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High Pressure Phase Behavior of Carbon Dioxide + 1-Methyl-2-pyrrolidinone and Carbon Dioxide + 1-Ethyl-2-pyrrolidinone Systems

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The high-pressure phase behavior of the carbon dioxide + 1-methyl-2-pyrrolidinone and carbon dioxide + 1-ethyl-2-pyrrolidinone systems has been studied. Pressure−composition isotherms were measured for binary mixtures of the carbon dioxide + 1-methyl-2-pyrrolidinone system at (45, 65, 85, 105, and 125) °C and pressures up to 250 bar and for the carbon dioxide + 1-ethyl-2-pyrrolidinone system at (40, 60, 80, 100, and 120) °C and pressures up to 232 bar. The solubility of 1-methyl-2-pyrrolidinone and 1-ethyl-2-pyrrolidinone for the carbon dioxide + 1-methyl-2-pyrrolidinone and carbon dioxide + 1-ethyl-2-pyrrolidinone systems increases as the temperatures increase at constant pressure. The carbon dioxide + 1-methyl-2-pyrrolidinone and carbon dioxide + 1-ethyl-2-pyrrolidinone systems exhibit type I phase behavior, characterized by a continuous critical line from pure carbon dioxide to the second component with a maximum in pressure. The experimental results for the carbon dioxide + 1-methyl-2-pyrrolidinone and carbon dioxide + 1-ethyl-2-pyrrolidinone systems have been modeled using the Peng−Robinson equation of state.

Introduction

The bubble- and dew-point behavior of monomer mixtures containing supercritical carbon dioxide is important for industrial application, supercritical fluid extraction, pharmaceutical industries, and process design. Recently, we have performed phase behavior experiments for mixtures containing supercritical carbon dioxide.[1−4] Supercritical carbon dioxide is a sustainable solvent for supercritical fluid processes because it is environmentally benign, nonhazardous, nontoxic, and readily available and because it can be used at relatively low temperatures and low pressures. Also, advances in supercritical fluid extraction technology often depend on experimental phase behavior measurements on vapor−liquid, liquid−liquid−vapor, and liquid−liquid equilibria. It is also important to determine three-phase equilibria in a binary system.

The main part of this work is the high-pressure experimental data for carbon dioxide + 1-methyl-2-pyrrolidinone and carbon dioxide + 1-ethyl-2-pyrrolidinone mixtures by investigating mixtures of carbon dioxide with two compounds: 1-methyl-2-pyrrolidinone and 1-ethyl-2-pyrrolidinone. Also presented is a portion of the pressure−temperature (p, T) trace of the mixture critical curve for the carbon dioxide + 1-methyl-2-pyrrolidinone and carbon dioxide + 1-ethyl-2-pyrrolidinone systems measured in the vicinity of the critical point of pure carbon dioxide. Three-phase, liquid−liquid−vapor regions occur with carbon dioxide + alcohol systems and with low-molecular-weight hydrocarbon solvent + alcohol mixtures near the critical point of the solvent.[5−9] A detailed description of the characteristics of this type of phase behavior can be found in McHugh and Krukonis.[10]

Also, to provide phase behavior information for high-pressure process design purposes the measured bubble- and dew-point data of binary systems are modeled using the Peng−Robinson equation of state. These results can give valuable information for rational process design and operation in the supercritical region.

Experimental Section

Apparatus and Procedure. Described in detail elsewhere are the experimental apparatus and techniques used to obtain bubble-, critical-, and dew-point curves using a high-pressure variable-volume view cell.[1,2] The experimental apparatus and method are briefly described here. The main part of the experimental apparatus is a variable-volume cell, high-pressure cell which is constructed of a high-nickel-content austenitic steel (Nitronic 50, 5.7 cm o.d., 1.59 cm i.d., working volume of ~28 cm^3) and is capable of operating to pressure of 2000 bar. Typically, the liquid 1-methyl-2-pyrrolidinone or 1-ethyl-2-pyrrolidinone was loaded into the cell to within ±0.002 g using a syringe after the empty cell was purged several times with carbon dioxide to remove traces of air and organic mixtures. Carbon dioxide was then added to the cell to within ±0.004 g using a high-pressure bomb.

The piston obtained of the desired pressure was moved using water pressurized by a high-pressure generator (HIP, model 37-5.75-60). The pressure in the cell was measured with a Heise gauge (Dresser Ind., model CM-53920, 0 to 340 bar) accurate to ±0.4 bar. The temperature of the cell was measured using a digital multimeter (Yokogawa, model 7563, accurate to ±0.005 °C). 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.

Phase behavior experimental data were detected visually in the following manner. At a fixed temperature, the solution in the cell was compressed to a single phase. The

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Table 1. Experimental Data for the Carbon Dioxide−1-Methyl-2-Pyrrolidinone System Measured in This Study

mole fraction of 1-methyl-2-pyrrolidinone	p/bar	transition	mole fraction of 1-methyl-2-pyrrolidinone	p/bar	transition
$t = 45$ °C					
0.012	103.3	bubble point	0.385	90.3	bubble point
0.019	103.3	bubble point	0.445	86.5	bubble point
0.043	102.4	bubble point	0.540	81.4	bubble point
0.067	101.9	bubble point	0.627	71.4	bubble point
0.117	100.8	bubble point	0.725	62.6	bubble point
0.137	100.7	bubble point	0.785	55.5	bubble point
0.220	97.6	bubble point	0.843	48.9	bubble point
0.318	96.6	bubble point			
$t = 65$ °C					
0.012	140.7	dew point	0.385	113.8	bubble point
0.019	142.1	bubble point	0.445	110.7	bubble point
0.043	141.4	bubble point	0.540	100.7	bubble point
0.067	140.8	bubble point	0.627	84.1	bubble point
0.117	142.9	bubble point	0.725	70.8	bubble point
0.137	142.4	bubble point	0.785	60.3	bubble point
0.220	138.9	bubble point	0.843	52.7	bubble point
0.318	125.5	bubble point			
$t = 85$ °C					
0.012	155.9	dew point	0.385	143.8	bubble point
0.019	159.0	dew point	0.445	135.2	bubble point
0.043	175.9	dew point	0.540	117.6	bubble point
0.067	182.9	critical point	0.627	99.7	bubble point
0.117	185.4	bubble point	0.725	78.4	bubble point
0.137	183.5	bubble point	0.785	67.4	bubble point
0.220	181.7	bubble point	0.843	55.5	bubble point
0.318	160.7	bubble point			
$t = 105$ °C					
0.012	157.7	dew point	0.385	172.4	bubble point
0.019	174.8	dew point	0.445	160.4	bubble point
0.043	205.2	dew point	0.540	137.2	bubble point
0.067	217.0	dew point	0.627	111.7	bubble point
0.117	223.8	bubble point	0.725	86.1	bubble point
0.137	222.8	bubble point	0.785	72.9	bubble point
0.220	217.2	bubble point	0.843	58.9	bubble point
0.318	193.8	bubble point			
$t = 125$ °C					
0.012	151.4	dew point	0.385	199.7	bubble point
0.019	182.4	dew point	0.445	183.5	bubble point
0.043	223.8	dew point	0.540	157.6	bubble point
0.067	240.9	dew point	0.627	126.2	bubble point
0.117	249.3	critical point	0.725	95.0	bubble point
0.137	249.3	bubble point	0.785	78.7	bubble point
0.220	246.6	bubble point	0.843	61.3	bubble point
0.318	225.9	bubble point			

solution was maintained in the single-phase (fluid) region at the desired temperature for at least 30 min for the cell to reach phase equilibrium. The pressure was then slowly decreased until a bubble point, critical point, and dew point appeared. The bubble-point pressure was obtained when small vapor bubbles appeared first in the cell, and a dew point was obtained when a fine mist appeared in the cell.

Materials. Carbon dioxide was obtained from Daesung Oxygen Co. (99.9% minimum purity) and used as received. The 1-methyl-2-pyrrolidinone (99.5% purity) and 1-ethyl-2-pyrrolidinone (99.5% purity) used in this work were obtained from Aldrich Chemical Co. Both components were used without further purification in the experiments.

Results and Discussion

Bubble-, dew-, and critical-point data for both the carbon dioxide + 1-methyl-2-pyrrolidinone and carbon dioxide + 1-ethyl-2-pyrrolidinone systems were measured and reproduced at least twice to within ±0.3 bar and 0.2 °C for a given loading of the cell. The mole fractions are accurate to ±0.002.

The carbon dioxide + 1-methyl-2-pyrrolidinone and carbon dioxide + 1-ethyl-2-pyrrolidinone mole fractions for the solubility isotherms at (40 to 125) °C were arranged according to the value of at least two independent data points that have an estimated accumulated error of less than ±1.0%.

Figure 1 and Table 1 show the experimental pressure−composition ($P-x$) isotherms at (45, 65, 85, 105, and 125) °C and the range of pressures of (48 to 250) bar for the carbon dioxide−1-methyl-2-pyrrolidinone system. This system was not observed on the three phases at any of the five temperatures. The $P-x$ isotherms shown in Figure 1 are consistent with those expected from a type I behavior[11] where a maximum occurs in the critical mixture curve.

Figure 2 and Table 2 show the phase behavior experimental data at (40, 60, 80, 100, and 120) °C and pressure up to 232 bar for the carbon dioxide−1-ethyl-2-pyrrolidinone mixture. The type I phase behavior is observed for the carbon dioxide−1-ethyl-2-pyrrolidinone system. The pressure of each mixture critical point continually increases as the temperature increases. The solubility of carbon dioxide decreases as temperatures increase at a constant pressure.

The $P-x$ isotherm experimental data in the carbon dioxide−1-methyl-2-pyrrolidinone and carbon dioxide−1-

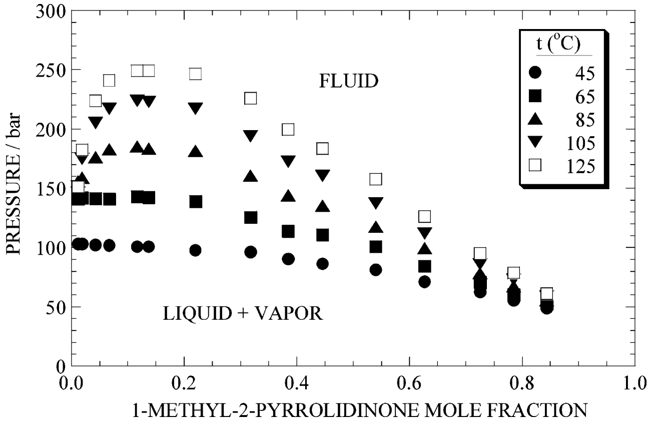

Figure 1. Experimental data isotherms for the carbon dioxide−1-methyl-2-pyrrolidinone system obtained in this work.

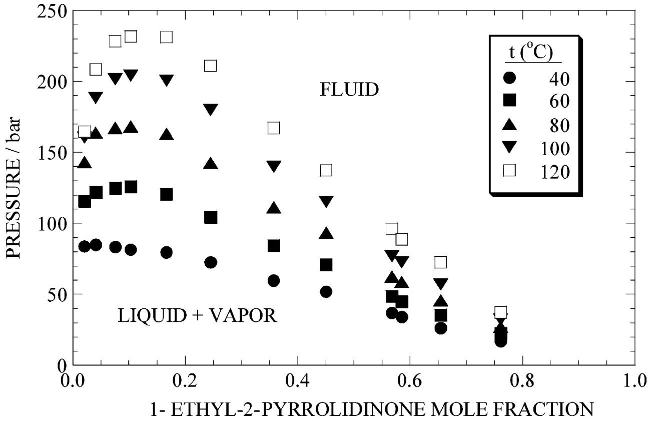

Figure 2. Pressure−composition isotherms for the carbon dioxide−1-ethyl-2-pyrrolidinone system obtained in this work.

ethyl-2-pyrrolidinone systems are modeled using the Peng−Robinson equation of state. The equation of state is briefly described here. For the correlation with the experimental data, we used the Peng−Robinson equation of state[12] with the following mixing rules:

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij} \tag{1}$$

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

$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij} \tag{3}$$

$$b_{ij} = 0.5[(b_{ii} + b_{jj})](1 - \eta_{ij}) \tag{4}$$

where k_{ij} and η_{ij} are interaction binary parameters that are determined by fitting $P-x$ experimental data and a_{ii} and b_{ii} are pure-component parameters as defined by Peng and Robinson. The expression for the fugacity coefficient using these mixing rules is given by Peng and Robinson[12] and is not reproduced here. The critical parameters T_c and P_c and acentric factors used in this work are reported in Table 3.[13−15] The critical property of 1-ethyl-2-pyrrolidinone is calculated by the group-contribution method.[13] Also, the boiling point of 1-ethyl-2-pyrrolidinone is reported by Aldrich Co.

Table 2. Experimental Data for the Carbon Dioxide-1-Ethyl-2-Pyrrolidinone System Measured in This Study

mole fraction of 1-ethyl-2-pyrrolidinone	p/bar	transition
	t = 40 °C	
0.020	83.7	bubble point
0.040	85.0	bubble point
0.075	83.5	bubble point
0.103	81.4	bubble point
0.166	79.6	bubble point
0.245	72.4	bubble point
0.357	59.8	bubble point
0.451	51.8	bubble point
0.568	36.9	bubble point
0.585	34.0	bubble point
0.654	26.2	bubble point
0.761	17.2	bubble point
	t = 60 °C	
0.020	115.9	dew point
0.040	122.0	dew point
0.075	125.0	critical point
0.103	125.7	bubble point
0.166	120.4	bubble point
0.245	104.5	bubble point
0.357	84.1	bubble point
0.451	70.9	bubble point
0.568	48.5	bubble point
0.585	44.8	bubble point
0.654	35.5	bubble point
0.761	22.4	bubble point
	t = 80 °C	
0.020	143.1	dew point
0.040	163.8	dew point
0.075	167.2	dew point
0.103	168.3	bubble point
0.166	163.0	bubble point
0.245	142.6	bubble point
0.357	111.4	bubble point
0.451	93.5	bubble point
0.568	62.6	bubble point
0.585	58.6	bubble point
0.654	45.6	bubble point
0.761	27.1	bubble point
	t = 100 °C	
0.020	160.5	dew point
0.040	188.3	dew point
0.075	201.6	dew point
0.103	204.1	bubble point
0.166	200.4	bubble point
0.245	179.8	bubble point
0.357	139.8	bubble point
0.451	115.2	bubble point
0.568	76.7	bubble point
0.585	72.4	bubble point
0.654	56.8	bubble point
0.761	32.1	bubble point
	t = 120 °C	
0.020	164.7	dew point
0.040	208.5	dew point
0.075	228.3	dew point
0.103	231.7	critical point
0.166	231.1	bubble point
0.245	211.0	bubble point
0.357	167.2	bubble point
0.451	137.4	bubble point
0.568	95.9	bubble point
0.585	88.8	bubble point
0.654	72.5	bubble point
0.761	37.2	bubble point

Figure 3 shows a comparison of carbon dioxide−1-ethyl-2-pyrrolidinone experimental results with calculations obtained using the Peng−Robinson equation at a temperature of 80 °C. The binary interaction parameters of the Peng−Robinson equation of state are fitted by the experimental data at 80 °C. The values of the adjusted parameters for the Peng−Robinson equation of state of the carbon dioxide−1-ethyl-2-pyrrolidinone system are $k_{ij} = 0.042$ and $\eta_{ij} = 0.0384$. A reasonable fit of the data is obtained over most of the composition range even if no mixture param-

Table 3. Pure-Component Critical Properties with the Peng–Robinson Equation of State[a]

component	M_w	t_c/°C	p_c/bar	acentric factor
carbon dioxide	44.01	31.1	73.9	0.225
methyl-2-pyrrolidinone	99.13	448.65	47.8	0.3950
ethyl-2-pyrrolidinone	113.16	366.08	40.41	0.4416

[a] References 13–15.

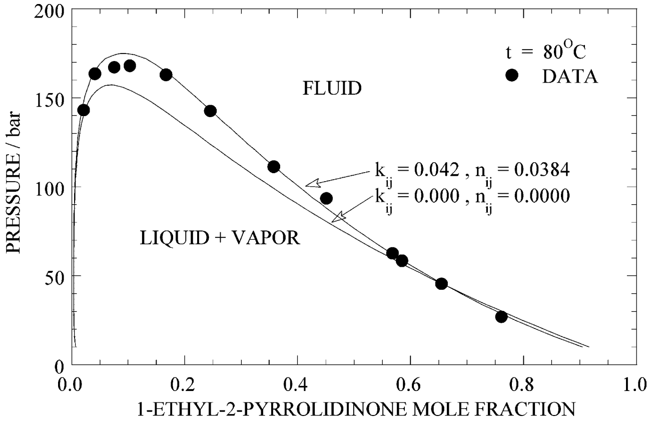

Figure 3. Comparison of the best fit of the Peng–Robinson equation of state to the carbon dioxide–1-ethyl-2-pyrrolidinone system obtained in this work (●) at 80 °C.

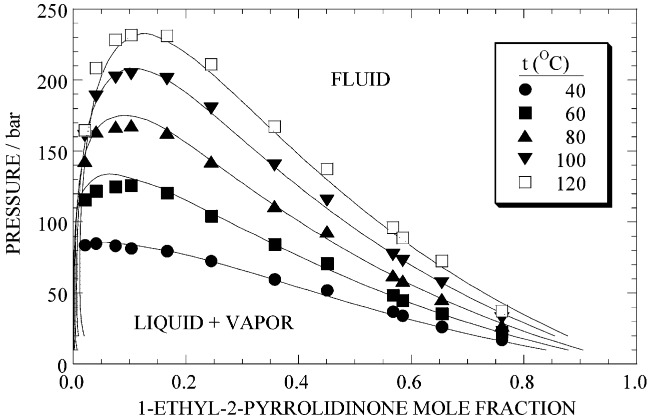

Figure 4. Comparison of the experimental data (symbols) for the carbon dioxide–1-ethyl-2-pyrrolidinone system with calculations (solid lines) obtained using the Peng–Robinson equation of state with $k_{ij} = 0.042$ and $\eta_{ij} = 0.0384$.

eters are used. But if two mixture parameters are used, the fit of the experimental results is significantly better. These sets of parameters are used to predict the vapor–liquid equilibria at other temperatures, namely, 40, 60, 100, and 120 °C.

Figure 4 shows a comparison of experimental data with calculated data at the temperatures of (40, 60, 80, 100, and 120) °C for the carbon dioxide–1-ethyl-2-pyrrolidinone mixture. These isotherms were calculated using the optimized values of $k_{ij} = 0.042$ and $\eta_{ij} = 0.0384$ determined at 80 °C. A good fit of the data was obtained with the Peng–Robinson equation of state using two adjustable mixture parameters for the carbon dioxide–1-ethyl-2-pyrrolidinone system.

Figure 5 shows a comparison of experimental data with calculated data at the temperatures of (45, 65, 85, 105, and 125) °C for the carbon dioxide–1-methyl-2-pyrrolidinone mixture. These isotherms are calculated using the optimized values of $k_{ij} = -0.0064$ and $\eta_{ij} = -0.0762$ determined at 85 °C by the above manner. A good fit of the data is obtained with the Peng–Robinson equation of state using two adjustable mixture parameters for the carbon dioxide–1-methyl-2-pyrrolidinone system.

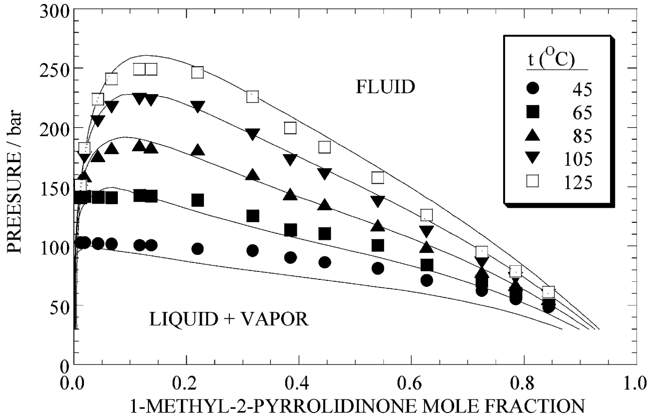

Figure 5. Comparison of the experimental data (symbols) for the carbon dioxide–1-methyl-2-pyrrolidinone system with calculations (solid lines) obtained using the Peng–Robinson equation of state with $k_{ij} = -0.0064$ and $\eta_{ij} = -0.0762$.

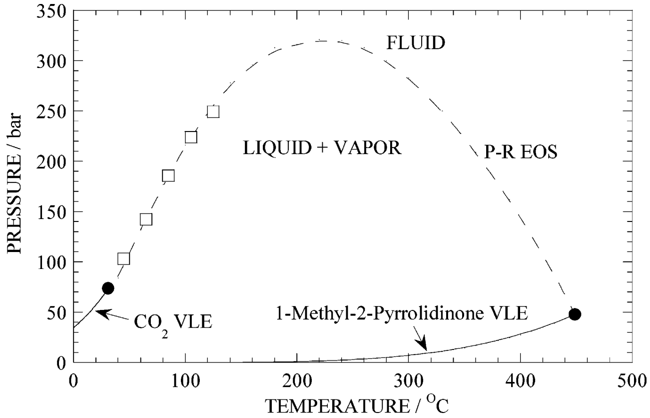

Figure 6. Pressure–temperature diagram for the carbon dioxide–1-methyl-2-pyrrolidinone system. The solid line and the solid circles represent the vapor–liquid line and the critical point for pure carbon dioxide and 1-methyl-2-pyrrolidinone. The open squares are critical points determined from isotherms measured in this study. The dashed line represents calculated values obtained using the Peng–Robinson equation of state with $k_{ij} = -0.0064$ and $\eta_{ij} = -0.0762$.

Figure 6 shows the mixture-critical curve for the carbon dioxide–1-methyl-2-pyrrolidinone system predicted by the Peng–Robinson equation of state. The calculated mixture-critical curve is type I, in agreement with experimental observations. As shown in Figure 6, the solid lines represent the vapor pressure for pure carbon dioxide[13,14] and 1-methyl-2-pyrrolidinone.[15] The solid circles represent the critical point for pure carbon dioxide and 1-methyl-2-pyrrolidinone. The upper part of the dashed line is single phase (fluid), and the lower part of it is two phase (vapor–liquid). The open squares are the mixture-critical points determined from isotherms measured in this experiment. The dashed lines represent the calculated value obtained using the Peng–Robinson equation of state. The binary mixture parameters are then obtained from the Peng–Robinson equation, with k_{ij} equal to -0.0064 and η_{ij} equal to -0.0762.

Figure 7 shows the mixture-critical curve for the carbon dioxide–1-ethyl-2-pyrrolidinone system predicted by the Peng–Robinson equation of state. The calculated mixture-critical curve is type I behavior, in agreement with experimental observations. As shown in Figure 7, the solid lines represent the vapor pressure for pure carbon dioxide[13,14]

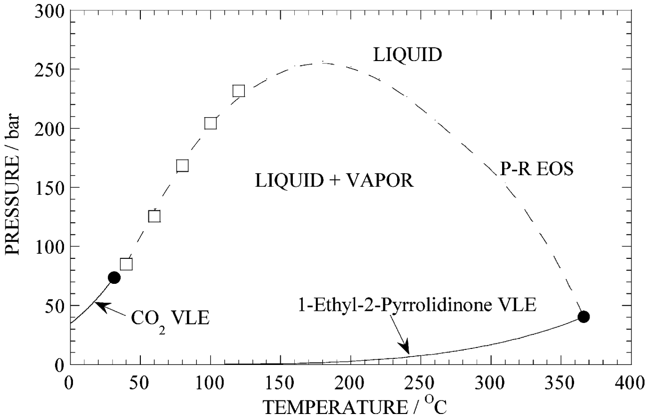

Figure 7. Pressure−temperature diagram for the carbon dioxide−1-ethyl-2-pyrrolidinone system. The solid line and the solid circles represent the vapor−liquid line and the critical point for pure carbon dioxide and 1-ethyl-2-pyrrolidinone. The open squares are critical points determined from isotherms measured in this study. The dashed line represents calculated values obtained using the Peng−Robinson equation of state with $k_{ij} = 0.042$ and $\eta_{ij} = 0.0384$.

and 1-ethyl-2-pyrrolidinone.[13] The vapor pressure of 1-ethyl-2-pyrrolidinone obtained by the Lee−Kesler method.[13] The dashed lines represent the calculated value obtained using the Peng−Robinson equation of state. The binary mixture parameters are then obtained by the Peng−Robinson equation, with $k_{ij} = 0.042$ and $\eta_{ij} = 0.0384$. The process of obtaining optimum binary interaction parameters is identified with the method in the carbon dioxide−1-ethyl-2-pyrrolidinone system.

Conclusion

We show phase behavior data for the carbon dioxide−1-methyl-2-pyrrolidinone and carbon dioxide−1-ethyl-2-pyrrolidinone systems. The experimental phase behavior data obtained for each mixture cover several compositions and different temperatures. The carbon dioxide−1-methyl-2-pyrrolidinone and carbon dioxide−1-ethyl-2-pyrrolidinone systems exhibit type I phase behavior, which is characterized by an uninterrupted critical-mixture curve. These two carbon dioxide−polar solute systems do not exhibit three-phase equilibria in the vicinity of the critical point of carbon dioxide. The Peng−Robinson equation is capable of accurately predicting the phase behavior for the carbon dioxide−1-methyl-2-pyrrolidinone and carbon dioxide−1-ethyl-2-pyrrolidinone systems studied using two independent-temperature mixture parameters.

Literature Cited

(1) Byun, H. S.; Shin, J. S. Bubble-Point Measurement for CO_2−Vinyl Acetate and CO_2−Vinyl Acrylate. *J. Chem. Eng. Data.* **2003**, *48*, 97−101.
(2) Byun, H. S.; Kim, K.; McHugh, M. A. Phase Behavior and Modeling of Supercritical Carbon Dioxide−Organic Acid Mixtures. *Ind. Eng. Chem. Res.* **2000**, *39*, 4580−4587.
(3) Byun, H. S. High-Pressure Phase Behavior and Modeling of CO_2−Propyl Acrylate and CO_2−Propyl Methacrylate Systems. *Fluid Phase Equilib.* **2002**, *198*, 299−312.
(4) Byun, H. S.; McHugh, M. A. Impact of "Free" Monomer Concentration on the Phase Behavior of Supercritical Carbon Dioxide−Polymer Mixtures. *Ind. Eng. Chem. Res.* **2000**, *39*, 4658−4662.
(5) Byun, H. S.; Kwak, C. High-Pressure Phase Behavior for Carbon Dioxide−1-Butanol and Carbon Dioxide−1-Octanol Systems. *Korean J. Chem. Eng.* **2002**, *19*, 1007−1013.
(6) Mallett, M. W.; Kohn, J. P.; McHugh, M. A. In *Chemical Engineering at Supercritical Fluid Conditions*; Paulaitis, M. E., Penninger, J. M. L., Gray, R. D., Davidson, P., Eds.; Ann Arbor Science: Ann Arbor, 1983.
(7) Diguet, R.; Deul, R.; Frank, E. U. Static Dielectric Constant and Density of Supercritical Methane−Methanol Mixtures to 200 MPa. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 551−556.
(8) Brunner, E.; Hultenschmidt, W. J. Fluid Mixtures at High Pressures. VIII. Isothermal Phase Equilibria in the Binary Mixtures (Ethanol + Hydrogen or Methane or Ethane). *J. Chem. Thermodyn.* **1990**, *22*, 73−84.
(9) Hasch, B. M.; Maurer, E. J.; Ansanelli, L. F.; McHugh, M. A. (Methanol + Ethene): Phase Behavior and Modeling with the SAFT Equation of State. *J. Chem. Thermodyn.* **1994**, *26*, 625−640.
(10) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth: Stoneham, MA, 1993.
(11) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1986.
(12) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−63.
(13) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Liquids and Gases*, 4th ed.; McGraw-Hill: New York, 1987.
(14) Vargaftik, N. B. *Handbook of Physical Properties of Liquid and Gases*; Springer-Verlag: Berlin, 1983.
(15) Daubert, T. F.; Danner, R. P. *Data Compilation of Properties of Pure Compounds*, Parts 1, 2, 3 and 4; DIPPR Project, AIChE: New York, 1985−1992.

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