

ACKNOWLEDGMENT

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Vapor-Liquid Equilibria of Methanol-Methyl Ethyl Ketone in the Presence of Diethyl Ketone

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Vapor-liquid equilibrium data are reported for the binary system methanol-methyl ethyl ketone at 760 mm. of Hg total pressure. The effect of various concentrations of diethyl ketone on the relative volatilities of methanol with respect to methyl ethyl ketone in normal binary azeotropic mixtures (84.7 mole % methanol) are shown. Vapor-liquid equilibrium data are also reported on a solvent (diethyl ketone) free basis for this binary system in the presence of 70 mole % diethyl ketone which breaks the binary azeotrope.

THE BINARY system methanol-methyl ethyl ketone forms an azeotrope at 760 mm. of Hg total pressure. Because of commercial interest, there was incentive to devise a technique to separate various mixtures of these materials into pure components. Sufficient data were obtained to illustrate that this can be done by extractive distillation using diethyl ketone as the extractive agent. These data were: the vapor-liquid equilibria of the binary system methanol-methyl ethyl ketone, the variation of the relative volatility of methanol with respect to methyl ethyl ketone at the binary azeotropic composition in the presence of various concentrations of diethyl ketone, the vapor-liquid equilibria of the system methanol-methyl ethyl ketone with 70 mole % diethyl ketone in the liquid phase, and a normal distillation of the binary systems methanol-diethyl ketone and methyl ethyl ketone-diethyl ketone into pure components to show that they could be separated. The equilibria data of the first three items are presented here.

EXPERIMENTAL

The vapor-liquid equilibrium data were determined on a Gillespie equilibrium still as modified by Foster (2). Tem-

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peratures were measured in the still by a calibrated thermistor while pressures were controlled at 760.0 ± 0.1 mm. of Hg by a Wallace and Tiernan Aneroid Manostat and measured by a Wallace and Tiernan Precision Mercurial Manometer. Reagent grade materials whose boiling points and refractive indices compared favorably with literature values were used as pure materials. The binary samples were analyzed by refractive index determinations using a Bausch and Lomb precision refractometer with a sodium lamp and a temperature controlled prism. The ternary samples obtained from the binary system in the presence of solvent (diethyl ketone) were analyzed for relative methanol-methyl ethyl ketone concentrations on a solvent-free basis. These data were determined by gas chromatography methods using a Perkin-Elmer Vapor Fractometer with a standard Perkin-Elmer "B" column. Peak areas were used in the chromatographic calibration. Total experimental errors were estimated to be less than ± 0.5 mole % methanol.

RESULTS AND DISCUSSION

Even though at least two sources of vapor-liquid equilibrium data for the binary system methanol-methyl ethyl ketone can be found in the literature (1, 4), an experimental investigation was conducted to ascertain these data since some discrepancy exists among those reported. Table I

Table I. Vapor-Liquid Equilibria of the System Methanol-Methyl Ethyl Ketone at 760 mm. of Hg

Methanol Concentration, Mole %		Temp., °C.	Activity Coefficients ^a	
Liquid	Vapor		Methanol	Methyl ethyl ketone
7.6	19.3	75.3	1.707	1.001
14.7	30.8	72.2	1.591	1.029
19.7	37.7	70.7	1.524	1.036
26.5	45.3	68.8	1.462	1.060
35.6	52.8	67.5	1.335	1.092
49.8	62.2	65.9	1.194	1.186
62.2	69.5	65.1	1.102	1.308
74.7	77.7	64.4	1.054	1.464
82.9	83.2	64.3	1.021	1.638
84.1	84.2	64.3	1.019	1.656
87.3	86.9	64.3	1.013	1.719
93.6	92.6	64.4	1.003	1.914

^aVapor pressure taken from Lange's Handbook of Chemistry, 9th edition.

lists the data obtained in this work at 760 mm. of Hg pressure. The activity coefficients are defined by

$$\gamma_i = \frac{y_i \pi}{x_i P_i} \quad (1)$$

where the vapor phase is assumed to be ideal.

As the *t-x-y* diagram in Figure 1 illustrates, the minimum boiling azeotrope at 760 mm. of Hg occurs at 64.3° C. and consists of 84.7 mole % methanol. The solid curves in Figure 2 show the excellent correlation of these vapor-liquid equilibrium data with the binary van Larr equations, viz.,

$$\log_{10} \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \quad (2)$$

and

$$\log_{10} \gamma_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \quad (3)$$

using $A = 0.270$ and $B = 0.325$.

These data are consistent according to the Redlich-Kister (6) consistency test as modified for isobaric data by Herrington (3). The binary azeotropic compositions reported by Hill and Van Winkle (4) and Britton, Nutting, and Horseley (1) are equal to that reported herein within

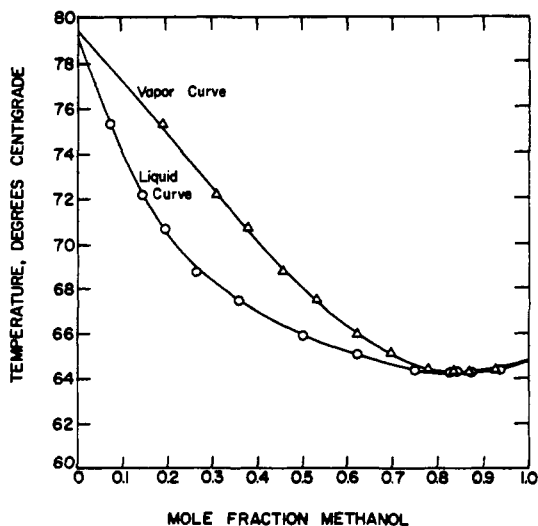


Figure 1. Boiling point diagram The system MeOH-MEK at 760 mm. of Hg

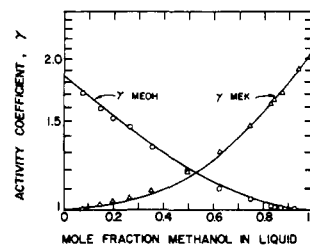


Figure 2. Activity coefficients The system MeOH-MEK at 760 mm. of Hg

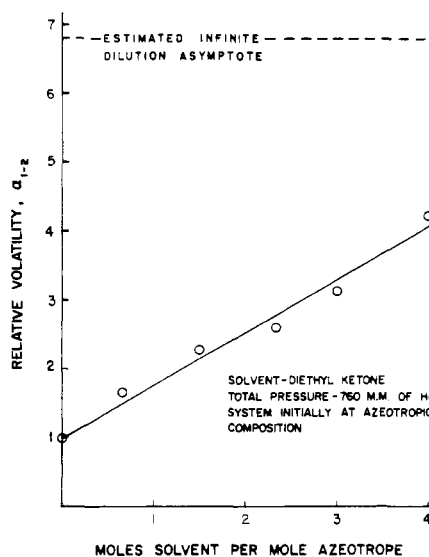


Figure 3. Effect of solvent concentration on relative volatility

Table II. Effect of Diethyl Ketone Concentration on the Vapor-Liquid Equilibria of the Binary System at 760 mm. of Hg.

Diethyl Ketone Concentration, Mole %	Phase	Methanol Concentration (Mole % on Diethyl Ketone Free Basis)	Relative Volatility of Methanol with respect to Methyl Ethyl Ketone
40	Liquid	83.6	1.67
	Vapor	89.5	
60	Liquid	82.6	2.28
	Vapor	91.4	
75	Liquid	82.6	3.13
	Vapor	93.7	
80	Liquid	79.7	4.22
	Vapor	94.3	

Table III. Vapor-Liquid Equilibria of Binary System in Presence of 70 Mole % Diethyl Ketone at 760 mm. of Hg

Vapor Composition, Mole % Methanol on Solvent-Free Basis	Liquid Composition, Mole % Methanol on Solvent-Free Basis	Temp., °C.
25.4	6.5	90.5
44.5	16.8	87.3
63.1	34.6	82.7
76.0	51.5	81.6
80.8	55.9	80.1
87.5	72.7	78.9
93.5	84.6	77.8
97.1	93.5	77.0

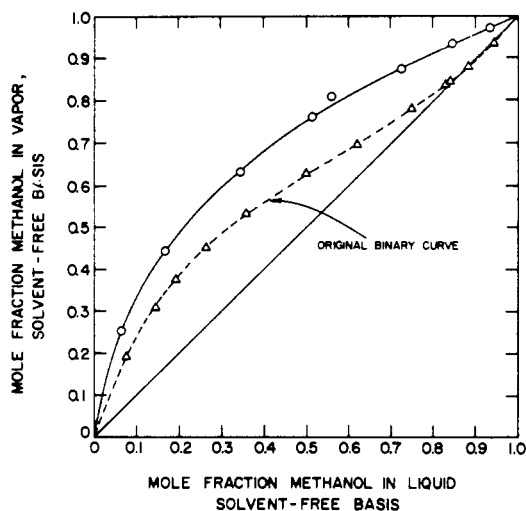


Figure 4. Altered vapor-liquid equilibrium
The system MeOH-MEK in the presence of 70 mole %
diethyl ketone at 760 mm. of Hg

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

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

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 non-polar 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 methanol- 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