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Critical Properties of Ethylene + Benzene + Ethylbenzene

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The critical temperature, pressure, and density of the ternary mixture ethylene + benzene + ethylbenzene have been measured. The hard-sphere three-parameter equation of state was used to calculate the critical points using the Hicks−Young method. The experimental data of the critical points of the three binary mixtures ethylene + benzene, benzene + ethylbenzene, and ethylene + ethylbenzene have been correlated. With the interaction coefficients obtained from the binary mixtures, the critical points of the ternary mixture (ethylene, benzene, and ethylbenzene) were predicted. The agreement between the predicted and the experimental values is satisfactory.

Introduction

In our laboratory, an investigation of the alkylation of benzene with ethylene over β zeolite in the near (super- and sub-) critical regions showed a low yield of ethylbenzene. This paper deals with the determination of the critical properties of benzene + ethylene + ethylbenzene where the mixture composition range corresponds to the compositions of the three components which would likely be encountered in the above reaction. To the authors' knowledge, the critical properties of this ternary mixture have not been previously reported.

The most commonly used techniques for measuring critical properties of mixtures include direct methods and indirect methods.[1] The former method is more accurate for determining the critical properties.[1] Depending on the apparatus, direct methods can be realized in a sealed tube or in an open-ended tube, both visually observable. The open-ended tube method is probably the most convenient method for determining the critical properties precisely because the volume of the sample in the cell can be adjusted by a screw press to reach the critical volume. However, it is very difficult to keep the cell airtight at high temperatures. The sealed tube method is a simple, generally reliable, and widely used method for determining the critical temperatures and pressures of both mixtures and pure substances.[2−4] Critical properties can be determined from the disappearance of an interphase meniscus when slowly heating the tube through the critical point or the reappearance of the meniscus when slowly cooling the tube. The reappearance of the meniscus is usually a more sensitive phenomenon than its disappearance.[1] For precise measurement of critical properties, the tube must be well stirred and as short as possible, and the final heating (or cooling) process must be carried out very slowly.[1]

For the ternary system, it is impractical to measure the critical properties over the whole composition range. Therefore, it is necessary to establish a reliable prediction method for the critical properties of the ternary mixtures based on the correlation of the experimental results of the three binary mixtures. The thermodynamic criteria for calculating the critical properties of mixtures have been discussed elsewhere.[5] Different equations of state such as the Peng−Robinson equation[6] and the Guggenheim equation[7] and different calculation methods such as the Newton method[6] and the Hicks−Young method[8] are used to calculate the critical properties of the mixtures. Here we applied the hard-sphere three-parameter equation,[9,10] the Powell method,[11] and the Hicks−Young method[8] to correlate the experimentally determined critical properties of the three binary mixtures: ethylene + benzene, benzene + ethylbenzene, and ethylene + ethylbenzene. Using the binary mixture interaction parameters, the critical points of the ternary mixture (ethylene + benzene + ethylbenzene) are predicted. The agreement between experiment and calculation is generally satisfactory.

Experimental Section

Experimental Setup and Procedures. In this work a stirred sealed cell of 28 mm in height was used to precisely determine the critical properties of the ternary mixture under investigation.

A schematic diagram of the apparatus is shown in Figure 1. Critical point measurements were conducted using a high-pressure view cell. 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 content. 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. This cell could be operated at temperatures up to 623 K and pressures up to 13 MPa. Loading of the chemicals was achieved by using high-pressure liquid metering pumps (Ruska Instrument Corporation, U.S.A.) at an accuracy of 0.01 cm^3. 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 Qisheng Instrument Limited Company, China), and a solid-state relay (Shanghai Qisheng Instrument Limited Company, China).

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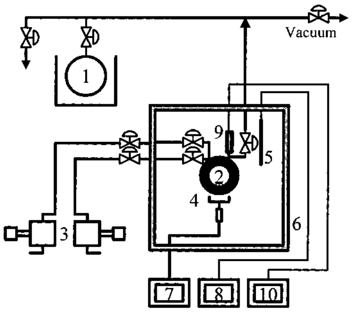

Figure 1. Schematic of the experimental setup: 1, liquid nitrogen degassing cell; 2, view cell; 3, high-pressure liquid pumps; 4, magnetic stirrer; 5, Pt resistance thermograph; 6, air thermostat; 7, stirring controller; 8, temperature controller; 9, pressure transducer; 10, digital multimeter.

A fan was installed in the air thermostat to ensure a uniform temperature. The cell's temperature was measured using a mercury thermometer at an accuracy of ±0.01 K, and the pressure was measured with a pressure transducer (NPI series, NOVA Corporation, U.S.A.) which could be operated at temperatures up to 623 K and was directly contacted with the fluids with an accuracy of ±0.02 MPa.[12]

The ternary mixtures were prepared by making a stock mixture of benzene and ethylbenzene which was diluted successively by ethylene. In this work the ethylbenzene to benzene mole ratio ranged from 1/11 to 1/6.4. This was the mole ratio range commonly found in the industrial alkylation process used for producing ethylbenzene.

The critical points for mixtures were based on visual observations. Ethylene and a mixture of benzene + ethylbenzene were loaded into separate pumps. Before loading, care was taken to degas the liquid mixture of benzene + ethylbenzene using freeze−pump−thaw cycles with liquid nitrogen as the coolant. Before being introduced into the cell, the temperatures of ethylene and the benzene + ethylbenzene mixture in separate pumps were maintained at 273 K and 308 K by two superthermostatic baths. Their pressures were maintained at 6.5 MPa and 0.5 MPa, respectively, to keep them in liquid form. The densities of both liquids at the specified temperature and pressure were obtained from literature values,[13,14] and from the volumes of the liquids introduced into the cell, their masses and the composition of the mixture were calculated.

In determining the critical condition of a binary mixture, a known volume of the component with a lower vapor pressure (benzene and/or ethylbenzene) was first introduced into the cell at 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 and the meniscus was observed. If the overall density was lower than the critical density, the meniscus would fall and eventually the liquid phase would disappear. 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 (less than ±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 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 the close vicinity of 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 single supercritical fluid phase. Then the temperature of the air thermostat was decreased about 30 K to cause the cell temperature to decrease slowly at a rate of less than 0.3 K·min^{-1}. 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, while the temperature was decreasing, the temperature and pressure readings could be made at the moment when complete darkness was observed[2] 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.

Table 1. Comparison of the Critical Constants from This Work with Those from the Literature[13]

	T_c/K		P_c/MPa		V_c/cm^3·mol^{-1}	
substance	this work	lit.	this work	lit.	this work	lit.
ethylene	282.75	282.343	5.06	5.040	133.57	130.99
benzene	563.65	562.160	5.01	4.898	263.01	258.65
ethylbenzene		617.146		3.609		374.49

Table 2. Critical Properties of Ethylene (1) + Benzene (2) + Ethylbenzene (3)

x_1	x_2	$T_{c,expt}$/K	$P_{c,expt}$/MPa	$\rho_{c,expt}$/g·cm^{-3}
0	0.864	572.3	5.02	0.300
0.101	0.819	561.4	5.67	0.313
0.300	0.626	533.7	7.97	0.325
0.500	0.447	486.9	10.63	0.338
0.673	0.298	442.3	11.92	0.345
0.892	0.099	347.5	9.72	0.290
1.000	0	282.8	5.07	0.210
0.907	0	350.3	11.26	0.334

The ethylene was obtained from the Shanghai Research Institute of Chemical Technology with a 99.9 mol % purity. The benzene and ethylbenzene from Shanghai Feida Chemicals were 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 ethylene and benzene. Our experimental results and literature values[13] shown in Table 1 were in excellent agreement with each other. The experimental critical properties of the ternary mixture (ethylene + benzene + ethylbenzene) are given in Table 2. Each experiment was repeated three times, and the average value was given. Usually the uncertainty of the critical temperature is no more than ±0.50 K and that of the critical pressure is less than ±0.07 MPa.

Calculation

Critical Conditions. The critical conditions for a ternary mixture[5,7] are

$$W\begin{vmatrix} -\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x_1,x_2} & -\left(\frac{\partial^2 A}{\partial V\,\partial x_1}\right)_{T,x_2} & -\left(\frac{\partial^2 A}{\partial V\,\partial x_2}\right)_{T,x_1} \\ \left(\frac{\partial^2 A}{\partial x_1\,\partial V}\right)_{T,x_2} & \left(\frac{\partial^2 A}{\partial {x_1}^2}\right)_{T,V,x_2} & \left(\frac{\partial^2 A}{\partial x_1\,\partial x_2}\right)_{T,V} \\ \left(\frac{\partial^2 A}{\partial x_2\,\partial V}\right)_{T,x_1} & \left(\frac{\partial^2 A}{\partial x_1\,\partial x_2}\right)_{T,V} & \left(\frac{\partial^2 A}{\partial {x_2}^2}\right)_{T,V,x_1} \end{vmatrix} = 0 \quad (1)$$

$$X\begin{vmatrix} \left(\frac{\partial W}{\partial V}\right)_T & \left(\frac{\partial W}{\partial x_1}\right)_T & \left(\frac{\partial W}{\partial x_2}\right)_T \\ \left(\frac{\partial^2 A}{\partial x_1\,\partial V}\right)_{T,x_2} & \left(\frac{\partial^2 A}{\partial {x_1}^2}\right)_{T,V,x_2} & \left(\frac{\partial^2 A}{\partial x_1\,\partial x_2}\right)_{T,V} \\ \left(\frac{\partial^2 A}{\partial x_2\,\partial V}\right)_{T,x_1} & \left(\frac{\partial^2 A}{\partial x_2\,\partial x_1}\right)_{T,V} & \left(\frac{\partial^2 A}{\partial {x_2}^2}\right)_{T,V,x_1} \end{vmatrix} = 0 \quad (2)$$

$$Y\begin{vmatrix} \left(\frac{\partial X}{\partial V}\right)_T & \left(\frac{\partial X}{\partial x_1}\right)_T & \left(\frac{\partial X}{\partial x_2}\right)_T \\ \left(\frac{\partial^2 A}{\partial x_1\,\partial V}\right)_{T,x_2} & \left(\frac{\partial^2 A}{\partial {x_1}^2}\right)_{T,V,x_2} & \left(\frac{\partial^2 A}{\partial x_1\,\partial x_2}\right)_{T,V} \\ \left(\frac{\partial^2 A}{\partial x_2\,\partial V}\right)_{T,x_1} & \left(\frac{\partial^2 A}{\partial x_2\,\partial x_1}\right)_{T,V} & \left(\frac{\partial^2 A}{\partial {x_2}^2}\right)_{T,V,x_1} \end{vmatrix} = 0 \quad (3)$$

where A and x denote the Helmholtz function and the composition, respectively. The condition $Y > 0$ is necessary for material stability. In addition, the following general tests for phase stability[5] are also applied:

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \quad (4)$$

$$\left(\frac{\partial^2 A}{\partial {x_1}^2}\right)_{T,V}\left(\frac{\partial^2 A}{\partial V^2}\right)_T - \left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_T > 0 \quad (5)$$

$$\left(\frac{\partial^2 A}{\partial {x_1}^2}\right)_{T,V} > 0 \quad (6)$$

CSPT EOS. When the Carnahan−Starling equation is combined as the repulsive term with the attractive term of the Patel−Teja equation, a new equation of state called the hard-sphere three-parameter equation of state is obtained,[9,10] which is abbreviated as CSPT EOS. The above derivatives are evaluated using this CSPT EOS. The basic equation can be expressed as follows:

$$P = \frac{RT}{V}\left[\frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}\right] - \frac{a}{V(V + b) + c(V - b)} \quad (7)$$

where

$$\eta = b/4V; \quad a = \Omega_{ac}\alpha(T_{r,w})\frac{(RT_c)^2}{P_c}; \quad b = \Omega_b\frac{RT_c}{P_c};$$

$$c = \Omega_c\frac{RT_c}{P_c}; \quad \Omega_{ac} = \gamma_c\zeta_c; \quad \Omega_b = 4\eta_c\zeta_c; \quad \Omega_c = 4\beta_c\zeta_c$$

Soave's correction factor for the temperature-dependence of the attractive parameter has been used:

$$\alpha(T_{r,w}) = [1 + F(1 - {T_r}^{0.5})]^2$$

F is the temperature-correction coefficient. ζ_c is the pseudocritical compressibility factor and is substance-dependent, and $\gamma_c = a_c/RT_cV_c$, $\beta_c = c/4V_c$, and $\eta_c = b/4V_c$ can be evaluated from ζ_c.[9]

Table 3. Parameters of the Pure Substances from the Literature[9]

substance	ζ_c	γ_c	β_c	η_c	F
ethylene	0.362	1.124 076	−0.086 831	0.080 415	0.610 849 9
benzene	0.357	1.155 813	−0.078 306	0.080 600	0.766 951 1
ethylbenzene	0.353	1.181 972	−0.071 340	0.080 763	0.869 090 4

For a mixture, a_m, b_m, and c_m can be calculated using the mixing rules

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

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

$$c_m = \sum_{i=1}^{n} x_i c_i$$

and k_{ij} is the binary interaction parameter between components i and j. The parameters for pure ethylene, benzene, and ethylbenzene used in the CSPT EOS are given in Table 1 (those from the literature[13]) and Table 3.

Correlation. The Powell method[11] is used to correlate the experimentally determined critical temperatures and pressures of the three binary mixtures ethylene + benzene,[12] benzene + ethylbenzene,[1] and ethylene + ethylbenzene (this work) to give the three binary interaction parameters k_{ij}. The form of the binary interaction parameters is expressed as

$$k_{ij} = \alpha_{ij} + \beta_{ij}t \quad (8)$$

The objective function is

$$\mathrm{OBJ} = (\mathrm{AADT} + \mathrm{AADP})/2 \quad (9)$$

where

$$\mathrm{AADT} = \left[\frac{1}{N}\sum_{j=1}^{N}\left|\frac{T_{c,expt} - T_{c,cal}}{T_{c,expt}}\right|_j\right] \quad (10)$$

$$\mathrm{AADP} = \left[\frac{1}{N}\sum_{j=1}^{N}\left|\frac{P_{c,expt} - P_{c,cal}}{P_{c,expt}}\right|_j\right] \quad (11)$$

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

Calculated Results

The experimental results of the three binary mixtures are correlated, and the results are shown in Table 4.

With the interaction parameters obtained from the three binary systems, the critical points of the ternary mixture have been predicted. The critical properties of the hypothetical binary mixture (ethylene and benzene + ethylbenzene) at some fixed mole ratio of ethylbenzene/benzene are calculated, and the results are shown in Figures 2 and 3. The deviations between the experimental data and the calculated results are shown in Figures 4 and 5. The

Table 4. Correlation Results of the Three Binary Mixtures via the CSPT EOS

binary mixture	no. of datum points	k_{ij}		AADT	AADP
		α_{ij}	β_{ij}		
ethylene + benzene	11	−0.081 580	−0.000 03	0.7%	2%
benzene + ethylbenzene	11	−0.008 823	0.0	0.02%	0.4%
ethylene + ethylbenzene	3	−0.020 702	0.0	0.7%	3.8%

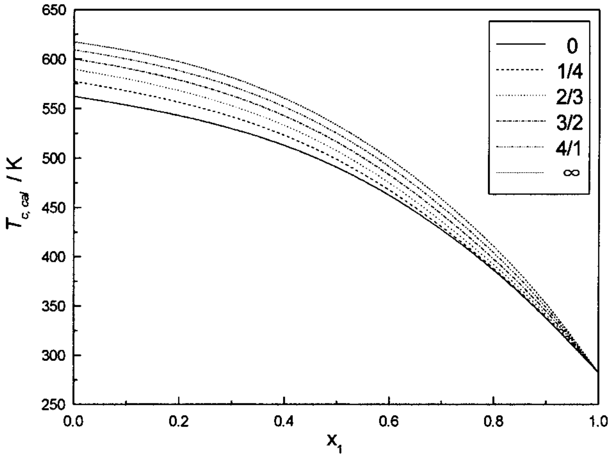

Figure 2. Calculated critical temperature ($T_{c,cal}$) with mole fraction (x_1) for the ethylene (1) + benzene (2) + ethylbenzene (3) system at x_3/x_2 = (0, 1/4, 2/3, 3/2, 4/1, and ∞).

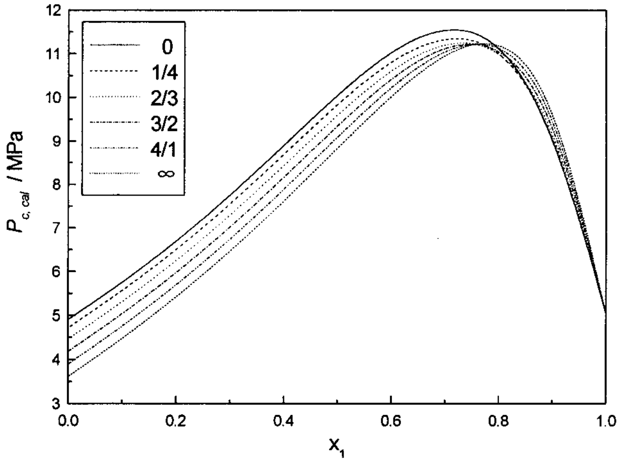

Figure 3. Calculated critical pressure ($P_{c,cal}$) with mole fraction (x_1) for the ethylene (1) + benzene (2) + ethylbenzene (3) system at x_3/x_2 = (0, 1/4, 2/3, 3/2, 4/1, and ∞).

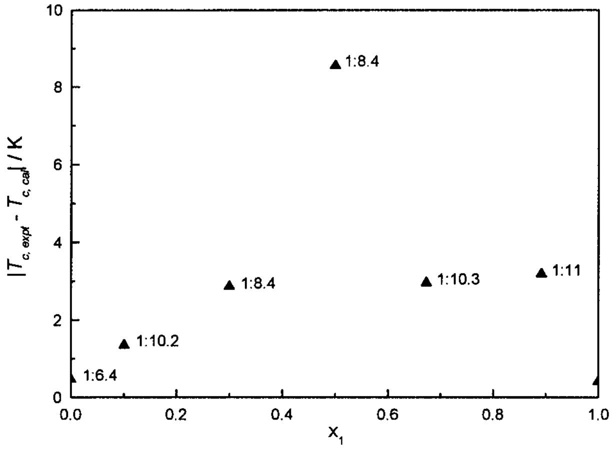

Figure 4. Critical temperature deviation between experimental values and calculation results ($|T_{c,expt} - T_{c,cal}|$) with mole fraction (x_1) for the ethylene (1) + benzene (2) + ethylbenzene (3) system at x_3/x_2 = (1:6.4, 1:10.2, 1:8.4, 1:8.4, 1:10.3, and 1:11).

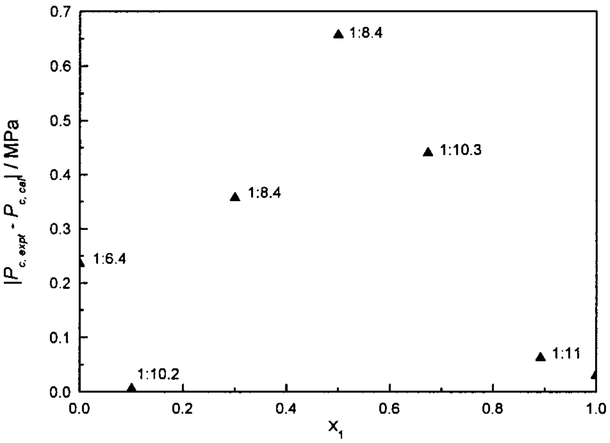

Figure 5. Critical pressure deviation between experimental values and calculation results ($|P_{c,expt} - P_{c,cal}|$) with mole fraction (x_1) for the ethylene (1) + benzene (2) + ethylbenzene (3) system at x_3/x_2 = (1:6.4, 1:10.2, 1:8.4, 1:8.4, 1:10.3, and 1:11).

average absolute deviations are

$$\mathrm{AADT} = 0.7\%; \quad \mathrm{AADP} = 2.7\%$$

Discussion

In this work, the CSPT equation of state is used to calculate the critical temperatures and pressures of the (ethylene + benzene + ethylbenzene) system. Figures 2 and 3 show that the calculated critical temperatures and pressures of this ternary mixture vary continuously over the whole composition range between the critical point of ethylene and the critical point of a benzene + ethylbenzene mixture of fixed composition. Each hypothetical binary mixture (ethylene and benzene + ethylbenzene) at a fixed mole ratio of ethylbenzene/benzene has a similar critical curve. Type I fluid phase behavior is displayed by both the ethylene + benzene + ethylbenzene mixture and the ethylene + benzene mixture.[12] The critical temperature of ethylbenzene is higher than that of benzene, but the critical pressure shows a different behavior, so the critical temperature of the hypothetical binary mixture should be higher than that of the ethylene + benzene mixture at the same ethylene composition, while the critical pressure is lower.

For this ternary mixture, Figures 4 and 5 show that the deviations were lower when x_1 was lower or higher. While $x_1 \approx x_2 + x_3$, the deviations show higher values. The average deviation of critical temperature between our experiments and calculation is 3.0 K, and that of pressure is 0.26 MPa. The average absolute deviation of temperature (AADT) is lower by 1%, and that of pressure (AADP) is lower by 3%. The agreement between our experiment and calculation is satisfactory.

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