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# Isobaric Vapor–Liquid Equilibrium Data for the Binary Systems 1,3,5-Trimethylbenzene/*N*-Formylmorpholine and *m*-Xylene/*N*-Formylmorpholine

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**Extractive rectification is one of the methods that can be applied when the system that is to be separated shows an azeotrope or a separation factor close to 1. The selective solvent must influence the activity coefficients of the compounds in such a way that the separation factor becomes different from unity. *N*-Formylmorpholine (NFM) often is used for these purposes, e.g., for the separation of butanes from butenes and aromatics from aliphatics. Quantitative vapor–liquid equilibrium (VLE) information is required for the design of the distillation columns. In this work VLE data for 1,3,5-trimethylbenzene and *m*-xylene with NFM at 150 mbar are reported.**

## Introduction

The design of distillation columns requires quantitative information about the *K* factors of each component on the different stages. With the modern expressions for the excess Gibbs energy (Wilson (*1*), NRTL (*2*), UNIQUAC (*3*)) these values can be obtained with binary data alone. When the binary data are missing, group contribution methods such as ASOG (*4*) or UNIFAC (*5*, *6*) can be applied. The parameters of these group contribution methods have been fitted by using VLE information published in the literature. When no consistent VLE data are available there are gaps in the parameter tables.

VLE data for the above-mentioned systems have been measured with a view extending the existing UNIFAC parameter table to selective solvents used for extractive distillation.

## Experimental Section

Commercial chemicals were used for these investigations. The purity of each chemical was tested by gas–liquid chromatography (GLC). *m*-Xylene was fractionated in a packed column. *N*-Formylmorpholine was dewatered simply by adding a molecular sieve 5A. The supplier and the obtained purity of each compound are presented in Table I.

## Vapor–Liquid Equilibrium Measurements

Vapor–liquid equilibrium measurements were performed for the two binary systems at isobaric conditions. The pressure was kept constant by a manostat (Normastat 75). A precision mercury manometer (Wallace and Tiernan) was used as a pressure measurement device as described in ref *7*. The temperature was measured by using a calibrated mercury-in-glass thermometer.

Equilibrium was attained in an all-glass equilibrium still with circulation of both the vapor and the liquid phase. The apparatus and the method of operation has been described earlier (*7*). For each data point approximately 45 min elapsed before equilibrium was attained and samples were taken by syringes.

Table I. Purity of Chemicals Used for This Investigation

| chemical | supplier | component | wt % by GLC |
|---|---|---|---|
| *N*-formylmorpholine | Krupp-Koppers | *N*-formylmorpholine | 99.94 |
| | | water | 0.06 |
| 1,3,5-trimethylbenzene | Riedel de Haen | 1,3,5-trimethylbenzene | 100 |
| *m*-xylene | Merck | *m*-xylene | 99.89 |
| | | ethylbenzene | 0.02 |
| | | *p*-xylene | 0.03 |
| | | *o*-xylene | 0.06 |

Liquid and vapor compositions were determined with a digital densimeter (DMA02D by Heraeus/Paar). It was calibrated by using air and doubly distilled water. The density measurement was carried out at 20 ± 0.01 °C. The precision at this temperature was better than $10^{-4}$ g/cm$^3$. The calibration curves were attained by measuring weighed samples of the binary hydrocarbon–NFM mixture. The measurements of the density (composition) of the equilibrium samples were repeated more than twice.

The data obtained were checked for thermodynamic consistency by using the integral test (*8*) and the point-to-point test developed by Van Ness et al. (*9*) and modified by Christiansen and Fredenslund (*10*). All data sets passed the consistency tests with good results using the criteria given in ref *11*.

## Pure Component Vapor Pressures

The dynamic still was also used for measuring the vapor pressures as a function of temperature. The data obtained were used to fit the parameters of the Antoine equation.

$$\log P_i^s = A - \frac{B}{\vartheta + C}$$

The experimental data together with the fitted Antoine constants are given in Table II. For fitting the Antoine constants the following objective function *F* was minimized by using the linear regression technique in combination with the golden section method.

$$F = \sum(\log P_{\mathrm{exp}} - \log P_{\mathrm{calc}})^2$$

## Results

The measurements for the systems 1,3,5-trimethylbenzene (1)/NFM (2) and *m*-xylene (1)/NFM (2) have been performed at a pressure of 150 mbar. Samples of each phase were analyzed by digital densimeter. Both data sets fulfilled the area and the point-to-point consistency test. The experimental data are given in Tables III and IV together with the parameters of the Margules, van Laar, Wilson, NRTL, and UNIQUAC equation, the calculated activity coefficients at infinite dilution for the different

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**Table II. Vapor Pressure Data and Fitted Antoine Constants [$P_i^s$ (mbar), $\vartheta$ (°C)]**

| 1,3,5-trimethylbenzene | | *m*-xylene | | *N*-formylmorpholine | |
|---|---|---|---|---|---|
| $\vartheta$, °C | $P_i^s$ | $\vartheta$, °C | $P_i^s$ | $\vartheta$, °C | $P_i^s$ |
| 75.500 | 49.98 | 54.000 | 50.00 | 127.700 | 30.18 |
| 81.100 | 63.00 | 64.000 | 78.08 | 129.800 | 33.13 |
| 86.800 | 80.00 | 69.700 | 99.90 | 133.150 | 38.30 |
| 91.050 | 95.00 | 75.800 | 128.20 | 136.200 | 43.30 |
| 96.900 | 119.88 | 79.780 | 150.00 | 138.700 | 48.10 |
| 102.780 | 149.05 | 87.370 | 199.78 | 140.600 | 53.20 |
| 102.850 | 150.00 | 93.480 | 248.78 | 143.300 | 58.00 |
| 108.200 | 180.00 | 98.720 | 299.90 | 146.000 | 64.90 |
| 115.800 | 234.00 | 103.310 | 348.58 | 152.800 | 84.40 |
| 123.280 | 299.80 | 107.450 | 398.60 | 156.300 | 94.80 |
| 130.500 | 377.70 | 110.020 | 428.75 | 157.900 | 99.10 |
| 135.100 | 436.18 | 114.300 | 489.18 | 160.700 | 109.15 |
| 139.650 | 500.90 | 117.350 | 539.20 | 163.350 | 119.80 |
| 142.820 | 549.90 | 122.850 | 638.08 | 165.650 | 130.00 |
| 145.800 | 599.30 | 132.000 | 837.25 | 167.600 | 139.65 |
| 148.530 | 648.70 | 136.420 | 942.65 | 169.750 | 150.00 |
| 151.200 | 699.80 | 137.900 | 978.10 | 170.750 | 154.90 |
| | | 139.200 | 1013.20 | | |

| | Antoine constants | | |
|---|---|---|---|
| | *A* | *B* | *C* |
| 1,3,5-trimethylbenzene | 7.426 85 | 1734.373 | 227.241 |
| *m*-xylene | 7.091 03 | 1437.156 | 212.552 |
| *N*-formylmorpholine | 5.998 66 | 1047.634 | 104.138 |

**Table III. Experimental Isobaric Vapor–Liquid Equilibrium Data at 150 mbar, $g^E$ Model Parameters, Calculated Activity Coefficients at Infinite Dilution, and Values for the Objective Function $F = \sum(\Delta P)^2$ (mmHg)$^2$ for the System 1,3,5-Trimethylbenzene (1)/*N*-Formylmorpholine (2)**

| | $A_{12}$ | $A_{21}$ | $\alpha_{12}$ | $\gamma_1^\infty$ | $\gamma_2^\infty$ | *F* |
|---|---|---|---|---|---|---|
| Margules | 1.1430 | 1.5105 | | 3.14 | 4.53 | 82.57*P* |
| van Laar | 1.1601 | 1.5350 | | 3.19 | 4.64 | 98.30*P* |
| Wilson | 323.6773 | 1008.6004 | | 3.13 | 5.19 | 97.72*P* |
| NRTL | 1282.5658 | -148.5446 | 0.0924 | 3.02 | 4.55 | 53.22*P* |
| UNIQUAC | 460.0740 | -120.0556 | | 3.08 | 4.62 | 67.53*P* |

| experimental data | | | experimental data | | |
|---|---|---|---|---|---|
| $\vartheta$, °C | $x_1$ | $y_1$ | $\vartheta$, °C | $x_1$ | $y_1$ |
| 169.75 | 0.0000 | 0.0000 | 113.83 | 0.3417 | 0.9223 |
| 168.70 | 0.0035 | 0.0599 | 111.75 | 0.4269 | 0.9323 |
| 167.32 | 0.0044 | 0.0906 | 109.80 | 0.5297 | 0.9436 |
| 161.90 | 0.0138 | 0.2518 | 109.02 | 0.5908 | 0.9469 |
| 153.42 | 0.0315 | 0.4486 | 108.10 | 0.6535 | 0.9525 |
| 145.50 | 0.0513 | 0.6038 | 107.00 | 0.7409 | 0.9620 |
| 140.30 | 0.0720 | 0.6825 | 106.20 | 0.7972 | 0.9677 |
| 132.35 | 0.1059 | 0.7793 | 104.90 | 0.8917 | 0.9798 |
| 129.35 | 0.1218 | 0.8099 | 104.40 | 0.9243 | 0.9852 |
| 122.85 | 0.1772 | 0.8636 | 103.72 | 0.9650 | 0.9943 |
| 120.00 | 0.2120 | 0.8850 | 102.85 | 1.0000 | 1.0000 |
| 115.80 | 0.2886 | 0.9092 | | | |

models, and the values for the objective function. The parameters of the local composition models are given in calories per mole. The parameters $A_{ij}$ do have the following meaning in the case of the local composition models (Wilson, $A_{ij} = (\lambda_{ij} - \lambda_{ii})$; NRTL, $A_{ij} = (g_{ij} - g_{jj})$; UNIQUAC, $A_{ij} = (u_{ij} - u_{jj})$).

For fitting the binary parameters the Simplex-Nelder-Mead method (*12*) was used to minimize the absolute pressure deviation. Ideal vapor-phase behavior was assumed to simplify the adjusting of the parameters. The required pure component properties for the Wilson and UNIQUAC equation are given in Table V.

Figures 1–4 show graphical representations of the experimental and the calculated data in the form of *y*–*x* and *T*–*xy* diagrams, whereby the calculated values have been obtained by means of the Wilson equation. As can be seen from the diagrams, there is in all cases good agreement between experimental and calculated values.

**Table IV. Experimental Isobaric Vapor–Liquid Equilibrium Data at 150 mbar, $g^E$ Model Parameters, Calculated Activity Coefficients at Infinite Dilution, and Values for the Objective Function $F = \sum(\Delta P)^2$ (mmHg)$^2$ for the System *m*-Xylene (1)/*N*-Formylmorpholine (2)**

| | $A_{12}$ | $A_{21}$ | $\alpha_{12}$ | $\gamma_1^\infty$ | $\gamma_2^\infty$ | *F* |
|---|---|---|---|---|---|---|
| Margules | 0.9956 | 1.4213 | | 2.71 | 4.14 | 19.58*P* |
| van Laar | 1.0128 | 1.4818 | | 2.75 | 4.40 | 17.65*P* |
| Wilson | 282.1131 | 880.5388 | | 2.63 | 4.86 | 24.33*P* |
| NRTL | 883.5631 | 173.4099 | 0.2907 | 2.58 | 4.44 | 26.87*P* |
| UNIQUAC | 390.4026 | -87.8979 | | 2.59 | 4.45 | 25.11*P* |

| experimental data | | | experimental data | | |
|---|---|---|---|---|---|
| $\vartheta$, °C | $x_1$ | $y_1$ | $\vartheta$, °C | $x_1$ | $y_1$ |
| 169.75 | 0.0000 | 0.0000 | 88.23 | 0.5094 | 0.9802 |
| 165.00 | 0.0033 | 0.1422 | 86.85 | 0.5803 | 0.9817 |
| 157.80 | 0.0112 | 0.3288 | 85.83 | 0.6399 | 0.9834 |
| 135.20 | 0.0476 | 0.7289 | 84.52 | 0.7280 | 0.9867 |
| 125.83 | 0.0711 | 0.8243 | 83.79 | 0.7810 | 0.9878 |
| 119.65 | 0.0920 | 0.8678 | 82.93 | 0.8350 | 0.9897 |
| 110.12 | 0.1412 | 0.9140 | 82.22 | 0.8809 | 0.9913 |
| 99.75 | 0.2287 | 0.9558 | 81.62 | 0.9123 | 0.9929 |
| 93.85 | 0.3243 | 0.9689 | 80.31 | 0.9776 | 0.9973 |
| 91.25 | 0.3940 | 0.9740 | 79.78 | 1.0000 | 1.0000 |

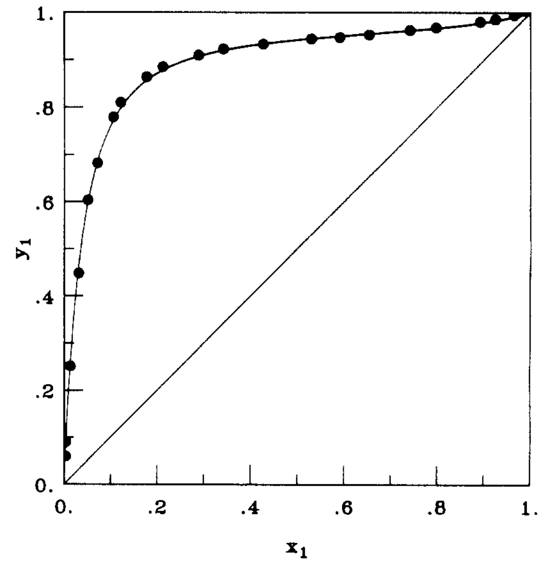

**Figure 1.** *y*–*x* diagram for the binary system 1,3,5-trimethylbenzene (1)/*N*-formylmorpholine (2) at 150 mbar.

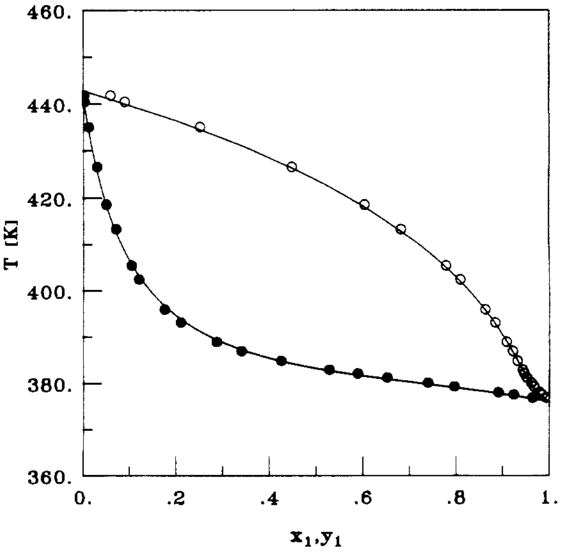

**Figure 2.** *T*–*xy* diagram for the binary system 1,3,5-trimethylbenzene (1)/*N*-formylmorpholine (2) at 150 mbar.

**Table V. Relative van der Waals Properties $r_i$ and $q_i$ and Molar Volumes $v_i$ for the Compounds Investigated**

| | $r_i$ | $q_i$ | $v_i$ |
|---|---|---|---|
| 1,3,5-trimethylbenzene | 5.3928 | 4.1044 | 138.93 |
| *m*-xylene | 4.6578 | 3.536 | 123.47 |
| *N*-formylmorpholine | 4.2248 | 3.44 | 121.06 |

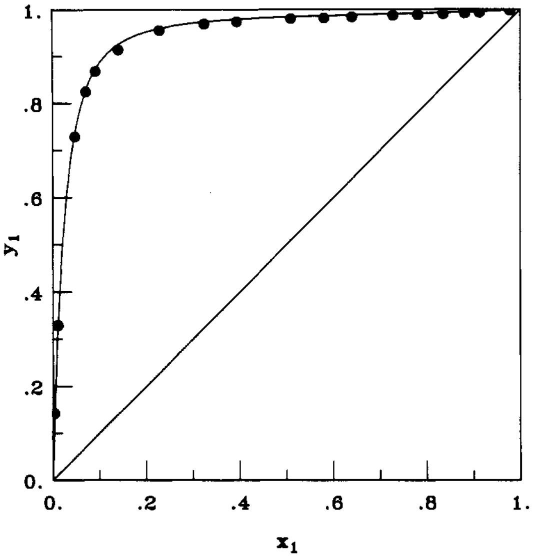

**Figure 3.** *y*-*x* diagram for the binary system *m*-xylene (1)/*N*-formylmorpholine (2) at 150 mbar.

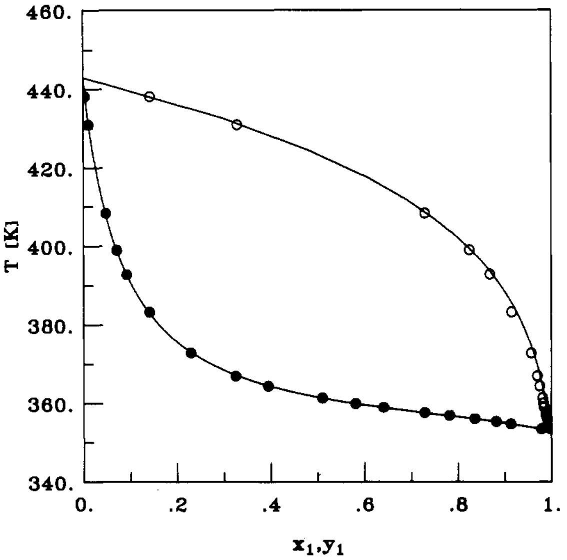

**Figure 4.** *T*-*xy* diagram for the binary system *m*-xylene (1)/*N*-formylmorpholine (2) at 150 mbar.

## Conclusion

Experimental VLE data have been obtained for the binary systems 1,3,5-trimethylbenzene/*N*-formylmorpholine and *m*-xylene/*N*-formylmorpholine. The calculated values for the activity coefficients at infinite dilution of the aromatics in *N*-formylmorpholine do agree with the data reported for the different aromatics, such as benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, and isopropylbenzene (*13*). It is intended to use these data together with other VLE data and activity coefficients at infinite dilution for the extension of the UNIFAC method to selective solvents for extractive distillation.

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## Glossary

| | |
|---|---|
| $A$, $B$, $C$ | parameters of the Antoine equation |
| $F$ | objective function |
| $g_{ij}$ | interaction parameter in the NRTL equation |
| $P$ | total pressure |
| $P_i^s$ | saturation vapor pressure |
| $q_i$ | relative van der Waals surface area of component $i$ |
| $r_i$ | relative van der Waals volume of component $i$ |
| $T$ | absolute temperature in K |
| $u_{ij}$ | interaction parameter in the UNIQUAC equation |
| $v_i$ | molar volume of component $i$ |
| $x_i$ | mole fraction of component $i$ in the liquid phase |
| $y_i$ | mole fraction of component $i$ in the vapor phase |
| $\alpha$ | nonrandomness factor in the NRTL equation |
| $\vartheta$ | temperature in °C |
| $\lambda_{ij}$ | interaction parameter in the Wilson equation |
| $\gamma_i^\infty$ | activity coefficient of component $i$ at infinite dilution |

**Registry No.** NFM, 4394-85-8; *m*-xylene, 108-38-3; 1,3,5-trimethylbenzene, 108-67-8.

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