

# Isobaric Vapor-Liquid Equilibria of Ethylbenzene + *m*-Xylene and Ethylbenzene + *o*-Xylene Systems at 6.66 and 26.66 kPa

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Vapor-liquid equilibrium data were obtained for systems of ethylbenzene with *m*- and *o*-xylenes at 6.66 and 26.66 kPa. The activity coefficients were found to be thermodynamically consistent. They were equally well correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations. The parameters of these equations are given.

## Introduction

Xylenes and ethylbenzene are C<sub>8</sub> benzene homologues with the molecular formula C<sub>8</sub>H<sub>10</sub>. The term "mixed xylenes" describes a mixture of ethylbenzene and the three xylene isomers. Mixed xylenes are largely derived from petroleum (*1*) and are a part of the commercial mixtures of liquid fuels for engines, due to their high octane index. These compounds have a great importance in petrochemical industries, since they are the main base for the synthesis of many organic compounds. For example, *p*-xylene is oxidized to terephthalic acid or to dimethyl terephthalate as the first step in a sequence that produces polyesters. *o*-Xylene is oxidized to phthalic anhydride which is converted to plasticizers. *m*-Xylene is oxidized to isophthalic acid for use in polyesters. Ethylbenzene is dehydrogenated to styrene.

In the last decades, the request for every one of these compounds has grown quickly; therefore, recuperation and purification of each isomer are required. However, this is technically quite complicated due to the large similarity of their physical properties. The distillation characteristics of the C<sub>8</sub> aromatic compounds are of considerable practical importance. Ethylbenzene can be separated from the remaining isomers by means of a column with more than 300 trays and a high reflux ratio. Ethylbenzene is a diluent which can accumulate in recycle processing schemes and, hence, has a strong impact on the separation of the individual xylene isomers. Equilibrium data of systems containing ethylbenzene and xylenes are needed for the correct design of the distillation columns, since the removal of ethylbenzene simplifies the subsequent separation of the C<sub>8</sub> aromatic compounds.

In this work, we report vapor-liquid equilibrium (VLE) data for two of these systems, ethylbenzene + *m*-xylene and ethylbenzene + *o*-xylene, at low pressure. Very few data for these systems are available (2-4).

## Experimental Section

**Chemicals.** Aldrich Chemical reactives were used in the experiments. Ethylbenzene and *m*-xylene (>99.0%) and *o*-xylene (>98%) were all high-purity grade. The physical properties of these components are listed in Table 1 together with literature values (5). Densities have been measured in a digital Anton Paar DMA55, German Weber S.A. densimeter and refractive indexes in an Abbe refractometer, Atago 3T.

**Apparatus and Procedure.** This apparatus used in this work was an all-glass, dynamic recirculating still described

Table 1. Densities *d*, Refractive Indexes *n*, and Boiling Points *T*<sub>b</sub> of the Compounds

| compound         | <i>d</i> (293.15 K)/<br>(g/cm <sup>3</sup> ) |          | <i>n</i> (D, 293.15 K) |          | <i>T</i> <sub>b</sub> (26.66 kPa)/K<br>exptl |
|------------------|--|----------|------------------------|----------|--|
|                  | exptl  | lit. (5) | exptl                  | lit. (5) |  |
| ethylbenzene     | 0.866 53                                     | 0.8670   | 1.4949                 | 1.4959   | 365.55                                       |
| <i>m</i> -xylene | 0.864 12                                     | 0.8642   | 1.4964                 | 1.4972   | 368.50                                       |
| <i>o</i> -xylene | 0.879 67                                     | 0.8802   | 1.5048                 | 1.5055   | 373.25                                       |

by Walas (6), equipped with a Cottrell pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures from 0.25 to 400 kPa, and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact and also in contact with the temperature-sensing element. The equilibrium temperature *T*, was measured with a digital Fisher thermometer with an accuracy of 0.1 K, and the pressure, *P*, with a digital manometer with an accuracy of 0.01 kPa. VLE data were obtained at two pressures (6.66 and 26.66 kPa) for both systems. The vapor pressures of the pure components were measured with the same recirculating still.

In each experiment the work pressure was fixed and the heating and shaking system of the liquid mixture was connected. This was kept at the boiling point for 15 min to ensure the stationary state. Once it was certain that the stationary state was reached, a sample of liquid and vapor of the Cottrell pump was taken. The extractions were carried out with special syringes which allowed us to take small volume samples in a system under partial vacuum.

Samples of 0.3 mL were withdrawn from the condensed vapor and liquid streams of the still, and were analyzed with a Hewlett-Packard 5700 A gas chromatograph (GC) with a thermal-conductivity detector. The GC response peaks were integrated by using a Hewlett-Packard 3394 A integrator. The GC column used was packed with 16% DC-200 methyl silicone oil and 3% Bentone-34 on Chromosorb W (80/100), of 3-m length and 1/8-in. diameter. Chromatographic analyses were carried out at 85 °C; the helium gas flow was 20 cm<sup>3</sup>/min.

The GC was calibrated with gravimetrically prepared standard solutions. A single analysis of the vapor or liquid composition by gas chromatography is frequently imprecise. However, with repeated measurements, the standard deviation of a composition analysis was usually less than 0.001 mole fraction. At least two analyses were made of each liquid and each vapor composition.

**Table 2. Vapor-Liquid Equilibrium Data, Liquid-Phase Mole Fraction  $x_1$ , Vapor-Phase Mole Fraction  $y_1$ , Temperature  $T$ , and Activity Coefficients  $\gamma_i$  for the Ethylbenzene (1) + *m*-Xylene (2) System at Constant Pressure  $P$**

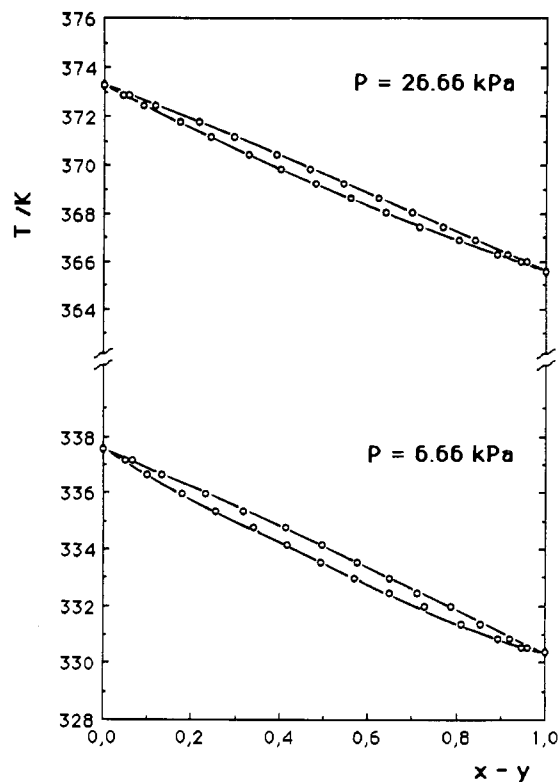
| $P/\text{kPa}$ | $x_1$ | $y_1$  | $T/\text{K}$ | $\gamma_1$ | $\gamma_2$ |
|----------------|-------|--------|--------------|------------|------------|
| 6.66           | 0.000 | 0.000  | 333.25       |            |            |
|                | 0.052 | 0.060  | 333.05       | 1.096      | 1.001      |
|                | 0.106 | 0.116  | 332.85       | 1.059      | 1.004      |
|                | 0.162 | 0.182  | 332.65       | 1.034      | 1.007      |
|                | 0.218 | 0.241  | 332.45       | 1.025      | 1.010      |
|                | 0.266 | 0.292  | 332.35       | 1.025      | 1.010      |
|                | 0.347 | 0.374  | 332.05       | 1.031      | 1.007      |
|                | 0.427 | 0.457  | 331.85       | 1.034      | 1.005      |
|                | 0.506 | 0.537  | 331.55       | 1.030      | 1.009      |
|                | 0.590 | 0.618  | 331.35       | 1.024      | 1.016      |
|                | 0.670 | 0.696  | 331.15       | 1.023      | 1.017      |
|                | 0.754 | 0.774  | 330.85       | 1.028      | 1.005      |
|                | 0.838 | 0.852  | 330.65       | 1.028      | 1.004      |
|                | 0.897 | 0.907  | 330.55       | 1.020      | 1.063      |
| 0.949          | 0.953 | 330.45 | 1.008        | 1.237      |            |
| 26.66          | 0.000 | 0.000  | 368.50       |            |            |
|                | 0.050 | 0.056  | 368.25       | 1.097      | 1.002      |
|                | 0.098 | 0.108  | 368.05       | 1.045      | 1.006      |
|                | 0.192 | 0.209  | 367.75       | 1.012      | 1.011      |
|                | 0.259 | 0.279  | 367.55       | 1.013      | 1.010      |
|                | 0.385 | 0.410  | 367.15       | 1.022      | 1.006      |
|                | 0.481 | 0.507  | 366.85       | 1.021      | 1.007      |
|                | 0.581 | 0.606  | 366.55       | 1.017      | 1.011      |
|                | 0.684 | 0.704  | 366.25       | 1.016      | 1.013      |
|                | 0.786 | 0.799  | 365.95       | 1.017      | 1.011      |
|                | 0.888 | 0.897  | 365.75       | 1.011      | 1.047      |
|                | 0.945 | 0.950  | 365.65       | 1.004      | 1.135      |
|                | 1.000 | 1.000  | 365.55       |            |            |

**Table 3. Vapor-Liquid Equilibrium Data, Liquid-Phase Mole Fraction  $x_1$ , Vapor-Phase Mole Fraction  $y_1$ , Temperature  $T$ , and Activity Coefficients  $\gamma_i$  for the Ethylbenzene (1) + *o*-Xylene (2) System at Constant Pressure  $P$**

| $P/\text{kPa}$ | $x_1$ | $y_1$ | $T/\text{K}$ | $\gamma_1$ | $\gamma_2$ |       |
|----------------|-------|-------|--------------|------------|------------|-------|
| 6.66           | 0.000 | 0.000 | 337.55       |            |            |       |
|                | 0.049 | 0.065 | 337.15       | 1.172      | 1.000      |       |
|                | 0.099 | 0.132 | 336.65       | 1.125      | 1.003      |       |
|                | 0.177 | 0.231 | 335.95       | 1.043      | 1.015      |       |
|                | 0.256 | 0.319 | 335.35       | 1.011      | 1.023      |       |
|                | 0.342 | 0.413 | 334.75       | 1.020      | 1.019      |       |
|                | 0.417 | 0.496 | 334.15       | 1.035      | 1.010      |       |
|                | 0.495 | 0.576 | 333.55       | 1.039      | 1.007      |       |
|                | 0.571 | 0.649 | 332.95       | 1.032      | 1.016      |       |
|                | 0.650 | 0.713 | 332.45       | 1.024      | 1.028      |       |
|                | 0.729 | 0.788 | 331.95       | 1.026      | 1.022      |       |
|                | 0.810 | 0.853 | 331.35       | 1.034      | 0.996      |       |
|                | 0.895 | 0.921 | 330.85       | 1.028      | 1.042      |       |
|                | 0.948 | 0.962 | 330.55       | 1.012      | 1.273      |       |
|                | 1.000 | 1.000 | 330.40       |            |            |       |
|                | 26.66 | 0.000 | 0.000        | 373.25     |            |       |
|                |       | 0.044 | 0.057        | 372.85     | 1.109      | 1.001 |
|                |       | 0.091 | 0.116        | 372.45     | 1.063      | 1.004 |
| 0.171          |       | 0.214 | 371.75       | 1.020      | 1.010      |       |
| 0.242          |       | 0.294 | 371.15       | 1.003      | 1.015      |       |
| 0.328          |       | 0.391 | 370.45       | 0.997      | 1.017      |       |
| 0.399          |       | 0.468 | 369.85       | 1.000      | 1.015      |       |
| 0.481          |       | 0.545 | 369.25       | 1.007      | 1.009      |       |
| 0.559          |       | 0.622 | 368.65       | 1.015      | 1.001      |       |
| 0.638          |       | 0.698 | 368.05       | 1.021      | 0.992      |       |
| 0.717          |       | 0.767 | 367.45       | 1.022      | 0.990      |       |
| 0.803          |       | 0.842 | 366.85       | 1.017      | 1.006      |       |
| 0.892          |       | 0.914 | 366.25       | 1.008      | 1.063      |       |
| 0.943          |       | 0.955 | 365.95       | 1.003      | 1.127      |       |
| 1.000          |       | 1.000 | 365.55       |            |            |       |

## Results and Discussion

The VLE data for both binary systems have been obtained at 6.66 and 26.66 kPa and are presented in Tables 2 and 3. The  $T$ - $x$ - $y$  diagram for ethylbenzene (1) + *o*-xylene (2) is shown in Figure 1.



**Figure 1. Vapor-liquid equilibrium temperature  $T$  of the system ethylbenzene (1) + *o*-xylene (2) at  $P = 6.66$  and  $26.66$  kPa as a function of the mole fraction of component 1.**

**Table 4. Test of Thermodynamic Consistency of the Experimental Data: Mean Average Deviation  $MAD(y)$  and Sum of the Squared Relative Deviations  $SSRD(P)$**

| system                          | $P/\text{kPa}$ | $MAD(y)$ | $SSRD(P)$ |
|---------------------------------|----------------|----------|-----------|
| ethylbenzene + <i>m</i> -xylene | 6.66           | 0.0033   | 2.20E-05  |
|                                 | 26.66          | 0.0024   | 3.01E-06  |
| ethylbenzene + <i>o</i> -xylene | 6.66           | 0.0043   | 3.18E-05  |
|                                 | 26.66          | 0.0044   | 6.36E-05  |

The activity coefficients  $\gamma_i$  of the components were calculated from

$$\gamma_i = y_i P / x_i P_i^\circ \quad (1)$$

The Poynting factor was considered as unity at the experimental conditions of this work (7), and the vapor pressures  $P_i^\circ$  were calculated with the equation

$$\ln(P_i^\circ/\text{kPa}) = A_i + B_i/(T/\text{K}) + C_i \ln(T/\text{K}) + D_i(T/\text{K})^{E_i} \quad (2)$$

using the coefficients given in the *AICHE Data Compilation Tables of Properties of Pure Compounds* (8). The fugacity coefficients calculated on the basis of the Redlich-Kwong equation of state (9), with the modification introduced by Soave (10), are nearly unity. The  $\gamma_i$  values are listed in Tables 2 and 3.

The thermodynamic consistency of the experimental data was checked by means of the point-to-point test of Van Ness et al. (11), modified by Fredenslund et al. (12), using a fifth-order Legendre polynomial where the objective function was the sum of the squared relative deviations in total pressure,  $SSRD(P)$ :

$$SSRD(P) = \sum \left( \frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}} \right)^2 \quad (3)$$

According to this test, the data are considered consistent if the mean absolute deviation in  $y$ ,  $MAD(y)$ , is less than 0.01.

**Table 5. Correlation Parameters for Activity Coefficients, Activity Coefficients at Infinite Dilution  $\gamma_i^\infty$ , and Mean Absolute Deviations MAD(y) and MAD(T)**

| P/kPa  |          | $A_{12}$             | $A_{21}$             | $\alpha_{12}$       | $\gamma_1^\infty$ | $\gamma_2^\infty$ | MAD(y) | MAD(T)/K |
|--|----------|----------------------|----------------------|---------------------|-------------------|-------------------|--------|----------|
| Ethylbenzene (1) + <i>m</i> -xylene (2) System |          |                      |                      |                     |                   |                   |        |          |
| 6.66   | Margules | 0.0365 <sup>a</sup>  | 0.1526 <sup>a</sup>  |                     | 1.04              | 1.16              | 0.0062 | 0.11     |
|  | Van Laar | 0.0381 <sup>a</sup>  | 0.2015 <sup>a</sup>  |                     | 1.04              | 1.22              | 0.0034 | 0.12     |
|  | Wilson   | -457.34 <sup>b</sup> | 809.45 <sup>b</sup>  |                     | 1.01              | 1.25              | 0.0041 | 0.12     |
|  | NRTL     | 796.48 <sup>b</sup>  | -535.14 <sup>b</sup> | 0.3051 <sup>a</sup> | 1.03              | 1.18              | 0.0051 | 0.08     |
|  | UNIQUAC  | 453.33 <sup>b</sup>  | -323.61 <sup>b</sup> |                     | 1.03              | 1.21              | 0.0051 | 0.07     |
| 26.66  | Margules | 0.0478               | 0.0880               |                     | 1.05              | 1.09              | 0.0035 | 0.10     |
|  | Van Laar | 0.0498               | 0.1398               |                     | 1.05              | 1.15              | 0.0037 | 0.09     |
|  | Wilson   | -377.12              | 589.11               |                     | 1.04              | 1.14              | 0.0028 | 0.07     |
|  | NRTL     | 610.87               | -445.30              | 0.3004              | 1.04              | 1.11              | 0.0034 | 0.09     |
|  | UNIQUAC  | 355.23               | -273.37              |                     | 1.04              | 1.12              | 0.0033 | 0.08     |
| Ethylbenzene (1) + <i>o</i> -xylene (2) System |          |                      |                      |                     |                   |                   |        |          |
| 6.66   | Margules | 0.0959               | 0.1161               |                     | 1.10              | 1.12              | 0.0062 | 0.16     |
|  | Van Laar | 0.0518               | 0.1615               |                     | 1.05              | 1.18              | 0.0047 | 0.18     |
|  | Wilson   | -390.93              | 650.09               |                     | 1.05              | 1.21              | 0.0063 | 0.13     |
|  | NRTL     | 528.05               | -366.02              | 0.3000              | 1.08              | 1.17              | 0.0062 | 0.14     |
|  | UNIQUAC  | 335.61               | -250.71              |                     | 1.07              | 1.18              | 0.0062 | 0.13     |
| 26.66  | Margules | 0.0531               | 0.0669               |                     | 1.05              | 1.07              | 0.0031 | 0.10     |
|  | Van Laar | 0.0292               | 0.0400               |                     | 1.03              | 1.04              | 0.0017 | 0.15     |
|  | Wilson   | -411.77              | 620.62               |                     | 1.02              | 1.11              | 0.0035 | 0.10     |
|  | NRTL     | 540.52               | -404.19              | 0.3007              | 1.04              | 1.09              | 0.0033 | 0.10     |
|  | UNIQUAC  | 354.06               | -274.20              |                     | 1.04              | 1.11              | 0.0034 | 0.10     |

<sup>a</sup> Dimensionless. <sup>b</sup> Calories per mole.

**Table 6. Relative Volatilities  $\alpha$  Estimated by a Polynomial Fit and Standard Deviations  $\sigma(\alpha)$** 

| system                          | P/kPa | $\alpha$ | $\sigma(\alpha)$ |
|---------------------------------|-------|----------|------------------|
| ethylbenzene + <i>m</i> -xylene | 6.66  | 1.145    | 0.026            |
|                                 | 26.66 | 1.113    | 0.008            |
| ethylbenzene + <i>o</i> -xylene | 6.66  | 1.393    | 0.068            |
|                                 | 26.66 | 1.311    | 0.040            |

In our work, for all the cases MAD(y) values obtained satisfactorily fulfill that condition as can be seen in Table 4, thereby showing them to be thermodynamically consistent.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (13). The adjustable parameters  $A_{12}$ ,  $A_{21}$ , and  $\alpha_{12}$  for the correlation data, mean absolute deviations, and activity coefficients at infinite dilution  $\gamma_i^\infty$  for the two systems are listed in Table 5. Mean absolute deviations between experimental and calculated temperatures, MAD(T), and vapor compositions, MAD(y), are of the order of estimated experimental uncertainties.

For fitting the binary parameters the Rosenbrok method (14) was used to minimize the following objective function, using the activity coefficients obtained from the consistency test as experimental values:

$$R = \sum \left( \frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}} \right)^2 \quad (4)$$

The relative volatilities  $\alpha$  calculated by means of eq 5 can be seen in Table 6; in both systems, the separation is more favorable at reduced pressures.

$$\alpha = \left[ \frac{dy_{\text{exptl}}}{dx_{\text{exptl}}} \right]_{x_{\text{exptl}} \rightarrow 0} \quad (5)$$

## Conclusions

The following conclusions can be extracted from the results obtained in this work: (1) The investigated systems show

small deviations from ideality, as can be seen from the activity coefficients at infinite dilution (Table 5). (2) The vapor-liquid equilibrium is slightly influenced by pressure.

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