rameters in Tables V and VII. These k_{ij} values were found by using a nonlinear least-squares regression technique to give the best fit between theory and experiment.

In Figure 4, the experimental benzoic acid mole fractions in supercritical carbon dioxide are shown as a function of temperature and pressure. These data are also well correlated with the Peng-Robinson equation of state. Also shown in this figure are the calculated benzoic acid concentrations for cases where the vapor phase is assumed to behave as an ideal gas.

The ideal-gas assumption (ϕ_1 of eq 1 is unity) is valid only at very low pressures. At high pressures, an ideal-gas assumption grossly underestimates the actual concentration.

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Glossary

a, b, A, B	variables in Peng-Robinson equation of state
k_{ij}	Peng-Robinson binary interaction parameter
P	pressure, bar
P_{vp}	vapor pressure, bar
R	gas constant
T	temperature, K
V	molar volume, cm^3/mol
y	fluid-phase mole fraction
Z	compressibility factor

Greek Letters

κ	parameter in Peng-Robinson equation of state
ϕ	fugacity coefficient
ω	acentric factor
Ω_a, Ω_b	constants in Peng-Robinson equation of state

Subscripts

1	solid component
2	fluid component
c	critical property
r	reduced property

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Critical Mixing of Decyl Alcohol with Dipolar Liquids

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The liquid-liquid coexistence curves for critical systems of decanol with five compounds covering a wide range of electric permittivity were determined and analyzed.

Introduction

Investigations of precritical phenomena which occur in the vicinity of the critical solubility point in binary systems call for mixtures with specific properties, e.g., with matched indexes

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of refraction, densities, etc. To verify the theories of effects induced by a strong electric field, it was necessary to find critical systems of chosen compounds with several other compounds covering a possibly wide range of electric permittivity (*1–3*). In particular, dipolar systems with a well-matched permittivity of compounds are needed, which to our best knowledge have not been noted in the literature.

There are many liquids, which with aliphatic hydrocarbons form solutions of high critical temperatures (*4*), e.g., nitromethane above 400 K. Since, in accordance with ref *5*, a decreasing of this temperature can be expected after introduction of weakly polar group such as -COO, -O-, -OH, -Cl, or -Br into the hydrocarbon chain, we undertook an investigation of the miscibility in the systems with decyl alcohol. In addition to the well-known systems with nitroethane and acetonitrile (*4*), we found a number of new ones with critical temperature close to room temperature (290–300 K). The phase-coexistence curves presented here are for mixtures of compounds which have relatively low electric conductivity and are therefore convenient for dielectric measurements.

Theory

The two-component mixture separates into two liquid phases if the temperature is lower than the upper critical solution temperature, T_c. When heated, both phases become identical at T_c, having the critical concentration X_c. The location of the critical point, where the fluctuational processes are extremely strong, is important in the investigation of precritical properties. The critical point can be determined in the sample characterized by the highest phase-separation temperature and for which the meniscus is in the middle of the bulk (*6*). Since this direct method is difficult to use successfully because of the flatness of the coexistence curve near the critical concentration and the scatter of the experimental data, the critical point should rather be determined by numerical analysis of the data (*6–8*).

The shape of the liquid–liquid equilibrium curve is determined by the dependence of the miscibility gap and the curve diameter on the reduced temperature t (*6*, *7*):

$$X_+ - X_- = A_1|-t|^{\beta}(1 + a_1|-t|^{\Delta} + ...) \qquad (1a)$$

$$0.5(X_+ + X_-) = X_c + A_2|-t|(1 + a_2|-t|^{-\alpha} + ...) \qquad (1b)$$

$$t = T/T_c - 1$$

where X_+ and X_- are equilibrium concentrations of the coexisting liquids. When the temperature is close to T_c, the curves for a large number of systems can be described by eq 2 (*2*).

$$X_{\pm} - X_c = \pm 0.5A_1|-t|^{\beta} + A_2|-t| \qquad (2)$$

This relation was used as the basis of our analysis. Concentrations have been expressed in volume fractions because then the curves become more symmetrical. Theories of the renormalization group and series expansion in the lattice model yield for the critical exponent $\beta = 0.325$ and $\beta = 0.312$, respectively (*9*).

Experimental Section

Procedure. Miscibility temperatures were determined by observing turbidity changes during heating and cooling of vigorously shaken solutions. The accuracy of the measurements was 0.05 K.

Materials. Reagents of initial purity 98%, if not otherwise stated, were purified as follows.

Decanol was preliminary dried and vacuum fractionated. The last fifth of the liquid was discarded, and the product was redistilled over CaH_2.

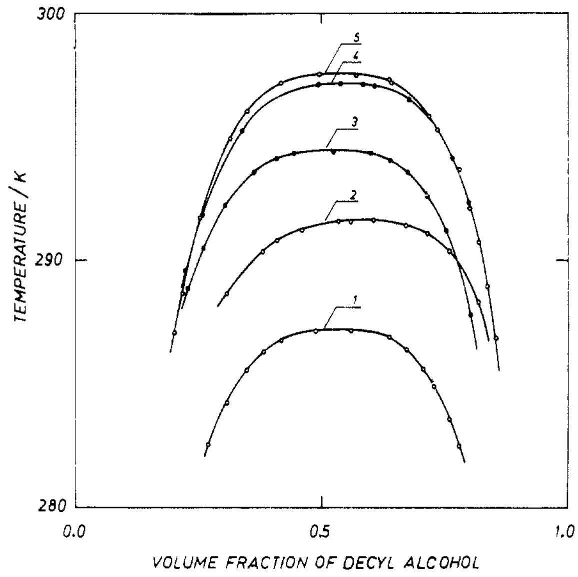

Figure 1. Liquid–liquid coexistence curves of decanol with dipolar solvents: (1) phenylacetonitrile; (2) 1,2-ethylene diacetate; (3) nitroethane; (4) acetonitrile; (5) dimethyl phthalate.

Table I. Systems of Decyl Alcohol with Dipolar Liquids[a]

liquid	ϵ[b]	A_1	A_2	T_c/K	ϕ_c
decanol	8.01				
1,2-ethylene diacetate	7.40	2.24	−1.708	291.60	0.577
dimethyl phthalate	8.61	2.00	−0.721	297.55	0.531
phenylacetonitrile	18.6_5	1.94	−0.382	287.20	0.531
nitroethane[c]	28.40	2.05	−0.352	294.40	0.517
acetonitrile	35.4_5	2.03	−0.447	297.10	0.541

[a] Electric permittivity (ϵ) and parameters of liquid–liquid coexistence curves from $\phi_{\pm} - \phi_c = \pm 0.5A_1|-t|^{\beta} + A_2|-t|$; $\beta = 0.325$. [b] Measured at 2 MHz, 298.16 K. [c] Fluka sample containing a few percent of 2-nitropropane. UCB sample of better purity gives $T_c = 295.0$ K.

1,2-Ethylene diacetate was dried by molecular sieves and vacuum distilled.

Dimethyl phthalate was shaken first with water and then with diluted potassium carbonate. After the addition of ether, the sample was washed and dried. The ether was removed, and methyl phthalate vacuum distilled over $CaSO_4$.

Phenylacetonitrile was purified in a similar manner as dimethyl phthalate. It was treated with 1:1 diluted sulfuric acid, and the dried product was vacuum fractionated over CaH_2.

Nitroethane was distilled under reduced pressure over $CaSO_4$, after agitation with sulfuric acid, washing, and drying. A Fluka sample of initial purity 95% was purified in a similar manner.

Acetonitrile (99.5% Fluka) was dried and distilled over CaH_2.

Results and Discussion

Phase-coexistence curves of the investigated systems are presented in Figure 1. The mean difference between experimental temperatures and temperatures calculated numerically from eq 2 with the help of our BETAPROX program (written by W. Jeute) is 0.03 K. Preliminary data analysis yielded reasonable values for the critical exponent: $\beta = 0.31$–0.33. However, determination of β with the desired accuracy on the order of 10^{-3} (*8*) requires phase-separation temperature measurements with one order better accuracy; such measurements are only now under way. Therefore, in further calculations, the theoretical value $\beta = 0.325$ was imposed and the remaining parameters were determined and listed in Table I. Critical concentrations of all systems are similar (0.52–0.58 volume fraction of decanol), and the curves are rather wide ($A_1 \sim 2$).

It is interesting to compare the critical temperatures of polar liquid-aliphatic alcohol and polar liquid-aliphatic hydrocarbon systems. The differences in critical-temperature decrease induced by the OH group are basically due to the formation of hydrogen bonds between components. The data necessary for estimation are not available for decane, but ref *4* gives the appropriate values for heptane. The critical-temperature changes after replacing heptane with decanol are -65, -61, -57, -41, and -14 K for dimethyl phthalate, acetonitrile, phenylacetonitrile, 1,2-ethylene diacetate, and nitroethane, respectively. The results are in agreement with the fact that the NO_2 group shows a weak ability to form hydrogen bonds.

The electric permittivity of the investigated liquids ranged from 7 to 35. Two of the systems have well-matched electric permittivities; for ethylene diacetate and dimethyl phthalate the difference $\Delta\epsilon$ at 298.16 K is ~0.60. Decanol also forms a critical system with *o*-nitroanisole ($\epsilon \sim 45$); however, the critical temperature is higher than 300 K.

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The advice and interest of Professor A. Piekara in the present work is greatly appreciated. One of the authors (W.P.) is also indebted to Dr. T. Krupkowski for critical discussion.

Glossary

A_1, A_2, a_1,a_2	constants of the coexistence-curve equations
T	absolute temperature, K
T_c	critical temperature
t	reduced temperature
X_c	critical concentration
$X_\pm$	equilibrium concentrations of coexisting liquids

Greek Letters

α	critical exponent for specific heat
β	critical exponent for coexistence curve
Δ	correction exponent in eq 1
ϵ	electric permittivity
$\Delta\epsilon$	electric permittivity difference between decanol and a dipolar liquid
ϕ	concentration in volume fraction
ϕ_c	critical concentration in volume fraction

Subscripts

c	critical

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Vapor-Liquid Phase Equilibrium for Carbon Dioxide-*n*-Hexane at 40, 80, and 120 °C

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Vapor and liquid equilibrium phase compositions have been measured for carbon dioxide-*n*-hexane at temperatures of 40, 80, and 120 °C. At each temperature, the pressure range from ~6.8 atm (100 psia) to near the system critical pressure was covered. Equilibrium *K* values for carbon dioxide and *n*-hexane were calculated from these data. The data from this work are well represented by the Soave equation of state. When one uses an optimum interaction parameter, C_{12} = 0.131, in the Soave equation, average errors in the predicted phase compositions (at fixed *T* and *P*) are 0.012 and 0.009 for the liquid and vapor phases, respectively.

Introduction

Carbon dioxide-hydrocarbon mixtures are found in numerous processes of importance to the production of fluids for use as energy sources. Prime process examples include the carbon dioxide flooding of petroleum reservoirs and the conversion of coal to liquid fuels. Furthermore, prediction of the behavior of mixtures which contain carbon dioxide is known to require modification of the simple mixing rules employed in commonly used solution models. To evaluate the parameters required to characterize carbon dioxide-hydrocarbon interactions requires experimental data on such systems. Systematic studies of selected carbon dioxide-hydrocarbon systems are especially valuable since such data can form the basis for generalizations of the interaction parameters in carbon dioxide systems.

Our recent study of the literature on phase equilibrium for carbon dioxide-*n*-paraffin hydrocarbons raised questions regarding the accuracy of the available data for carbon dioxide-*n*-hexane. As a result, the present study was undertaken to provide additional information on this binary system.

Experimental Method

The experimental measurements were done in a variable-volume, windowed, phase equilibrium cell. The cell is constructed of A286 stainless steel and has a maximum volume of 600 cm^3. The cell is basically a 2.0-in. i.d., 4.5-in. o.d. piston-cylinder assembly, with the cylinder closed at one end by a metal plug. The opposite end contains a 2.75-in. diameter, 1.0-in. thick quartz window, backed by a metal plug except for

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