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Isobaric Vapor–Liquid Equilibria of 1-Butanol–*p*-Xylene System[1]

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Isobaric vapor–liquid equilibrium data were obtained for 1-butanol–*p*-xylene system at 97.3 kPa using a vapor recirculating type (modified Othmer's) equilibrium still. The activity coefficients were obtained by taking into consideration vapor-phase imperfections. The experimental data for this system were tested for thermodynamic consistency and were correlated by various equations. The system forms a minimum boiling azeotrope.

KEY WORDS: activity coefficients; binary parameters; 1-butanol; equilibrium still; *p*-xylene; vapor-liquid equilibrium.

1. INTRODUCTION

Vapor–liquid equilibrium of alcohols with aromatic hydrocarbons is important in studying the possible hydrocarbon–non-hydrocarbon relationships and the extractive distillation of hydrocarbons. Isobaric vapor–liquid equilibrium data for 1-butanol–*p*-xylene system have not been reported to date at 97.3 kPa, whereas isothermal vapor–liquid equilibrium data at 308.15 K [1] and 313.15 K [2] and bubble temperature measurements at 95.1 kPa [3] have been reported earlier for the system studied. The experimental data generated in this study is comparable to the earlier reported data.

In the present work isobaric vapor–liquid equilibrium data were obtained for the 1-butanol–*p*-xylene system at 97.3 kPa using a modified

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version of the recirculating type equilibrium described earlier [4, 5]. The system has a boiling range of 20.6 K.

This study forms part of a program to study the thermodynamic properties of liquid mixtures with a C_8 or C_9 aromatic hydrocarbon as one of the components.

2. EXPERIMENTAL

1-Butanol, laboratory reagent grade (BDH, India) and *p*-xylene (Riedel, Germany) were dried using suitable drying agents and then purified by distillation in a glass column as described elsewhere [6]. Table I summarizes some of the physical properties of the reagents used.

A modified version of the equilibrium still described by Raju and co-workers [5] was used for obtaining the vapor–liquid equilibrium data. The equilibrated mixtures were analyzed by the refractive index method using a Bausch and Lomb Abbe-3L refractometer. The apparatus, modifications, and analytical techniques have already been described [6]. The estimated uncertainties in the measurements were 0.0002 mole fraction in composition, 0.1 K in temperature, and 0.27 kPa in pressure. Refractive index readings were taken on samples with sufficient time allowed for the sample to come to thermal equilibrium at 298.15 K with the help of a circulating type cryostat (Type MK70, MLW, Germany) maintained at a given temperature within ±0.02 K.

3. RESULTS AND DISCUSSION

The liquid-phase activity coefficients were estimated from the experimental data taking into consideration the non-ideality of the vapor phase using Eqs. (1) and (2) as given below:

Table I. Physical Properties of Pure Components

Property	1-Butanol	*p*-Xylene
Molar Mass	74.123	106.168
T_b (K)	390.9	411.5
$RI_{298.15}$	1.3973	1.49325
$d_{298.15}$ ($g \cdot cm^{-3}$)	0.8060	0.85669
T_c (K)	562.9	616.2
P_c (kPa)	4.41×10^3	3.51×10^3
V_c ($cm^3 \cdot mol^{-1}$)	274.0	379.0
ω	0.590	0.324
μ (Debye)	1.8	0.1

$$\gamma_1 = (Py_1/P_1^0x_1)\exp[(B_{11} - V_1)(P - P_1^0)/RT + P\delta_{12}y_2^2/\mathrm{R}T] \tag{1}$$

$$\gamma_2 = (Py_2/P_2^0x_2)\exp[(B_{22} - V_2)(P - P_2^0)/RT + P\delta_{12}y_1^2/\mathrm{R}T] \tag{2}$$

where x_1, x_2 and y_1, y_2 are the equilibrium mole fractions of components 1 and 2 in the liquid and vapor phases, respectively, T and P are the boiling point and the total pressure, V_1 and V_2 are the molar liquid volumes, B_{11} and B_{22} are the second virial coefficients of the pure components, B_{12} is the cross second virial coefficient, and

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}$$

Vapor pressures were calculated for different temperatures from the Antoine equation of the form,

$$\log P^0 = A - [B/(C + T)] \tag{3}$$

where T is in K, P^0 is in mm Hg, and A, B, C are Antoine constants given in Ref. 7.

The surface-tension method was used for the estimation of liquid molar volumes. The Pitzer and Curl [8] correlation as modified by Tsonopoulos [9] was used for estimating second virial coefficients.

Table II gives the experimental T, x_1, y_1 and activity coefficient data. The x_1, y_1 and T, x_1, y_1 plots for the 1-butanol–*p*-xylene system at

Table II. Vapor–Liquid Equilibrium Data of 1-Butanol–*p*-Xylene System at 97.3 kPa

T (K)	x_1	y_1	$\ln \gamma_1$	$\ln \gamma_2$
389.5	1.0000	1.0000	−0.0030	0.9500
389.4	0.9317	0.9100	−0.0400	0.8380
389.2	0.8708	0.8400	−0.0390	0.7748
389.0	0.8117	0.8117	−0.0053	0.6300
389.1	0.7875	0.7833	−0.0124	0.5768
389.1	0.7333	0.7117	−0.0421	0.5200
389.2	0.6983	0.7317	0.0327	0.4343
389.4	0.6500	0.7083	0.0668	0.3647
389.7	0.6117	0.6850	0.0872	0.3319
390.2	0.5583	0.6708	0.1402	0.2327
391.3	0.4717	0.6183	0.2101	0.1870
391.7	0.4333	0.5867	0.2217	0.1793
393.2	0.3400	0.5467	0.3542	0.0862
395.9	0.2358	0.4100	0.3330	0.1195
401.7	0.1000	0.1900	0.3380	0.0830
406.2	0.0325	0.0775	0.4340	0.0360
410.0	0.0000	0.0000	0.4100	0.0000

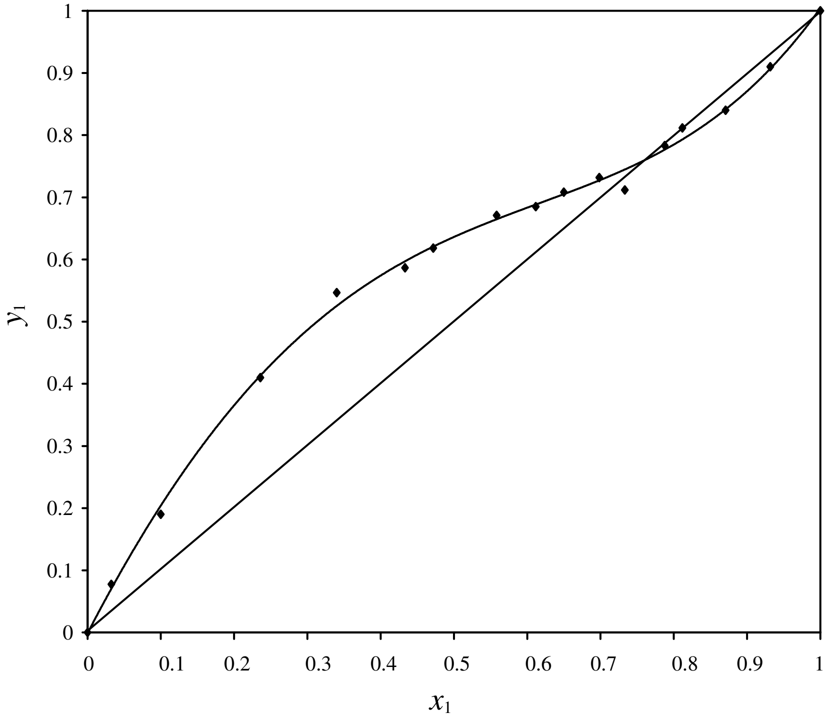

Fig. 1. Vapor–liquid equilibrium curve for 1-butanol–*p*-xylene system.

97.3 kPa are given in Figs. 1 and 2, respectively. Figure 3 shows a plot of $x_1, \ln\gamma_1$ and $x_1, \ln\gamma_2$.

The data for the system were assessed for thermodynamic consistency by applying the equal area test and found to be thermodynamically consistent. Figure 3 gives a comparison of experimental activity coefficient data with those calculated using the UNIFAC method [10]. The present study shows that an azeotrope is formed at 0.769 mole fraction of 1-butanol with a minimum boiling point of 389.05 K.

The experimental vapor–liquid equilibrium data were used to obtain binary parameters in various activity coefficient models. The Margules [11], Redlich–Kister [12], Black [13], and Wilson [14] correlations were used to fit the data. The deviations in vapor phase compositions are reasonably small for the Margules and Redlich–Kister equations (given below), and this indicates that these two activity coefficient models are suitable to represent the binary experimental data. However, the Black and Wilson models are not suitable for the system studied as the deviations in

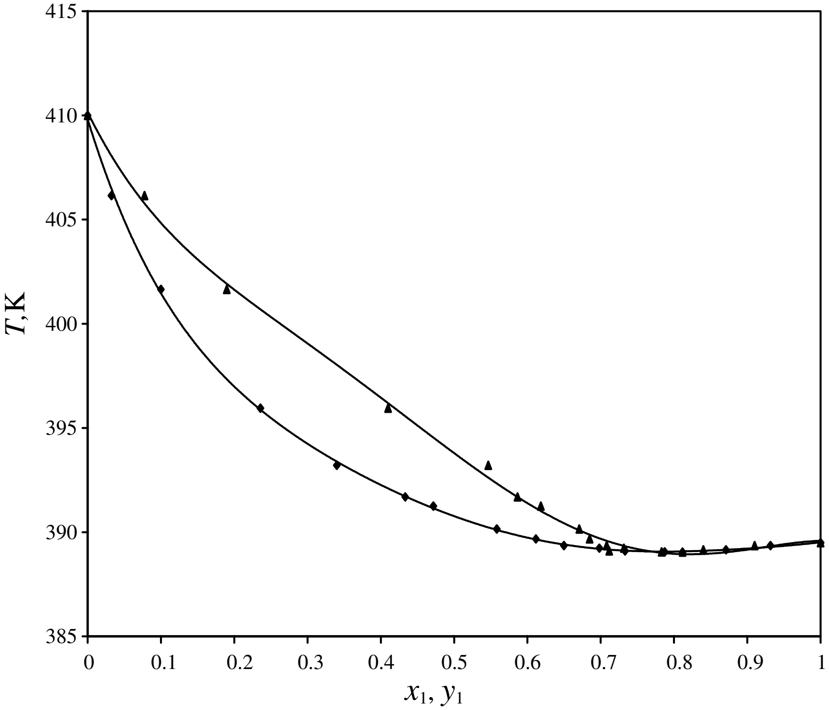

Fig. 2. T, x_1, y_1 diagram for 1-butanol–*p*-xylene system.

vapor phase compositions are relatively large. The values of the correlation parameters and absolute root-mean-square deviations in vapor phase mole fraction Δy are given in Table III.

Margules Equation:

$$\ln \gamma_1 = x_2^2[A_1 + 2(A_2 - A_1 - A_3)x_1 + 3A_3x_1^2] \tag{4}$$

$$\ln \gamma_2 = x_1^2[A_2 + 2(A_1 - A_2 - A_3)x_2 + 3A_3x_2^2] \tag{5}$$

Redlich–Kister Equation:

$$\ln \gamma_1 = x_2^2[A_1 + A_2(4x_1 - 1) + A_3(2x_1 - 1)(6x_1 - 1)] \tag{6}$$

$$\ln \gamma_2 = x_1^2[A_1 + A_2(4x_1 - 3) + A_3(2x_1 - 1)(6x_1 - 5)] \tag{7}$$

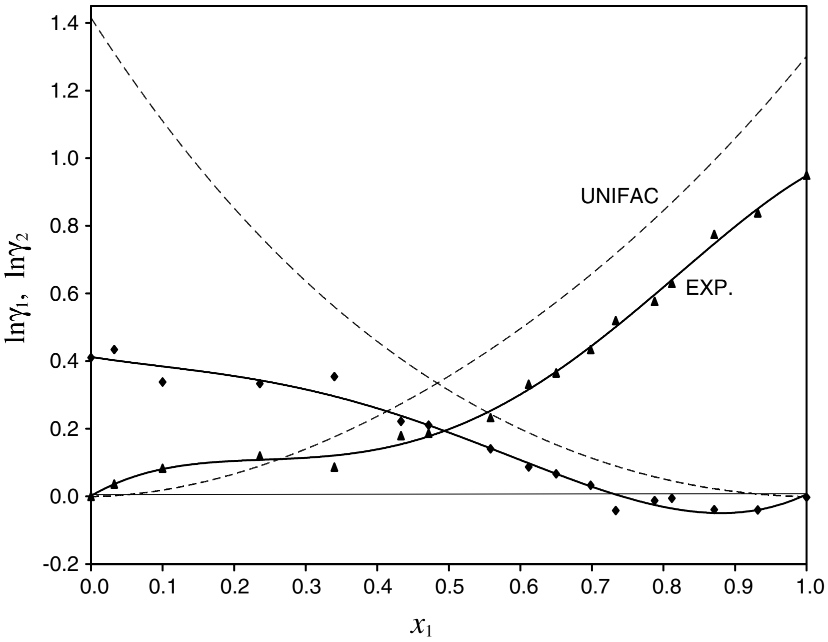

Fig. 3. ln γ_1, ln γ_2 versus x_1 diagram for 1-butanol–*p*-xylene system at 97.3 kPa: experimental (—) and UNIFAC (---).

Table III. Correlation Parameters for Activity Coefficients and Deviations in Vapor Phase Composition

Correlations	A_1	A_2	A_3	deviation (Δy)
Margules	0.39951	0.74583	−0.98955	0.040
Redlich–Kister	0.82006	0.17316	−0.24739	0.041

NOMENCLATURE

A_1, A_2, A_3	coefficients of correlations given in Table III
B	second virial coefficient of pure component, $cm^3 \cdot mol^{-1}$
$d_{298.15}$	density at 298.15 K
P^0	vapor pressure of pure component
P_c	critical pressure, kPa
R	universal gas constant
$RI_{298.15}$	refractive index at 298.15 K
T	temperature, K

T_c	critical temperature, K
T_b	normal boiling temperature of the pure component, K
V_c	critical volume, $cm^3 \cdot mol^{-1}$
Δy	root-mean-square deviation in vapor phase mole fraction
γ	activity coefficient
μ	dipole moment, Debye
ω	Pitzer's acentric factor

Subscripts

1	more volatile component
2	less volatile component

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