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# Isobaric Vapor–Liquid Equilibria of Methyl Ethyl Ketone (1) + *o*-Dichlorobenzene (2), + Bromobenzene (2), and + Nitrobenzene (2)

**Ramanjaneyulu Kalluru and Krishnaiah Abburi***

*Department of Chemistry, College of Engineering, Sri Venkateswara University, Tirupati 517 502, India*

**Ramakrishna Machiraju**

*Regional Research Laboratory, Hyderabad 500 007, India*

**Boiling temperatures were measured for the binary systems methyl ethyl ketone (MEK) with *o*-dichlorobenzene, bromobenzene, and nitrobenzene at 300, 500, and 700 mmHg. The data were correlated by Wilson equation and the excess Gibbs energies at 25 °C were calculated.**

## Introduction

The present work forms part of a program of measurement of excess thermodynamic properties of nonelectrolyte binary solutions. In this paper we present boiling temperature measurement and derived excess Gibbs energies for three binary systems of methyl ethyl ketone with substituted benzenes.

## Experimental Section

A Swietoslawski ebulliometer was used for the measurement of the boiling points of the mixtures. The condenser of the ebulliometer was connected through a ballast to a vaccum system to ensure the required pressure. The pressure was regulated by a valve at the required constant value which is then determined with a U-tube mercury manometer. The temperatures of the boiling mixtures were measured with a precalibrated platinum resistance thermometer, connected to a digital display with 0.1 °C resolution.

Mixtures of known composition were prepared gravimetrically and introduced into the ebulliometer. When a steady state was reached, the temperature was read.

All the chemicals were purified by the methods described by Riddick and Bunger (*1*). Methyl ethyl ketone (BDH) was treated several times with saturated potassium carbonate solution. The two layers were then separated and the organic layer was distilled to remove water. It was then dried for 1 day over anhydrous potassium carbonate and finally fractionated. *o*-Dichlorobenzene (Riedel) was purified by fractional distillation under reduced pressure. Bromobenzene (BDH) was repeatedly washed with concentrated sulfuric acid until the acid developed no more color. It was then washed first with water and then with dilute potassium carbonate solution. After drying over anhydrous calcium chloride it was subjected to fractional distillation. Nitrobenzene (BDH) was dried over anhydrous calcium chloride for 2 days and the dried sample was subjected to fractional distillation. The purity of the samples was checked by comparing the measured densities and the boiling points with those reported in the literature (*2*). The data are presented in Table I.

## Results and Discussion

For the three binary systems the boiling point curves were determined at 300, 500, and 700 mmHg. The experimental data are reported in Tables II–IV.

The vapor-phase compositions and excess Gibbs free energies can be calculated if a model is assumed for the activity coefficients in the liquid phase. The empirical parameters of the model can then be calculated from the experimental data by minimizing the objective function

$$F = \sum_{i=1}^{N} \left( \frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}} \right) \tag{1}$$

where $P_{\text{exptl}}$ and $P_{\text{calcd}}$ are the experimental and calculated values of the total boiling pressures at the $i$th run for a mixture at composition $x$ and temperature $t$ and $N$ is the number of experimental data. The calculation of the boiling pressure at each point was made by solving the following equation

$$P_{\text{calcd}} = \frac{\gamma_1(x,t)\, x f^\circ_{1,\text{L}}(t,P)}{\hat{\phi}_1(y,P,t)} + \frac{\gamma_2(x,t)(1-x) f^\circ_{2,\text{L}}(t,P)}{\hat{\phi}_2(y,P,t)} \tag{2}$$

In eq 2 $\gamma_1$ and $\gamma_2$ are the activity coefficients given by the liquid-phase model chosen, $f^\circ_{i,\text{L}}$ is the standard-state fugacity of component $i$ at temperature $t$ and pressure $P$ and $\hat{\phi}_i$ is the fugacity coefficient for component $i$ in the vapor mixture. For normal liquids, the standard-state fugacity $f^\circ_{i,\text{L}}$ at temperature $t$ and pressure $P$ is given by

$$f^\circ_{i,\text{L}} = P_{\text{s},i}(t)\, \phi_{\text{s},i}(t) \exp\left[ V_{i,\text{L}} \left( \frac{P - P_{\text{s},i}}{RT} \right) \right] \tag{3}$$

Here $P_{\text{s},i}$ is the vapor pressure of component $i$ at temperature $t$, $\phi_{\text{s},i}$ is the fugacity coefficient of pure component $i$ at saturation condition, and $V_{i,\text{L}}$ is the liquid molar volume of component $i$, which is estimated by the modified Rackett equation (*3*). The vapor pressures of pure components can be calculated by means of Antoine's equation. The Antoine constants are given in Table I.

The fugacity coefficients $\hat{\phi}_i$ and $\phi_{\text{s},i}$ were calculated by means of the virial equation of state

$$\ln \phi_{\text{s},i} = B_i P_{\text{s},i} \tag{4}$$

$$\ln \hat{\phi}_i = (P/RT)[B_i + (1 - y_i)^2 \delta_{12}] \tag{5}$$

with

$$\delta_{12} = 2B_{12} - B_1 - B_2 \tag{6}$$

where $B_1$ and $B_2$ are the second virial coefficients of components 1 and 2, respectively, and $B_{12}$ is the cross virial coefficient. The second virial coefficients were calculated by Tsonopoulous (*4*) correlation. For calculating the cross virial

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**Table I. Densities, Boiling Points, and Antoine Constants of Pure Components**

| substance | density, g/cm$^3$ present work | density, g/cm$^3$ lit. | boiling point, K present work | boiling point, K lit. | Antoine constants[e] *A* | Antoine constants[e] *B* | Antoine constants[e] *C* |
|---|---|---|---|---|---|---|---|
| methyl ethyl ketone | 0.794 56 | 0.794 52[a] | 352.6 | 352.8 | 7.063 56 | 1261.34 | 221.969 |
| *o*-dichlorobenzene | 1.294 54 | 1.294 57[b] | 453.4 | 453.6 | 7.070 26 | 1649.55 | 213.310 |
| bromobenzene | 1.481 54 | 1.481 50[c] | 429.1 | 429.1 | 6.860 64 | 1438.82 | 205.441 |
| nitrobenzene | 1.193 46 | 1.193 41[d] | 483.7 | 483.9 | 7.115 62 | 1746.59 | 201.783 |

[a] Ceuterick, P. *Bull. Soc. Chim. Belg.* **1936**, *45*, 553. [b] Reddy, K. D. Ph.D. Thesis, S. V. University, India, 1985. [c] Young, S. *Sci. Proc. R. Dublin Soc.* **1910**, *12*, 374. [d] Timmermans, J.; Roland, H. M. *J. Chim. Phys.* **1935**, *32*, 589. [e] Reference *6*.

**Table II. Boiling Temperatures of Mixtures of Methyl Ethyl Ketone (1)–*o*-Dichlorobenzene (2) at 300, 500, and 700 mmHg**

| $X_1$ | *T*, °C | $X_1$ | *T*, °C | $X_1$ | *T*, °C |
|---|---|---|---|---|---|
| | | *P* = 300 mmHg | | | |
| 0.1114 | 106.6 | 0.4782 | 69.3 | 0.9196 | 54.6 |
| 0.2702 | 84.2 | 0.5597 | 66.0 | 0.9529 | 54.0 |
| 0.3065 | 80.9 | 0.6426 | 62.3 | | |
| 0.3803 | 75.5 | 0.7835 | 58.7 | | |
| | | *P* = 500 mmHg | | | |
| 0.1114 | 126.4 | 0.4782 | 84.5 | 0.9196 | 69.1 |
| 0.2702 | 100.4 | 0.5597 | 80.5 | 0.9529 | 67.9 |
| 0.3065 | 97.2 | 0.6426 | 77.8 | | |
| 0.3803 | 91.3 | 0.7835 | 73.0 | | |
| | | *P* = 700 mmHg | | | |
| 0.1114 | 139.6 | 0.4782 | 95.6 | 0.9196 | 78.8 |
| 0.2702 | 113.3 | 0.5597 | 91.5 | 0.9529 | 78.2 |
| 0.3065 | 109.6 | 0.6426 | 88.2 | | |
| 0.3803 | 103.7 | 0.7835 | 83.7 | | |

**Table III. Boiling Temperatures of Mixtures of Methyl Ethyl Ketone (1)–Bromobenzene (2) at 300, 500, and 700 mmHg**

| $X_1$ | *T*, °C | $X_1$ | *T*, °C | $X_1$ | *T*, °C |
|---|---|---|---|---|---|
| | | *P* = 300 mmHg | | | |
| 0.1137 | 96.0 | 0.5254 | 66.1 | 0.8963 | 55.2 |
| 0.2217 | 83.7 | 0.6335 | 62.7 | 0.9521 | 54.0 |
| 0.3338 | 75.5 | 0.7404 | 59.4 | | |
| 0.4355 | 69.6 | 0.8184 | 56.9 | | |
| | | *P* = 500 mmHg | | | |
| 0.1137 | 113.5 | 0.5254 | 81.0 | 0.8963 | 69.4 |
| 0.2217 | 99.7 | 0.6335 | 77.1 | 0.9521 | 67.6 |
| 0.3338 | 90.9 | 0.7404 | 73.8 | | |
| 0.4355 | 85.8 | 0.8184 | 71.5 | | |
| | | *P* = 700 mmHg | | | |
| 0.1137 | 126.8 | 0.5254 | 91.6 | 0.8963 | 79.8 |
| 0.2217 | 111.8 | 0.6335 | 87.6 | 0.9521 | 78.1 |
| 0.3338 | 102.7 | 0.7404 | 84.2 | | |
| 0.4355 | 96.8 | 0.8184 | 81.8 | | |

**Table IV. Boiling Temperatures of Mixtures of Methyl Ethyl Ketone (1)–Nitrobenzene (2) at 300, 500, and 700 mmHg**

| $X_1$ | *T*, °C | $X_1$ | *T*, °C | $X_1$ | *T*, °C |
|---|---|---|---|---|---|
| | | *P* = 300 mmHg | | | |
| 0.1264 | 111.9 | 0.4737 | 70.7 | 0.8375 | 57.0 |
| 0.1906 | 97.6 | 0.5206 | 67.8 | 0.9123 | 54.4 |
| 0.3057 | 83.0 | 0.6524 | 63.8 | | |
| 0.3843 | 76.3 | 0.7695 | 59.4 | | |
| | | *P* = 500 mmHg | | | |
| 0.1264 | 132.2 | 0.4737 | 86.1 | 0.8375 | 71.6 |
| 0.1906 | 116.6 | 0.5206 | 83.7 | 0.9123 | 68.9 |
| 0.3057 | 99.6 | 0.6524 | 78.6 | | |
| 0.3843 | 92.9 | 0.7695 | 73.0 | | |
| | | *P* = 700 mmHg | | | |
| 0.1264 | 147.2 | 0.4737 | 98.3 | 0.8375 | 81.9 |
| 0.1906 | 129.3 | 0.5206 | 95.4 | 0.9123 | 79.2 |
| 0.3057 | 112.3 | 0.6524 | 89.5 | | |
| 0.3843 | 104.8 | 0.7695 | 84.1 | | |

**Table V. Wilson Constants $(\lambda_{12} - \lambda_{11})/R$ and $(\lambda_{21} - \lambda_{22})/R$ for the Three Systems**

| system | $(\lambda_{12} - \lambda_{11})/R$, K | $(\lambda_{21} - \lambda_{22})/R$, K |
|---|---|---|
| methyl ethyl ketone (1)–dichlorobenzene (2) | −101.28 | 361.34 |
| methyl ethyl ketone (1)–bromobenzene (2) | 53.164 | 126.38 |
| methyl ethyl ketone (1)–nitrobenzene (2) | −148.05 | 413.02 |

**Table VI. Excess Gibbs Energy Data at 25 °C for the Mixtures Methyl Ethyl Ketone (1)–1,2-Dichlorobenzene (2), Methyl Ethyl Ketone (1)–Bromobenzene (2), and Methyl Ethyl Ketone (1)–Nitrobenzene (2)**

| $X_1$ | $G^E$, J/mol | $X_1$ | $G^E$, J/mol | $X_1$ | $G^E$, J/mol |
|---|---|---|---|---|---|
| | | MEK–Dichlorobenzene | | | |
| 0.00 | 0.0 | 0.35 | 161.9 | 0.70 | 219.6 |
| 0.05 | 26.2 | 0.40 | 179.2 | 0.75 | 209.7 |
| 0.10 | 51.6 | 0.45 | 194.2 | 0.80 | 192.1 |
| 0.15 | 76.1 | 0.50 | 206.7 | 0.85 | 165.2 |
| 0.20 | 99.6 | 0.55 | 216.1 | 0.90 | 126.5 |
| 0.25 | 121.8 | 0.60 | 221.9 | 0.95 | 73.0 |
| 0.30 | 142.7 | 0.65 | 223.3 | 1.00 | 0.0 |
| | | MEK–Bromobenzene | | | |
| 0.00 | 0.0 | 0.35 | 275.6 | 0.70 | 279.0 |
| 0.05 | 53.7 | 0.40 | 294.3 | 0.75 | 252.8 |
| 0.10 | 102.9 | 0.45 | 307.4 | 0.80 | 219.0 |
| 0.15 | 147.4 | 0.50 | 314.5 | 0.85 | 177.2 |
| 0.20 | 187.1 | 0.55 | 315.5 | 0.90 | 127.1 |
| 0.25 | 221.8 | 0.60 | 310.0 | 0.95 | 68.2 |
| 0.30 | 251.4 | 0.65 | 298.0 | 1.00 | 0.0 |
| | | MEK–Nitrobenzene | | | |
| 0.00 | 0.0 | 0.35 | 120.6 | 0.70 | 179.3 |
| 0.05 | 18.3 | 0.40 | 135.1 | 0.75 | 173.9 |
| 0.10 | 36.5 | 0.45 | 148.2 | 0.80 | 162.0 |
| 0.15 | 54.3 | 0.50 | 159.7 | 0.85 | 141.9 |
| 0.20 | 71.8 | 0.55 | 169.1 | 0.90 | 110.9 |
| 0.25 | 88.8 | 0.60 | 176.0 | 0.95 | 65.4 |
| 0.30 | 105.1 | 0.65 | 179.0 | 1.00 | 0.0 |

coefficient, $B_{12}$, the interaction parameter $k_{12}$ is taken as 0.12, which was suggested by Tsonopoulous (*4*) for similar systems. The effect of uncertainty in this value on *y* values is negligible and is less than 0.2% even when $k_{12}$ was taken as zero (*5*, *6*).

The model chosen to describe the activity coefficients in the liquid phase is the Wilson model (*7*)

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right) \qquad (7)$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) + x_1 \left( \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} \right) \qquad (8)$$

where

$$\Lambda_{12} = \frac{V_{2,L}}{V_{1,L}} \exp\left( \frac{-\lambda_{12} - \lambda_{11}}{RT} \right) \qquad (9)$$

$$\Lambda_{21} = \frac{V_{1,L}}{V_{2,L}} \exp\left(\frac{-\lambda_{21} - \lambda_{22}}{RT}\right) \qquad (10)$$

Here $V_{1,L}$ and $V_{2,L}$ are the liquid molar volumes and $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ are the model parameters with $\lambda_{12} = \lambda_{21}$. The Wilson parameters, obtained by minimizing the objective function defined by eq 1, are reported in Table V. All the three sets of data at 300, 500, and 700 mmHg were used in data reduction.

The excess Gibbs energies at 25 °C for the three systems were also calculated with these model parameters by using the equation

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (11)$$

and are presented in Table VI.

### Glossary

| | |
|---|---|
| $A$, $B$, $C$ | Antoine constants |
| $p$ | pressure, mmHg |
| $t$ | temperature, °C |
| $x$ | mole fraction in liquid phase |
| $y$ | vapor composition |

*Greek Letters*

| | |
|---|---|
| $\gamma$ | activity coefficient |
| $\Lambda$ | Wilson parameter |

*Subscripts*

| | |
|---|---|
| 1 | methyl ethyl ketone |
| 2 | substituted benzene |

**Registry No.** MEK, 78-93-3; *o*-dichlorobenzene, 95-50-1; bromobenzene, 108-86-1; nitrobenzene, 98-95-3.

### Literature Cited

(1) Riddick, J. A.; Bunger, W. B. *Organic Solvents*, 3rd ed.; Wiley Interscience: New York, 1970.
(2) Timmermans, J. *Physico-chemical Properties of Pure Organic Compounds*; Elsevier: Amsterdam, 1950.
(3) Spencer, C. F.; Danner, R. P. *J. Chem. Eng. Data* **1972**, *17*, 236.
(4) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(5) Boublik, T.; Fried, V.; Hala, E. *The Vapour Pressures of Pure Substances*; Elsevier: Amsterdam, 1973.
(6) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1977.
(7) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.

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# Vapor–Liquid Equilibria for *m*-Cresol/Tetralin and Tetralin/Quinoline at Temperatures between 523 and 598 K

**Vicki G. Niesen and Victor F. Yesavage***
*Chemical Engineering and Petroleum Refining Department, Colorado School of Mines, Golden, Colorado 80033*

**Binary vapor–liquid equilibria are reported for the binary systems of *m*-cresol/tetralin and tetralin/quinoline at 523.15, 548.15, 573.15, and 598.15 K as well as tetralin vapor pressures over the same temperature region. These compounds are of interest because they form highly nonideal mixtures and are also models for coal liquids. Due to hydrogen-bonding capabilities, both *m*-cresol and quinoline are quite hygroscopic. Water was found to be a major impurity and had very large effects on the vapor–liquid equilibria measurements, even at extremely low concentrations. The *m*-cresol/tetralin data indicated a low-boiling azeotrope that moved toward higher *m*-cresol concentrations and eventually disappeared as the temperature increased. The tetralin/quinoline system exhibited small departures from ideal behavior.**

## Introduction

As part of a continuing effort (*1*, *2*) to study the phase behavior of coal-derived liquid model compounds, vapor–liquid equilibria (VLE) measurements were generated for the binary systems *m*-cresol/1,2,3,4-tetrahydronaphthalene (tetralin) and tetralin/quinoline at the four isotherms 523.15, 548.15, 573.15, and 598.15 K as well as vapor pressure data for tetralin. Phase behavior data are important not only for use in engineering design and analysis, but also to check thermodynamic property correlations. Only a limited amount of phase behavior data is available for highly nonideal systems and even less data exist at elevated conditions where many chemical processes operate.

Previously reported work (*2*) studied the binary system of *m*-cresol/quinoline to model the interactions between an acidic oxygen compound and a basic nitrogen compound which are likely to be found in coal liquids. Both binary vapor–liquid equilibrium (VlE) data at 523.15, 548.15, 573.15, and 598.15 K and vapor pressure data over the same temperature range for pure *m*-cresol and quinoline were reported. The present study considers the interactions between an acidic oxygen compound (*m*-cresol) and a naphthenic compound (tetralin) as well as the interactions between a basic nitrogen compound (quinoline) and a naphthenic compound (tetralin). Complementary enthalpy data for the *m*-cresol/quinoline, *m*-cresol/tetralin, and tetralin/quinoline systems have been obtained at the Colorado School of Mines (*3*, *4*) over a temperature range of 291–650 K and pressures of 101.3–10342 kPa.

A major problem in obtaining the VLE data was that both *m*-cresol and quinoline are capable of hydrogen bonding and consequently are hygroscopic. Trace amounts of water can significantly affect the measured vapor pressure especially for systems containing *m*-cresol. Estimations of the effects of water on our measurements have been previously reported (*2*).

## Experimental Details

The experimental apparatus for obtaining these measurements has been discussed in detail previously (*1*). The measurements were made on a flow vapor–liquid equilibrium apparatus and analyzed on a Hewlett-Packard 5710A gas chromatograph with a flame ionization detector. The flow system is advantageous for compounds that decompose at high temperatures since the residence time in the heated portion of the flow system is only about 5 min. Estimated experimental error

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