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Received for review February 4, 1982. Accepted May 18, 1982. The DSC facility used in this work and the acquisition and design of the computer accessories were made possible, in large part, by support received from the U.S. Department of Energy, Division of Materials Research.

Vapor–Liquid Equilibrium in the System Methyl Ethyl Ketone–*p*-Xylene

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New vapor–liquid equilibrium data have been obtained for the binary system methyl ethyl ketone–*p*-xylene at 760 mmHg to compare with previously reported data assumed to be thermodynamically inconsistent. The system presents slight positive deviations from ideal solution behavior. The activity coefficients are well correlated by a three-constant Redlich–Kister equation and by the Wilson equation. Boiling points are adequately described by a four-constant equation, and vapor composition is very accurately predicted by the UNIFAC method.

Introduction

Chandrashekara and Seshadri (*1*) have recently reported vapor–liquid equilibria data for the system methyl ethyl ketone (MEK)–*p*-xylene and chlorobenzene–*p*-xylene at 685-mmHg pressure. They have analyzed the thermodynamic consistency of their data using the Herington criteria (*2*) based on an empirical evaluation of heats of mixing effects. On this basis, they claim that their data are consistent in spite of the fact that, for MEK concentrations of less than $X_1 = 0.35$, γ_i is larger than unity for MEK and smaller than unity for *p*-xylene. The same behavior, although much less pronounced, is reported for the binary chlorobenzene–*p*-xylene.

The system MEK–*p*-xylene is not believed to exhibit such strong deviations from ideal solution behavior to justify the behavior observed; we believe that it is due to poor, inconsistent data and not to heat effects. We have measured the vapor–liquid equilibrium data at 760 mmHg to verify our assumptions.

No other data are available on the MEK–*p*-xylene system for further comparison.

We can mention that Burke et al. (*3*) observed the same behavior in their measurement of the vapor–liquid equilibrium of the system methanol–toluene. Further measurements by Ocon et al. (*4*) showed that the data of Burke are not reliable.

Experimental Section

Purity of Materials. Analytical-grade reagents purchased from Merck and Fluka were used without further purification after gas-chromatography analysis failed to show any significant impurities.

Table I. Physical Constants of Pure Compounds

index	compd	refractive index at 25 °C	bp(760 mmHg), °C	% purity GLC (min)
1	methyl ethyl	1.378^a	79.56^a	99.5
	ketone	1.376^b	79.60^b	
2	*p*-xylene	1.494^a	138.3^a	99.0
		1.493^b	138.4^b	

^{a} Measured. ^{b} Reference 8.

Table II. Experimental Vapor-Liquid Equilibria Data

T, °C	x_1	y_1	y_1-(UNIFAC)^a	calcd (eq 1) γ_1	calcd (eq 1) γ_2
129.45	0.048	0.208	0.218	1.203	1.049
125.42	0.079	0.317	0.324	1.215	1.043
123.25	0.102	0.381	0.394	1.187	1.030
116.80	0.161	0.511	0.524	1.169	1.048
112.44	0.210	0.594	0.604	1.155	1.052
105.55	0.305	0.710	0.719	1.127	1.056
101.15	0.387	0.755	0.793	1.087	1.070
95.30	0.506	0.852	0.861	1.068	1.061
93.90	0.546	0.872	0.886	1.053	1.047
89.45	0.670	0.917	0.934	1.023	1.091
86.55	0.770	0.947	0.971	0.999	1.108
85.02	0.815	0.959	0.976	1.000	1.126
84.58	0.831	0.962	0.972	0.996	1.161
80.65	0.970	0.994	1.000	0.992	1.194

^{a} $y_1(\mathrm{UNIFAC}) = p^\circ{}_1 x_1 \gamma_1(\mathrm{UNIFAC})/P$.

Physical properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublikova recirculation still (*5*) was used in the equilibrium determinations. The experimental features have been described previously (*6*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm diameter and was packed with SP 1200 on 80–100 Supelcoport and operated isothermally at 105 °C.

Injector temperature was 270 °C and the detector operated at 150 mA and 280 °C. Calibration analyses were carried on

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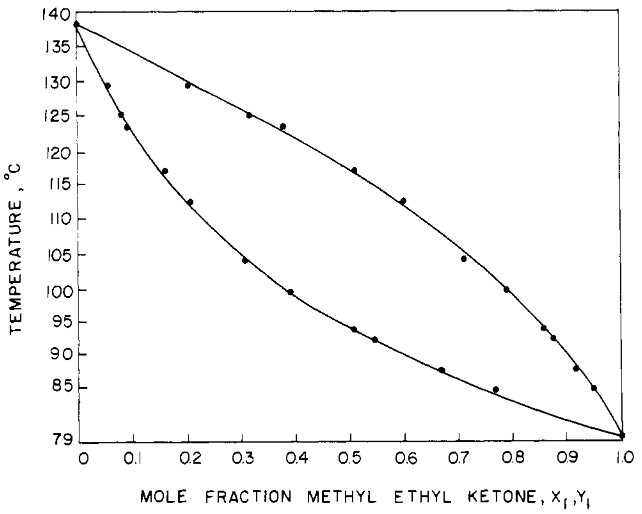

Figure 1. Boiling-point diagram.

Table III. Vapor Pressure Constants (8)

compd	α_i	β_i	γ_i
methyl ethyl ketone	7.063 56	1261.34	221.969
p-xylene	6.990 53	1453.43	215.310

to convert the peak area ratio to the weight composition of the mixture. Concentration measurements were generally accurate to ±0.5%.

Results

Constant-pressure equilibria determinations were made at 760 mmHg, and the experimental results are reported in Figure 1 and Table II.

Activity coefficients were calculated from the equation (7)

$$\ln \gamma_i = \ln (Py_i/P^0_i x_i) + (B_i - v^0_i)(P - P^0_i)/RT + (1 - y_i)^2 P\delta/RT \qquad (1)$$

where

$$\delta = 2B_{ij} - B_i - B_j \qquad (2)$$

Vapor pressures P^0_i were calculated by using Antoine's equation

$$\log P^0_i = \alpha_i - \beta_i/(\gamma_i + t) \qquad (3)$$

where the constants appear in Table III (8). The virial coefficients B_{11} and B_{22} and the mixed coefficient B_{12} were estimated by the method of Tsonopoulos (9, 10) using the molecular parameters suggestsed by the author. In general, the contribution of the last two terms accounted for less than 3% of the activity coefficients, their influence being marked only at dilute concentrations.

The activity coefficients calculated from eq 1 show that the system exhibits slight positive deviations from ideal behavior in all of the concentration range. Area and slope tests indicated that the data satisfied the Gibbs-Duhem equation for thermodynamic consistency. An additional check of the quality of the data was performed comparing the experimental vapor composition with the calculated vapor composition using obtained UNIFAC (11) predicted activity coefficients. The excellent agreement between both sets of data gives strength to our claims.

The analysis method (GLC) used in this work is assumed to be more reliable than that of Chandrashekara and Seshadri (1), who used density measurements to determine the sample composition. Although both sets of data were obtained at slightly different pressures, we feel that this difference cannot account for the abnormal behavior of Chandrashekara's data and that the latter are in error. Our activity coefficient data and those of Chandrashekara appear in Figure 2.

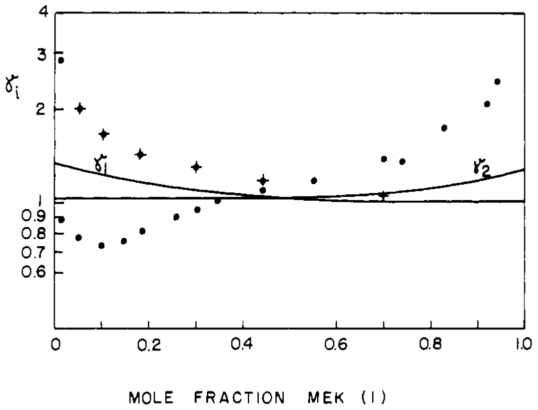

Figure 2. Activity coefficients: smooth curve, this work; points (●), Chandrashebara (1).

The following activity coefficients reported in Table II were correlated with the following three-constant Redlich-Kister equation (12)

$$\ln \gamma_1 = 0.47948x_2^2 - 2.6932x_2^3 + 2.49732x_2^4 \qquad (4)$$

$$\ln \gamma_2 = 2.07014x_1^2 - 4.39020x_1^3 + 2.49732x_2^4 \qquad (5)$$

with a relative error of less than 4%, and a Wilson correlation (13)

$$\ln \gamma_1 = -\ln (x_1 + x_2\Lambda_{12}) + x_2\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right] \qquad (6)$$

$$\ln \gamma_2 = -\ln (x_2 + x_1\Lambda_{21}) - x_1\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right] \qquad (7)$$

with a relative error smaller than 2% and parameter values $\Lambda_{12} = 0.8373$ and $\Lambda_{21} = 1.0643$.

Boiling points were correlated with the equation suggested by Wisniak and Tamir (14):

$$T = x_1T^0_1 + x_2T^0_2 + w + x_1x_2 \sum_{k=0}^{l} C_k(x_1 - x_2)^k \qquad (8)$$

$$w = x_1 \ln (y_1/x_1) + x_2 \ln (y_2/x_2) \qquad (9)$$

The value of w was found to be negligible. A Simplex optimization technique was used to determine the following values of the constants in eq 8:

$$c_0 = -52.719 \qquad c_1 = 30.396 \qquad c_2 = -21.484 \qquad c_3 = 26.682 \qquad (10)$$

The root mean square deviation of the fit was 0.279 (sum of squares SS = 1.087), which is very good if we consider that the first point (x_1 = 0.048) contributes 0.507 to SS.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical determinations.

Glossary

α, β, δ	constants, eq 3
B_{ii}, B_{ij}	second virial coefficient for pure component and the mixed virial coefficient, respectively
C_k	constant, eq 8
l	number of terms in the series expansion of $x_1 - x_2$
P	overall pressure, mmHg

P^0_i	vapor pressure of component *i* pure, mmHg
rmsd	root mean square deviation $[\sum(T_{\text{exptl}} - T_{\text{calcd}})^2/n]^{1/2}$
n	number of experimental points
t, T	temperature, °C, K
T^0_i	boiling temperature of component *i* pure at pressure P, K
V^0_i	molar volume of liquid pure component
x_i, y_i	mole fraction composition of component *i* in the liquid and vapor phases
γ_i	activity coefficient of component *i*
Λ_{ij}, Λ_{ji}	Wilson constants, eq 6 and 7
Subscript	
i	component *i*

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Received for review November 17, 1981. Accepted June 4, 1982.

Vapor–Liquid Equilibrium in the Systems Propyl Bromide–Acetic Acid, Propyl Bromide–Propionic Acid, and Propyl Bromide–Acetic Acid–Propionic Acid

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The vapor–liquid equilibria for the title systems were determined at 760 mmHg. Activity coefficients were calculated by assuming association in the vapor phase. Boiling points of the systems were correlated by empirical expressions; none of the systems studied exhibited azeotropic behavior. Tentative UNIFAC interaction parameters are reported for the pairs COOH, Br and Br, COOH.

In previous investigations on systems containing fatty acids, we have studied the vapor–liquid equilibrium properties of the systems formic acid–acetic acid–propionic acid (*1*), water–formic acid–propionic acid (*2*), water–formic acid–acetic acid (*3*), water–acetic acid–propionic acid (*3*), propionic acid–carbon tetrachloride (*4*), propionic acid–methyl isobutyl ketone (*4*), and acetic acid–carbon tetrachloride (*5*).

Inspection of the UNIFAC parameter table has indicated that the interaction parameters for the acid group COOH and bromine are not available (*6*). The aim of the present work is to initiate the accumulation of experimental data that will allow filling the missing information. For this purpose we have selected for study the vapor–liquid equilibrium of the systems indicated in the title.

Experimental Section

Purity of Materials. Analytical-grade fatty acids (99.5% +) were purchased from Fluka; propyl bromide (99.6% +) was supplied by Bromine Compounds Ltd., Beer-Sheva. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*7*) was used in the equilibrium determination. The experimental features have been described in previous publications (*3–5*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm in diameter, was packed with SP-1200 on 80–100 mesh Supelcoport, and was operated isothermally at 75 °C. Injector and detector temperatures were 200 and 210 °C, respectively. Very good separation was achieved under these conditions, and calibration analyses were carried to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta t = \pm 0.02$ °C.

Table I. Physical Properties of Pure Compounds

compd	refractive index at 20 °C	bp, °C
propyl bromide (1)	1.4316[a]	70.55[a]
	1.4317[b]	70.8[b]
acetic acid (2)	1.3717[a]	117.0[a]
	1.3716[b]	117.1[b]
propionic acid (3)	1.3860[a]	140.85[a]
	1.3865[b]	140.83[b]

[a] This work. [b] Reference *16*.

Results

The temperature–concentration measurements at 760 mmHg for the systems under consideration are presented in Tables III–V. Preliminary calculations showed that the activity coefficients calculated without taking into account the association effects were thermodynamically inconsistent. Fatty acids are known to undergo extensive association already at room temperature so that the real species present in the system are different from the nominal ones. The mathematics of associ-

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