

rather constant $\alpha = 8.29$, in the midrange of Smith's values.

Glossary

AN	acrylonitrile
m, n	slope and intercept, respectively, in the Othmer-Tobias plot, eq 3
R^2	correlation coefficient in linear regressions
ST	styrene
x	mass fraction of the component in solvent-rich phase in equilibrium with y , kg/kg of organic phase
y	as above, in the water-rich phase, kg/kg of aqueous phase
α	distribution coefficient of AN defined by eq 4

Subscripts

A	acrylonitrile
S	styrene

W water

Registry No. ST, 100-42-5; AN, 107-13-1.

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Vapor-Liquid Critical Curve of the System Ethane + 2-Methylpropane

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The vapor-liquid critical curve of the binary system ethane + 2-methylpropane was determined from the critical temperature of ethane up to the critical temperature of 2-methylpropane. The results are compared with vapor-liquid equilibrium data reported earlier on this system and with the critical curve that is predicted for this system from the Peng-Robinson equation of state.

Introduction

Vapor-liquid equilibria in the binary system ethane + 2-methylpropane are of interest to the petroleum and natural gas processing industry since both components are present in the multicomponent systems that are handled by these industries. Experimental data at temperatures below the critical temperatures of ethane are reported by Skripa et al. (1). Besserer and Robinson (2) reported four isotherms in the temperature region 310-395 K, at temperatures above the critical temperature of ethane. These authors have used the analytical method for the measurements of the vapor-liquid equilibria in this system and therefore they were not able to measure critical points. In this paper experimentally determined critical points are presented and the Peng-Robinson equation of state (3) is used to describe the critical curve.

Experimental Section

The measurements were carried out in an apparatus for use with pressures up to 20 MPa and temperature up to 473 K described earlier by de Loos et al. (4). With this so-called Cailletet apparatus, which is shown in Figure 1, dew points and bubble points of mixtures of known composition can be determined visually. The sample of the mixture M is confined over

mercury in the sealed end of a thick-walled, capillary Pyrex glass tube C, 4 × 12 mm and 50 cm long. At about $2/3$ of its length this tube has a conical thickening which fits in the closing plug P of the stainless-steel autoclave A. Glass to metal and metal to metal sealing is achieved by using Viton O-rings R. The autoclave is filled with mercury up to the line to the pressure generating system. The open end of the tube is immersed in the mercury; thus the mercury in the tube and of the autoclave serves as a pressure intermediate between the sample and the hydraulic oil. The sample can be agitated by a small stirrer which consists of a soft-iron rod, sealed in with glass, with a slightly smaller diameter than the bore of the glass capillary tube. This stirrer is activated by two button magnets B which move up and down.

The glass capillary tube is kept at the desired temperature by a thermostat with circulating oil. The temperature was measured to an accuracy within ± 0.01 K by using a platinum resistance thermometer; it was maintained constant to better than ± 0.02 K. The pressure is generated hydraulically with screw pump H and is measured with a dead-weight pressure gauge to accuracy within 0.001 MPa.

During an experiment the mixture is first brought to the temperature and pressure conditions corresponding to the two-phase fluid region. Then the pressure is changed slowly until one of the phases just disappears. By observing the descent or ascent of the meniscus at constant temperature as function of pressure it can be ascertained whether the observed phase behavior is characteristic of a dew point or of a bubble point. The same procedure is followed at other temperatures. The critical point can be located in that temperature interval in which the observed phase behavior changes from bubble-point to dew-point behavior. For a given composition the accuracy in the measured critical temperature is 0.1 K and in the critical pressure 0.02 MPa. The mixture can be prepared with an accuracy in the mole fraction of 0.002.

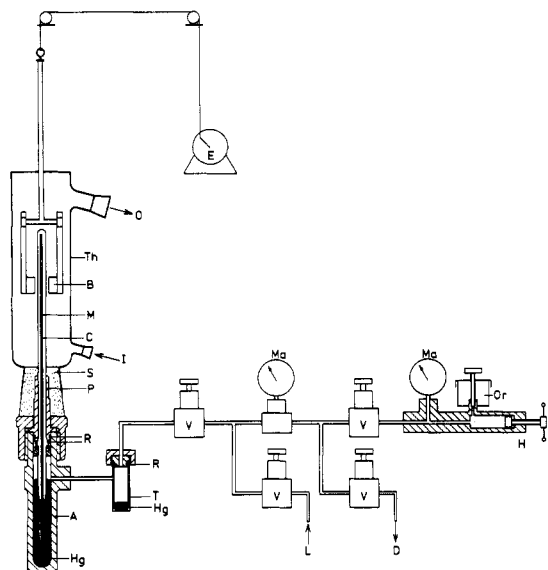


Figure 1. The Calletet equipment; A, autoclave; B, button magnets; C, capillary glass tube; D, drain; H, rotating hand pump; Hg, mercury; I, thermostatic liquid in; L, line to dead weight pressure gauge; M, mixture being investigated; Ma, manometers; O, thermostatic liquid out; Or, hydraulic oil reservoir; P, closing plug; R, Viton O-rings; S, silicone rubber stopper; T, mercury trap; Th, glass thermostat; V, valve.

The mole fraction purity of the ethane used was greater than 0.9996, that of the 2-methylpropane greater than 0.9996. Both gases were research grade gases supplied by Matheson Gas Products.

Results

The experimentally determined critical pressure and critical temperature of mixtures of known composition are given in Table I. The p, T and T, x projections of the critical curve are

Table I. Vapor-Liquid Equilibria for (1 - x)2-Methylpropane + x Ethane: Values of Critical Temperature T_c , Critical Pressure p_c , and Critical Mole Fraction x_c .

x_c	T_c/K	P_c/MPa	x_c	T_c/K	P_c/MPa
0.960	311.2	5.04	0.571	362.6	5.28
0.913	319.6	5.21	0.506	369.1	5.18
0.854	328.2	5.36	0.447	374.2	5.02
0.819	333.1	5.40	0.408	378.4	4.93
0.768	339.8	5.44	0.309	387.2	4.61
0.747	342.7	5.45	0.252	391.3	4.47
0.701	348.3	5.45	0.207	394.0	4.33
0.649	353.9	5.41	0.149	398.4	4.12
0.609	359.8	5.34	0.094	401.7	4.01

shown in Figure 2. From this figure it can be seen that the critical temperature varies almost linearly with the critical mole fraction. In the p, T projection the critical curve exhibits a pressure maximum.

Discussion

In Figure 3 the experimental vapor-liquid equilibrium data of Besserer and Robinson are plotted at three constant temperatures together with the critical points at these temperatures found by interpolation from Figure 2. This figure shows that the two sets of data match reasonably. The critical curve of binary systems can be predicted by using a suitable equation of state (5, 6). In this study the well-known Peng-Robinson equation of state is used (3). According to Beegle et al. (7) and Reid and Beegle (8) the two general critical point criteria of Gibbs (9) for a binary system can be written in terms of the derivatives of the molar Helmholtz free energy $A = A(T, v, x)$ with respect to the molar volume v and the mole fraction x of the second component:

$$A_{vv}A_{xx} - A_{vx}^2 = 0 \quad (1)$$

$$A_{vv}A_{xx}A_{vxx} + A_{vv}^2A_{xxx} - 3A_{vv}A_{vx}A_{vxx} - 3A_{xx}A_{vx}A_{vv} + 2A_{vx}^2A_{vxx} = 0 \quad (2)$$

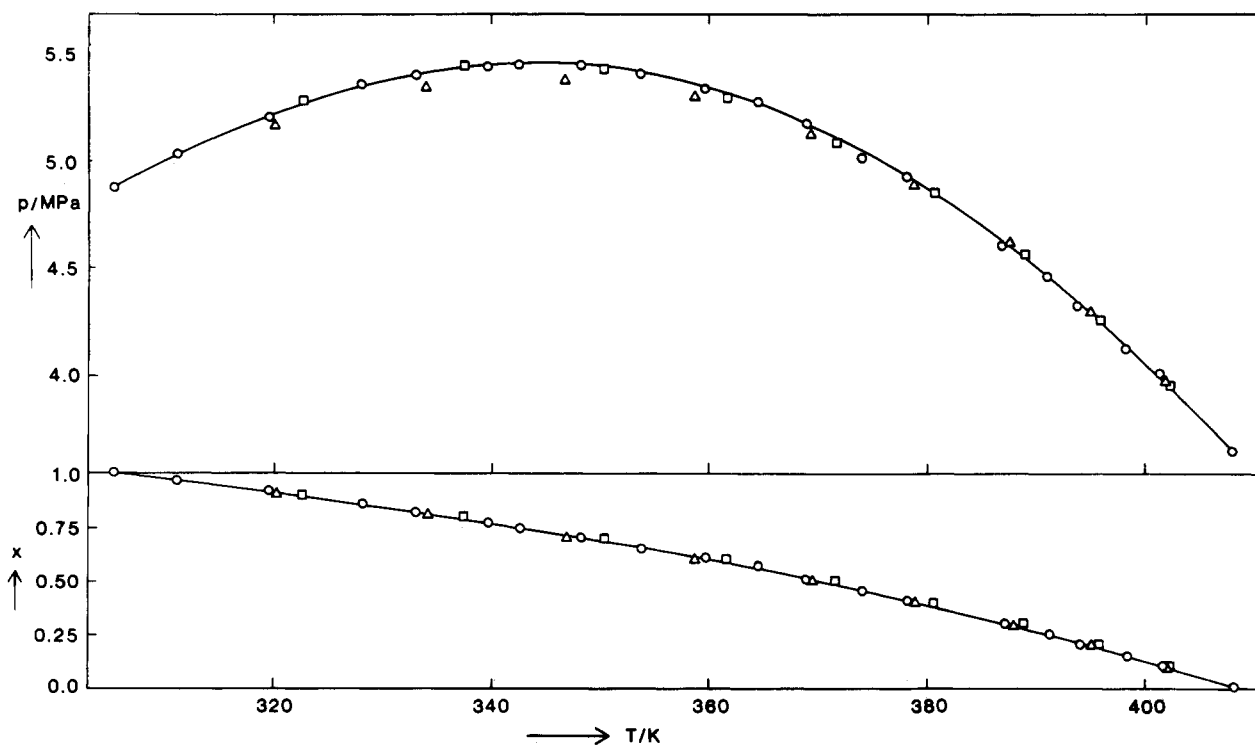


Figure 2. Vapor-liquid critical curve in the system (1 - x)2-methylpropane + x ethane, p, T and T, x projections: O, experiments; □, calculated by using the Peng-Robinson equation (3) with $\delta_{ij} = 0$; Δ, calculated by using the Peng-Robinson equation (3) with $\delta_{ij} = 0.031$.

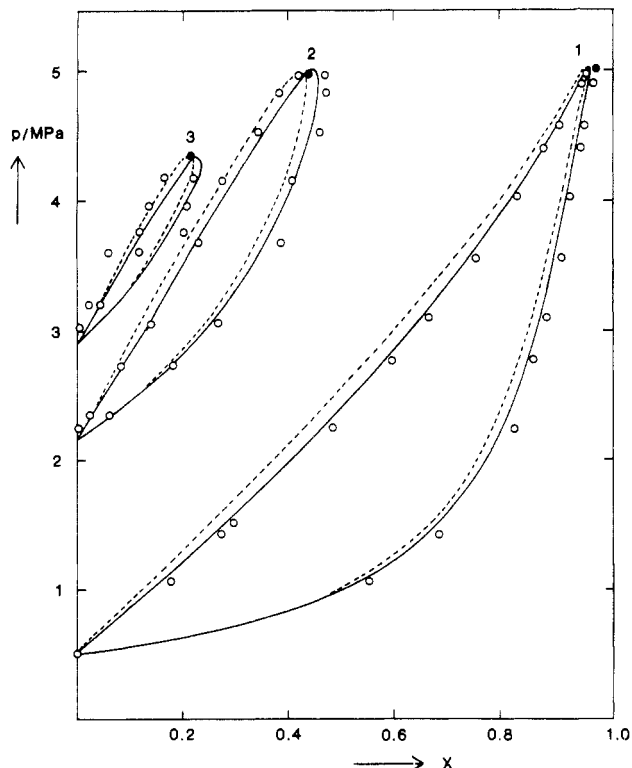


Figure 3. Vapor-liquid equilibria in the system (1-x)2-methylpropane + x ethane, isothermal p, x diagrams: O, experiments (2), ●, experimental critical points (this work); —, calculated by using Peng-Robinson equation (3) with $\delta_{ij} = 0$; ----, calculated by using Peng-Robinson equation (3) with $\delta_{ij} = 0.031$. 1, 311.26 K, 2, 377.43 K, 3, 394.04 K.

For the Peng-Robinson equation of state the derivatives in eq 1 and 2 are given by Hong et al. (10). Evaluation of eq 1 and 2 leads to a set of two equations in three variables T , x , and v . From these equations v and x can be calculated numerically at a given T . The critical pressure can now be calculated from the equation of state.

In Figure 2 the experimental critical curve is compared with the calculated critical points for two values of the binary interaction coefficient δ_{ij} (3). For $\delta_{ij} = 0$ one gets an excellent prediction of the p, T projection of the critical curve, but the critical temperature predicted for a given composition can deviate 3.5 K from the experimental critical temperature. For $\delta_{ij} = 0.031$, a value calculated from the experimental critical temperature at $x = 0.5$, the prediction of the T, x projection of the critical curve is very good, but the predicted critical pressures can be 0.1 MPa too low.

Figure 3 shows experimental isothermal phase envelopes at 311.26, 377.43, and 394.04 K and isothermal phase envelopes calculated at these temperatures by using the Peng-Robinson equation with $\delta_{ij} = 0$ and $\delta_{ij} = 0.031$. A value of $\delta_{ij} = 0$ results in a somewhat better overall prediction of the phase envelopes, particularly at lower temperatures.

Registry No. Ethane, 74-84-0; 2-methylpropane, 75-28-5.

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Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for CO₂ + Hydrocarbon Systems. 2. CO₂ + *n*-Decane

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Experimental vapor-liquid equilibrium phase compositions, phase densities, and interfacial tensions are presented for CO₂ + *n*-decane at 160 and 220 °F at pressures to the critical point (interfacial tensions as low as 0.008 mN/m). The phase compositions are in excellent agreement with the data of Reamer and Sage; however, the phase densities exhibit significant differences, with the present data yielding a substantially higher critical-point density. The interfacial tensions represent data not previously available in the literature.

Introduction

The motivation for the work presented here is the need for fundamental data on interfacial tensions (IFT) in CO₂-hydro-

carbon systems to serve as the basis for better understanding of the effects of temperature, pressure, and composition on the IFT in such systems. These data could also lead to improved understanding of the process of miscible (or near-miscible, low-IFT) displacement of reservoir oils by CO₂ injection.

The data on CO₂ + *n*-decane presented here is the second in a planned series of studies on CO₂ + hydrocarbon systems which will include measurements on CO₂ with pure and mixed hydrocarbons and on CO₂ with reservoir oils. The first part of this series (1) presented data on CO₂ + *n*-butane.

Experimental Method

The apparatus and procedures for the measurements have been described in detail previously (1). The only change in procedures employed in the present study involved density