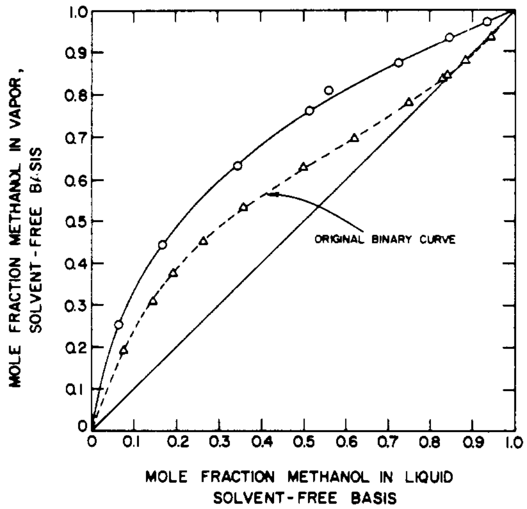

Figure 4. Altered vapor-liquid equilibrium

The system MeOH-MEK in the presence of 70 mole % diethyl ketone at 760 mm. of Hg

1 mole %, but there is some disagreement among the data of the three sources for low methanol concentrations.

To explore the effectiveness of diethyl ketone in breaking the methanol–methyl ethyl ketone azeotrope at 760 mm. of Hg pressure, vapor-liquid equilibrium data were obtained when the still was charged with normal azeotropic compositions of the binary mixture along with various relative concentrations of diethyl ketone. The samples were analyzed on a solvent (diethyl ketone) free basis. These data are listed in Table II, and the relative volatility of methanol with respect to methyl ethyl ketone, defined by

$$\alpha_{1-2} = \frac{y_1/x_1}{y_2/x_2} \qquad (4)$$

is shown as a function of the diethyl ketone concentration in Figure 3. Also shown in this figure is an estimated limiting relative volatility, for infinite dilution of azeotrope in solvent, calculated by normal solution theory neglecting polarity effects as discussed by Prausnitz (*5*).

The solvent-free vapor-liquid equilibrium relationships of the binary system methanol–methyl ethyl ketone were obtained in the presence of 70 mole % solvent. These data at 760 mm. of Hg total pressure are listed in Table III. Figure 4 shows the alteration in the binary *x*-*y* diagram achieved by the introduction of 70 mole % of the third component. These curves clearly demonstrate that diethyl ketone can be used successfully as an extractive agent for the extractive distillation of methanol–methyl ethyl ketone at 760 mm. of Hg provided the solvent does not form an azeotrope with either of the binary components. The latter was shown not to be the case by actual distillation.

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NOMENCLATURE

A, B = Van Laar constants (Carlson and Colburn modification)
γ_i = activity coefficient of component i
x_i = mole fraction of i in liquid
y_i = mole fraction of i in vapor
p_i = vapor pressure of i (mm. of Hg)
π = total pressure (mm. of Hg)
α = relative volatility

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Partial Miscibility Phenomena in Binary Hydrocarbon Systems Involving Ethane

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THE significant recent work of Rowlinson on mutual solubility of liquids, particularly the study of the partial miscibility of methane and ethane with certain hydrocarbons (*2, 6, 7*), has motivated considerable interest in partial miscibility behavior.

In the past, numerous examples of partial miscibility in liquid mixtures of polar and nonpolar liquids have been found. Partial miscibility observations on systems in which all the components are nonpolar have been relatively rare. Rowlinson (*6*) has cited the experimental work on the nonpolar systems in which partial miscibility has been observed. Davenport (*2*) has studied the solubility of hydrocarbons in liquid methane and found partial miscibility in many binary systems of methane with components of higher molecular weight than pentane. Kohn (*4*) has reported partial miscibility phenomena in the binary system methand-*n*-heptane. Rowlinson (*7*) has reported immiscibility of ethane with a series of high molecular weight hydrocarbons and complete miscibility of these same components with propane.

Further studies on the partial miscibility of light hydrocarbons with higher hydrocarbon components are useful not only for their value in understanding miscibility phenomena but also because such studies supply data which are necessary in the design of separation processes.

EXPERIMENTAL

The apparatus was the same as in other recent studies on binary systems (*3, 4*). Briefly, the heavier component

Solutions of ethane from 0 to 99.8 mole % in binary mixtures with *n*-heptadecane, *n*-octadecane, *n*-nonadecane, and *n*-eicosane were examined in the temperature range from 25° to 38° C. for partial miscibility behavior in the liquid phase. Ethane was found to be partially miscible with *n*-nonadecane and *n*-eicosane over small temperature ranges near the critical temperature of ethane. The compositions and molar volumes of the two liquid phases are presented at selected temperatures over the range of their coexistence. Absolutely no evidence was found for partial miscibility of ethane with *n*-heptadecane and *n*-octadecane. The complete miscibility behavior of these two systems appears to be positive evidence that *n*-nonadecane is the normal paraffin hydrocarbon of lowest molecular weight, which is partially miscible with ethane.

was added as a liquid to calibrated 12-ml. borosilicate glass equilibrium cells. The ethane was added as a superheated gas to the thermostated cell from a high pressure gas reservoir by a calibrated positive displacement mercury pump. The experimental procedure for obtaining the compositions of the L_1 and L_2 liquid phases is described by Ma (*5*) and Kim (*3*). The relatively few vapor compositions were obtained in special dew point equilibrium cells using a technique similar to that described by Kohn (*4*).

The ethane was material of 99 mole % minimum purity, supplied in cylinders by the Matheson Chemical Co. The impurities were stated to be methane, nitrogen, carbon dioxide, and propane. The ethane was treated by passing the saturated vapor at room temperature through a 75-ml. stainless steel bomb packed with 5-A. molecular sieves. The effluent gas from the bomb was condensed inside a 100-ml. volume sight glass gage. Approximately 20% of the condensed liquid was allowed to vaporize and the vapor discarded. Approximately 60 ml. of the remaining liquid was distilled into a dry evacuated stainless steel bomb for use in the experiments, with the remaining liquid discarded. Typical isotherms on the purified ethane which were run at 25° C. indicated a pressure difference of approximately 0.25 atm. between the bubble point and the dew point pressures with the final 95 volume % condensing over a 0.07-atm. pressure difference. From these data, it appears probable that the purified ethane contained less than 0.4 mole % impurities. The heavy hydrocarbons were obtained as 99% minimum purity, petroleum-derived material from the Humphrey-Wilkinson Corp. The heavy hydrocarbons were used without further purification.

Table I. Smoothed Values of Pressure, Composition, and Molar Volume of the Liquid Phases in the Three-Phase (L_1-L_2-V) Region

Ethane-*n*-nonadecane system

		L_1 Phase		L_2 Phase	
Temp., ° C.	Press., Atm.	Compn. mole fract. ethane	Mol. vol., ml./g. mole	Compn. mole fract. ethane	Mol. vol., ml./g. mole
36.60[a]	51.819	0.9750	96.00	0.9750	96.00
36.7	51.933	0.9647	94.10	0.9832	98.58
36.8	52.051	0.9615	93.65	0.9857	99.78
37.0	52.282	0.9576	93.48	0.9888	101.80
37.2	52.520	0.9547	93.42	0.9910	103.81
37.4	52.753	0.9522	93.37	0.9928	106.00
37.6	52.987	0.9498	93.12	0.9946	108.71
37.7	53.102	0.9487	92.95	0.9953	110.80
37.78[b]	53.200	0.9478	92.78	0.9960	115.10

[a] LCST point. [b] Type K singular point.

RESULTS

Binary mixtures of *n*-heptadecane in ethane, and *n*-octadecane in ethane, at compositions between 0 and 0.99 mole fraction ethane were completely miscible in the range from 25° to 38° C. Experimental isotherms in the temperature range appeared to be typical. As ethane was added to the glass cell containing the heavy component, it was absorbed into the liquid phase. After each addition of ethane and equilibration by magnetic stirring, the pressure rose to a new equilibrium value. There was only a gas phase and a single liquid phase in equilibrium. At over-all compositions of ethane up to 99 mole %, no second liquid phase was observed for the ethane–*n*-octadecane systems.

Both of the binary systems, ethane–*n*-nonadecane and ethane–*n*-eicosane, had miscibility gaps over small temperature ranges. Table I presents the smoothed pressure, temperature, composition, and molar volume data of the two liquid phases which coexist over a 1.18° C. temperature range for the ethane–*n*-nonadecane system. Table II presents similar information over a 2.89° C. temperature range for the ethane–*n*-eicosane system. The raw experimental data on the liquid phases were reproducible to ±0.0005 mole fraction ±0.02° C., and ±0.05 atm. The molar volumes of the L_2 liquid phase were reproducible to ±0.2 ml. per gram mole, while those of the L_1 liquid phase were reproducible to ±0.6 ml. per gram mole. The vapor phase molar volumes reported in Table II were reproducible to ±1.0 ml. per gram mole. Only a few experimental determinations

Table II. Smoothed Values of Pressure, Composition, and Molar Volume in the Three-Phase (L_1-L_2-V)Region

		L_1 Phase		L_2 Phase		V Phase	
Temp., ° C.	Press., Atm.	Compn., mole fract. ethane	Mol. vol., ml./g. mole	Compn. mole fract. ethane	Mol. vol., ml./g. mole	Compn., mole fract. ethane	Mol. vol., ml./g. mole
33.74[a]	48.887	0.9705	93.40	0.9705	93.40	0.9996	203.5
34.0	49.180	0.9568	92.75	0.9836	95.71	0.9992	200.0
34.4	49.638	0.9503	93.44	0.9884	96.90	0.9991	193.4
34.8	50.090	0.9457	94.29	0.9908	98.59	0.9990	186.7
35.2	50.542	0.9416	95.22	0.9925	100.80	0.9990	179.1
35.6	51.000	0.9379	96.08	0.9940	103.77	0.9989	171.0
36.0	51.452	0.9351	96.68	0.9954	107.80	0.9985	162.0
36.4	51.908	0.9327	96.24	0.9967	114.90	0.9983	150.5
36.63[b]	52.179	0.9315	95.17	0.9974	127.60	0.9974	127.60

[a] LCST point. [b] Type K singular point.

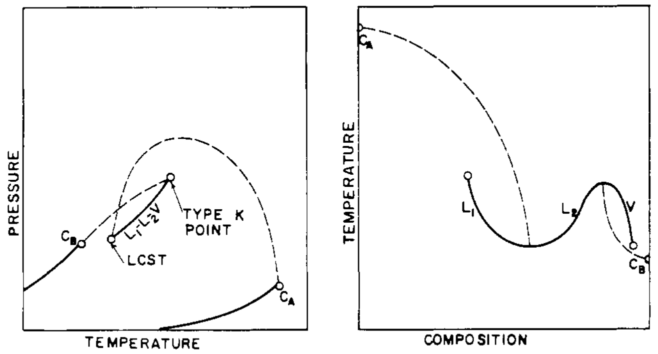

Figure 1. Phase behavior in the three-phase regions

were done on the vapor phase, since it was the most difficult phase upon which to obtain reproducible molar volume information. For all practical purposes, the vapor phases coexisting with the two liquid phases for both systems may be regarded as pure ethane gas.

Figure 1 shows schematic sketches of the phase behavior in the three-phase region. The dashed lines are vapor-liquid critical loci. Actually only one vapor-liquid critical point was experimentally determined. The critical phase was at a temperature of 37.51° C. and a pressure of 55.96 atm. and had a composition of 0.9668 mole fraction ethane and a molar volume of 93.79 ml. per gram mole. From the figure, it is apparent that there is a discontinuity in the vapor-liquid critical locus.

Three-phase behavior of the type presented here has been discussed at some length by Rowlinson (*7*). The results obtained here further confirm Rowlinson's observation that this type of miscibility is found in mixtures of nonpolar molecules of the same chemical type if the molecular sizes and energies of interaction of the components are sufficiently different. The data definitely prove, however, that these two systems do not follow the Bronsted and Koefoed "principle of congruence" (*1*) nor do they follow regular solution theory even when the compositions are expressed in volume fractions.

NOMENCLATURE

C_A = vapor-liquid critical point of pure high boiling hydrocarbon
C_B = vapor-liquid critical point of pure ethane
L_1 = liquid phase less rich in ethane (higher density)
L_2 = liquid phase richest in ethane
LCST = lower critical solution temperature (L_1 is in critical identity with L_2 in presence of vapor phase)
Type K = singular point (L_2 is in critical identity with V in presence of L_1 phase)
V = vapor phase

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Ternary Liquid Equilibria

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Phase equilibrium data for the ternary liquid-liquid systems acetic acid–water–methyl butyrate, propionic acid–water–methyl butyrate, and *n*-butyric acid–water–methyl butyrate at 30° C. are presented. The tie line data are well correlated by the methods of Hand and Othmer and Tobias.

IN CONTINUATION of studies on liquid-liquid equilibria of fatty acid-water-solvent systems (*5*), the systems acetic acid-water-methyl butyrate, propionic acid-water-methyl butyrate, and *n*-butyric acid-water-methyl butyrate have been studied at 30° C. and atmospheric pressure and the data are presented here.

Acetic acid (British Drug Houses, Analar grade, 99.8%), propionic acid (Eastman Kodak Co., 99.9%), butyric acid (Narden Co., 99.8%), and methyl butyrate (Narden Co., $d^{30°}$ 0.8821, $n_D^{30°}$ 1.3822) with negligible free acidity were used. The method suggested by Othmer, White, and Truegar (*3*) was followed for the determination of saturation isotherm and tie-line data. The acid content of aqueous and ester layers was determined by titration.