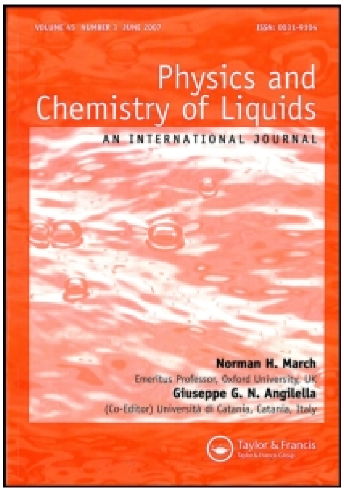

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Isothermal Phase Equilibrium Studies on the Binary Mixtures of N-Butanol and N-Pentanol with Alkylbenzenes

S. M. Ashraf[a]; D. H. L. Prasad[a]
[a] Properties Group, Indian Institute of Chemical Technology, Hyderabad, India

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ISOTHERMAL PHASE EQUILIBRIUM STUDIES ON THE BINARY MIXTURES OF N-BUTANOL AND N-PENTANOL WITH ALKYLBENZENES

S. M. ASHRAF and D. H. L. PRASAD*

Properties Group, Indian Institute of Chemical Technology,
Hyderabad – 500 007, India

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The gas chromatographic method proposed by us for simple and accurate measurement of isothermal phase equilibria has been applied to: aliphatic alcohol (*n*-butanol and *n*-pentanol) + alkylbenzene (benzene, toluene, *o*-xylene, *p*-xylene and ethylbenzene) binary mixtures. The present measurements on: benzene with *n*-butanol, and toluene with *n*-butanol and *n*-pentanol are in good agreement with the isothermal phase equilibrium data available in the literature.

Keywords: Phase equilibria; aliphatic alcohols; alkylbenzenes; infinite dilution activity coefficients

INTRODUCTION

In continuation of our work on the isothermal phase equilibria of binary mixtures using gas chromatographic techniques [1], this investigation on the binary mixtures of *n*-butanol and *n*-pentanol with benzene, toluene, *o*-xylene, *p*-xylene and ethylbenzene has been taken up.

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*Author for Correspondence.

EXPERIMENTAL

Solvents and Solutes

Analar/Spectroscopic grade: *n*-butanol, *n*-pentanol, benzene, toluene, *o*-xylene, *p*-xylene and ethyl benzene, procured from M/s E. Merck, Darmstadt (FRG) are used in the present study. While the other substances have been used without further purification, *n*-butanol and *n*-pentanol are purified further by drying over a molecular sieve and calcium chloride, and distillation. No significant second peak has been observed when the substances have been injected to the 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 [2, 3] 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 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 experiments. The contents are kept in a cold environment (a refrigerator) overnight. The solvent in excess

TABLE I Comparison of the Refractive-index and Density of the Pure Liquids with the Literature Data [2, 3]

Substance	*Refractive-index* *This work*	*Literature (Source)*	*Density, g/ml* *This work*	*Literature (Source)*
Benzene	1.5015	1.5011(2)	0.8794	0.8790(2)
Toluene	1.4978	1.4969(2)	0.8672	0.8669(2)
o-Xylene	1.5056	1.5054(2)	0.8805	0.8802(2)
p-Xylene	1.4956	1.4958(2)	0.8612	0.8610(2)
Ethylbenzene	1.4961	1.4959(2)	0.8673	0.8670(2)
n-Butanol	1.3995	1.3993(3)	0.8097	0.8096(3)
n-Pentanol	1.4100	1.4099(3)	0.8145	0.8144(3)

of the desired percent loading, is removed by bubbling pure nitrogen gas. The coated support material is then filled carefully inside the column. The column is installed inside the oven of the Model-5840 A Hewlett Packard make micro-processor 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 pre-saturated 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 the present work. Presaturated helium gas is run through the main column of the chromatograph at a constant ambient temperature of the value 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, whereas the detector temperature in 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 the experiment.

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 re-installed 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 inside the column 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 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 given by Ashraf *et al.* [1]. The infinite dilution activity coefficients of eight binary systems studied in this work are presented in Table II. The values 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

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

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

The Wilson model equations for the activity coefficients

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

TABLE II Infinite Dilution Activity Coefficients and the Wilson Parameters of the Binary Systems Studied in the Present Work

Component 1	*Component 2*	*Temperature/°C*	γ_1	γ_2	Λ_{12}	Λ_{21}
Benzene	*n*-Butanol	25	3.786	10.404	0.6242	0.1400
Toluene	*n*-Butanol	90	1.939	5.459	1.2080	0.1489
Toluene	*n*-Pentanol	50	2.991	6.398	1.1024	0.1847
n-Butanol	*O*-Xylene	40	9.378	3.129	0.1358	0.7585
n-Butanol	*p*-Xylene	60	7.236	4.972	0.2448	0.4281
n-Butanol	Ethylbenzene	50	5.958	3.841	0.2651	0.5430
Benzene	*n*-Pentanol	60	2.455	11.054	0.7434	0.2032
n-Pentanol	*o*-Xylene	40	8.127	4.449	0.2031	0.4988

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) + *n*-Butanol (2) at 25°C			Toluene (1) + *n*-Butanol (2) at 90°C		
6.1	0.00	0.00	255.2	0.00	0.00
35.8	0.10	0.84	304.4	0.10	0.24
53.7	0.20	0.90	345.7	0.20	0.40
66.2	0.30	0.93	379.4	0.30	0.51
74.5	0.40	0.94	406.0	0.40	0.59
80.2	0.50	0.95	426.0	0.50	0.65
84.2	0.60	0.95	440.0	0.60	0.71
87.0	0.70	0.96	448.1	0.70	0.75
89.0	0.80	0.96	450.7	0.80	0.78
92.0	0.90	0.97	445.4	0.90	0.85
95.2	1.00	1.00	406.7	1.00	1.00
Toluene (1) + *n*-Pentanol (2) at 50°C			*n*-Butanol (1) + *o*-Xylene (2) at 40°C		
14.2	0.00	0.00	15.3	0.00	0.00
30.3	0.10	0.58	21.2	0.10	0.32
43.8	0.20	0.74	22.5	0.20	0.38
55.0	0.30	0.81	23.0	0.30	0.42
64.2	0.40	0.85	23.2	0.40	0.45
71.6	0.50	0.88	23.3	0.50	0.49
77.5	0.60	0.91	23.2	0.60	0.53
82.1	0.70	0.92	22.7	0.70	0.59
85.8	0.80	0.94	21.7	0.80	0.67
89.1	0.90	0.96	20.1	0.90	0.79
92.1	1.00	1.00	17.7	1.00	1.00
n-Butanol (1) + *p*-Xylene (2) at 50°C			*n*-Butanol (1) + Ethylbenzene (2) at 50°C		
51.4	0.00	0.00	35.1	0.00	0.00
71.9	0.10	0.34	44.3	0.10	0.27
78.3	0.20	0.42	47.3	0.20	0.35
80.9	0.30	0.46	48.5	0.30	0.40
82.1	0.40	0.49	49.0	0.40	0.43
82.6	0.50	0.52	49.0	0.50	0.46
82.4	0.60	0.54	48.5	0.60	0.50
81.3	0.70	0.58	47.3	0.70	0.55
78.5	0.80	0.64	45.0	0.80	0.62
72.3	0.90	0.74	40.8	0.90	0.74
58.8	1.00	1.00	33.1	1.00	1.00
Benzene (1) + *n*-Pentanol (2) at 60°C			*n*-Pentanol (1) + *o*-Xylene (2) at 40°C		
26.0	0.00	0.00	15.3	0.00	0.00
123.4	0.10	0.81	17.3	0.10	0.18
193.4	0.20	0.89	17.7	0.20	0.23
244.0	0.30	0.92	17.6	0.30	0.25
280.6	0.40	0.93	17.5	0.40	0.28
307.5	0.50	0.94	17.2	0.50	0.30
327.5	0.60	0.95	16.7	0.60	0.32
343.4	0.70	0.96	15.8	0.70	0.36
357.3	0.80	0.97	14.4	0.80	0.43
372.1	0.90	0.98	11.8	0.90	0.56
391.4	1.00	1.00	7.3	1.00	1.00

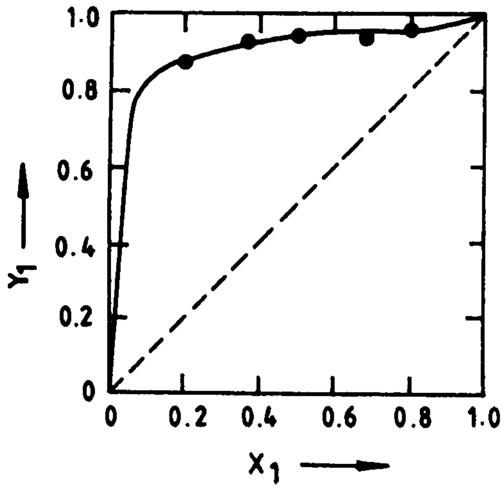

FIGURE 1 Equilibrium Diagram for Benzene(1)+*n*-Butanol (2) System at 25°C (— This work ● Literature).

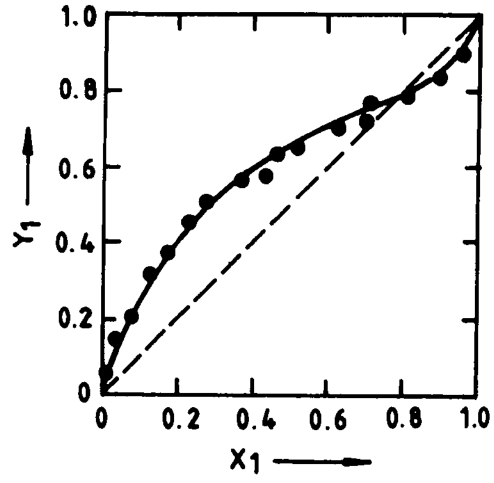

FIGURE 2 Equilibrium Diagram for Toluene(1)+*n*-Butanol (2) System at 90°C (— This work ● Literature).

and

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

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

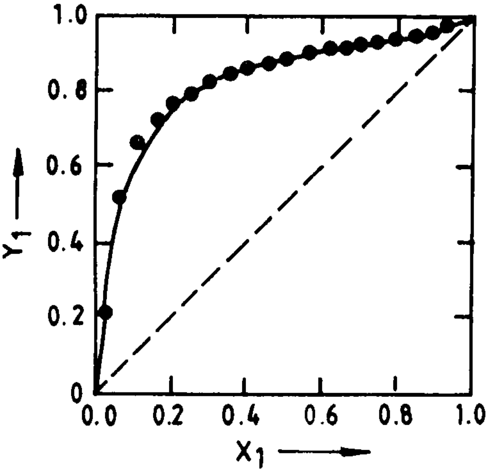

FIGURE 3 Equilibrium Diagram for Toluene(1) + *n*-Pentanol (2) System at 50°C (— This work • Literature).

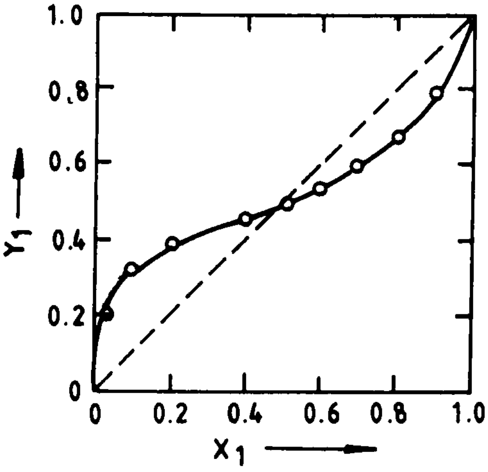

FIGURE 4 Equilibrium Diagram for *n*-Butanol (1) + *o*-Xylene(2) System at 40°C (— This work).

phase diagrams. The total pressure at each point (P_{total}) 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. The values of the vapor pressures are calculated

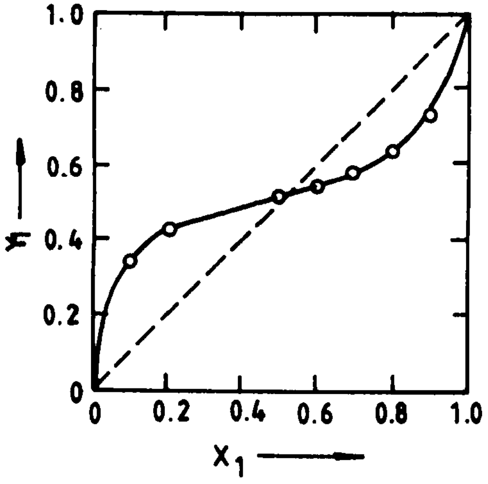

FIGURE 5 Equilibrium Diagram for *n*-Butanol (1) + *p*-Xylene (2) System at 50°C (— This work).

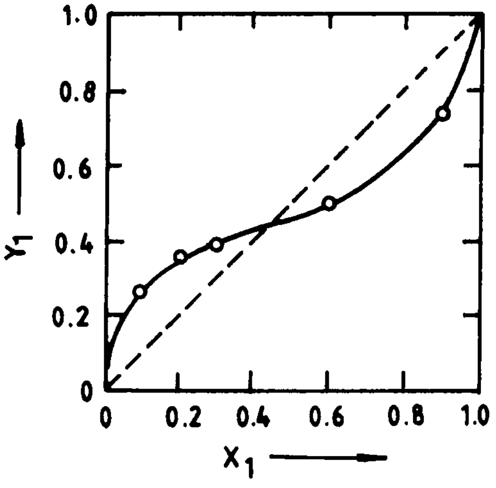

FIGURE 6 Equilibrium Diagram for *n*-Butanol (1) + Ethylbenzene System at 50°C (— This work).

from the Antoine equation and the set of constants given in Reid *et al.* [4].

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

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

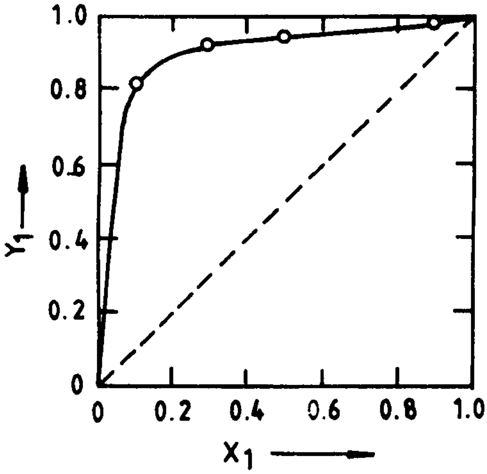

FIGURE 7 Equilibrium Diagram for Benzene (1)+*n*-Pentanol (2) System at 60°C (— This work).

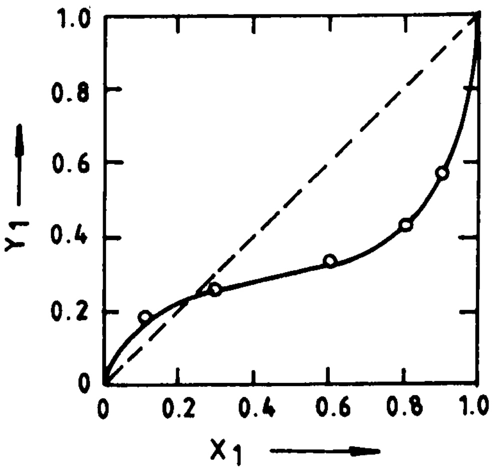

FIGURE 8 Equilibrium Diagram for *n*-Pentanol (1)+*o*-Xylene (2) System at 40°C (— This work).

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 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

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

Plots of $x_1$vs y_1 are drawn in Figures 1 to 8. In Figures 1 to 3, the $x_1$vs y_1 data measured by the conventional methods and published in the literature [5 – 7] are shown by •. It can be seen from the figures that the agreement of the present work with the literature data is good.

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