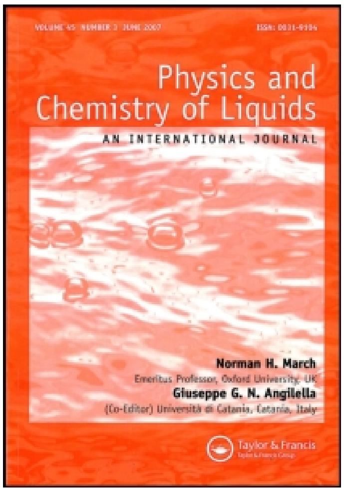

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ISOTHERMAL PHASE EQUILIBRIUM STUDIES ON THE BINARY MIXTURES OF SOME ALKYLBENZENES

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The gas chromatographic method proposed by us for simple and accurate measurement of isothermal phase equilibria has been applied to the binary mixtures formed by alkylbenzenes amongst themselves. Results on the binary mixtures of: benzene + toluene, toluene + *o*-xylene, toluene + *p*-xylene, toluene + ethylbenzene, ethylbenzene + *o*-xylene and ethylbenzene + *p*-xylene are presented in this paper. The present measurements on benzene + toluene system at 40°C are in good agreement with the isothermal phase equilibrium data available in the literature.

Keywords: Phase equilibria; alkyl benzenes; activity coefficients

INTRODUCTION

In continuation of our work on the isothermal phase equilibria of binary mixtures using gas chromatographic techniques [1 – 3] this investigation on the binary mixtures formed by the alkylbenzenes amongst themselves, noted in the abstract has been taken up.

EXPERIMENTAL

Solvents and Solutes

Analar grade/Spectroscopic grade: benzene, toluene, *o*-xylene, *p*-xylene and ethylbenzene, procured from M/s E. Merck, Darmstadt

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* Corresponding author.

(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 [4] as shown in Table I.

Support Material

Chromosorb-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 to 4 hours 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 Model 5840 A Hewlett Packard make microprocessor controlled gas chromatograph.

Carrier Gas and Presaturation

Pure helium gas supplied by M/s Indian Oxygen Limeted, Special Gases Division, Bombay (India) is used as the carrier gas. The gas

TABLE I Comparison of the Refractive-index and Density of the pure liquids with literature data from Driesbach [4] at 293.15 K

	Refractive-index		*Density, g/ml*	
Substance	*This work*	*Literature*	*This work*	*Literature*
Benzene	1.5015	1.5011	0.8794	0.8790
Toluene	1.4978	1.4969	0.8682	0.8669
o-Xylene	1.5056	1.5054	0.8805	0.8802
p-Xylene	1.4956	1.4958	0.8612	0.8610
Ethylbenzene	1.4961	1.4959	0.8673	0.8670

is initially presaturated with the solvent by passing 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 dioxide 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 main column of the chromatograph at a constant ambient temperature between 293 and 298 K. The gas is allowed through the column for 10 to 15 minutes, and its flow rate 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 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 set conditions of the injection port, thermal conductivity detector and column temperature are reached, the system is ready for use.

Initially, a solute with a small retention time like acetone or diethylether is injected into the column. After elution of the corresponding peak, the column is removed from the oven and its weight noted. The column is reinstalled in the oven and the same solute 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 accurately. As the thermal conductivity detector is used in these investigations, the retention time due to the dead volume caused by the porosity inside the column is detected by injecting one micro-litre of air. One micro-litre of the solute is subsequently injected and its retention time noted.

RESULTS AND DISCUSSION

The value of the infinite dilution activity coefficients γ_1^∞ and γ_2^∞ are calculated from the observations, using the method of treatment of the data described earlier [1]. The infinite dilution activity coefficients of the six binary systems studied in this work are presented in Table II. The value of γ_1^∞ and γ_2^∞ are used to calculate the Wilson parameters Λ_{12} and Λ_{21} by the simultaneous solution of the equations

$$\ln\gamma_1^\infty = -\ln\Lambda_{12} - \Lambda_{21} + 1 \qquad (1)$$

$$\ln\gamma_2^\infty = -\ln\Lambda_{21} - \Lambda_{12} + 1 \qquad (2)$$

The Wilson model equations for the activity coefficients

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

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

and 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 calcualted from

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

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

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^∞	γ_2^∞	Λ_{12}	Λ_{21}
Benzene	Toluene	40	0.927	0.888	0.3118	2.2412
Toluene	*o*-Xylene	40	0.965	0.857	0.2221	2.5402
Toluene	*p*-Xylene	40	1.481	0.898	0.1279	2.6636
Toluene	Ethylbenzene	40	0.988	1.060	1.8024	0.4229
Ethylbenzene	*o*-Xylene	40	0.851	1.861	2.9614	0.0757
Ethylbenzene	*p*-Xylene	40	0.893	1.588	2.9664	0.0882

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

Total pressure/mm Hg	x_1	y_1	*Total pressure/mm Hg*	x_1	y_1
Benzene(1) + Toluene (2)			Toluene (1) + *o*-Xylene (2)		
60.5	0.0	0.00	15.3	0.0	0.00
71.2	0.1	0.23	19.3	0.1	0.28
82.0	0.2	0.41	23.1	0.2	0.47
93.5	0.3	0.55	27.3	0.3	0.61
105.4	0.4	0.66	31.7	0.4	0.71
117.9	0.5	0.75	36.4	0.5	0.79
130.7	0.6	0.82	41.2	0.6	0.86
143.7	0.7	0.88	46.0	0.7	0.91
156.7	0.8	0.93	50.1	0.8	0.94
169.8	0.9	0.97	55.7	0.9	0.97
182.8	1.0	1.00	60.5	1.0	1.00
Toluene(1) + *p*-Xylene (2)			Toluene (1) + Ethylbenzene (2)		
19.8	0.0	0.00	21.5	0.0	0.00
24.3	0.1	0.25	25.3	0.1	0.24
27.7	0.2	0.41	29.3	0.2	0.41
31.2	0.3	0.54	33.2	0.3	0.55
35.0	0.4	0.65	37.2	0.4	0.65
39.1	0.5	0.74	41.2	0.5	0.74
43.3	0.6	0.82	45.2	0.6	0.81
47.5	0.7	0.88	49.1	0.7	0.87
51.9	0.8	0.93	53.0	0.8	0.92
56.2	0.9	0.97	56.8	0.9	0.96
60.5	1.0	1.00	60.5	1.0	1.00
Ethylbenzene (1) + *o*-Xylene			Ethylbenzene (1) + *p*-Xylene (2)		
15.3	0.0	0.00	19.8	0.0	0.00
15.8	0.1	0.13	19.8	0.1	0.10
16.4	0.2	0.26	19.9	0.2	0.21
17.0	0.3	0.38	20.0	0.3	0.32
17.8	0.4	0.50	20.3	0.4	0.43
18.7	0.5	0.61	20.7	0.5	0.55
19.7	0.6	0.71	21.2	0.6	0.66
20.8	0.7	0.80	21.8	0.7	0.76
21.9	0.8	0.88	22.5	0.8	0.85
22.7	0.9	0.93	23.0	0.9	0.92
23.1	1.0	1.00	23.1	1.0	1.00

calculated from the Antoine equation from the set of constants given in Reid *et al.* [5].

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

$$f_1^L = x_1\gamma_1 P_1^{\text{sat}} \tag{7}$$

As the present set of measurements 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 Figures 1 to 6. In Figure 1, the x_1 versus y_1 data for the benzene + toluene binary mixtures measured in

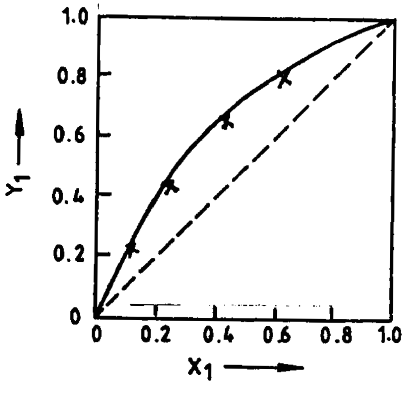

FIGURE 1 Phase diagram for benzene(1) + toluene(2) at 40°C.

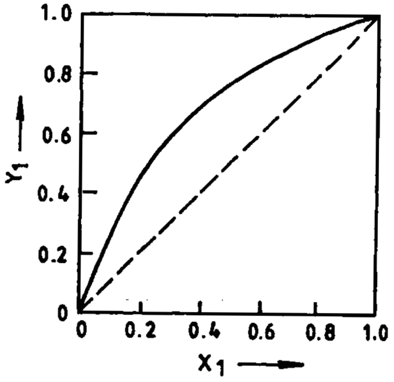

FIGURE 2 Phase diagram for toluene(1) + *o*-xylene(2) at 40°C.

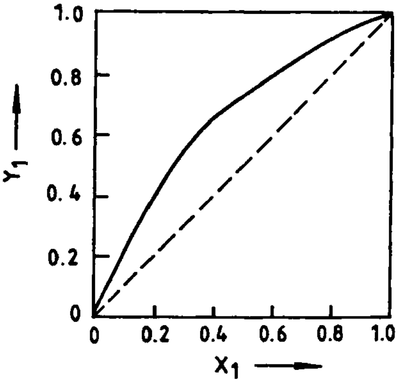

FIGURE 3 Phase diagram for toluene(1) + *p*-oxylene(2) at 40°C.

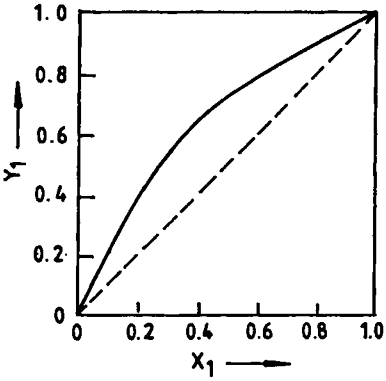

FIGURE 4 Phase diagram for toluene(1) + ethylbenzene(2) at 40°C.

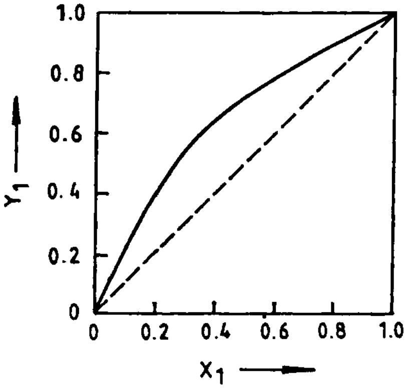

FIGURE 5 Phase diagram for ethylbenzene(1) + *o*-xylene(2) at 40°C.

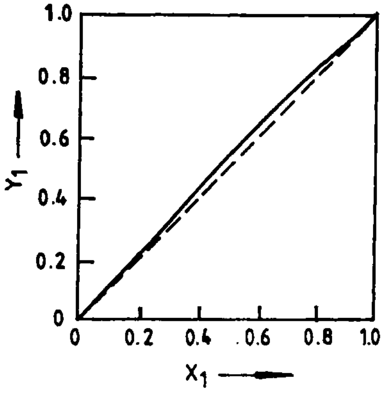

FIGURE 6 Phase diagram for ethylbenzene(1) + *p*-xylene(2) at 40°C.

the conventional way by Griswold *et al.* [6] are shown by *X* marks. It can be seen from the figure that the agreement of the present work with the literature data is good.

References

[1] Ashraf, S. M., Ramakrishna, M. and Prasad, D. H. L. (1997). *Physics and Chemistry of Liquids*, **34**, 89.

[2] Ashraf, S. M. and Prasad, D. H. L. (1997). *Physics and Chemistry of Liquids* (in Press).

[3] Ashraf, S. M. and Prasad, D. H. L. *Physics and Chemistry of Liquids* (accepted for publication).

[4] Driesbach, R. R. (1955, 1957). *Physical Properties of Chemical Compounds*, **I** & **II**, American Chemical Society, Washington D C.

[5] Reid, R. C., Prausnitz, J. M. and Sherwood, T. K. (1977). *The properties of Gases and Liquids*, Third Edition, Mc Graw-Hill, New York.

[6] Griswold, J., Anders, D. and Klein, V. A. (1943). *Transactions of the American Institute of Chemical Engineers*, **39**, 223.