

## Isobaric Vapour-Liquid Equilibria of *p*-Xylene-2-Nitrotoluene System at $730 \pm 2$ mm Hg

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Isobaric vapour-liquid equilibrium data were obtained for the system *p*-xylene-2-nitrotoluene at  $730 \pm 2$  mm Hg pressure using a vapour recirculating type (modified Othmers) equilibrium still. The activity coefficients were obtained by taking into consideration the vapour phase non-ideality based on the pure component and mixture properties. The experimental data for the system was tested for thermodynamic consistency and correlated by various equations.

**Key Words:** Vapour-liquid equilibrium, Binary mixtures.

### INTRODUCTION

The vapour-liquid equilibrium studies are important because they serve as a basis for the success of many operations like distillation, both azeotropic and extractive, gas absorption, humidification and dehumidification and many chemical reactions which are carried out with a gas or vapour in intimate contact with the liquid phase. In recent years, there has been a considerable upsurge in the theoretical and experimental investigations of the vapour-liquid equilibria of binary and multicomponent mixtures. The thermodynamic properties associated with the liquids and liquid mixtures like vapour-liquid equilibria and liquid-liquid equilibria directly depend upon the nature of the molecules that constitute it; so a thorough knowledge of molecular behaviour is essential to understand completely the physical or chemical behaviour of a substance. The study of these properties is used as a tool for investigating the properties of the mixture and the nature of intermolecular interactions between the components constituting the mixture.

In the present work, isobaric vapour-liquid equilibrium data were obtained for *p*-xylene-2-nitrotoluene system at  $730 \pm 2$  mm Hg pressure using a modified version of the recirculating type equilibrium still described earlier<sup>1,2</sup>. It is a wide boiling system with a boiling range of 83.35°C. The system does not form an azeotrope. The experimental results are given in Table-2.

This study forms part of a program to study the thermodynamic and thermo-physical properties of liquid mixtures with a C<sub>8</sub> or C<sub>9</sub> aromatic hydrocarbon as one of the components.

TABLE-1  
PHYSICAL PROPERTIES OF PURE COMPONENTS

Property	<i>p</i> -Xylene	2-Nitrotoluene
m.w.	106.169 <sup>3</sup>	137.1 <sup>13</sup>
T <sub>b</sub> , K (at 760 mm Hg)	411.50 <sup>3</sup>	494.85 <sup>13</sup>
Refractive index (25°C)	1.49325 <sup>3</sup>	1.5466 (20°C) <sup>13</sup>
T <sub>c</sub> , K	616.2 <sup>11</sup>	722.0 <sup>14</sup>
P <sub>c</sub> , atm	34.641 <sup>11</sup>	39.58 <sup>14</sup>
V <sub>c</sub> , cm <sup>3</sup> mol <sup>-1</sup>	379.00 <sup>11</sup>	395.1 <sup>14</sup>
Acentric factor, ω	0.32 <sup>11</sup>	0.492 <sup>14</sup>
Dipole moment, μ, Debye	0 <sup>11</sup>	3.72 <sup>15</sup>
Antoine constants		
A	6.98820 <sup>12</sup>	5.85126 <sup>12</sup>
B	1451.792 <sup>12</sup>	946.255 <sup>12</sup>
C	215.111 <sup>12</sup>	96.072 <sup>12</sup>

TABLE-2  
VAPOUR-LIQUID EQUILIBRIUM DATA OF *p*-XYLENE (1)-  
2-NITROTOLUENE (2) SYSTEM AT 730 ± 2 mm Hg

t (°C)	x <sub>1</sub>	y <sub>1</sub>	ln γ <sub>1</sub>	ln γ <sub>2</sub>
136.85	1.0000	1.0000	0.0000	2.3200
138.95	0.9900	0.9910	-0.0530	2.2264
141.64	0.9750	0.9800	-0.1171	2.0066
147.92	0.9250	0.9590	-0.2407	1.3940
150.94	0.8850	0.9480	-0.2806	1.0978
152.80	0.8480	0.9423	-0.2861	0.8529
156.09	0.7550	0.9310	-0.2581	0.4421
158.30	0.6855	0.9256	-0.2176	0.1945
160.77	0.6050	0.9200	-0.1543	-0.0409
163.20	0.5202	0.9113	-0.0663	-0.2100
168.10	0.3976	0.8875	0.0699	-0.3515
169.40	0.3652	0.8767	0.1149	-0.3514
173.60	0.2988	0.8530	0.2005	-0.3997
177.70	0.2525	0.8310	0.2594	-0.4419
192.71	0.1500	0.7220	0.3508	-0.4743
197.55	0.1200	0.6630	0.4010	-0.4373
205.25	0.0800	0.5300	0.4490	-0.3333
211.21	0.0500	0.4034	0.5471	-0.2624
216.07	0.0250	0.2519	0.6919	-0.1686
220.62	0.0000	0.0000	1.0000	0.0000

## EXPERIMENTAL

*p*-Xylene (Riedel, Germany) and 2-nitrotoluene (S.D. Fine Chem., Mumbai, India), AR grade, were purified using standard procedures<sup>3</sup> and stored over molecular sieves. Table-1 summarizes some of the physical properties of the pure components used.

A modified version of the equilibrium still<sup>2</sup> was used for obtaining the vapour-liquid equilibrium data. The equilibrated mixtures were analyzed by the refractive index method using a Bausch & Lomb Abbe-3L refractometer. The apparatus, modifications and analytical techniques have already been described earlier<sup>4</sup>. The estimated uncertainties in the measurements of composition were 0.002 mol fraction, in temperature were 0.1°C and in pressure were ±2.0 mm Hg. Refractive index readings were taken on samples with sufficient time allowed for the sample to come to thermal equilibrium at 25°C with the help of a circulating type cryostat (Type MK70, MLW, Germany) maintained at a temperature within ±0.02 K.

## RESULTS AND DISCUSSION

The liquid phase activity coefficients were calculated from the experimental data using the equations given below, which take into account the vapour phase non-ideality along with the liquid phase:

$$\gamma_1 = (\pi y_1 / P_1^0 x_1) \exp [(B_1 - V_1)(\pi - P_1^0) / RT + \pi \delta_{12} y_2^2 / RT] \quad (1)$$

$$\gamma_2 = (\pi y_2 / P_2^0 x_2) \exp [(B_2 - V_2)(\pi - P_2^0) / RT + \pi \delta_{12} y_1^2 / RT] \quad (2)$$

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

The interactions  $B_{11}$ ,  $B_{12}$  and  $B_{22}$  are the second virial coefficients for pairs of molecules in collisions 1-1, 1-2 and 2-2 respectively.

Vapour pressures were calculated at different temperatures from Antoine's equation of the form:

$$\log P^0 = A - [B / (C + t)]$$

where  $t$  is in °C,  $P^0$  is vapour pressure in mm Hg and  $A$ ,  $B$  and  $C$  are Antoine's constants<sup>12</sup> given in Table-1.

Lyckman, Eckerts and Prausnitz<sup>5</sup> correlation was used for the estimation of liquid molar volumes. Pitzer and Curl equation modified by Tsonopoulos<sup>6</sup> was used in the evaluation of second virial coefficients as well as cross virial coefficients in this work.

Table-2 gives the experimental  $t$ - $x$ - $y$  and activity coefficients data. The  $x$ - $y$  and  $t$ - $x$ - $y$  plots for *p*-xylene and 2-nitrotoluene system at  $730 \pm 2$  mm Hg are given in Figs. 1 and 2 respectively. Fig. 3 shows the plot of  $x_1 - \ln \gamma_1$  and  $x_2 - \ln \gamma_2$ . The data for the system was assessed for thermodynamic consistency by applying the Herington area test<sup>7</sup> (Fig. 4) and Hirata test<sup>8</sup> and were found to be thermodynamically consistent. Hirata's method (Fig. 5) gave three straight lines, the upper line extending from  $x = 0.755$ , with a slope of 0.7078, the middle line

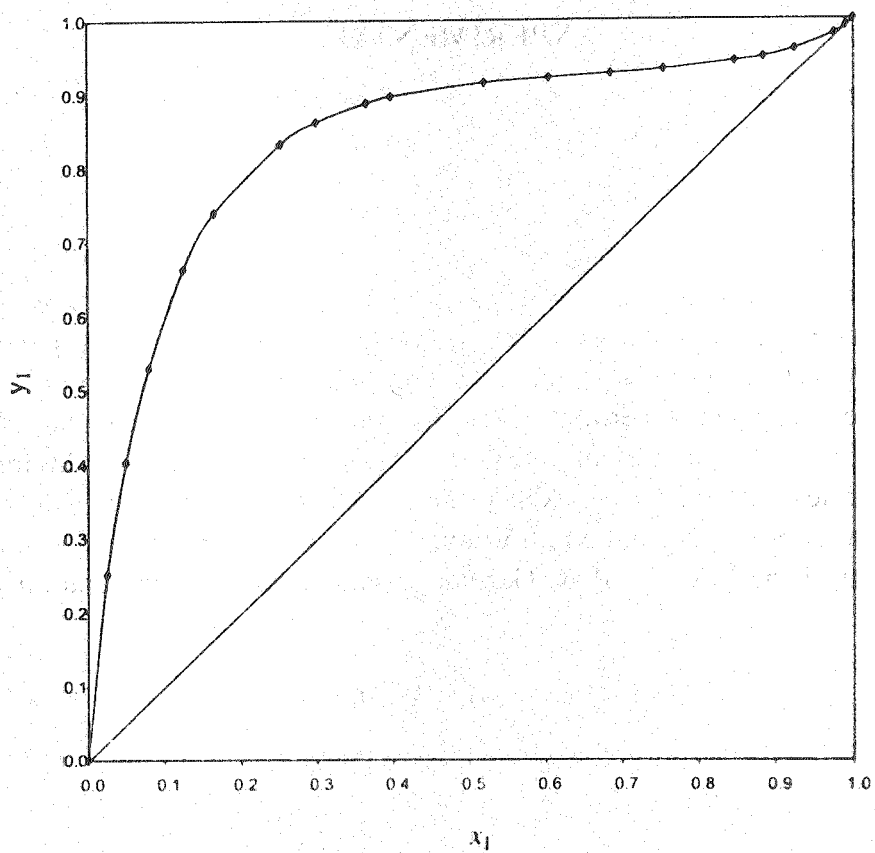


Fig. 1. Plot of vapour-liquid equilibrium data for the system p-xylene (1)-2-Nitrotoluene (2) at  $730 \pm 2$  mm Hg pressure

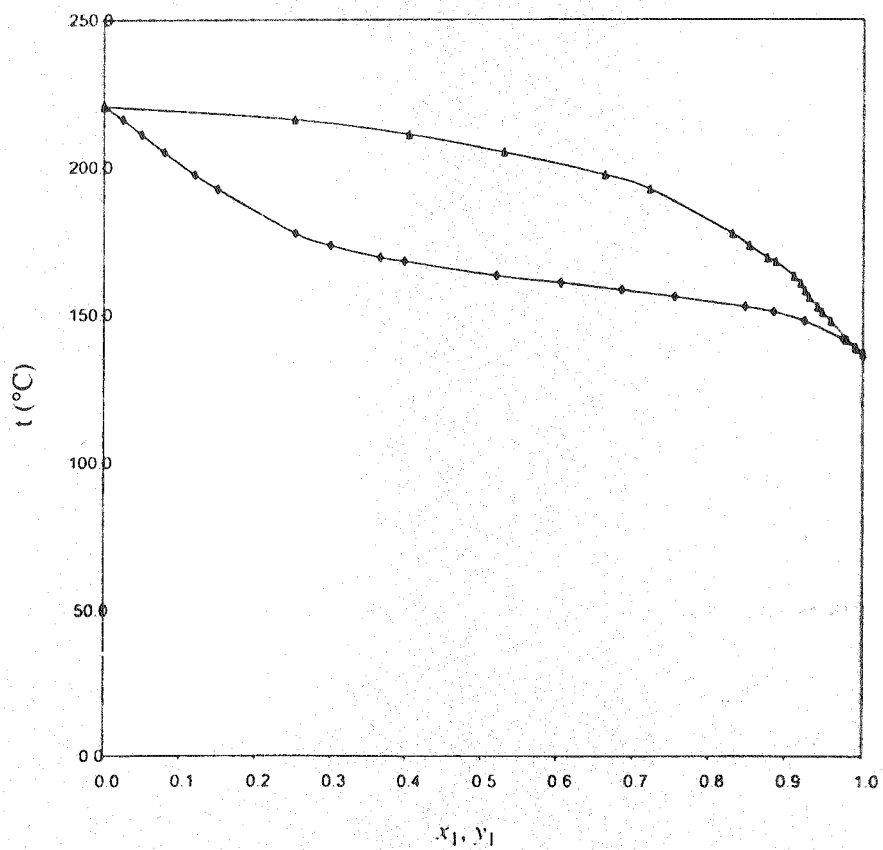


Fig. 2. Plot of  $t$  vs.  $x_1, y_1$  data for the system p-Xylene (1)-2-nitrotoluene (2)

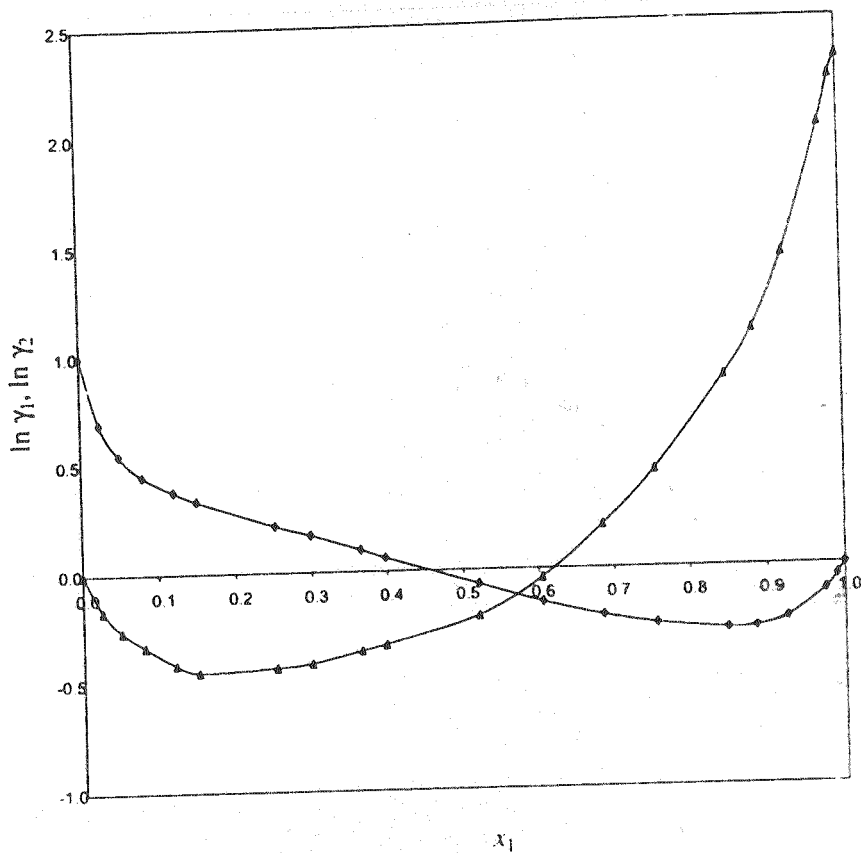


Fig. 3. Plot of  $\ln \gamma_1, \ln \gamma_2$  vs.  $x_1$  for the system *p*-xylene (1)-2-nitrotoluene (2) at  $730 \pm 2$  mm Hg

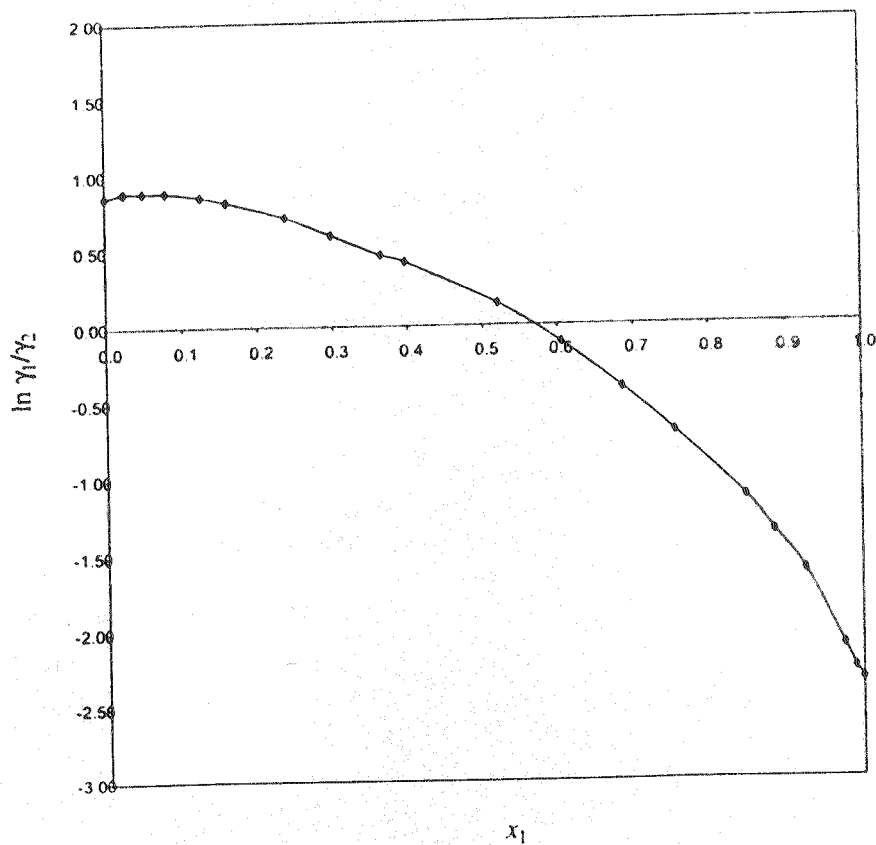


Fig. 4. Plot of  $\ln \gamma_1/\gamma_2$  vs.  $x_1$  for the system *p*-xylene (1)-2-nitrotoluene (2)

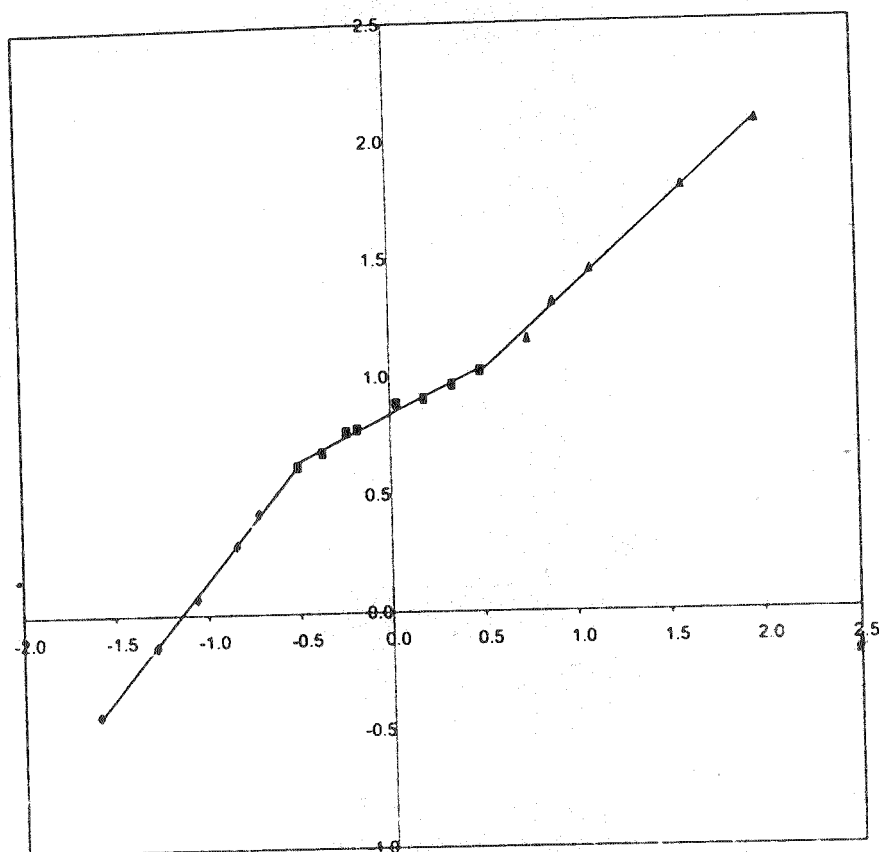


Fig. 5. Plot of  $\log(y_1/(1-y_1))$  vs.  $\log(x_1/(1-x_1))$  for the system *p*-xylene (1)-2-nitrotoluene (2) at  $730 \pm 2$  mm Hg

extending from  $x = 0.238$  to  $x = 0.755$ , with a slope of 0.3909 and the lower line extending from  $x < 0.238$ , with a slope of 0.9754.

The experimental vapour-liquid equilibrium data were used to obtain the binary parameters in various activity coefficient correlations. The deviation in vapour phase compositions for Margules<sup>9</sup> and Redlich-Kister<sup>10</sup> correlations is reasonably smaller than other correlations, which indicates that these two activity coefficient models are suitable to represent the binary experimental data. The values of these correlation parameters and absolute root mean square deviation in vapour phase mole fraction,  $\Delta y$ , are given in Table-3.

TABLE-3  
CORRELATION PARAMETERS FOR ACTIVITY COEFFICIENT AND  
DEVIATION IN VAPOUR PHASE COMPOSITION

Correlations	$A_1$	$A_2$	$A_3$	Deviation ( $\Delta y$ )
Margules	0.96159	2.28729	0.8942	0.33098
Redlich-Kister	1.40089	0.66285	0.22355	0.36990

#### Nomenclature

- $A_1, A_2, A_3$  Coefficients of correlations given in Table-3  
 B Second virial coefficient of pure component,  $\text{cm}^3 \cdot \text{mol}^{-1}$

$P^0$	Vapour pressure of pure component, mm Hg
$P^c$	Critical pressure, atm
$R$	Gas constant
$T$	Absolute temperature, K
$T_c$	Critical temperature, K
$t$	System temperature, °C
$T_b$	Normal boiling temperature of the pure component, K
$V$	Liquid molar volume of pure component, $\text{cm}^3 \cdot \text{mol}^{-1}$
$V_c$	Critical volume, $\text{cm}^3 \cdot \text{mol}^{-1}$
$x$	Mole fraction in liquid phase
$y$	Mole fraction in vapour phase
$\Delta y$	Root mean square deviation in vapour phase mole fraction
$\gamma$	Activity coefficient
$\mu$	Dipole moment, debye units
$\pi$	System pressure
$\omega$	Pitzer's acentric factor

### Subscripts

1	More volatile component
2	Less volatile component

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