x	liquid mole fraction
y	vapor mole fraction

Subscripts

1, 2	component 1 or 2
e, c	experimental or calculated

Registry No. 2,2,2-Trifluoroethanol, 75-89-8; 1-propanol, 71-23-8.

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Solubilities of Solid *n*-Nonacosane and *n*-Tritriacontane in Supercritical Ethane

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The solubilities of solid *n*-nonacosane (*n*-$C_{29}H_{60}$) and *n*-tritriacontane (*n*-$C_{33}H_{68}$) in supercritical ethane at temperatures between 308.1 and 318.1 K and pressures up to 20 MPa have been measured and are reported in this paper. The results complement our previous results for the solubilities of *n*-octacosane (*n*-$C_{26}H_{58}$), *n*-tritriacontane (*n*-$C_{30}H_{62}$), and *n*-dotriacontane (*n*-$C_{32}H_{66}$) in ethane.

Introduction

As outlined elsewhere (*1*) odd-numbered *n*-alkanes exhibit different trends in their solid-state properties than even-numbered members of the *n*-alkane series. It may therefore be attractive to exploit these differences to separate close-boiling members of the series using supercritical fluids.

We have studied the solubilities of five solid *n*-alkanes having 28–33 carbon atoms in supercritical ethane, near the critical point of ethane. The solubilities of *n*-nonacosane (*n*-$C_{29}H_{60}$) and *n*-tritriacontane (*n*-$C_{33}H_{68}$) in supercritical ethane are reported here. The solubilities of even-numbered *n*-alkanes (*n*-$C_{26}H_{58}$, *n*-$C_{30}H_{62}$, *n*-$C_{32}H_{64}$) in ethane were reported in an earlier publication (*1*).

Experimental Section

The apparatus and experimental procedure have been described in detail elsewhere (*1*). The apparatus is a single-pass flow system of the type used by Kurnik et al (*2*), McHugh and Paulaitis (*3*), and Adachi et al. (*4*), with the solubilities of the solid determined gravimetrically.

Ethane was first liquefied and then compressed to the desired pressure by means of a Milton Roy minipump. Its temperature was increased to the desired value in a heat exchange coil immersed in a constant temperature bath. The temperature in the bath was maintained constant within ±0.1 K. The supercritical fluid was then brought into contact with the solid solute in a high-pressure view cell which was also immersed in the constant temperature bath. Layers of glass beads were packed with the solute in the equilibrium cell to increase contact between the supercritical ethane and the solid solute. The loaded supercritical fluid was then depressurized by using a micrometering valve and the deposited solute was collected in a separation vessel. The temperature in the equilibrium cell was measured with a copper-constantan thermocouple calibrated against an NBS-certified platinum resistance thermometer, and the pressure was measured with a Heise gauge calibrated against a dead weight gauge. We estimate the precision of our temperature and pressure measurements to be ±0.1 K and ±0.05 MPa, respectively. The depressurized solvent volume was measured with an estimated precision of 0.5% by using a wet test meter. The accuracies were typically twice the values given above.

Table I. Experimental Solubilities ($y_2 \times 10^3$) of Solid *n*-Alkanes in Supercritical Ethane

	T = 308.1 K		T = 313.1 K	T = 318.1 K
P, MPa	q = 29	q = 33	q = 33	q = 33
6.47	2.32 ± 0.04	0.371 ± 0.01	0.228 ± 0.01	0.183 ± 0.01
10.20	4.32 ± 0.05	0.963 ± 0.01	1.15 ± 0.02	1.54 ± 0.01
12.12	8.29 ± 0.14	1.14 ± 0.01	1.47 ± 0.02	1.96 ± 0.02
13.64	9.91 ± 0.14	1.36 ± 0.02	1.72 ± 0.02	2.97 ± 0.04
16.67	14.2 ± 0.32	1.64 ± 0.02	2.24 ± 0.03	
20.20		2.37 ± 0.03	2.93 ± 0.05	

Source and Purity of the Materials

The solid *n*-nonacosane and *n*-tritriacontane were obtained from Wiley Organics and Fluka Chemical Corp. and had a stated purity of 99% and 97%, respectively. They were used without further purification. Ethane was furnished by the Matheson Gas Co. with a purity of 99+% and was also used without further purification.

The crystallinity of the solid samples was confirmed in two ways. First, a melting–freezing point check was carried out on a Thomas Hoover capillary apparatus. Both the melting and freezing of each hydrocarbon occurred at a single temperature which was within ±0.5 °C of the value reported by the supplier. In addition, one sample of each hydrocarbon was analyzed on a Philips θ-2θ X-ray diffractometer. Sharp peaks in the X-ray diffraction scans were noted in each case, confirming that the hydrocarbons were crystalline.

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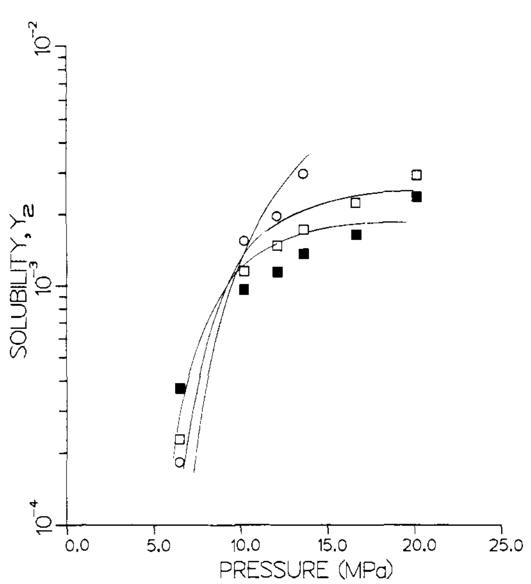

Figure 1. Experimental and calculated solubilities of *n*-tritriacontane in supercritical ethane. The solid lines were calculated by using the Patel-Teja equation of state. (■) 308 K, (□) -313 K, (○) 318 K.

Results

For comparison purposes the solubilities of 2,3-dimethylnaphthalene in carbon dioxide at three temperatures were first measured and the results compared with those of Kurnik et al. (*2*). The results have been presented elsewhere (*1*). The average difference between our solubilities and those of Kurnik et al. was about 1% and the maximum difference was 3.6%. In turn, Kurnik et al.'s data agreed with the data of Tsekhanskaya et al. (*5*) with an average deviation of 1.3%. All three sets of data therefore are in agreement, within experimental error. Our results for the C_2H_6 + *n*-$C_{29}H_{60}$ and C_2H_6 + *n*-$C_{33}H_{68}$ systems are given in Table I. Experimental uncertainties are also shown in Table I.

The region of the C_2H_6 + *n*-alkane phase diagram covered in the experiments is similar to that in our previous work on even-numbered *n*-alkane + ethane binary systems (*1*). The region is bounded by the solid-liquid-gas curve at higher pressures and this limits the range of pressures and temperatures which can be studied in this type of apparatus.

Data Correlation. Experimental data were correlated as follows: (1) by using the Patel-Teja equation of state (*6*); and (2) by using an empirical relationship similar to that developed for the even-numbered alkanes.

Equation of State Calculations. For a pure solid phase in equilibrium with a supercritical gas phase, we may write (*7*)

$$P_2^s\phi_2^s \exp\left\{\int_{P_2^s}^{P} \frac{V_2^s}{RT}\,dP\right\} = y_2\phi_2^F P \qquad (1)$$

where P_2^s is the sublimation (vapor) pressure of the solute 2, ϕ_2^s the fugacity coefficient of the solute at its sublimation pressure, V_2^s the molar volume of the solute, y_2 the composition (solubility) of the solute in the supercritical solvent, ϕ_2^F the fugacity coefficient of the solute in the supercritical solvent, P the pressure, and all properties are evaluated at the system temperature. Since the sublimation pressure is usually very small, we may assume $\phi_2^s \simeq 1$ and the integral to be evaluated from zero pressure to the system pressure P. Also, since the solid molar volume is approximately constant with pressure, we can integrate and rewrite eq 1 as follows:

$$y_2 = \frac{P_2^s \exp[PV_2^s/RT]}{P\phi_2^F} \qquad (2)$$

Table II. Binary Interaction Coefficients Required in the Calculation of Solubilities Using the Patel-Teja Equation of State

q	T = 308.1 K	T = 313.1 K	T = 318.1 K
28	-0.0405		
30	-0.0307	-0.0265	
32	-0.0383	-0.0315	
29	-0.0049		
33	-0.0037	-0.0007	-0.0008

Table III. Properties of the *n*-Alkanes Used in the Calculations

	q = 29	q = 33	comments
V^s, L mol^{-1}	0.5058	0.571	supplied by manufacturer
P_c, kPa	864.3	768.1	estimated (*9*)
T_c, K	846.1	874.0	estimated (*9*)
ω	1.298	1.471	estimated (*9*)
T_t, K	336.8	344.6	from normal melting temp
P_t, kPa × 10^7	3.112	0.5275	estimated using eq 3

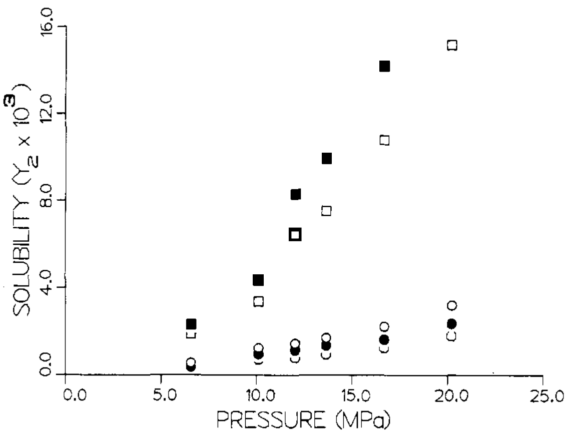

Figure 2. Experimental solubilities of five *n*-alkanes in supercritical ethane at 308.15 K: (■) C_{29}, (□) *n*-C_{28}, (○) *n*-C_{30}, (●) *n*-C_{33}, (○) *n*-C_{32}.

Thus, if the solid-phase properties (density and sublimation pressure) are known, then the solubility of the solute in the supercritical solvent at any pressure and temperature can be calculated provided an equation of state is available for the calculation of ϕ_2^F. Typical results obtained by using the Patel-Teja equation of state are shown in Figure 1. Note that a temperature-dependent binary interaction coefficient (k_{ij}) is required in the equation of state calculations. At a given temperature, the binary interaction coefficient decreases as the number of carbon atoms in the solute increases, denoting increasing deviations from the geometric mean rule with increasing size difference. In addition the binary interaction coefficient of odd-numbered *n*-alkane + ethane mixtures is one order of magnitude less than that of the even-number *n*-alkane + ethane systems as can be seen in Table II. The solubilities of five *n*-alkanes at 308.15 K are plotted against pressure in Figure 2. Note that the solubilities of even- and odd-numbered alkanes follow different trends. Thus the solubility of *n*-C_{29} is higher than that of *n*-C_{28} at the same conditions. Our equation of state calculations show that these solubility differences between odd- and even-numbered *n*-alkanes in supercritical ethane apparently depend on differences in binary pair interactions as well as on vapor pressure differences. Solid densities and critical properties (T_c and P_c) and accentric factors (ω) used in the solubility calculations are given in Table III. The critical properties and acentric factor were estimated by using the correlations developed by Robinson and Peng (*8*) for *n*-paraffins. The densities were supplied by the manufacturer whereas the sublimation pressures were estimated as follows. The reported sublimation pressures of methane and *n*-heptadecane (n-$C_{17}H_{36}$) of Bradley and Shellard (*9*) and Armstrong et al. (*10*) were fitted to the following equations (having the same functional form as reported for the even-numbered n-alkanes)

$$\ln P^{\rm s} = C + D/T \qquad (3)$$

where

$$C = 6.56653 + 1.76232q \qquad (4)$$

$$D = -244.831 - 915.569q \qquad (5)$$

In eq 3-5, q is the number of carbon atoms in the (odd-numbered) n-alkanes and the units of P and T are MPa and K, respectively. The overall absolute deviation between experimental and calculated sublimation pressures was found to be 0.71% for the two paraffins studied. These equations allow the estimation of the sublimation pressures of other odd-numbered n-alkanes (e.g., n-$C_{29}H_{60}$ and n-$C_{33}H_{68}$) and are similar to those used successfully for the even-numbered n-alkanes in our earlier work.

Empirical Correlation for the Solubility. Because of the need to estimate T_c, P_c, ω, and $P_2^{\rm s}$ in the equation of state calculations, the solubility was correlated directly with solid-state properties by using the relationship

$$\ln y = A + B(P_{\rm t}V^{\rm s}/RT_{\rm t}) \qquad (6)$$

where $P_{\rm t}$ and $T_{\rm t}$ are the triple point pressure and temperature, respectively, and $V^{\rm s}$ is the molar volume of the solid. The triple point temperature $T_{\rm t}$ can be approximated by the normal melting temperature and, once this is known, the triple point pressure can be estimated from eq 3-5. Thus the solubility of any odd-numbered n-alkane (e.g., n-C_{31} or n-C_{35}) in supercritical ethane near the critical point of ethane can be predicted solely from a knowledge (or estimates) of $P_{\rm t}$, $T_{\rm t}$, and $V^{\rm s}$. Values of $P_{\rm t}$, $T_{\rm t}$, and $V^{\rm s}$ used in our calculations are given in Table III.

A similar correlation was developed for even-numbered n-alkanes by Moradinia and Teja (*1*). Because of the ability of the previous correlation for interpolation and (judicious) extrapolation of data, we believe that the correlation presented above can also be used for such purposes, although this obviously cannot be shown from data on two odd-numbered n-alkanes. In addition, it should be emphasized that the correlation is valid only over a limited range of pressures and temperatures.

Registry No. n-$C_{29}H_{60}$, 630-03-5; n-$C_{33}H_{68}$, 630-05-7; ethane, 74-84-0.

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Phase Behavior in the Critical Region of Six Binary Mixtures of 2-Methylalkanes

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The *PTx* diagrams of six binary systems formed from 2-methylpentane, 2-methylhexane, 2-methylheptane, and 2-methyloctane were determined in the critical region. The critical properties and vapor pressures of the pure components were also determined and compared with literature values. A plot of the critical constants of the pure components against the carbon number yielded parallel curves for the *n*-alkane and the 2-methylalkane homologous series. The *PTx* diagrams of the binary systems also closely resemble those of the corresponding *n*-alkane systems. The Peng–Robinson equation was used to model the behavior of these systems with reasonable success. However, there are distinct limitations to the use of this equation in the critical region.

Introduction

The *PVTx* diagrams of mixtures at elevated pressures are of great practical as well as theoretical interest. Of particular interest are systems of close-boiling components since such mixtures are difficult to separate by using conventional distillation techniques. From a theoretical point of view, the study of these mixtures in the critical region yields fundamental information on molecular interactions in fluids and on the critical exponents.

This work was undertaken in an effort to determine the effect of molecular size and shape on the behavior of binary mixtures in the critical region. Six binary systems formed from 2-methylpentane, 2-methylhexane, 2-methylheptane, and 2-methyloctane were studied. The ability of the Peng–Robinson (*1*) equation to correlate and predict the data was also examined.

Experimental Section

The P–T border curves for a series of mixtures of known composition were determined experimentally. The apparatus and experimental techniques were the same as those employed in previous studies (*2*, *3*). Briefly, a sample of known composition (prepared gravimetrically) was confined over mercury in the sealed end of a thick-walled precision-bore glass tube. The tube was secured in one leg of a steel U-tube, with the

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