J. Chem. Eng. Data **2001,** *46*, 809−812

Gas−Liquid Critical Properties of Ethylene + Benzene

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Gas−liquid critical properties of ethylene + benzene have been measured over the whole composition range by using a high-pressure view cell with direct visual observation. The critical points of the two pure components are in good agreement with literature values. Critical lines show the expected type I fluid phase behavior. Our results are compared with those of Lyubetski,[1] who obtained critical property values through extrapolation of vapor−liquid-phase equilibrium data. Using the Peng−Robinson equation of state, the binary interaction parameter k_{ij}, obtained from vapor−liquid equilibrium data at 348.15 K,[2] was used to calculate the critical temperature and the critical pressure. The agreement between our experimental values and the calculated values is satisfactory.

Introduction

Critical properties of fluid mixtures are of much interest in chemical engineering. In the reaction engineering field, critical properties of the reactant mixture are particularly important when the reaction is carried out in the near critical region.

In our laboratory, alkylation of ethylene and benzene in the near (super- and sub-) critical regions is under investigation. Therefore, the critical properties of the reactant mixture need to be known. This paper presents accurate values of the critical properties of this binary mixture.

The most commonly used techniques for measuring critical properties of mixtures include direct methods and indirect methods. The former method determines critical properties through the direct observation of the critical point such as via the visual method[3] or the acoustic method.[4] The latter method has been used to determine the critical properties through extrapolation from the dew points and bubble points of the mixtures. The former is generally more reliable than the latter.[5] Depending on the apparatus used, direct observation can be done using either sealed tubes or open-ended tubes.

Because of the simplicity of the apparatus, the sealed tube method has been most widely used for both mixtures and pure substances.[3,4,6] Critical properties can be determined from disappearance of the liquid meniscus by slowly heating the cell or from the reappearance of the meniscus when slowly cooling the cell. The reappearance of the meniscus is usually sharper than its disappearance.[5] In addition, for precise determination of the critical properties, the cell must be sufficiently short and well stirred to prevent temperature gradients. Heating (or cooling) of the cell during the final stage approaching the critical state must be carried out very slowly.[5]

In this paper we report results with a sealed cell which is sufficiently short (28 mm high) and well stirred. The authors' critical properties of the ethylene + benzene binary mixture have shown differences from those of Lyubetski,[1] who obtained the critical properties through extrapolation of vapor−liquid equilibrium data.

The thermodynamic criteria for calculating the critical properties of mixtures have been discussed in the literature.[7] Different equations of state, such as the Peng−Robinson equation[8] and the Guggenheim equation,[9] and different calculation methods, such as the Newton method[8] and the Hicks−Young method,[10] have been used to calculate the critical properties of mixtures. In this work, the Peng−Robinson equation and the Hicks−Young method have been used to calculate the critical temperatures and pressures of the ethylene + benzene mixture at various compositions using the binary interaction parameter correlated from the vapor−liquid equilibrium data at 348.15 K.[2] The agreement between our experimental results and calculations is basically satisfactory.

Experimental Section

Experimental Setup. Critical point measurements were conducted using a high-pressure view cell. The cell can be operated at temperatures up to 623 K and pressures up to 13 MPa.

A schematic diagram of the apparatus is shown in Figures 1 and 2. The cell was made from a stainless steel block 50 mm in diameter with a chamber hole of 28 mm drilled in its longitudinal direction. Two quartz windows (18 mm thick and 49 mm in diameter) at both ends of the hole permitted visual observation of the contents. The quartz windows were sealed with a special nonasbestos gasket on both sides. The cell was horizontally installed. Located at the center of the bottom was a terrace on which a magnetic stirring bar was mounted. Loading was achieved by two separate high-pressure liquid metering pumps (Ruska Instrument Corporation, U.S.A.) at an accuracy of 0.01 cm^3. The cell pressure was measured at an accuracy of ±0.02 MPa by a pressure transducer (NPI series, NOVA, U.S.A.). The temperature was measured at an accuracy of ±0.01 K by a mercury thermometer which had been calibrated. The cell was placed in an air thermostat, whose temperature was controlled at an accuracy of ±0.2 K by a temperature control system consisting of a Pt resistance thermograph (WZP-280, No.3 Shanghai Automatic Instruments, China), a temperature controller (AI-708, Shanghai

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10.1021/je000309y CCC: $20.00

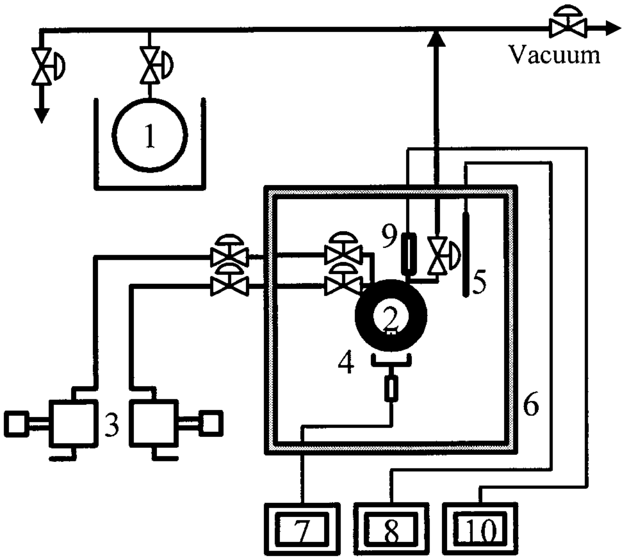

Figure 1. Schematic of the experimental setup: 1, liquid nitrogen degassing cell; 2, view cell; 3, high-pressure liquid pumps; 4, magnetic stirrer; 5, Pt resistance thermograph; 6, constant temperature air bath; 7, stirring controller; 8, temperature controller; 9, pressure transducer; 10, digital multimeter.

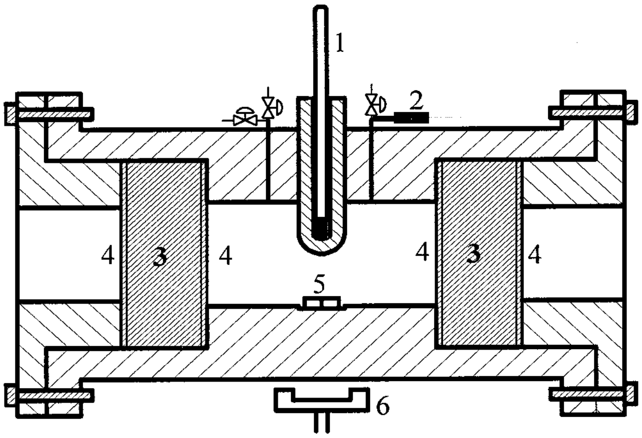

Figure 2. View cell (which is placed in the air thermostat) used in the experiments: 1, mercury thermometer; 2, pressure transducer; 3, quartz windows; 4, gasket; 5, stirring bar; 6, magnetic stirrer.

Qisheng Instrument Limited Company, China), and a solid-state relay (Shanghai Qisheng Instrument Limited Company, China). A fan was installed in the air thermostat to make the system more isothermal. The pressure transducer which could be operated at temperatures up to 623 K was directly contacted with the fluids. The vacuum line was used to degas benzene and to evacuate the cell before adding the materials. The internal volume of the cell was 39.963 cm^3, calibrated with distilled water when the magnetic stirring bar was in place.

Experimental Procedures. Gas−liquid critical points for pure substances and mixtures were determined on the basis of visual observations. Ethylene and benzene were loaded in separate pumps. Before loading, care was taken to degas the liquid benzene using freeze−pump−thaw cycles with liquid nitrogen as the coolant. Before being introduced into the cell, the temperatures of ethylene and benzene in separate pumps were maintained at 273.15 K and 308.15 K by two superthermostatic baths. Their pressures were maintained at 6.5 MPa and 0.5 MPa to keep them in liquid form. The densities of both liquids at the specified temperature and pressure were calibrated from literature values[11,12] and from the volumes of the liquids introduced into the cell, so their masses were determined as well as the composition of the mixture.

Table 1. Comparison of the Critical Constants of This Work with Those from the Literature[12]

	T_c/K		P_c/MPa		ρ_c/g·cm^{-3}	
substance	this work	lit.	this work	lit.	this work	lit.
ethylene	282.75	282.343	5.06	5.040	0.210	0.2141
benzene	563.65	562.160	5.01	4.898	0.297	0.3020

In determining the critical condition of a binary mixture, a known volume of the component with a lower vapor pressure (benzene) was first introduced into the cell at a constant temperature. Then a known volume of the second component (ethylene) was added and the stirrer was turned on. The amount of the mixture in the cell was controlled in such a way that the density of the mixture should be close to (or slightly higher than) its critical density, which was *a priori* unknown. After filling, the temperature of the air bath was increased gradually while observing the existence of the meniscus. If the overall density was lower than the critical density, the meniscus would fall and eventually the liquid phase would evaporate. If the overall density was considerably greater than the critical density, then the meniscus would rise and eventually the liquid would completely fill the cell. If the overall density was close to the critical density ($< \pm 0.005$ g·cm^{-3}), the location of the meniscus would remain unchanged or slightly rise to the middle of the view cell, where the meniscus would become flatter and fainter and would finally disappear as soon as the critical point was reached. Usually, the mixture must be reloaded several times so as to guarantee that the overall density in the cell was close to the critical density. In close vicinity to the critical point, the strong red-glow critical opalescence could be observed. The intensities of the opalescence in the liquid phase and that in the vapor phase were almost the same, and there was no intensity and color difference between mixtures of different compositions. The temperature sequentially rose to a little above the critical temperature to reach a uniform phase of a supercritical fluid. Then the temperature of the air thermostat was decreased about 30 K so as to cause the cell temperature to decrease slowly at a rate of <0.3 K/min. Before the two-phase region was reached, in the temperature-decreasing process a strong critical opalescence could also be observed when the temperature was gradually decreasing. The color of the fluid would go from colorless to yellow, to red glow, and to black. Then the meniscus would reappear at the middle of the view cell. These temperature-increasing and -decreasing processes needed to be repeated several times for a more precise reading. Eventually, in the temperature-decreasing process the temperature and pressure readings could be made at the moment when complete darkness was observed [3] before the meniscus reappeared. Generally, the difference of the temperature between the disappearance of the meniscus and the complete darkness of the fluid was within ±0.3 K.

Materials. The ethylene was obtained from the Shanghai Research Institute of Chemical Technology with a 99.9 mol % purity. The benzene from Shanghai Feida Chemicals was purified before application to guarantee a purity of higher than 99.5 mol %.

Experimental Results

The apparatus and the technique were checked by measuring the critical temperature and pressure of ethyl-

Table 2. Critical Properties of Ethylene (1) + Benzene (2)

x_1	T_c/K	P_c/MPa	ρ_c/g·cm^{-3}
1.000	282.75	5.07	0.210
0.911	331.25	8.43	0.304
0.831	372.47	10.78	0.352
0.700	438.25	11.53	0.379
0.600	461.21	10.97	0.380
0.500	488.25	9.93	0.378
0.402	511.85	9.15	0.370
0.300	528.25	7.72	0.348
0.197	542.65	6.71	0.340
0.100	552.75	6.06	0.318
0.000	563.65	5.01	0.297

Table 3. Critical Properties of Ethylene (1) + Benzene (2) from the Literature[1]

x_1	T_c/K	P_c/MPa	ρ_c/g·cm^{-3}
1.000	282.75	5.14	0.210
0.940	307.75	6.43	0.255
0.760	357.55	9.05	0.319
0.652	397.95	9.80	0.330
0.466	449.15	9.60	0.329
0.244	514.45	6.97	0.314
0.000	563.65	5.08	0.297

Table 4. Parameters of the Pure Substances Used in the P−R EOS from the Literature[12]

substance	T_c/K	P_c/MPa	V_c/cm^3·mol^{-1}	Z_c[a]	ω[b]
ethylene	282.343	5.040	130.99	0.2813	0.0870
benzene	562.160	4.898	258.65	0.2710	0.2092

[a] Z_c denotes the critical compressibility factor. [b] ω denotes the acentric factor.

ene and benzene. Table 1 shows the experimental results. The critical temperature and pressure are in excellent agreement with the literature values.[12] Table 2 gives the critical properties for ethylene (1) + benzene (2). Each experimental point is repeated three times, and their average taken as the final value. Usually the deviation of critical temperature is no more than ±0.4 K and that of critical pressure is no more than ±0.06 MPa. Table 3 presents the values[1] obtained by extrapolation of the vapor−liquid equilibrium data. Figures 3−5 show that the critical lines are continuous over the whole composition range between the critical points of the two pure components. The critical pressure passes through a maximum at $x_1 \approx 0.7$; the critical densities show a maximum at $x_1 \approx 0.6$.

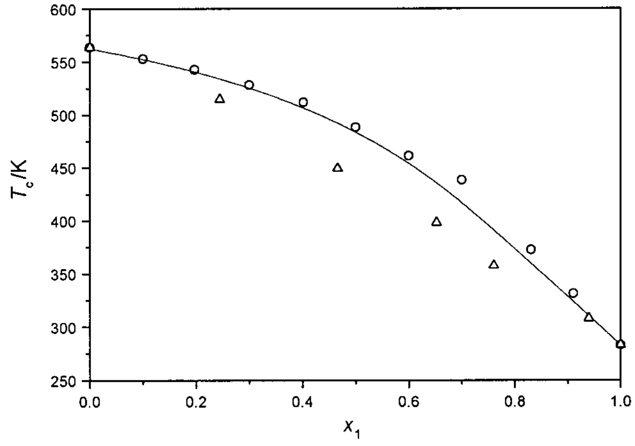

Figure 3. Critical temperature for ethylene (1) + benzene (2) (△, Lyubetski's experiments; ○, this work; —, calculation results via P−R EOS with k_{12} = 0.031 20).

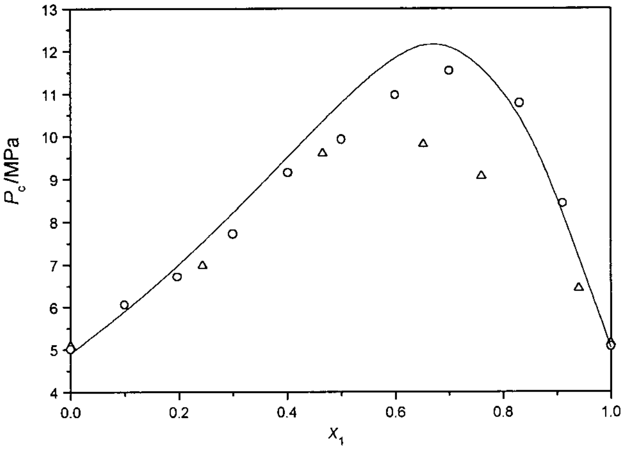

Figure 4. Critical pressure for ethylene (1) + benzene (2) (△, Lyubetski's experiments; ○, this work; —, calculation results via P−R EOS with k_{12} = 0.031 20).

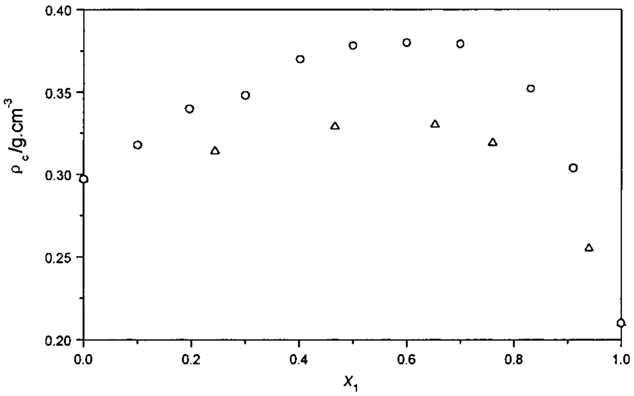

Figure 5. Critical density for ethylene (1) + benzene (2) (△, Lyubetski's experiments; ○, this work).

Calculation of Critical Properties

Critical Conditions. The critical conditions for a binary mixture can be determined as follows:[7]

$$W = \begin{bmatrix} -\left(\dfrac{\partial^2 A}{\partial V^2}\right)_{T,x_1} & -\left(\dfrac{\partial^2 A}{\partial V\,\partial x_1}\right)_T \\ \left(\dfrac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \left(\dfrac{\partial^2 A}{\partial x_1^{\,2}}\right)_{T,V} \end{bmatrix} = 0 \qquad (1)$$

$$X = \begin{bmatrix} \left(\dfrac{\partial W}{\partial V}\right)_T & \left(\dfrac{\partial W}{\partial x_1}\right)_T \\ \left(\dfrac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \left(\dfrac{\partial^2 A}{\partial x_1^{\,2}}\right)_{T,V} \end{bmatrix} = 0 \qquad (2)$$

The mechanical stable condition can be expressed in eq 3, and the material stable conditions are presented in eqs 4 and 5:

$$(\partial P/\partial V)_T < 0 \qquad (3)$$

$$W_1 = (\partial^2 A/\partial x_1^{\,2})_{T,V} > 0 \qquad (4)$$

$$Y = \begin{bmatrix} \left(\dfrac{\partial X}{\partial V}\right)_T & \left(\dfrac{\partial X}{\partial x_1}\right)_T \\ \left(\dfrac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \left(\dfrac{\partial^2 A}{\partial x_1^{\,2}}\right)_{T,V} \end{bmatrix} > 0 \qquad (5)$$

where A and x denote the Helmholtz function and the mole fraction.

Peng−Robinson EOS. The above derivatives have been evaluated using the Peng−Robinson equation of state.[8] The binary critical conditions were solved by a general procedure reported by Hicks and Young.[10] All the critical points of any composition could be located by tracking the locus specified either by eq 1 or by eq 2 over a certain range of temperature and specific volume. The critical point is also tested for mechanical and material stability.

For mixtures, the following mixing rules have been used:

$$a_m = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij}, \quad a_{ij} = (1 - k_{ij})\sqrt{a_i a_j}, \quad k_{ij} = k_{ji}$$

$$b_m = \sum_{i=1}^{n} x_i b_j$$

k_{ij} is the binary interaction parameter. While $i = j$, we have $k_{ij} = 0$.

Calculation Results. The vapor−liquid equilibrium data of this binary mixture at 348.15 K[2] were correlated using the Peng−Robinson EOS, and the binary interaction parameter was obtained:

$$k_{ij} = 0.03120 \quad (i \neq j)$$

Then value of k_{ij} was used to calculate the critical temperature and pressure. The calculation results can be seen from Figures 3 and 4. The parameters of pure ethylene and pure benzene used in the Peng−Robinson equation are shown in Table 4. Deviations between experimental work and calculation can be expressed as

$$\text{AADT} = \left[\frac{1}{N}\sum_{j=1}^{N}\left|\frac{T_{c,exp} - T_{c,cal}}{T_{c,exp}}\right|_j\right] \qquad (6)$$

$$\text{AADP} = \left[\frac{1}{N}\sum_{j=1}^{N}\left|\frac{P_{c,exp} - P_{c,cal}}{P_{c,exp}}\right|_j\right] \qquad (7)$$

AADT and AADP represent the average absolute deviation of temperature and pressure between experiments and calculation, and N is the number of data. $T_{c,exp}$ and $P_{c,exp}$ denote the experimental critical temperature and critical pressure, while $T_{c,cal}$ and $P_{c,cal}$ denote the calculated critical temperature and critical pressure.

For our experimental results

$$\text{AADT} = 1.4\% \qquad \text{AADP} = 4.4\%$$

While for Lyubetski's results

$$\text{AADT} = 16.2\% \qquad \text{AADP} = 13.4\%$$

Discussions

It is clearly observed that there are obvious differences between our work and Lyubetski's.[1] Results are discussed from three aspects as follows:

(1) Our experimental results were obtained by using a direct method. In Lyubetski's work, the critical properties were not measured but extrapolated from the vapor−liquid equilibrium curve. The direct method is more reliable than the indirect method for determining the critical properties of the mixtures.[5]

(2) Near the critical point, the compressibility of the fluid tends to be infinite as the effect of the gravitational force becomes so large as to cause a great density gradient in the vessel even if it is only a few centimeters high, and the infinite values of C_p and C_v make it hard to reach thermal equilibrium. The effect of the density gradient in a mixture is greater than that in a pure substance. In our experiments, we have noticed that when the fluids are not stirred, the fluids in the cell in the near (super- and sub-) critical regions would divide into several layers, and it is difficult to observe the disappearance or reappearance of the meniscus. Therefore, the authors' experimental cell was of the shortest possible height. The stirrer was used to speed up thermal equilibrium and to prevent the gravitational force effects to the greatest possible extent. In the present work, each measurement has been repeated three to five times and is only accepted when only negligible differences appear. In Lyubetski's work a long glass capillary was used in which the fluids were not stirred. Hence, his vapor−liquid equilibria in the near critical regions were possibly not reliable and so could lead to unreliability of his extrapolated critical data.

(3) For the mixture ethylene (1) + benzene (2) at 348.15 K, there are systematical differences between the values of Lyubetski[1] and Knapp et al.[2]. Extrapolating the data of Knapp et al. to T_c of 348.15 K, $x_1 = 0.85 \pm 0.05$ and $P_c > 9.5$ MPa. Extrapolating the results of Lyubetski to $T_c = 348.15$ K, $x_1 = 0.80 \pm 0.02$ and $P_c < 8.5$ MPa.

(4) The average deviation gives experimental values of T_c and P_c much closer to those calculated from a k_{ij} derived from the results of Knapp et al. by using the Peng−Robinson EOS.

Acknowledgment

This work is supported by the National Science Foundation of China (NSFC) and the China Petrochemical Corporation (SINOPEC) (Contract No. 29792077).

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Received for review September 19, 2000. Accepted March 6, 2001.

JE000309Y