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Received for review March 3, 1981. Revised manuscript received December 28, 1981. Accepted February 2, 1982.

# Isobaric Vapor–Liquid Equilibria of Toluene–Butyl Cellosolve Mixtures

**K. Venkateswara Rao,* A. Raviprasad, and C. Chiranjivi**

*Department of Chemical Engineering, Andhra University, Visakhapatnam 530003, India*

**Isobaric vapor–liquid equilibria of the system toluene–butyl cellosolve at 760 ± 1 mmHg have been reported. This system exhibits positive deviations from Raoult's law. The vapor composition is predicted from experimental *t*–*x* data using the Wilson equation as well as UNIFAC parameters. The Wilson equation predicted the vapor composition well, whereas the UNIFAC method predicted the vapor composition with an average absolute error of 0.034 mole fraction.**

Toluene is used as a diluent for butyl cellosolve in its application as an industrial solvent. The vapor–liquid equilibrium data for the system toluene–butyl cellosolve is of use in designing a solvent recovery system. So far the vapor–liquid equilibrium data of this system have not been reported. Hence, the vapor–liquid equilibrium data at 760 ± 1 mmHg pressure are determined and reported here.

## Experimental Section

***Materials.*** Analytical-grade toluene from the British Drug House Co. (India) is double distilled in a laboratory distillation column. Butyl cellosolve supplied by Naarden (Holland) is distilled under vacuum, and the middle fraction whose boiling point at atmospheric pressure coincides with that reported in the literature is collected and used. Table I compares the physical properties of the chemicals with the literature values.

***Equilibrium Still.*** A vapor recirculating still of Jones as modified by Ward (*1*) is used to determine the vapor–liquid equilibrium compositions. A still with a total capacity of about 60 mL is used. The still and the experimental technique have been described elsewhere (*2*). When the equilibrium temperature is attained in the still, this temperature is maintained for 2 h to ensure equilibrium conditions. The equilibrium temperature is measured by using a standard mercury-in-glass thermometer having an accuracy of ±0.1 °C.

***Analysis.*** The composition of the equilibrium samples is determined by refractive index. Refractive index measurements are taken at 30 ± 0.1 °C for sodium light with an Abbe precision refractometer capable of reading up to 0.0005. Water from a constant-temperature bath maintained at 30 ± 0.1 °C is circulated through the prism of the refractometer. The compositions in mole percent are determined from a standard plot of refractive index vs. composition prepared earlier by using mixtures of known composition. The maximum error in the composition measurement by refractive index is estimated to be ±0.007 mole fraction.

## Results and Discussion

The vapor–liquid equilibrium data at 760 ± 1 mmHg pressure are presented in Table II.

The liquid-phase activity coefficient of each component is calculated from the expression

$$\gamma_i = \frac{\phi_i{}^V \pi y_i}{\phi_i{}^S P^\circ x_i [V_i{}^L(\pi - P^\circ{}_i)/RT]} \qquad (1)$$

The fugacity coefficients are calculated by using the virial equation truncated after the second term. The second virial coefficient and molar volume data are estimated from Hayden and O'Connel (*3*) and Yen and Woods (*4*) correlations, respectively. The Antoine constants (*5*) for toluene and butyl cellosolve are modified to fit the experimental boiling temperatures and are used to compute the vapor pressures.

From the activity coefficient data it is found that this system exhibits small positive deviation from Raoult's law.

The data are found to be consistent by the point-to-point method (*6*).

The Wilson equation (*7*) and the UNIFAC method are used to predict the vapor compositions from *t*–*x* data. As the fugacity coefficient ratio $\phi_i{}^V/\phi_i{}^S$ and the Poynting factor in eq 1 are found to be around unity, these correction factors are neglected in the prediction of vapor composition by the two methods.

In the case of the Wilson equation, a nonlinear least-squares minimization procedure (*8*) which optimizes Wilson parameters while predicting the vapor compositions is used with the following objective function:

$$F = \sum_{1}^{N} [1 - (y_{1,\text{calcd}} + y_{2,\text{calcd}})]^2 \qquad (2)$$

The estimated vapor composition is presented in Table II. The

0021-9568/82/1727-0281$01.25/0

**Table I. Physical Properties of the Chemicals Used**

| chemical | bp, °C |  |  | refractive index |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  | exptl | lit. | ref | exptl | lit. | ref | vapor press. eq | ref |
| toluene | 110.6 | 110.6 | *11* | 1.4912 at 30 °C | 1.4912 at 30 °C | *11* | $\log P = 6.95105 - 1342.310/(t + 219.187)$ | *5* |
| butyl cellosolve | 170.6 | 170.6 | *12* | 1.4190 at 25 °C | 1.4190 at 25 °C | *12* | $\log P = 7.84562 - 1988.900/(t + 230.000)$ | *5* |

**Table II. Vapor-Liquid Equilibrium Data for the System Toluene-Butyl Cellosolve at 760 ± 1 mmHg**

| $t$, °C | $x_1$ | $y_{1,\text{exptl}}$ | $y_{1,\text{calcd}}$ (Wilson) | $y_{1,\text{calcd}}$ (UNIFAC) |
|---|---|---|---|---|
| 157.1 | 0.103 | 0.411 | 0.423 | 0.487 |
| 154.4 | 0.118 | 0.440 | 0.455 | 0.528 |
| 151.4 | 0.146 | 0.513 | 0.522 | 0.591 |
| 148.6 | 0.173 | 0.568 | 0.575 | 0.641 |
| 145.3 | 0.202 | 0.622 | 0.617 | 0.685 |
| 142.0 | 0.241 | 0.681 | 0.673 | 0.732 |
| 140.2 | 0.258 | 0.705 | 0.686 | 0.747 |
| 136.5 | 0.312 | 0.760 | 0.746 | 0.794 |
| 134.7 | 0.348 | 0.780 | 0.786 | 0.817 |
| 131.8 | 0.397 | 0.814 | 0.821 | 0.843 |
| 128.8 | 0.452 | 0.848 | 0.850 | 0.866 |
| 126.2 | 0.504 | 0.869 | 0.871 | 0.883 |
| 124.9 | 0.540 | 0.882 | 0.892 | 0.874 |
| 121.1 | 0.637 | 0.917 | 0.922 | 0.917 |
| 117.3 | 0.756 | 0.955 | 0.952 | 0.939 |
| 114.5 | 0.840 | 0.973 | 0.958 | 0.955 |
| 112.0 | 0.950 | 0.990 | 0.992 | 0.981 |

absolute average error in $y_1$ is 0.0081. The temperature-independent Wilson parameters are

$$\Lambda_{12} = 1.3877 \qquad \Lambda_{21} = 0.3870$$

For the UNIFAC method (*9*) the required parameters are taken from the data of Gmehling et al. (*10*). The groups considered are $CH_3$ (or $CH_2$), OH, $CH_2O$ for butyl cellosolve, and ACH and $ACCH_3$ for toluene. The predicted values of $y_1$ from UNIFAC are presented in Table II. The UNIFAC method predicts the vapor composition with an average absolute error of 0.0348.

The comparison of the experimental, Wilson, and UNIFAC vapor compositions is given in Figure 1.

The system toluene-butyl cellosolve is a typical example as it contains alcohol, ether, aromatic hydrocarbon, and methyl groups, and as such it provides a good test for the ability of the UNIFAC method to predict vapor-liquid equilibria. The higher values of vapor composition predicted by this method are apparently due to the use of group interaction parameters derived from compounds containing the alcohol group only or the ether group only. If group interaction parameters had been evaluated from the data of a homologue of butyl cellosolve, the prediction would have been better.

### Glossary

| | |
|---|---|
| $P°$ | vapor pressure of the pure component, mmHg |
| $R$ | universal gas constant |
| $t$ | temperature, °C |
| $T$ | temperature, K |
| $V$ | molar volume, $cm^3$/mol |
| $x$ | equilibrium liquid composition, mole fraction |
| $y$ | equilibrium vapor composition, mole fraction |

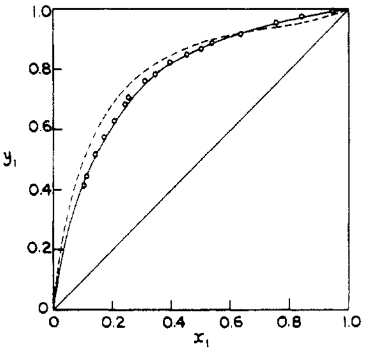

**Figure 1.** Equilibrium diagram for toluene-butyl cellosolve at 760 mmHg: (O) experimental, (—) Wilson equation, (- - -) UNIFAC.

*Greek Letters*

| | |
|---|---|
| $\gamma$ | activity coefficient |
| $\Lambda$ | Wilson parameter |
| $\pi$ | total pressure, mmHg |
| $\phi$ | fugacity coefficient |

*Superscripts*

| | |
|---|---|
| L | liquid |
| S | standard state |
| V | vapor phase |

*Subscripts*

| | |
|---|---|
| $i$ | any component |
| 1 | more-volatile component |
| 2 | less-volatile component |
| calcd | calculated |

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Received for review March 11, 1980. Revised manuscript received January 15, 1982. Accepted February 16, 1982.