Critical Properties for Binary Mixtures of Ethane Containing Low Concentrations of *n*-Alkane

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The critical temperature and pressure for binary mixtures of ethane containing *n*-alkanes (C_5 to C_{10}) at low concentrations (up to 5.2 mol %) have been determined. A visual technique was used where the observation of mixture critical opalescence followed by the appearance of a vapor−liquid meniscus in a constant volume sight gauge was observed. The absolute errors in the measurements of the mixture critical temperature and pressure were ±2 K and ±0.5 bar, respectively, with an estimated relative error of ±1.5% for the composition of the organic compounds used. The binary mixture critical temperature and pressure were estimated using a correlation based on the theory of conformal solutions and a dilute-mixture Soave−Redlich−Kwong (SRK) equation of state approach. Both methods correlated the critical mixture temperature to an absolute error of within 3 K. However, the mixture critical pressure was correlated to an absolute error of within 10 and 4 bar using the conformal solutions correlation and a dilute-mixture SRK equation of state, respectively.

Introduction

Critical properties are important design and characterization parameters for pure substances and mixtures. These properties provide the boundary conditions for the supercritical region in which supercritical fluid (SCF) extraction can be performed.

The determination of the critical temperature (T_c) and pressure (P_c) of binary mixtures at low cosolvent concentrations is particularly relevant in SCF extraction due to the increased use of small amounts of simple organic compounds for use as cosolvents (or modifiers) to increase solubility and/or selectivity of solutes. Polar and nonpolar compounds at concentrations below 15 mol % have been used successfully as cosolvents (Schmitt and Reid, 1986; Dobbs et al., 1986, 1987; Smith and Wormald, 1990). The addition of cosolvent changes the physical and chemical properties of the primary solvent, thereby affecting solute−solvent interactions and solubility. It is important to choose the right cosolvent because the mixture T_c, P_c, and phase behavior can be different from those of the primary solvent, affecting the operating conditions.

Most of the binary mixture critical locus work reported has focused on the entire range of mixture composition (Kay, 1964; Mehra and Thodos, 1965; Pak and Kay, 1972; Reamer and Sage, 1962). A compilation of the critical properties of various binary mixtures and the use of visually observed opalescence for the determination of critical properties are described elsewhere (Hicks and Young, 1975; Pak and Kay, 1972; Li and Kiran, 1988; Garcia-Sanchez and Trejo, 1979; Gurdial et al., 1991). Experimental data for binary mixtures of CO_2 containing *n*-alkanes, *n*-alcohols and acetone demonstrate that, even at low cosolvent concentrations (<7 mol %), the mixture critical properties can differ significantly from those of the primary SCF. For example, the addition of 4.9 mol % hexane to CO_2 increased the mixture T_c by 4% and P_c by 15% (Gurdial et al., 1991). Recently, critical properties for $CO_2 + n$-alkane mixtures using a variable-volume view cell have also been determined (Choi and Yeo, 1998).

Ethane has similar critical properties to CO_2 and has been shown to be a powerful solvent for the extraction of hydrocarbons (Singh et al., 1993). Most work on the determination of binary critical properties has concentrated on the use of CO_2 as the primary solvent. In this work, we present new experimental data on the critical properties of binary mixtures of ethane containing *n*-alkanes such as pentane, hexane, heptane, octane, nonane, and decane at low concentrations (up to 5.2 mol %). In addition, these data were estimated using a correlation based on the theory of conformal solutions and a dilute-mixture Soave−Redlich−Kwong (SRK) equation of state approach.

Data Correlation

Critical properties have been estimated by various empirical and semiempirical methods and group contribution methods. Two estimation methods used in this study are described below.

Conformal Solution Theory. Kreglewski and Kay (1969) have derived expressions for T_c and P_c based on the theory of conformal solutions, which uses the corresponding states principle and conforms to certain simple postulates of statistical mechanics. The mixture T_c and P_c can be estimated from pure component data without the use of any binary interaction parameter. The expression has been satisfactorily tested for mixtures containing molecules that differ in both size and shape over a wide range. The liquid molar volume required in the expression can be found using the modified Rackett method (Reid et al., 1987).

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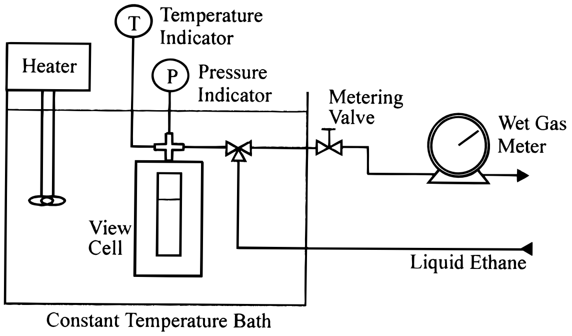

Figure 1. Apparatus used for determination of binary mixture T_c and P_c.

EOS Approach. Critical properties can also be correlated using a rigorous solution of the molar Gibbs free energy criteria and an appropriate equation of state (EOS). For mixtures, the determination of critical properties also involves the use of appropriate mixing rules. Gualtieri et al. (1982) have greatly reduced the complexity of the resulting equations by employing a dilute-mixture thermodynamic framework. In their work, the van der Waals EOS (vdW EOS) was used to derive analytical expressions for the critical properties of dilute mixtures. However, the agreement between theory and experiment is only qualitative (Morrison and Kincaid, 1984). More recently, the vdW EOS has been used successfully with the thermodynamically consistent Wong−Sandler mixing rules, for the determination of critical properties (Castier and Sandler, 1997a, 1997b).

In this study, a similar procedure was adopted based on the Soave−Redlich−Kwong (SRK) EOS. Anselme and Teja (1990) have derived expressions for the T_c and V_c (critical volume) of dilute multicomponent mixtures using a dilute-mixture SRK EOS (DM SRK EOS). After calculating values for T_c and V_c using these expressions, the mixture P_c was then determined using the SRK EOS.

Experimental Section

Materials. Ethane was supplied by Matheson with a purity of 99.5%. The cosolvents were supplied by BDH with a purity of 99.5%, except for octane and nonane, which were supplied with a purity of 99.0%. All of the solvents were used without further purification.

Equipment. A schematic diagram of the experimental apparatus is shown in Figure 1. It consists of a high-pressure sight gauge (Jerguson model 13-R-32) which contained the binary mixture and some glass beads to improve mixing when the sight gauge was rocked. The sight gauge with an internal volume of about 55 mL had a clear borosilicate glass window for visual observation of the phases present. A type K thermocouple was fitted into the sight gauge, which enabled the mixture temperature to be monitored to within ±0.2 K using a Jenco temperature indicator (model 7000CH). The system pressure was monitored with a Druck pressure transducer (model PDCR 911) and a Druck pressure indicator (model DPI 260).

Liquid ethane was introduced into the Jerguson via a three-way Whitey valve. A Sno-Trik shut-off valve was used to isolate the system. The volume of liquid ethane used was measured by venting the gas (at room temperature) through a wet gas meter (model DM 3A, Alexander Wright and Co.) after the critical conditions were determined. The temperature of the water bath was maintained with a Thermoline Unistat heater/circulator to ±0.2 K.

Table 1. Comparison of Experimental and Literature Data

system	lit.		this work	
	T_c/K	P_c/bar	T_c/K	P_c/bar
ethane[a]	305.3	48.7	305.6	49.0
ethane + 0.5 mol % decane[b]	310.9	53.6		
ethane + 0.42 mol % decane			309.4	53.1

[a] Data from Ambrose and Tsonopoulos (1995). [b] Data from Reamer and Sage (1962).

Procedure. The mixture T_c and P_c were obtained by first introducing a known volume of cosolvent (typically between 0.5 and 3.25 mL) into the sight gauge using a syringe. Liquid ethane was then added to a depth of $^2/_3$ of the viewing length of the sight gauge. This liquid level was found to correspond to a volume which was close to the critical density of the mixture. The sight gauge was then shaken by inverting it several times to ensure mixing and the formation of a single phase (Type I), after which it was immersed into the water bath. The temperature of the water bath was gradually increased to about two degrees above the temperature at which opalescence or cloudiness appeared. As the temperature was raised, the liquid−gas interface disappeared upon heating. The water bath was then cooled at a rate of about 0.1 K/min by switching off the temperature controller.

As the mixture was cooled, opalescence (milky-white color) was observed at the critical conditions as the gas−liquid interface reappeared. The pressure and temperature readings were recorded at the first appearance of the meniscus upon cooling. The procedure was repeated until the differences between the observed critical conditions were <0.2 K and <1 bar for temperature and pressure, respectively. During both the heating and cooling processes, the sight gauge was frequently shaken to maintain mixture homogeneity and to prevent the formation of metastable phases or density gradients. For all of the binary systems investigated the reproducibilities of the T_c, P_c, and composition measurements were estimated to be ±0.2 K, ±0.5 bar, and ±1.5% (relative), respectively.

It was important to add the correct amount of liquid ethane into the sight gauge. An insufficient quantity of ethane lead to an overall density which was less than the critical density. This resulted in a gradual lowering of the meniscus level as the critical point was approached. Under these conditions all of the liquid evaporated, thus preventing the observation of the disappearance of the vapor−liquid interface at the critical point. An excess amount of ethane had the opposite effect, causing the meniscus to rise until all of the vapor had condensed. In both instances, the most important criterion for the determination of the critical point when using a visual technique, that is the occurrence of opalescence or cloudiness of the mixture, was not met.

Comparison with Literature Data. The accuracy of the experimental technique was validated by comparing the experimentally determined critical point for pure ethane and an ethane + decane binary mixture with literature values, as shown in Table 1. The results show reasonable agreement with published data. The impurities present in the ethane used in this study consist mainly of low molecular weight compounds such as methane and ethylene which did not significantly affect the critical properties of ethane.

Results and Discussion

In this study filling $^2/_3$ of the viewing length of the Jerguson with liquid ethane provided an overall density

Table 2. Experimental T_c-P_c-x for Binary Mixtures of Ethane + *n*-Alkanes

ethane + pentane			ethane + hexane			ethane + heptane		
mol % pentane	T_c/K	P_c/bar	mol % hexane	T_c/K	P_c/bar	mol % heptane	T_c/K	P_c/bar
0.48	306.6	49.9	0.65	308.1	51.2	0.87	310.4	52.8
1.09	308.8	51.1	1.31	311.3	53.3	1.51	315.0	56.4
2.10	312.4	53.0	1.96	314.1	54.9	2.02	318.0	57.9
2.85	314.7	54.3	2.62	317.5	57.0	2.87	322.4	61.3
3.45	316.5	55.0	3.27	320.5	58.7	3.50	325.8	64.8
4.05	318.6	56.2	3.99	324.0	60.3			
4.25	319.0	56.9						
5.22	324.5	58.5						

ethane + octane			ethane + nonane			ethane + decane		
mol % octane	T_c/K	P_c/bar	mol % nonane	T_c/K	P_c/bar	mol % decane	T_c/K	P_c/bar
0.41	308.4	51.5	0.72	312.0	54.7	0.42	309.4	53.1
0.79	311.3	54.1	1.02	314.7	57.1	0.87	314.8	57.3
1.24	314.8	56.4	1.43	319.1	59.8	1.26	318.1	59.8
1.60	318.3	58.6	1.53	321.6	62.3	1.61	321.5	62.8
1.82	319.1	59.8	1.72	322.9	63.1	1.85	324.8	65.6
2.10	322.0	61.6	2.16	327.1	65.7			
2.52	326.3	64.2						

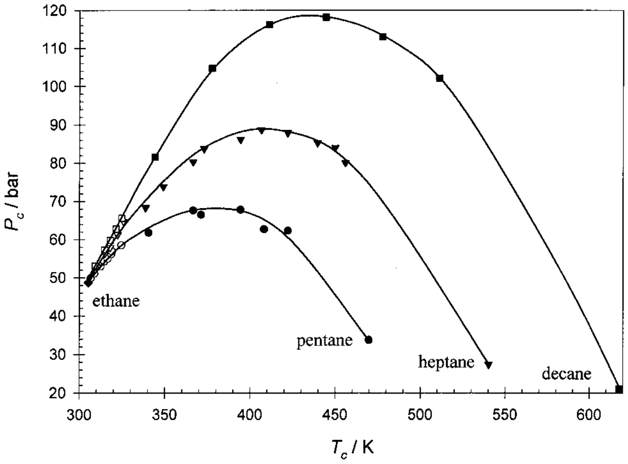

Figure 2. Critical loci of ethane + *n*-alkane binary mixtures: (○) pentane (this work); (●) pentane (Ekiner and Thodos, 1966; Reamer et al., 1960); (▽) heptane (this work); (▼) heptane (Mehra and Thodos, 1965; Ekiner and Thodos, 1965); (□) decane (this work); (■) decane (Reamer and Sage, 1962); (◆) pure ethane.

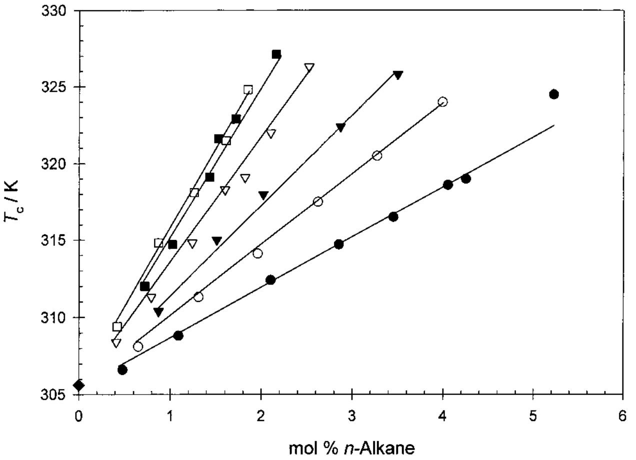

Figure 3. Plots of T_c versus x for ethane + *n*-alkane binary mixtures: (●) pentane; (○) hexane; (▼) heptane; (▽) octane; (■) nonane; (□) decane; (◆) pure ethane (this work).

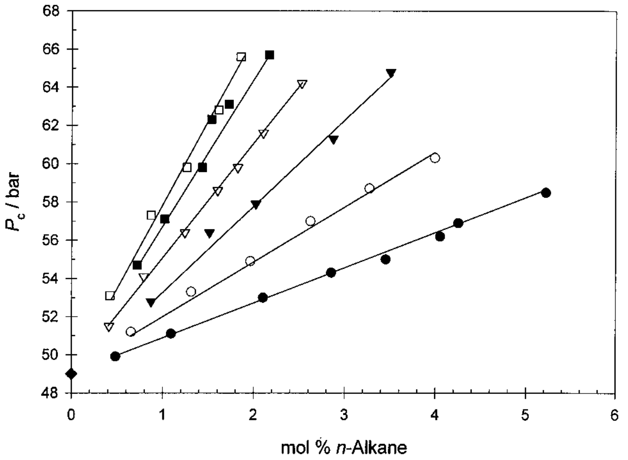

Figure 4. Plots of P_c versus x for ethane + *n*-alkane binary mixtures: (●) pentane; (○) hexane; (▼) heptane; (▽) octane; (■) nonane; (□) decane; (◆) pure ethane (this work).

close to the critical density and also resulted in the meniscus reappearing near the center of the view cell on cooling. The opalescence or cloudiness is a density phenomenon. As a result of the large scale density fluctuations near the critical point, the fluid becomes a suspension, where particles from one phase are present in the other phase. Light scattering occurs when these particles are of the size of the wavelength of light, resulting in the cloudiness which is referred to as critical opalescence.

The experimental T_c and P_c results obtained for the ethane + *n*-alkane binary mixtures studied are shown in Table 2. A comparison of the experimental data for the ethane + pentane, ethane + heptane, and ethane + decane systems with published data which covers the whole composition range is shown in Figure 2. The plots in Figure 2 are continuous between the critical points of ethane and the respective *n*-alkanes. It can be seen that the low-concentration data obtained in this study are consistent with the critical loci covering the whole composition range. Furthermore, an almost linear relationship exists between T_c and P_c. The lower carbon number *n*-alkanes have a smaller slope compared to that of the larger *n*-alkanes, and this is consistent with published data for components belonging to the same homologous series (Kay, 1968).

The T_c-x and P_c-x relationships for the ethane-*n*-alkane binary mixtures are shown in Figures 3 and 4, respectively. These plots indicate that the addition of small amounts of *n*-alkanes can significantly change the critical conditions of a binary mixture with ethane. Both the plots exhibit an almost linear relationship because the *n*-alkane concentrations are low. The addition of *n*-alkanes to ethane resulted in a larger overall percent change for the mixture P_c compared with the mixture T_c. For example, with the addition of 2.16 mol % nonane, the binary mixture T_c and P_c increase by about 7% and 35%, respectively, compared to the values for pure ethane.

The increase in the critical conditions is greater with the addition of larger *n*-alkanes. For example, the addition of about 2.1 mol % pentane increases the mixture T_c and P_c by about 2% and 9%, respectively. However, a similar addition of octane increases the mixture T_c and P_c by about 6% and 26%, respectively. As the relative size of the components in a homologous series increases, the critical conditions also increase.

This study indicates that the addition of small amounts (up to 5.2 mol %) of C_5 to C_{10} *n*-alkanes as cosolvents to ethane can significantly change the conditions necessary for extraction at supercritical conditions. This suggests that small amounts of impurities (e.g., water, dissolved air, organic compounds) present in a supercritical solvent can

Table 3. Dilute Mixture SRK EOS k_{ij}

cosolvent	optimized k_{ij}[a]	lit. k_{ij}[b]
pentane	0.057	0.100
hexane	0.077	0.034
heptane	0.099	0.078
octane	0.103	0.017[c]
nonane	0.109	−0.044
decane	0.148	0.025

[a] Optimized from experimental data for T_c from this work. [b] Obtained from Galicia-Luna and Perez (1987). [c] Obtained from ASPEN Plus R. 9.3.

Table 4. AARD (%) Using Conformal Solutions and the Dilute Mixture SRK EOS

	AARD (%)			
	conformal solutions		DM SRK EOS[a]	
n-alkane	T_c	P_c	T_c	P_c
pentane	0.27	5.4	0.12	0.632
hexane	0.28	6.8	0.05	1.4
heptane	0.41	9.3	0.11	1.7
octane	0.60	8.9	0.13	3.5
nonane	0.94	10.3	0.17	5.0
decane	0.47	10.1	0.11	3.2

[a] T_c and P_c values obtained using optimized k_{ij}.

affect critical conditions and should be minimized.

Data Correlation. Since only low concentrations of n-alkanes were used, the mixture T_c and P_c were first estimated using a naive estimation method: the pseudocritical temperature (Kay's rule) and pressure method. The T_c was estimated to an AARD of within 3.5%, and the P_c, to within 20%. Larger deviations were generally obtained for the higher n-alkanes. To improve the estimation of T_c and P_c, the data obtained from this study were then correlated using a conformal solutions correlation and the dilute mixture SRK EOS. The former method requires no adjustable parameters whereas the latter method requires the knowledge of binary pair interaction parameters k_{ij} for each n-alkane studied, which compensates for the inadequacies of the combining and mixing rules. The k_{ij} can be obtained from the literature or by fitting the SRK EOS to experimental mixture data by using the van der Waals one-fluid mixing rules. The data were optimized by minimizing the average absolute relative deviation (AARD) for each binary mixture:

$$\text{AARD} = \frac{1}{N}\sum\frac{|y_{\text{corr}} - y_{\text{exp}}|}{y_{\text{exp}}} \tag{1}$$

where y_{corr} and y_{exp} are the correlated and experimental critical values, respectively, and N is the number of data points.

The optimized and literature k_{ij} values obtained for the ethane + n-alkane mixtures are given in Table 3. As a comparison, literature k_{ij} values obtained by Galicia-Luna and Perez (1987) by fitting various critical loci data using the discreet SRK EOS are also shown in this table.

The AARDs obtained using the conformal solutions correlation and dilute mixture SRK EOS methods are shown in Table 4. It can be seen that both methods are able to satisfactorily estimate the T_c to within 1% AARD. The conformal solution correlation is preferred because no knowledge of interaction parameters is required. However, for the estimation of P_c, this approach yields large errors (up to 10% AARD). Large errors were also obtained for systems containing methane (Reid et al., 1987). The conformal solutions correlation generally underestimated all the T_c and P_c data. The dilute mixture SRK EOS reasonably correlated the P_c (up to 5% AARD). Larger errors for P_c were particularly observed for the ethane + octane and ethane + nonane binary mixtures. This is attributed to the lower purity of the cosolvents used in these systems. Figures 5 and 6 show the plots for T_c−x and P_c−x for the experimental and regressed values (using the SRK EOS with k_{ij} optimized for temperature) for the octane and nonane systems. A large deviation is observed as the n-alkane concentration increases. The k_{ij} values used may not truly reflect the interaction of the unlike pair in the system. When literature k_{ij} values were used in the dilute mixture SRK EOS for the determination of mixture T_c and P_c, an AARD of up to 4% was obtained for the determination of T_c. However, a less satisfactory AARD was obtained for the determination of P_c (above 20%), especially for the ethane + octane and nonane binary mixtures.

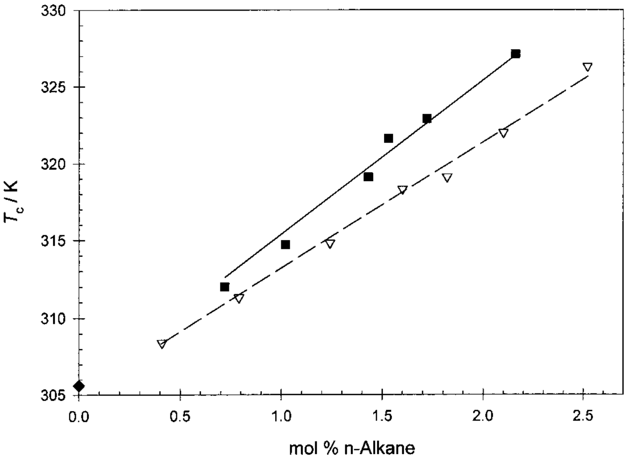

Figure 5. Comparison of experimental and SRK EOS correlated binary mixture T_c−x plots for ethane + octane [(▽) exptl; (- - -) correlated] and ethane + nonane [(■) exptl; (—) correlated; (◆) pure ethane (this work)].

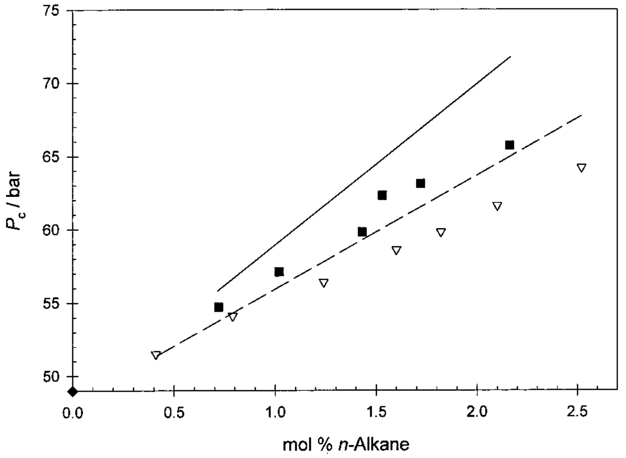

Figure 6. Comparison of experimental and SRK EOS correlated binary mixture P_c−x plots for ethane + octane [(▽) exptl; (- - -) correlated] and ethane + nonane [(■) exptl; (—) correlated; (◆) pure ethane (this work)].

Conclusion

The addition of small amounts of organic cosolvents was shown to substantially increase the ethane + n-alkane binary mixture T_c and P_c (by up to 6% and 26%, respectively, with the addition of 2.1 mol % octane). As the relative size of n-alkanes in a homologous series increased (at constant composition), the T_c and P_c of the binary mixtures with ethane also increased. At constant composition, a large overall relative change was observed in the mixture P_c over T_c compared to the pure ethane critical conditions. For the ethane + *n*-alkane binary mixtures studied, the T_c was accurately predicted by the correlation based on the theory of conformal solutions and the dilute mixture SRK EOS approach. For correlation of the binary mixture P_c at low alkane concentrations, the dilute mixture SRK EOS is better, although it requires the knowledge of an optimized parameter.

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