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### A Simple and Accurate Method for Isothermal Phase Equilibrium Studies

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# A SIMPLE AND ACCURATE METHOD FOR ISOTHERMAL PHASE EQUILIBRIUM STUDIES

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A gas chromatographic method for simple and accurate measurement of isothermal phase equilibrium studies has been proposed and applied to: aliphatic alcohol (methanol, ethanol and n-propanol) + aromatic hydrocarbon (benzene, toluene, o-xylene, p-xylene and ethylbenzene) binary mixtures. The present measurements on: benzene with methanol, ethanol and n-propanol and toluene with ethanol are in good agreement with the isothermal phase equilibrium data available in the literature.

*Keywords:* Phase equilibrium; aliphatic alcohols; aromatic hydrocarbons; infinite dilution activity coefficients

## INTRODUCTION

Studies on phase equilibria have been a topic of continued interest for about a century for chemists and chemical Technologists/Engineers. Depending on the specific need and/or interest, the studies have been carried out isothermally or isobarically—the chemists preferring to carry out isothermal measurements in their quest to understand the nature and type of interaction between different molecular species, and the chemical Technologists/Engineers concentrating on isobaric measurements for direct use in the design of the conventional

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separation operations—although good data of one type might be useful for the other purpose as well. The recent studies of Barker and Hilmi [1], Conder and Young [2], Eckert *et al.* [3], Eugene *et al.* [4], Kanger *et al.* [5] and Kwantes and Rijnders [6] utilized the gas-liquid chromatographic technique to determine the infinite dilution activity coefficients of volatile solutes in non-volatile or volatile solvents, and contributed significantly to the experimental methodology. The present work is aimed at the determination of the infinite dilution activity coefficient of both the components of the binary mixtures (mentioned in the abstract) and utilizing them to calculate the isothermal phase equilibrium data through the use of the Wilson model.

## EXPERIMENTAL

### Solvents and Solutes

Analar/Spectroscopic grade: methanol, ethanol, n-propanol, benzene, toluene, o-xylene, p-xylene and ethylbenzene, supplied by E. Merck, Darmstadt (FRG) are used in the present study. While the other substances have been used without further purification, n-propanol is purified further by drying over a molecular sieve and calcium chloride, and distillation. No significant second peaks have been noticed when the substances have been injected to the gas-chromatograph with the object of determining the purity. As an additional check on the purity of the substances, the refractive-index for Sodium-D line and density have been measured at 293.15 K. They compare favourably with the literature data as shown in Table I.

### Support Material and the Column

Chromosorb-W(40/60), procured from Alltech, Arlington Heights, Illinois (USA), is employed as the support material. Drawing from the experience of Barker and Hilmi [1], regarding the ease of handling, filling and removal of the support material, and proper separation, a stainless steel column of 60.96 cm length and 6.35 mm inner diameter has been chosen for use. The support material is initially dried for 3 to 4 hours in an oven at  $373 \pm 5$  K. A known mass of the dry support

TABLE I Comparison of Refractive-index and Density of the pure Liquids with the Literature Data from Dreisbach 11 at 20 C

<i>Substance</i>	<i>Refractive-index</i>		<i>Density, g/ml</i>	
	<i>This work</i>	<i>Literature</i>	<i>This work</i>	<i>Literature</i>
Methanol	1.3287	1.3286	0.7916	0.7915
Ethanol	1.3618	1.3614	0.7904	0.7905
n-Propanol	1.3854	1.3856	0.8036	0.8036
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

material is soaked in an excess quantity of the stationary phase being used for the experiments. The contents are kept in a 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 column. The column is installed in 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 presaturated with the solvent by passing through a specially designed presaturator. The presaturator is fabricated from two tubes. The bottom of the first tube is fused with standard sintered glass of 0.1 mm pore diameter. This tube is filled with the solvent under study and the carrier gas is passed through the sintered pores in the form of minute bubbles. The top end of the second tube is connected to the main stream near the injection port of the main experimental column. The support material, placed inside the second tube is fully saturated with the desired solvent. An injection point is also provided near the bottom of the second tube to inject the solvent whenever required.

Before entering the presaturator, the carrier gas is passed through the purifiers, containing a molecular sieve and manganous dioxide to remove traces of moisture and oxygen, which are 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 between 293 to 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  $\pm 0.05$  ml/min. Three or four measurements are carried out to calculate a reliable value of specific retention volume ( $v_g^0$ ).

### Actual Experiment

The injection port, detector and column temperatures of the chromatograph are set at the desired levels by means of the micro-processor. The injection port temperature is maintained 25 K above the boiling point of the solute, whereas 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 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 retention time in such successive experiments helps in the measurement of the quantity of the solvent present on the support inside the column accurately. As the thermal conductivity detector is used in these investigations, the retention time ( $t_0$ ) for the dead volume due to the porosity inside the column is detected by injecting one micro-litre of air. One micro-litre of solute is subsequently injected and its retention time ( $t_r$ ) noted.

### TREATMENT OF THE DATA

The specific retention volume ( $v_g^0$ ) is calculated from Equation (1) suggested by Desty and Swanson [7]

$$v_g^0 = (JF_m/w)(P_0 - P_{H_2O})/P_0(273/T_m)(t_r - t_0) \quad (1)$$

Where  $F_m$  is the flow rate of the carrier gas (m/s) at the ambient temperature  $T_m$  (K),  $W$ (kg) is the mass of the stationary phase,  $P_o$  ( $P_a$ ) is the pressure at the out-let of the column,  $P_{H_2O}$  ( $P_a$ ) is the vapour pressure of water at  $T_m$ ,  $t_r$  (s) and  $t_o$  (s) are the retention times of the solute and inert respectively.  $J$  is the James-Martin correction factor given by

$$J = (3/2) [(P_i/P_o)^2 - 1]/[(P_i/P_o)^3 - 1] \quad (2)$$

where  $P_i$  ( $P_a$ ) is the column inlet pressure. The infinite dilution activity coefficient ( $\gamma^{\infty}$ ) of the solute is calculated from

$$\ln \gamma^{\infty} = \ln(273R/P_2^{\circ} M_1 v_g^{\circ}) - [(B_{22} - v_2^{\circ})/RT_{\text{Expt}}] \quad (3)$$

where  $R$  is the universal gas constant (8.314 J/mol K),  $P_2^{\circ}$  is the vapour pressure of the solute at the experimental column temperature ( $T_{\text{Expt}}$ ),  $M_1$  is the molecular weight of the stationary phase,  $v_2^{\circ}$  ( $m^3/mol$ ) is the molar volume of the solute. The second term on the right hand side of the equation, takes into account the vapour phase non-ideality. Second virial coefficient of the solute  $B_{22}$  is calculated using the method suggested by Hayden and O'Connell [8]. The other properties such as molar volumes and critical properties are collected from or estimated according to the methods recommended by Reid *et al.* [9].

## RESULTS AND DISCUSSION

The experimentally determined infinite dilution activity coefficients of ten binary mixtures are presented in Table II. The values of  $\gamma_1^{\infty}$  and  $\gamma_2^{\infty}$  are used to calculate with Wilson [12] parameters  $\Lambda_{12}$  and  $\Lambda_{21}$  by the simultaneous solution of the equations

$$\ln \gamma_1^{\infty} = -\ln \Lambda_{12} - \Lambda_{21} + 1 \quad (4)$$

$$\ln \gamma_2^{\infty} = -\ln \Lambda_{21} - \Lambda_{12} + 1 \quad (5)$$

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	$\gamma_1^\infty$	$\gamma_2^\infty$	$\Lambda_{12}$	$\Lambda_{21}$
Methanol	Benzene	20	13.872	8.472	0.1486	0.2766
Ethanol	Benzene	25	11.091	3.898	0.1351	0.5954
Benzene	n-Propanol	20	4.131	7.979	0.5394	0.1987
Ethanol	Toluene	35	12.270	4.550	0.1312	0.5241
Methanol	Toluene	25	20.390	11.482	0.1078	0.2126
Ethanol	Ethylbenzene	40	17.816	8.745	0.1154	0.2770
n-Propanol	Toluene	40	7.680	5.106	0.2320	0.4220
n-Propanol	o-Xylene	40	11.148	4.426	0.1432	0.5322
n-Propanol	p-Xylene	40	5.749	2.153	0.1615	1.0774
n-Propanol	Ethylbenzene	40	9.220	5.148	0.1906	0.4364

TABLE III Isothermal Vapour-Liquid Equilibrium Predicted from Infinite Dilution Activity Coefficient Measurements

Total Pressure (mm Hg)	$x_1$	$y_1$	Total Pressure (mm Hg)	$x_1$	$y_1$
Methanol(1) + Benzene(2) at 20°C			Ethanol(1) + Benzene(2) at 25°C		
75.2	0.0	0.0	95.4	0.0	0.0
126.9	0.1	0.44	116.0	0.1	0.23
136.8	0.2	0.50	119.1	0.2	0.27
139.9	0.3	0.52	119.6	0.3	0.30
141.3	0.4	0.54	119.1	0.4	0.32
141.9	0.5	0.55	117.5	0.5	0.34
141.9	0.6	0.56	114.4	0.6	0.38
140.9	0.7	0.58	108.9	0.7	0.42
137.6	0.8	0.62	99.6	0.8	0.50
129.7	0.9	0.70	84.4	0.9	0.64
97.3	1.0	0.0	59.1	1.0	1.0
Benzene(1) + n-Propanol(2) at 20°C			Ethanol(1) + Toluene(2) at 35°C		
14.6	0.0	0.0	46.8	0.0	0.0
37.5	0.1	0.65	93.5	0.1	0.53
51.3	0.2	0.76	102.7	0.2	0.58
59.8	0.3	0.81	106.6	0.3	0.61
65.3	0.4	0.83	109.2	0.4	0.63
68.9	0.5	0.85	111.2	0.5	0.65
71.3	0.6	0.87	112.7	0.6	0.68
73.2	0.7	0.88	113.6	0.7	0.72
74.7	0.8	0.89	113.3	0.8	0.77
75.9	0.9	0.92	110.5	0.9	0.85
75.2	1.0	1.0	103.2	1.0	1.0

TABLE III (Continued)

<i>Total Pressure</i> (mm Hg)	$x_1$	$y_1$	<i>Total Pressure</i> (mm Hg)	$x_1$	$y_1$
Methanol(1) + Toluene(2) at 25 C			Ethanol(1) + Ethylbenzene(2) at 40 C		
28.4	0.0	0.0	21.5	0.0	0.0
112.5	0.1	0.76	104.0	0.1	0.80
124.3	0.2	0.79	117.0	0.2	0.83
128.0	0.3	0.80	121.5	0.3	0.84
129.9	0.4	0.80	124.2	0.4	0.84
131.3	0.5	0.81	126.3	0.5	0.85
132.6	0.6	0.81	128.3	0.6	0.86
133.9	0.7	0.82	130.6	0.7	0.87
135.0	0.8	0.84	133.0	0.8	0.88
134.9	0.9	0.87	135.2	0.9	0.92
126.9	1.0	1.0	134.2	1.0	1.0
n-Propanol(1) + Toluene(2) at 40 C			n-Propanol(1) + o-Xylene(2) at 40 C		
59.2	0.0	0.0	15.4	0.0	0.0
77.0	0.1	0.29	38.6	0.1	0.63
82.1	0.2	0.36	43.8	0.2	0.68
83.9	0.3	0.40	46.1	0.3	0.71
84.4	0.4	0.43	47.7	0.4	0.72
84.3	0.5	0.45	49.0	0.5	0.74
85.3	0.6	0.48	50.3	0.6	0.77
81.6	0.7	0.51	51.5	0.7	0.80
77.6	0.8	0.57	52.4	0.8	0.84
69.4	0.9	0.69	52.8	0.9	0.90
52.2	1.0	1.0	52.2	1.0	1.0
n-Propanol(1) + p-Xylene(2) at 40 C			n-Propanol(1) + Ethylbenzene(2) at 40 C		
19.9	0.0	0.0	21.5	0.0	0.0
33.2	0.1	0.44	43.8	0.1	0.54
37.6	0.2	0.53	50.0	0.2	0.62
40.4	0.3	0.59	52.6	0.3	0.65
42.7	0.4	0.64	54.1	0.4	0.67
44.7	0.5	0.69	55.2	0.5	0.69
46.6	0.6	0.74	56.1	0.6	0.71
48.3	0.7	0.79	56.7	0.7	0.74
49.8	0.8	0.85	56.8	0.8	0.78
51.8	0.9	0.92	55.8	0.9	0.86
52.2	1.0	1.0	52.2	1.0	1.0



The Wilson model equations for activity coefficients

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

and

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

are used to calculate the values of  $\gamma_1$  and  $\gamma_2$  at regular intervals of the liquid phase composition ( $x_1$ ) to facilitate the construction of the phase diagrams. The total pressure at each point ( $P_{\text{total}}$ ) is calculated from

$$P_{\text{total}} = \gamma_1 x_1 P_1^{\text{sat}} + \gamma_2 x_2 P_2^{\text{sat}}. \quad (8)$$

where  $P_1^{\text{sat}}$  and  $P_2^{\text{sat}}$  are the saturated vapour pressures of the pure components 1 and 2. The values of the vapour pressure are calculated from the Antoine equation and the set of constants recommended in Reid *et al.* [9]

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

$$f_1^v = y_1 \Phi_{1v} P_{\text{total}} \quad (9)$$

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

$$f_1^l = x_1 \gamma_1 P_1^{\text{sat}} \quad (10)$$

As the present set of experiments are carried out at atmospheric pressure, the vapour phase imperfection coefficient  $\Phi_{1v}$  is assumed to be unity enabling us to calculate the vapour phase composition from

$$y_1 = x_1 \gamma_1 P_1^{\text{sat}} / P_{\text{total}} \quad (11)$$

Plots of  $x_1$  vs  $y_1$  are drawn in Figures 1 to 10. In Figures 1 to 4, the  $x_1$  vs  $y_1$  data measured employing the conventional ebullimetric, circulation type apparatus, collected from the literature and compiled

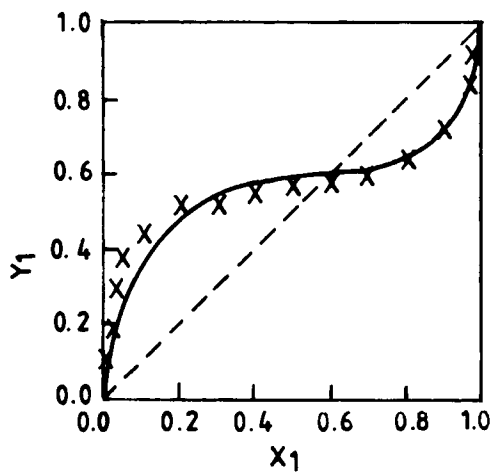


FIGURE 1 Equilibrium Diagram for Methanol (1) + Benzene (2) System at 20°C (----- This work, x Literature).

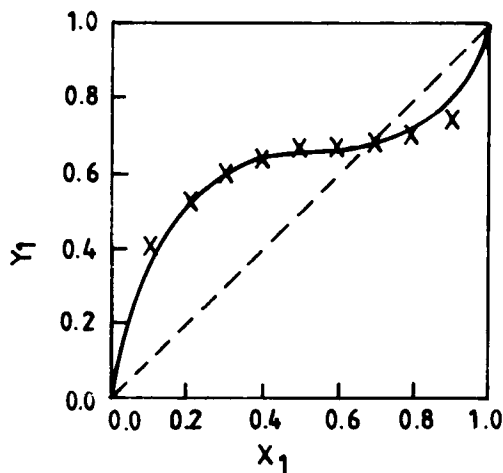


FIGURE 2 Equilibrium Diagram for Ethanol (1) + Benzene (2) System at 25°C (----- This work, x Literature).

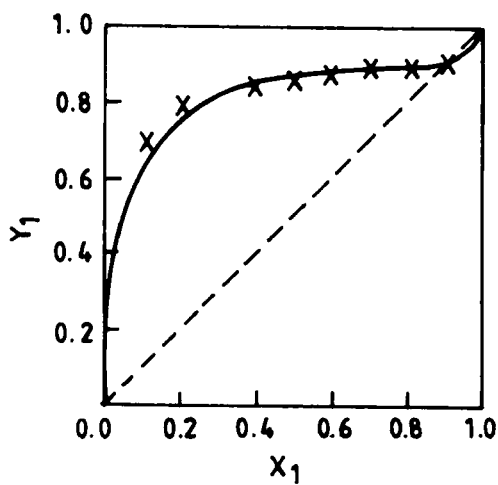


FIGURE 3 Equilibrium Diagram for Benzene (1) + n-Propanol (2) System at 20 C (- - - This work, x Literature).

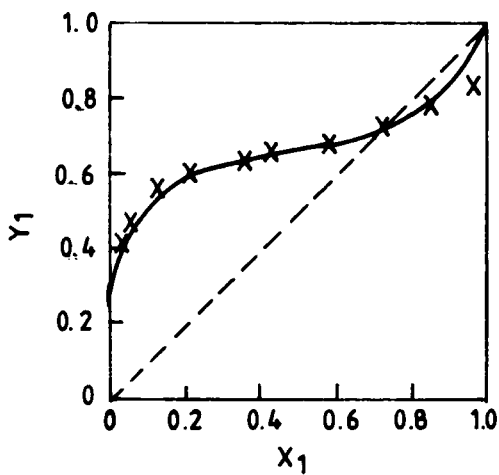


FIGURE 4 Equilibrium Diagram for Ethanol (1) + Toluene (2) System at 35 C (- - - This work, x Literature).

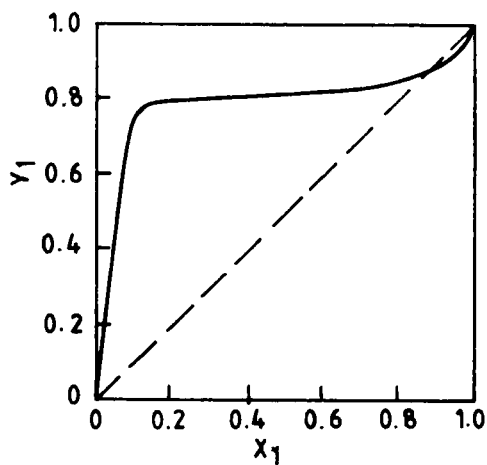


FIGURE 5 Equilibrium Diagram for Methanol (1) + Toluene (2) System at 25 °C (--- This work).

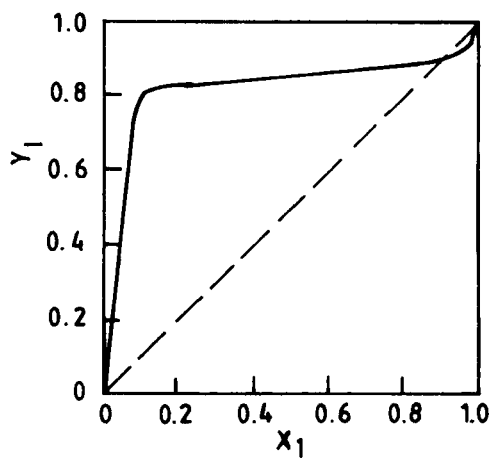


FIGURE 6 Equilibrium Diagram for Ethanol (1) + Ethylbenzene (2) System at 40 °C (--- This work).

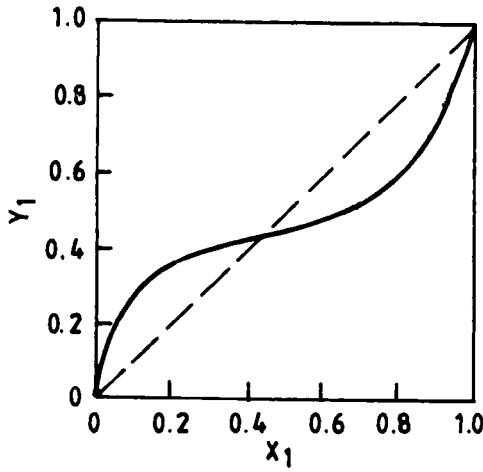


FIGURE 7 Equilibrium Diagram for n-Propanol (1) + Toluene (2) System at 40°C (- - -  
 - - This work).

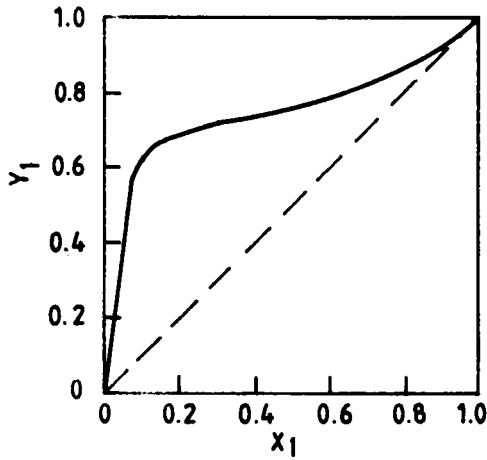


FIGURE 8 Equilibrium Diagram for n-Propanol (1) + o-Xylene (2) System at 40°C (- - -  
 - - This work).

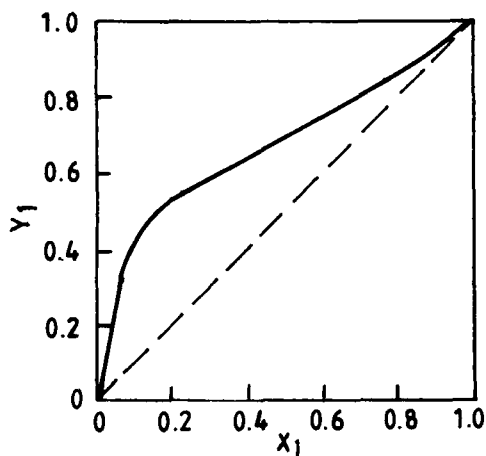


FIGURE 9 Equilibrium Diagram for n-Propanol (1) + p-Xylene (2) System at 40 °C (--- This work).

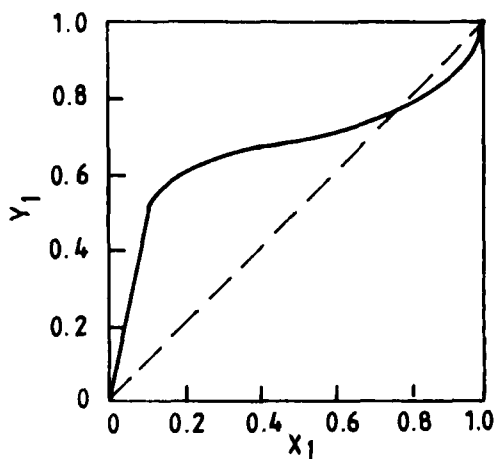


FIGURE 10 Equilibrium Diagram for n-Propanol (1) + Ethylbenzene (2) System at 40 °C (---- This work).

by Gmehling and Onken [13] are indicated by small crosses ( $\times$ ). It can be seen from the figures that the agreement of the present work plots with literature data is good. Based on this study, the method proposed

in this paper is recommended for the generation of reliable isothermal phase equilibrium data in an easy yet accurate manner.

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