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Phase Behavior of the Carbon Dioxide–Styrene System

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Pressure–composition isotherms for the carbon dioxide–styrene system are obtained at 35, 55, 80, and 100 °C. A portion of the critical-mixture curve is also obtained in the vicinity of the critical point of pure carbon dioxide. The resulting experimental data are modeled by using the Peng–Robinson equation of state. Two temperature-independent model parameters are used to obtain good agreement between calculated and experimental data.

Introduction

Experimental information available for the carbon dioxide–benzene (*1*), –toluene (*2*, *3*), –*m*-xylene (*4*), and –isopropylbenzene (*5*) systems show that these systems exhibit type I phase behavior (*6*, *7*). The focus of this work is to add to this series of CO_2–aromatic systems by determining the phase behavior of the CO_2–styrene system.

Experimental Section

The experimental apparatus and techniques used in this study are described in detail elsewhere (*5*) and are briefly described here. Figure 1 shows a schematic diagram of the experimental apparatus used to obtain dew, bubble, and critical points using the synthetic method. The main component of the experimental apparatus is a high-pressure, variable-volume, cell (316 stainless steel, 5.1 cm o.d. × 1.9 cm i.d., 45-cm^3 working volume) maintained at a constant temperature to within ±0.1 °C. The cell is initially loaded with a measured amount of styrene (Aldrich Chemical Co., 99% purity, used as received) to within ±0.002 g. Carbon dioxide (Linde Co., bone-dry grade, 99.8% minimum purity, used as received) is transferred into the cell gravimetrically to within ±0.002 g by use of a high-pressure bomb. The CO_2–styrene mixture in the cell is viewed through a borescope (Olympus Corp., Model D100-048-000-90) placed against a Pyrex window secured at one end of the cell. The contents of the cell are mixed by a glass-encased stirring bar activated by a magnet located below the cell.

The solution can be compressed to the desired operating pressure by a movable piston fitted within the cell. System pressure is measured with a Heise gauge accurate to within ±0.69 bar. The carbon dioxide–styrene solutions are isolated from the pressure gauge with a gauge protector (Hyett Instrument Co.) located within the air bath near the cell to minimize dead volume. The system temperature is measured to within ±0.1 °C with a Pt-resistance device connected to a digital multimeter.

Dew, bubble, and mixture-critical points are obtained in the following manner. At a fixed temperature the CO_2–styrene mixture in the cell is compressed to a single phase. The pressure is then slowly decreased until a second phase appears. If a fine mist appears, a dew point is obtained; however, if a small vapor bubble is observed, a bubble point is obtained. In either case, the composition of the major phase present is equal to the composition of the overall solution since the small amount of mass in the precipitated phase can be neglected. The transition is a mixture critical point if critical opalescence is observed during the transition process and if two phases of equal volume are present when the mixture phase separates.

Table I. Pressure–Composition Data for the Carbon Dioxide–Styrene System Obtained in This Study

mole fracn styrene	*P*, bar 35.0 °C	55.0 °C	80.0 °C	100.0 °C
0.0092	77.4	88.9		
0.0245	75.6	98.6	114.8	125.1
0.0611	73.1	100.5	134.0	
0.0726	70.8	100.1	136.1	157.0
0.1169	69.5	98.4	136.7	
0.1392				162.4
0.1656				162.3
0.2650	63.5	89.5	123.7	
0.3831				132.4
0.4879	53.5	71.9	94.1	110.4
0.6338	43.8	54.6	68.7	78.9
0.8245	26.9	31.6	38.8	43.6

Table II. Critical-Mixture Data for the Carbon Dioxide–Styrene System Obtained in This Study

mole fracn styrene	*T*, °C	*P*, bar
0.0245	41.5	84.3
0.0611	58.0	106.1
0.0726	70.0	122.5
0.1392	100.0	162.4

Results and Discussion

Experimental *P*–*T*–*x* data at 35, 55, 80, and 100 °C are shown in Figures 2 and 3 and are listed in Tables I and II. The mole fractions reported in this work are accurate to within ±0.0025 and the pressures for each bubble and dew point are generally reproducible to within ±0.3 bar. The isotherms in Figure 2 show that the CO_2–styrene system exhibits type I phase behavior. Type I phase behavior has a continuous critical-mixture curve as shown in Figure 3.

The phase equilibrium data obtained in this study are modeled with the Peng–Robinson (*8*) equation of state. The Peng–Robinson equation of state is used with the following mixing rules

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

$$a_{ij} = (a_{ii} a_{jj})^{0.5}(1 - k_{ij}) \tag{2}$$

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

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

where k_{ij} and η_{ij} are mixture parameters which are determined by fitting pressure–composition data and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson (*8*). With these mixing rules the expression for the fugacity coefficient becomes

$$\ln \phi_i = \frac{b'_i}{b_{\mathrm{mix}}}(Z - 1) - \ln (Z - B) - \frac{A}{2.828B}\left(\frac{2\sum_j x_j a_{ij}}{a} - \frac{b'_i}{b_{\mathrm{mix}}}\right) \ln \left(\frac{Z + 2.414B}{Z - 0.414B}\right) \tag{5}$$

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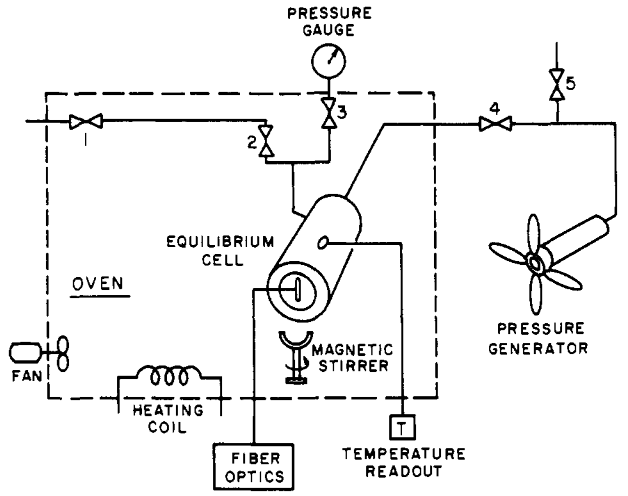

Figure 1. Schematic diagram of the experimental apparatus used to obtain phase equilibrium data.

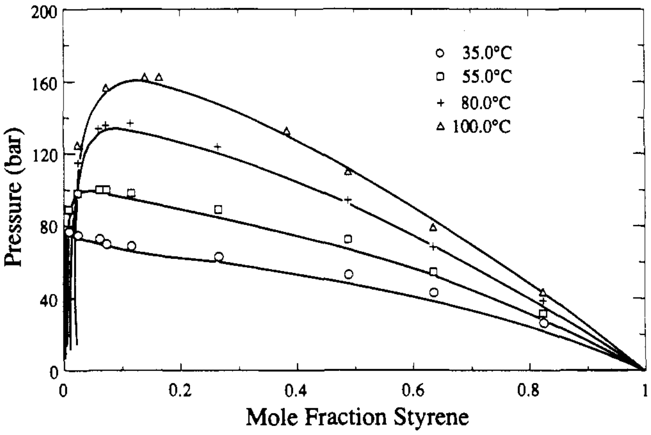

Figure 2. Comparison of experimental and calculated P–x data for the carbon dioxide–styrene system. The solid lines represent calculations with the Peng–Robinson equation with k_{ij} = 0.046 and n_{ij} = −0.067.

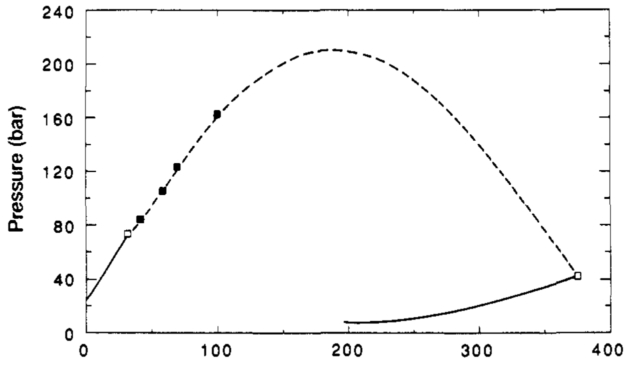

Figure 3. Comparison of experimental and calculated P–T data for the carbon dioxide–styrene system. The open squares represent the pure component critical conditions for carbon dioxide and styrene (*9*), and the filled squares represent experimentally observed mixture critical points. The dashed line represents calculations with the Peng–Robinson equation with k_{ij} = 0.046 and η_{ij} = −0.067.

Table III. Pure Component Parameters (*9*) Used with the Peng-Robinson Equation of State

component	T_c, °C	P_c, bar	acentric factor
CO_2	31.1	73.8	0.225
styrene	373.9	39.9	0.257

where

$$Z = \frac{Pv}{RT}$$

$$A = \frac{a_{mix}R^2T^2}{P}$$

and

$$B = \frac{b_{mix}RT}{P}$$

The term b'_i is defined as

$$b'_i = \left(\frac{\partial(b_{mix}N)}{\partial N_i}\right)_{T,V,N_{j\neq i}} = 2\sum_k x_k b_{ik} - b_{mix} \qquad (6)$$

where N is the total number of moles in the mixture. If η_{ij} is set equal to zero, the mixing rule for b_{mix} reduces to a single summation in mole fraction, b'_i becomes equal to b_i, and the equation for the fugacity coefficient of component i reduces to the expression given by Peng and Robinson (*8*). Table III shows the pure component critical temperatures, critical pressures, and the acentric factors needed with the Peng–Robinson equation.

The values of k_{ij} and η_{ij} were obtained by minimizing the sum of the absolute differences between the calculated and observed pressures. For a fixed value of η_{ij}, the calculated values of the mixture-critical pressure and composition increase with increasing values of k_{ij}. For a fixed value of k_{ij}, increasing η_{ij} increases the calculated mixture-critical pressure and lowers the bubble point pressure for a given isotherm.

The fit of the P–x isotherms and the critical-mixture curve using the Peng–Robinson equation is shown in Figures 2 and 3 with the optimized values of 0.046 for k_{ij} and −0.067 for η_{ij}. The calculated and experimental isotherms and critical-mixture curves are in good agreement. Both parameters are needed to obtain a good fit of the data. A better fit of the data could be obtained with temperature-dependent mixture parameters, although this result was not reported since the increase in the number of fitted parameters did not seem warranted. The values of k_{ij} and η_{ij} for the CO_2–styrene system are close to those found for the CO_2–benzene (*10*, *11*), -toluene, -*m*-xylene, and -isopropylbenzene systems (*5*, *11*).

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Glossary

a_{ii}	pure component parameter for component i used in the Peng–Robinson equation of state
b_{ii}	pure component parameter for component i used in the Peng–Robinson equation of state
k_{ij}	mixture parameter accounting for interaction between mixture components
N	total number of moles of the mixture
P	pressure
R	gas constant
T	temperature
v	molar volume
V	total volume
Z	compressibility factor

Greek Letters

ϕ_i	fugacity coefficient of component i
η_{ij}	mixture parameter accounting for differences in the sizes of the mixture components

Registry No. CO_2, 124-38-9; styrene, 100-42-5.

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Three-Phase Liquid–Liquid–Vapor Equilibria in the Nitrogen + Methane + *n*-Heptane System

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The three-phase liquid–liquid–vapor (L_1–L_2–V) phase equilibria behavior of the ternary mixture nitrogen + methane + *n*-heptane is presented, with special attention directed toward identifying the boundaries of the three-phase region. This ternary system has a constituent binary mixture, methane + *n*-heptane, which exhibits L_1–L_2–V immiscibility. The presence of nitrogen creates a three-sided L_1–L_2–V region extending in pressure–temperature space down in temperature, over a range of 169–192 K, from the binary L_1–L_2–V locus. The other two boundaries of the three-phase region are type K point (L_1–L_2=V) and Q point (S–L_1–L_2–V) loci. Liquid-phase compositions and molar volumes are reported as a function of temperature and pressure within the three-phase region and along the boundaries.

Introduction

We have been engaged in an extensive study of liquid–liquid–vapor (L_1–L_2–V) phenomena in well-defined ternary prototype mixtures of liquefied natural gas (LNG) (*1*–*7*), in order to help understand the possible occurrence of multiphase equilibria in LNG process systems. To date, we have studied five ternary mixtures containing nitrogen + methane (*4*, *5*, *7*), with the third component being the solutes ethane, propane, *n*-butane, *n*-pentane, and *n*-hexane, respectively.

In this paper, we present results for the L_1–L_2–V phase equilibria of the ternary mixture nitrogen + methane + *n*-heptane. The binary constituent mixture methane + *n*-heptane exhibits L_1–L_2–V immiscibility. *n*-Heptane is the largest *n*-paraffin that is partially miscible with methane. Since nitrogen is more volatile than methane, *n*-heptane is therefore the largest *n*-paraffin to be immiscible with mixtures of nitrogen + methane. The role of nitrogen is to create a three-phase L_1–L_2–V region (surface) in thermodynamic phase space, extending down in temperature from the binary L_1–L_2–V locus. Liquid-phase compositions and molar volumes are reported herein for the L_1 and L_2 phases in the three-phase region including along its boundaries.

Experimental Section

The experimental study was performed using and apparatus originally developed by Kohn and co-workers (*8*). The experimental procedures are detailed in ref *1* and *2*.

The multiphase equilibria phenomena were observed in a glass visual cell of approximately 12 mL internal volume, marked and calibrated so that phase volumes could be determined by direct visual inspection. Stoichiometric and phase volumetric measurements were made on the liquid phases in the cell which permitted the computation of the composition and molar volume of each of those phases. In order to calculate these properties accurately, the amount of the vapor phase was kept small during any run, and the composition of the vapor phase was assumed to be a mixture of nitrogen and methane only. This assumption appears justified given the very low vapor phase mole fraction of *n*-heptane in the phase equilibria of the binary mixture methane + *n*-heptane at comparable temperatures (*8*). Further justification for the assumption is found in Table II, where the composition of the L_2 phase at L_2=V in the presence of L_1 phase is given for several conditions. The maximum composition of *n*-heptane at any conditions given is 0.0044 mole fraction and generally averages asound 0.003 mole fraction. Since the composition of *n*-heptane in all of the noncritical vapor phases must be lower than that in the critical (L_2=V) phase and this composition of the critical vapor phase is obtained without invoking the simplifying assumption of zero *n*-heptane, the upper limit for composition of *n*-heptane in all the gas phases is clearly established. The vapor-phase nitrogen + methane composition was assumed to be the same as that for the nitrogen + methane binary vapor–liquid system as reported by Kidnay et al. (*9*) at the same temperature and pressure. Given this assumption, the vapor-phase compressibility factor, and then the amount of material in the vapor phase, was estimated by using the Soave–Redlich–Kwong equation of state as modified by Graboski and Daubert (*10*, *11*).

The temperature of the liquid bath housing the visual cell was measured with a Pt-resistance thermometer, calibrated to the IPTS-1968 scale; cell temperatures were estimated to be accurate to ±0.03 K. The system pressure was measured with a Heise bourdon tube gauge, accurate to ±0.07 bar. Liquid-phase volumes in the visual cell could be read to ±0.02 mL.

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