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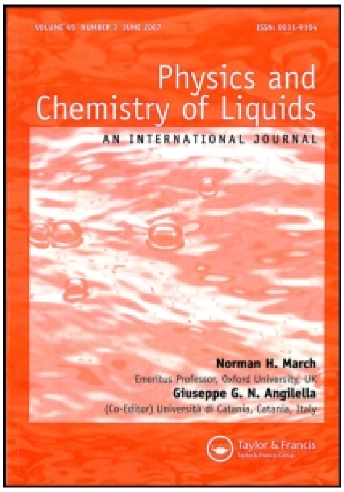

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Isothermal Phase Equilibria in the Binary Systems Formed by Methyl-Iso-Butyl Ketone with Alkylbenzenes

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ISOTHERMAL PHASE EQUILIBRIA IN THE BINARY SYSTEMS FORMED BY METHYL-ISO-BUTYL KETONE WITH ALKYLBENZENES

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The gas chromatographic method proposed by us for simple and accurate measurement of isothermal phase equilibrium has been applied to the binary mixtures formed by alkylbenzenes with methyl-iso-butyl ketone. Results on the binary mixtures of methyl-iso-butyl ketone with benzene, toluene, *o*-xylene, *p*-xylene and ethylbenzene are presented in this paper.

Keywords: Phase equilibria; Alkylbenzenes; Methyl-iso-butyl ketone;
Activity coefficients

INTRODUCTION

In continuation of our work on isothermal phase equilibria of binary mixtures using gas chromatographic techniques [1–4] this work on the binary mixtures formed by methyl-iso-butyl ketone with alkylbenzenes noted in the abstract has been taken up.

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EXPERIMENTAL

Solvents and Solutes

Analar/Spectroscopic grade: benzene, toluene, *o*-xylene, *p*-xylene and ethylbenzene as well as methyl-iso-butyl ketone procured from E. Merck, Darmsdat (FRG) are used in the present study. No significant second peaks have been observed when the substances have been injected to the gas chromatograph with the object of determining the purity. As an additional check, the refractive-index and density of the substances have been measured at 293.15 K. The values compare favourably with the literature data [5,6] as shown in Table I.

Support Material

Chromosdrb-W(40/60), procured from Alltech, Arlington Heights, Illinois (USA), is employed as the support material. A stainless steel column of 60.96 cm length and 6.35 mm inner diameter has been chosen for use, to provide for the ease of handling, filling and removal of the support material and proper separation. The support material is initially dried for 3–4 h in an oven maintained at 373 ± 5 K. A known mass of the dry support material is soaked in an excess quantity of the stationary phase being used in the experiment. The contents are kept in cold environment (a refrigerator) overnight. The solvent in excess of the desired percent loading is removed by bubbling pure nitrogen gas. The coated support material is then filled carefully inside the stainless steel column. The column is installed inside the oven of the

TABLE I Comparison of the refractive-index and density of the substances used with the literature data at 293.15 K

Substance	*Refractive-index*		*Density* (g/ml)	
	This work	*Literature [Source]*	*This work*	*Literature [Source]*
Benzene	1.5105	1.5011 [5]	0.8794	0.8790 [5]
Toluene	1.4978	1.4969 [5]	0.8682	0.8669 [5]
o-Xylene	1.5056	1.5054 [5]	0.8805	0.8802 [5]
p-Xylene	1.4956	1.4958 [5]	0.8612	0.8610 [5]
Ethylbenzene	1.4961	1.4959 [5]	0.8673	0.8670 [5]
Methyl-iso-butylketone	1.3967	1.3962 [6]	0.7975	0.7978 [6]

Model 5840 A Hewelett Packard make microprocessor controlled gas chromatograph.

Carrier Gas and Presaturation

Pure helium gas supplied by Indian Oxygen Limited, Special Gases Division, Bombay (India) is used as the carrier gas. The gas is initially presaturated with the solvent by passing it through a specially designed presaturator described earlier [1]. Before entering the presaturator, the carrier gas is passed through the purifiers containing a molecular sieve and manganous oxide to remove the traces of moisture and oxygen likely to interfere with the functioning of the thermal conductivity detector being used as the sensing element in this work. Presaturated helium gas is run through the column for 10–15 min at an ambient temperature maintained between 293 and 298 K, and its flow rate is recorded. The flow rate is measured using a soap-bubble flow meter to an accuracy of 0.05 ml/min. Three or four measurements are carried out to be able to calculate a reliable value of the specific retention volume.

Actual Experiment

The injection port, detector and column temperatures of the chromatograph are set at the desired levels by means of the microprocessor. The injection port temperature is maintained 25 K above the boiling point of the solute while the detector temperature is maintained 50 K above the boiling point of the solute. When the injection port, thermal conductivity detector and column temperature conditions are set the system is ready for use.

Initially a solute with small retention time like acetone or diethyl ether is injected into the column. After elution of the corresponding peak, the column is removed from the oven and weighed. The column is reinstalled in the oven and the same solute is injected again. The constancy of the retention time in such successive experiments helps in the measurement of the quantity of solvent present on the support material accurately. As the thermal conductivity detector is used in these experiments, the retention time due the dead volume of the porosity inside the column is detected by injecting 1 μl of air.

One micro-litre of the solute is subsequently injected to determine its retention time.

RESULTS AND DISCUSSION

The values of the infinite dilution activity coefficients γ_1^α and γ_2^α are calculated from the observations, using the method of treatment of the data described earlier [1]. The infinite dilution activity coefficients of the five binary systems studied in this work are given in Table II.

The values of γ_1^α and γ_2^α are used to calculate the Wilson parameters Λ_{12} and Λ_{21} by the simultaneous solution of

$$\ln \gamma_1^\alpha = -\ln \Lambda_{12} - \Lambda_{21} + 1 \tag{1}$$

and

$$\ln \gamma_2^\alpha = -\ln \Lambda_{21} - \Lambda_{12} + 1 \tag{2}$$

The Wilson model equations for the activity coefficients

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \tag{3}$$

and

$$\ln \gamma_2 = -\ln(x_1 + \Lambda_{21}x_1) + x_1\left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right] \tag{4}$$

TABLE II Infinite dilution activity coefficients and Wilson parameters of the binary systems studied in this work

Component 1	*Component 2*	*Temperature,* °C	γ_1^α	γ_2^α	Λ_{12}	Λ_{21}
Benzene	Methyl-iso-butyl ketone	40	1.840	4.184	1.2192	0.1920
Toluene	Methyl-iso-butyl ketone	40	2.002	1.781	0.5754	0.8585
Methyl-iso-butyl ketone	*o*-Xylene	50	2.045	4.316	1.0712	0.2158
Methyl-iso-butyl ketone	*p*-Xylene	50	1.814	5.151	1.2972	0.1442
Methyl-iso-butyl ketone	Ethylbenzene	50	1.799	5.151	1.3104	0.1424

are used to calculate the values of γ_1 and γ_2 at regular intervals of the liquid phase composition (x_1) to facilitate the construction of the phase diagrams. The total pressure at each point is calculated from

$$P_{\text{total}} = \gamma_1 x_1 P_1^{\text{sat}} + \gamma_2 x_2 P_2^{\text{sat}} \tag{5}$$

where P_1^{sat} and P_2^{sat} are the saturated vapor pressures of the pure components 1 and 2 respectively. The values of the vapor pressures are calculated from the Antoine constants given in Reid *et al.* [7].

At equilibrium, the fugacity of the component 1 in the vapor phase

$$f_1^V = y_1 \phi_{1V} P_{\text{total}} \tag{6}$$

is equated to the fugacity of the same component in the liquid phase

$$f_1^L = x_1 \gamma_1 P_1^{\text{sat}}$$

As the present set of experiments are carried out at the atmospheric pressure, the vapor phase imperfection coefficient ϕ_{1V} is assumed to be unity, enabling us to calculate the vapor phase composition from

$$y_1 = x_1 \gamma_1 P_1^{\text{sat}} / P_{\text{total}} \tag{8}$$

Plots of x_1 versus y_1 are drawn in Figs. 1–5. Based on the comparisons of the results of our method presented in our earlier papers [1–4] the isothermal phase equilibrium data presented in this paper are expected to be reliable.

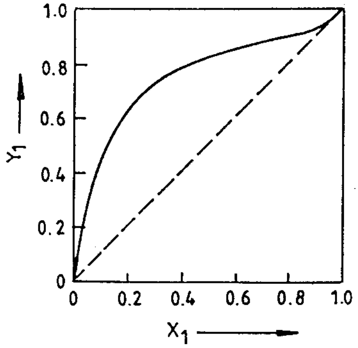

FIGURE 1 Phase diagram for benzene (1) + methylisobutyl ketone (2) at 40°C.

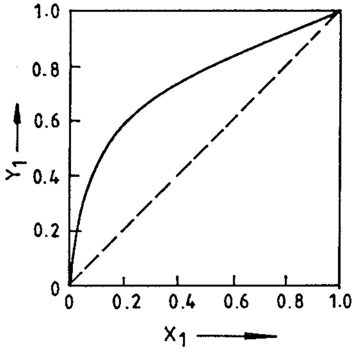

FIGURE 2 Phase diagram for toluene (1) + methylisobutyl ketone (2) at 40°C.

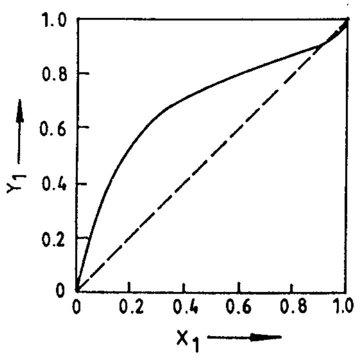

FIGURE 3 Phase diagram for methylisobutyl ketone (1) + *o*-xylene (2) at 50°C.

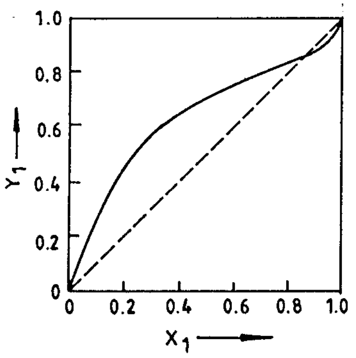

FIGURE 4 Phase diagram for methylisobutyl ketone (1) + *p*-xylene (2) at 50°C.

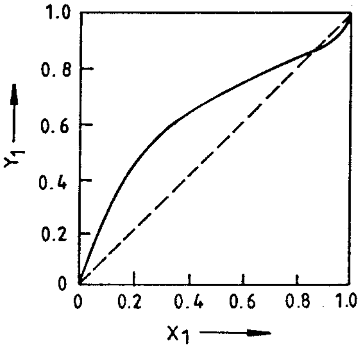

FIGURE 5 Phase diagram for methylisobutyl ketone (1) + ethylbenzene (2) at 50°C.

TABLE III Isothermal vapor-liquid equilibria predicted from infinite dilution activity coefficient measurements

Total pressure (mm Hg)	x_1	y_1
Benzene(1) + Methyl-iso-butyl ketone(2) at 40°C		
43.8	0.0	0.00
71.1	0.1	0.44
94.9	0.2	0.62
115.2	0.3	0.72
132.2	0.4	0.79
146.3	0.5	0.83
157.7	0.6	0.86
166.7	0.7	0.89
173.7	0.8	0.91
179.4	0.9	0.94
182.8	1.0	1.00
Methyl-iso-butyl ketone(1) + *o*-Xylene(2) at 50°C		
25.5	0.0	0.00
36.3	0.1	0.36
45.1	0.2	0.54
52.3	0.3	0.64
58.1	0.4	0.71
62.6	0.5	0.76
66.0	0.6	0.80
68.5	0.7	0.83
70.3	0.8	0.87
71.3	0.9	0.91
70.2	1.0	1.00
Methyl-iso-butyl ketone(1) + Ethylbenzene (2) at 50°C		
35.1	0.0	0.00
43.7	0.1	0.27
51.2	0.2	0.44

(*Continued*)

TABLE III Continued

Total pressure (mm Hg)	x_1	y_1
57.5	0.3	0.56
62.8	0.4	0.64
67.1	0.5	0.70
70.3	0.6	0.75
72.5	0.7	0.80
73.8	0.8	0.84
74.0	0.9	0.88
70.2	1.0	1.00
Toluene(1) + Methyl-iso-ketone(2) at 40°C		
43.8	0.0	0.00
70.9	0.1	0.44
90.9	0.2	0.60
106.6	0.3	0.69
119.7	0.4	0.75
131.3	0.5	0.80
141.9	0.6	0.84
152.1	0.7	0.88
162.2	0.8	0.92
172.4	0.9	0.94
182.8	1.0	1.00
Methyl-iso-butyl ketone(1) + *p*-Xylene(2) at 50°C		
32.5	0.0	0.00
41.4	0.1	0.29
49.2	0.2	0.46
55.8	0.3	0.58
61.3	0.4	0.66
65.7	0.5	0.72
69.1	0.6	0.77
71.5	0.7	0.81
73.0	0.8	0.85
73.4	0.9	0.89
70.2	1.0	1.00

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