values of optimized parameters of the Peng-Robinson EOS for the (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) systems are $k_{ij} = 0.071$ and $\eta_{ij} = -0.015$ (RMSD = 0.79 %, data point no. = 12), $k_{ij} = 0.066$ and $\eta_{ij} = -0.025$ (RMSD = 2.14 %, data point no. = 13), and $k_{ij} = 0.070$ and $\eta_{ij} = -0.026$ (RMSD = 2.59 %, data point no. = 15), respectively.

Figure 3(a) ~ 3(c) compares experimental results with calculated $P - x$ isotherms at temperatures of $T = (313.2, 333.2, 353.2, 373.2 \text{ and } 393.2)$ K for the (carbon dioxide + valeronitrile) (a), (carbon dioxide + capronitrile) (b) and (carbon dioxide + lauronitrile) (c) systems using the optimized values of k_{ij} and η_{ij} determined at $T = 353.2$ K. As shown in Figure 3(a) ~ 3(c), a good fit of the data are obtained with Peng-Robinson equation using an adjustable mixture parameters for the (carbon dioxide + valeronitrile) (a), (carbon dioxide + capronitrile) (b) and (carbon dioxide + lauronitrile) (c) systems.

Figure 4(a) ~ 4(c) plots pressures against mole fraction to illustrate the comparison of the experimental data (symbols) for the (carbon dioxide + valeronitrile) (a), (carbon dioxide + capronitrile) (b) and (carbon dioxide + lauronitrile) (c) systems with calculations (solid lines) obtained with the Peng-Robinson EOS at each temperature. As shown in Figure 4(a) ~ 4(c),

these curves are calculated using optimized values of determined at each temperatures. The comparison between experimental data and calculated curve shows in good agreement at five temperatures. According to calculated result the mixture-critical curve is type-I.[14]

Figure 5(a) ~ 5(c) compare the mixture-critical curves of the experimental data with calculated values by the Peng-Robinson EOS for the (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) systems. The calculated mixture-critical curve is type-I region. In Figure 5(a) ~ 5(c), the solid lines represent the vapor pressure for pure carbon dioxide [10], valeronitrile, capronitrile and lauronitrile. [13] The solid lines represented for the vapor pressure of pure valeronitrile, capronitrile and lauronitrile were obtained by Lee-Kesler method.[10] The solid circles represent the critical point for pure carbon dioxide and valeronitrile, carbon dioxide and capronitrile, and carbon dioxide and lauronitrile. The upper part of the dash line is single phase (fluid), the lower part vapor-liquid (two-phases). The dash lines represent the calculated value obtained using the Peng-Robinson EOS, with $k_{ij} = 0.071$ and $\eta_{ij} = -0.015$ (carbon dioxide + valeronitrile), $k_{ij} = 0.066$ and $\eta_{ij} = -0.025$ (carbon dioxide + capronitrile), and $k_{ij} = 0.070$ and $\eta_{ij} = -0.026$ (carbon dioxide + lauronitrile), respectively. The open squares are for the mixture-critical points determined from isotherms measured in this experiment.

CONCLUSIONS

High pressure phase equilibria data of (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) systems has been studied using a high-pressure, variable-volume view cell. The (carbon dioxide + valeronitrile), (carbon dioxide + capronitrile) and (carbon dioxide + lauronitrile) mixtures do not exhibit three phases at any five temperatures. The Peng-Robinson equation of state is capable of accurately predicting the phase behavior for both of these two systems using two temperature-independent mixture interaction parameters. The agreement between calculated and experimental mixture-critical curves is reasonably good for using two optimized parameters with Peng-Robinson equation of state.

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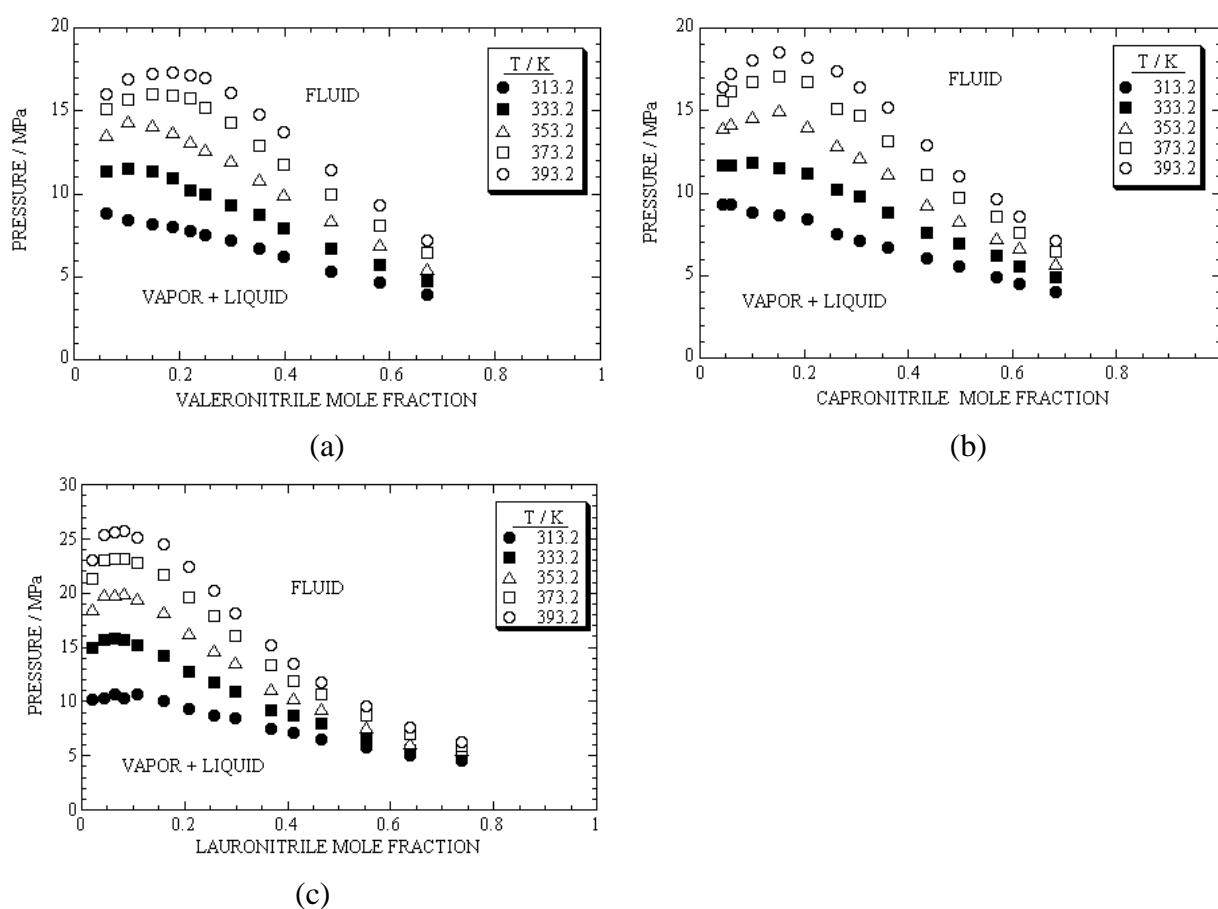
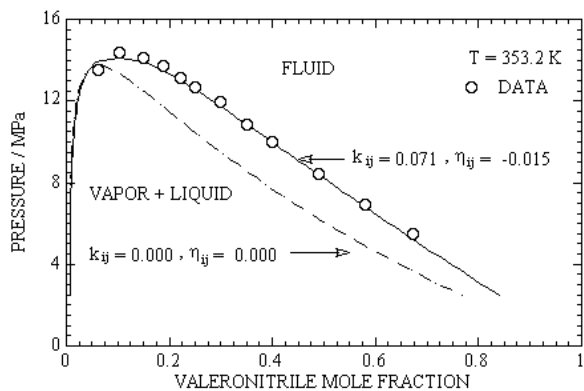
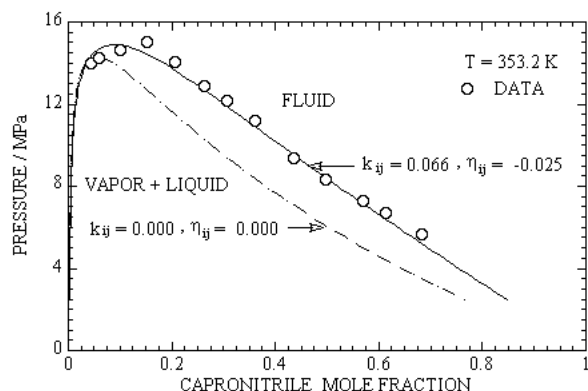


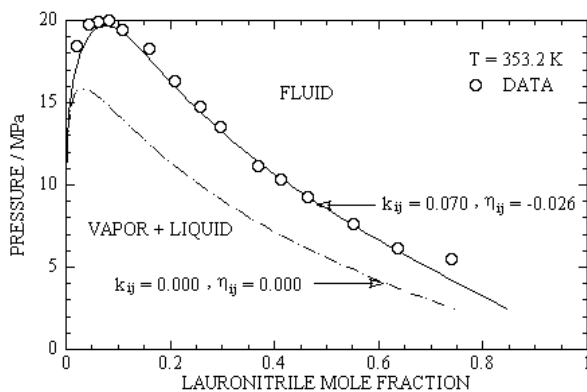
Figure 1. Experimental data for the carbon dioxide + valeronitrile (a), carbon dioxide + capronitrile (b) and carbon dioxide + lauronitrile (c) systems at 313.2 K, 333.2 K, 353.2 K, 373.2 K and 393.2 K obtained in this work.



(a)



(b)



(c)

Figure 2. Plot of pressure against mole fraction to illustrate the comparison of experimental data (symbols) for the (carbon dioxide + valeronitrile) (a), (carbon dioxide + capronitrile) (b) and (carbon dioxide + lauronitrile) (c) with calculation obtained from the Peng-Robinson equation of state by k_{ij} and η_{ij} set equal to zero (dashed lines), and $k_{ij} = 0.071$, $\eta_{ij} = -0.015$ ((carbon dioxide + valeronitrile) (a), $k_{ij} = 0.066$, $\eta_{ij} = -0.025$ (carbon dioxide + capronitrile) (b) and $k_{ij} = 0.070$, $\eta_{ij} = -0.026$ (carbon dioxide + lauronitrile) (c) at 353.2 K.

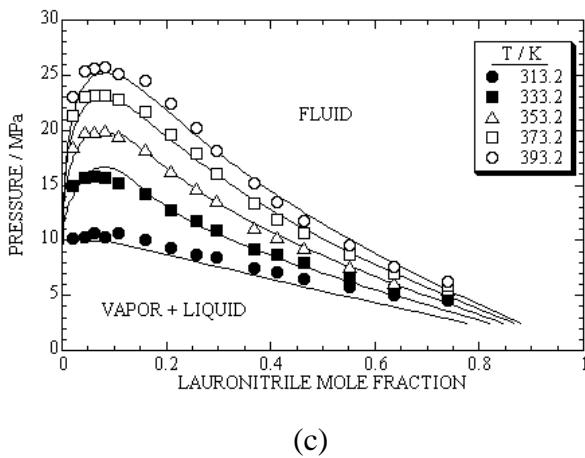
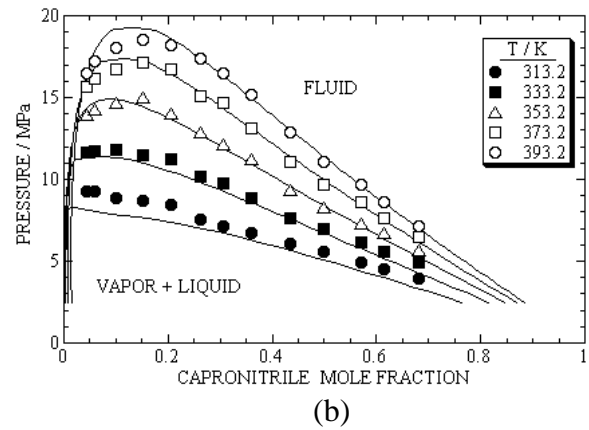
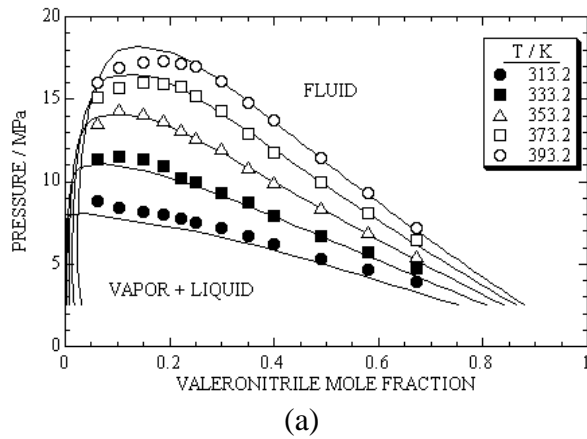
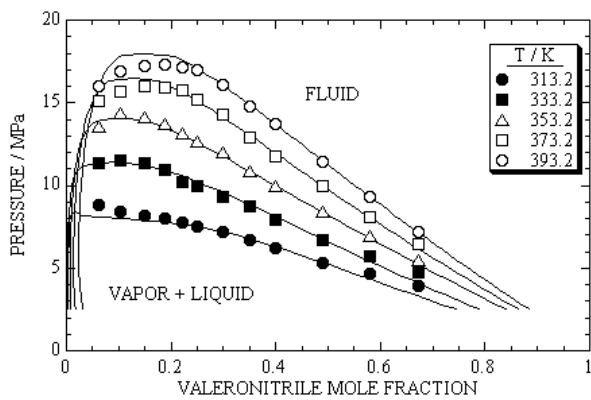
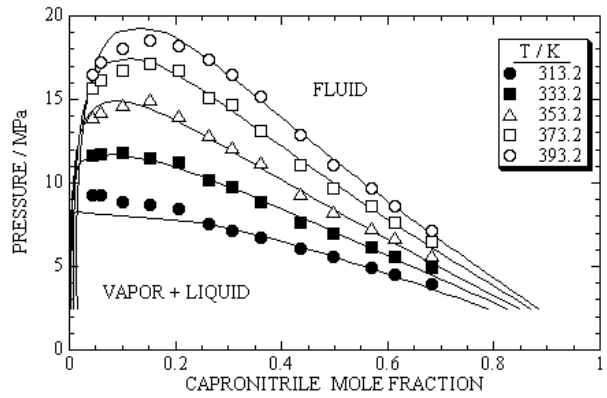


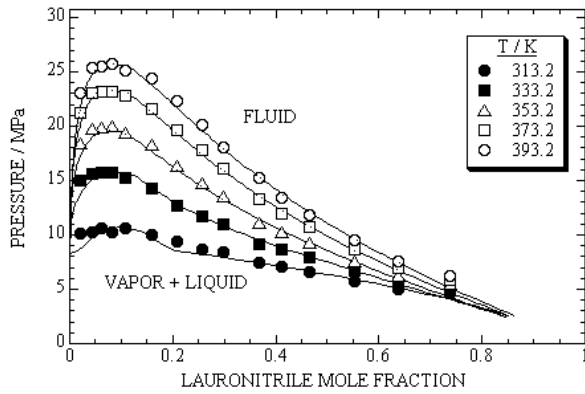
Figure 3. Plot of pressure against mole fraction to illustrate the comparison of the experimental data (symbols) for the (carbon dioxide + valeronitrile) (a), (carbon dioxide + capronitrile) (b) and (carbon dioxide + lauronitrile) (c) systems with calculations (solid lines) obtained with the Peng-Robinson equation of state k_{ij} equal to 0.071 and η_{ij} equal to -0.015, k_{ij} equal to 0.066 and η_{ij} equal to -0.025, and k_{ij} equal to 0.070 and η_{ij} equal to -0.026. ●, 313.2 K; ■, 333.2 K; △, 353.2 K; □, 373.2 K; ○, 393.2 K.



(a)



(b)



(c)

Figure 4. Plot of pressure against mole fraction to illustrate the comparison of the experimental data (symbols) for the (carbon dioxide + valeronitrile) (a), (carbon dioxide + capronitrile) (b) and (carbon dioxide + lauronitrile) (c) systems with calculations (solid lines) obtained with the Peng-Robinson equation of state using optimum parameters (k_{ij} and η_{ij}) at each temperatures: ●, 313.2 K; ■, 333.2 K; △, 353.2 K; □, 373.2 K; ○, 393.2 K.

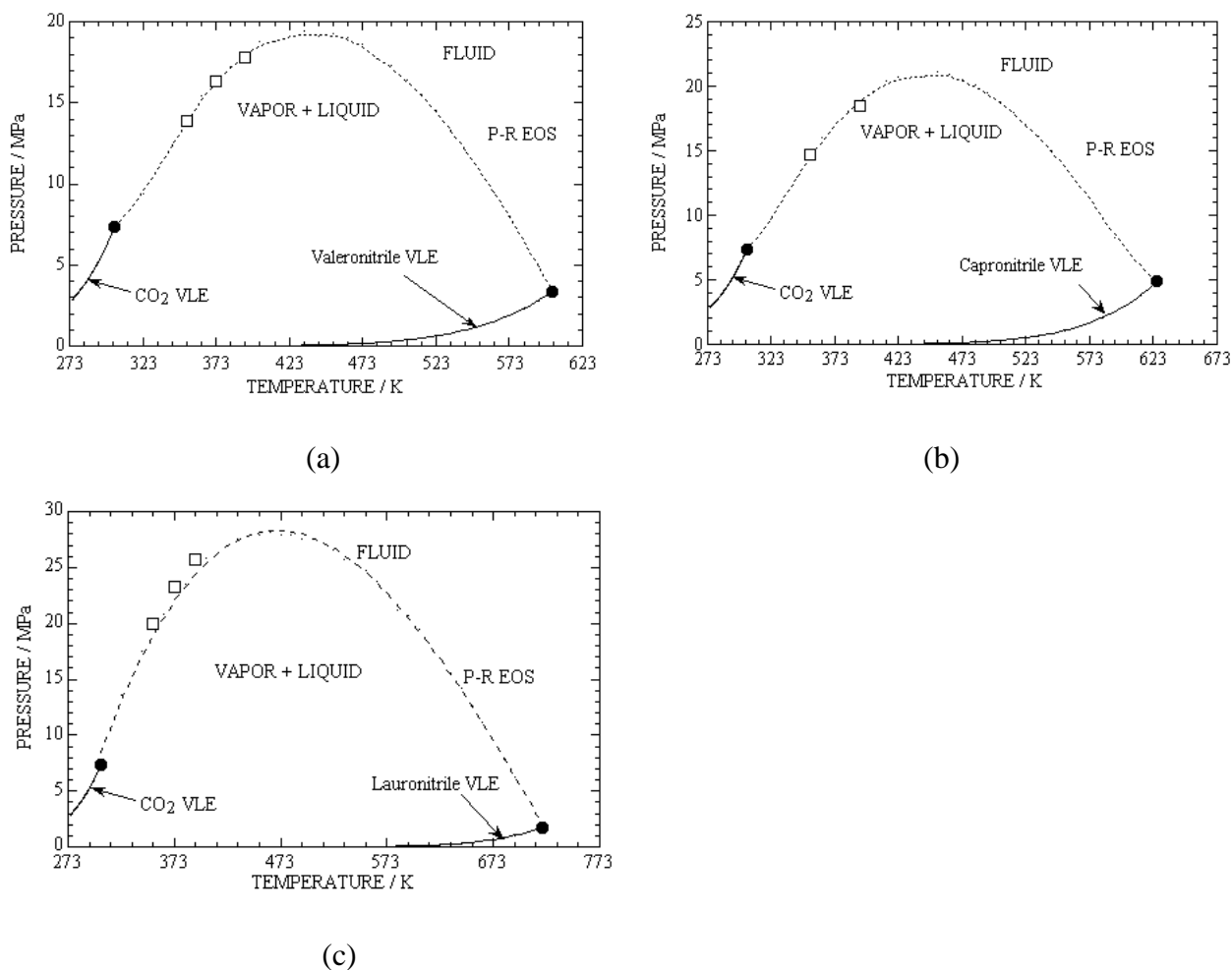


Figure 5. Plot of pressure against temperature for the the (carbon dioxide + valeronitrile) (a), (carbon dioxide + capronitrile) (b) and (carbon dioxide + lauronitrile) (c) systems. The solid lines and the solid circles represent the vapor-liquid lines and the critical points for pure carbon dioxide and the valeronitrile or capronitrile or lauronitrile. The open squares are critical points determined from isotherms measured in this work. The dashed lines represent calculations obtained using Peng-Robinson equation of state with k_{ij} equal to 0.071 and η_{ij} equal to -0.015 (carbon dioxide + valeronitrile), k_{ij} equal to 0.066 and η_{ij} equal to -0.025 (carbon dioxide + capronitrile), and k_{ij} equal to 0.070 and η_{ij} equal to -0.026 (carbon dioxide + lauronitrile).