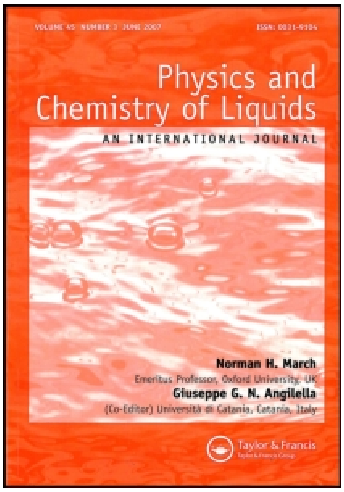

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ISOTHERMAL PHASE EQUILIBRIA THROUGH GAS CHROMATOGRAPHY FOR PETROCHEMICAL PROCESSING

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A gas chromatographic technique has been used to measure the isothermal phase equilibria likely to be of importance in petrochemical processing. The measurements on the binary mixtures formed by chlorobenzene with some aromatic hydrocarbons (toluene, *o*-xylene, *p*-xylene) and aliphatic alcohols (ethanol, 1-propanol, 1-butanol) are given in this paper. Our measurements on chlorobenzene + 1-propanol mixtures are in good agreement with the literature data.

Keywords: Phase equilibrium; aliphatic alcohols; aromatic hydrocarbons; activity coefficients

INTRODUCTION

Aromatic hydrocarbons, aliphatic alcohols and halogenated compounds are among the several thousands of compounds currently classified as petrochemicals. Chemical processes involving the production of these compounds require phase equilibrium data of the multicomponent systems which can be computed from binary data, for the economical design of the separation and purification equipments and their operation. Isothermal phase equilibrium data on the binary mixtures formed by chlorobenzene with: ethanol, 1-propanol, 1-butanol, toluene, *o*-xylene and *p*-xylene dilution activity coefficients are presented in this paper.

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EXPERIMENTAL

While our earlier paper [1] describes the details of the experimentation for the measurement of infinite dilution activity coefficient, a brief account follows.

Solvents and Solutes

Analar/Spectroscopic grade toluene, *o*-xylene, *p*-xylene, ethanol, 1-propanol, 1-butanol, procured from E. Merck Darmsdat (FRG) are used in the present study. While the other substances have been used without any further purification, 1-butanol has been purified further by drying over a molecular sieve and calcium chloride and distillation. No significant second peaks have 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-about 61 cm long and about 6 mm diameter-has been chosen for use, to provide ease of handling, filling and removal of the support material as well as proper separation. The support material is initially

TABLE I Comparison of the refractive-index and density with literature data [2, 3]

Substance	*Refractive-index*		*Density, g/mL*	
	This work	*Literature*	*This work*	*Literature*
Ethanol	1.3618	1.3614 [2]	0.7916	0.7915 [2]
1-Propanol	1.3854	1.3856 [2]	0.8036	0.8036 [2]
1-Butanol	1.3995	1.3993 [2]	0.8097	0.8096 [2]
Toluene	1.4973	1.4969 [3]	0.8687	0.8669 [3]
o-Xylene	1.5056	1.5054 [3]	0.8805	0.8802 [3]
p-Xylene	1.4956	1.4958 [3]	0.8612	0.8610 [3]
Chlorobenzene	1.5242	1.5241 [3]	1.1058	1.1057 [3]

dried for 4 h 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 studied. The contents are kept in a cold environment (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 inside the oven of the Model 5840 A Hewlett 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. 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 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 port is also provided near the bottom of second tube to inject the solvent whenever required. Before entering the presaturator, the carrier gas is passed through 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 the present experiments. 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 by means of a soap-bubble flow meter to an accuracy of 0.05 ml/min. Three or four measurements are taken to calculate a reliable value of the 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 is maintained 50 K above the boiling point of the solute. When the set conditions of the injection port, thermal conductivity detector 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 reinstalled into the oven and the same solute injected again. The constancy of the retention time in such experiments helps in the accurate measurement of the quantity of solute present in the column. As the thermal conductivity detector is used, the dead volume caused by the porosity inside the column is detected by injecting 1 microlitre of air. One microlitre of the solute is subsequently injected and its retention time noted.

TREATMENT OF THE DATA

The specific retention volume (V_g^o) is calculated from the equation proposed by Desty and Swanton [4]:

$$V_g^o = (JF_m/W)(P_o - P_{\mathrm{H_2O}})/P_o(273/T_m)(t_r - t_o) \qquad (1)$$

where F_m is the flow rate of the carried gas (m/s) at the ambient temperature T_m(K), W(kg) is the mass of the stationary phase, P_o(Pa) is the pressure at the outlet of the column, $P_{\mathrm{H_2O}}$(Pa) is the vapor pressure of water at T_m(K). $t_r(s)$ and $t_o(s)$ are the retention times of the solute and the inert respectively. J is the James-Martin correction factor given by:

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

where P_i(Pa) is the column inlet pressure. The infinite dilution activity coefficient (γ^∞) of the solute is calculated from:

$$\ln\gamma^\infty = \ln(273R/P_2^o M_1 V_g^o) - [(B_{22} - V_2^o)/RT_{\mathrm{Expt}}] \qquad (3)$$

where R is the universal gas constant (8.314 J/mol K), P_2^o is vapor pressure of the solute at the experimental temperature (T_{Expt}(K), M_1 is the molecular mass of the stationary phase, V_2^o(ml/mol) is the molar volume of the solute. The second term on the right side of the equation takes into account the vapor phase non-ideality. The second virial coefficient of the solute B_{22} is calculated using the method suggested by Hayden and O'Connel [5]. The properties required for the calculations such as: molar volumes and critical properties are collected from or estimated by the methods recommended by Reid *et al.* [6].

RESULTS AND DISCUSSION

The values of the infinite dilution activity coefficients γ_1^∞ and γ_2^∞ are used to calculate the Wilson parameters Λ_{12} Λ_{21} by the simultaneous solution of the equations:

$$\ln \gamma_1^\infty = -\ln \Lambda_{12} - \Lambda_{21} - 1 \tag{4}$$

and

$$\ln \gamma_2^\infty = -\ln \Lambda_{21} - \Lambda_{12} - 1. \tag{5}$$

The Wilson model equations for the activity coefficients

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

and

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

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:

$$P_{\text{total}} = \gamma_1 x_1 P_1^{\text{sat}} + \gamma_2 x_2 P_2^{\text{sat}} \tag{8}$$

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 pressure are calculated from the Antoine equation with the constants given in Reid *et al.* [6].

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

$$f_1^V = y_1 \phi_{1V} P_{\text{total}} \tag{9}$$

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

$$f_1^L = x_1 \gamma_1 P_1^{\text{sat}}. \tag{10}$$

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 mole fraction from

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

Plots of x_1 *versus* y_1 are drawn in Figures 1 to 6. Computed phase equilibrium information is given in Tables II and III.

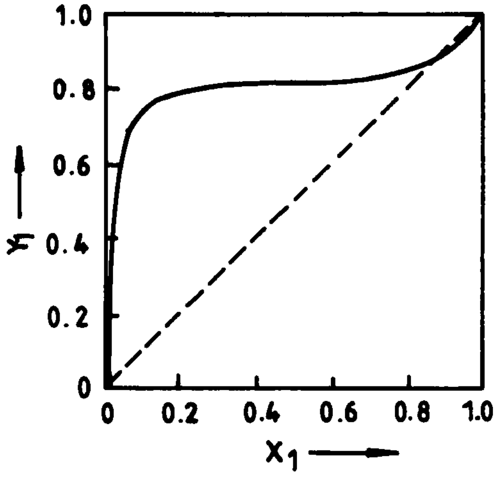

FIGURE 1 Phase diagram for ethanol (1) + chlorobenzene (2) at 40°C.

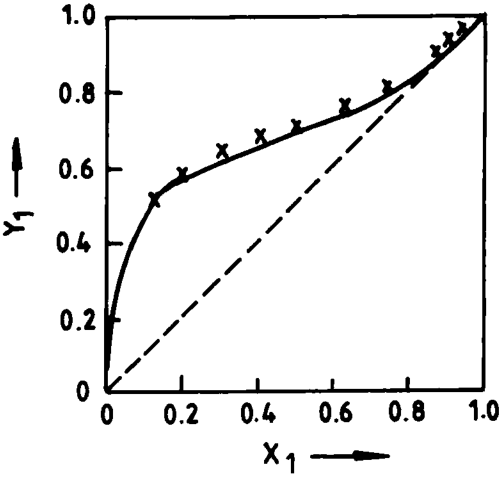

FIGURE 2 Phase diagram for 1-propanol (1) + chlorobenzene (2) at 95°C (*x* literature).

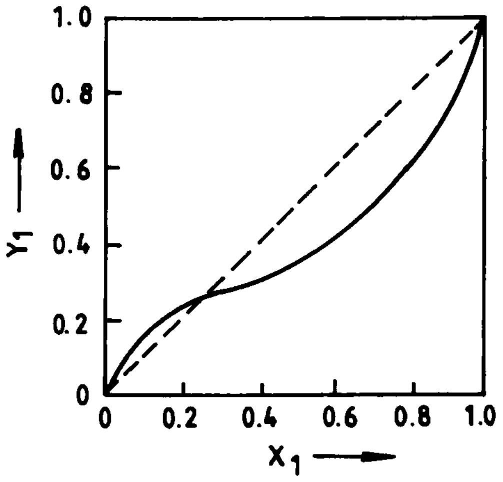

FIGURE 3 Phase diagram for 1-butanol (1) + chlorobenzene (2) at 40°C.

In Figure 1, x_1 *versus* y_1 data measured by the conventional method and published in the literature, collected from the complication of Gmehling and Onken [7] are shown by *x* marks. It can be seen from

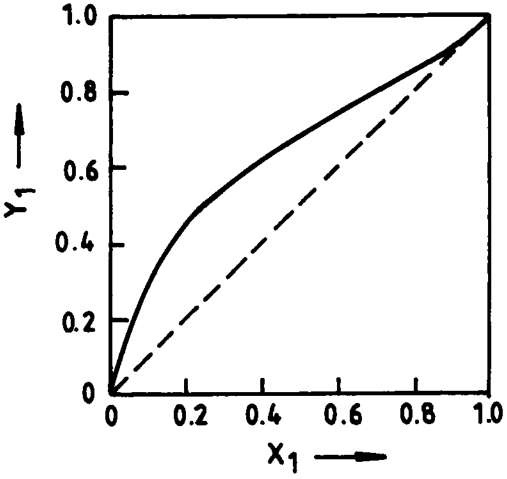

FIGURE 4 Phase diagram for toluene (1) + chlorobenzene (2) at 40°C.

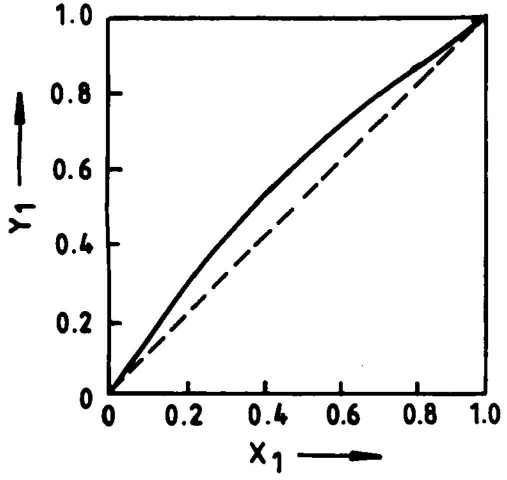

FIGURE 5 Phase diagram for chlorobenzene (1) + *o*-xylene (2) at 40°C.

the figure that the agreement between the present work and the literature observations is good. The measurements and the approach described in this paper for the determination of the isothermal phase equilibria are useful in the generation of the data for design purposes.

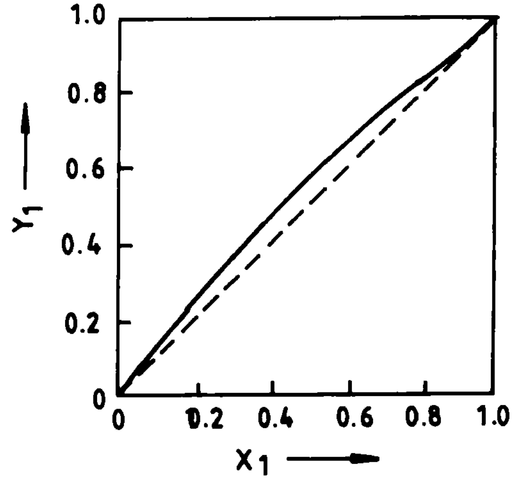

FIGURE 6 Phase diagram for chlorobenzene (1) + *p*-xylene (2) at 40°C.

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}
Ethanol	Chlorobenzene	40	17.41	9.15	0.120	0.264
1-Propanol	Chlorobenzene	95	7.52	2.46	0.167	0.909
1-Butanol	Chlorobenzene	40	6.89	1.94	0.113	1.251
Toluene	Chlorobenzene	40	2.00	1.78	0.575	0.859
Chlorobenzene	*o*-Xylene	40	0.98	1.02	0.176	0.459
Chlorobenzene	*p*-Xylene	40	1.07	1.16	1.537	0.504

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
Ethanol (1) + Chlorobenzene (2) at 40°C			1-Propanol (1) + Chlorobenzene (2) at 95°C		
26.4	0.0	0.00	250.8	0.0	0.00
108.9	0.1	0.77	456.6	0.1	0.49
122.2	0.2	0.80	520.8	0.2	0.57
126.9	0.3	0.81	558.1	0.3	0.62
129.4	0.4	0.82	587.1	0.4	0.66
131.4	0.5	0.82	612.3	0.5	0.70
133.3	0.6	0.83	635.9	0.6	0.74
135.2	0.7	0.84	656.9	0.7	0.79
137.1	0.8	0.86	675.0	0.8	0.85
138.2	0.9	0.89	689.5	0.9	0.91
134.2	1.0	1.00	698.9	1.0	1.00

TABLE III (Continued)

Total pressure mm Hg	x_1	y_1	*Total pressure mm Hg*	x_1	y_1
1-Butanol (1) + Chlorobenzene (2) at 40°C			Toluene (1) + Chlorobenzene (2) at 40°C		
26.4	0.0	0.00	26.8	0.0	0.00
29.6	0.1	0.16	34.1	0.1	0.30
30.0	0.2	0.30	39.5	0.2	0.45
29.9	0.3	0.25	43.7	0.3	0.55
29.4	0.4	0.30	47.0	0.4	0.62
28.6	0.5	0.35	50.0	0.5	0.68
27.3	0.6	0.42	52.0	0.6	0.74
25.6	0.7	0.50	54.0	0.7	0.80
23.4	0.8	0.61	56.1	0.8	0.86
20.8	0.9	0.77	57.8	0.9	0.93
17.7	1.0	1.00	59.1	1.0	1.00
Chlorobenzene (1) + *o*-Xylene (2) at 40°C			Chlorobenzene (1) + *p*-Xylene (2) at 40°C		
15.3	0.0	0.00	19.8	0.0	0.00
16.4	0.1	0.16	20.7	0.1	0.13
17.5	0.2	0.30	21.5	0.2	0.26
18.6	0.3	0.42	22.2	0.3	0.37
19.7	0.4	0.53	23.0	0.4	0.48
20.8	0.5	0.63	23.7	0.5	0.57
21.9	0.6	0.72	24.4	0.6	0.67
23.1	0.7	0.80	25.0	0.7	0.75
24.2	0.8	0.90	25.5	0.8	0.83
25.3	0.9	0.94	26.0	0.9	0.92
26.4	1.0	1.00	26.4	1.0	1.00

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