# Thermodynamics of Ternary Liquid Mixtures Containing Toluene, Ethylbenzene, and Chlorobenzene

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Excess molar enthalpy ($H^E$) data and vapor−liquid equilibria (VLE) were measured for the ternary system toluene + ethylbenzene + chlorobenzene. Ternary $H^E$ values were measured with a Calvet-type microcalorimeter at 298.15 K. These results together with literature $H^E$ data of constituent binaries were used for a correlation with the modified Redlich−Kister equation. Boiling temperature ($T$)−liquid composition ($x$) relations were obtained at (26.66, 53.33, 79.99, and 101.32) kPa by using a semimicroebulliometer. The modified Wilson model with parameters that linearly depend on temperature was used to correlate the binary $T-x$ data and to predict VLE in the ternary system. Excess functions at 298.15 K were compared.

## Introduction

The determination of thermodynamic properties of mixtures represents an important topic of both scientific and industrial interest, linked to testing and extension of model theories of mixtures on one side and to the design of separation and purification processes on the other. In previous work,[1,2] we reported experimental excess molar enthalpy ($H^E$) and vapor−liquid equilibrium (VLE) in the ternary system containing toluene, *p*-xylene, and 1,2-dichloroethane. To obtain further information on the thermodynamic properties of ternary mixtures that contain aromatic compounds, we measured molar excess enthalpy at the temperature 298.15 K and vapor−liquid equilibria at the pressures (26.66, 53.33, 79.99, and 101.32) kPa for the system toluene + ethylbenzene + chlorobenzene. Such information for this ternary system has not been found in the literature, but there are several data sets for all constituent binaries. Among them are the $H^E$ data of interest at 298.15 K for toluene + ethylbenzene reported by Recko and Sadowska,[3] Woicicki,[4] and Tanaka and Benson,[5] for toluene + chlorobenzene reported by Tanaka and Benson,[6] Münsch,[7] and Fujihara et al.,[8] and for ethylbenzene + chlorobenzene reported by the above-mentioned authors.[3,6,7] Comparable $T-x$ data at 101.32 kPa were reported for the system toluene + ethylbenzene by Makh and Azarova, [9] Martirosyan et al.,[10] Wohland and Pape,[11] and Kutsarov et al.[12] For the system toluene + chlorobenzene the VLE data at 101.32 kPa were obtained by Wohland and Pape[11] and Borisova et al.,[13] and for ethylbenzene + chlorobenzene data were obtained by Wohland and Pape[11] and Machova et al.[14] We have not found data in the literature investigated at other pressures chosen by us.

VLE data obtained here were used to test the reliability of the modified Wilson equation with the binary parameters depending linearly on temperature, to predict excess Gibbs energy, $G^E$, and to connect it with ternary excess enthalpy measured at 298.15 K.

## Experimental Section

***Materials.*** All substances were twice purified by vacuum rectification. Their purity was checked by gas chromatography and found to be better than 99.5 mass %. Densities measured at 298.15 K in a capillary pycnometer were (862.2, 862.5, and 1100.8) kg·m$^{-3}$ for toluene, ethylbenzene, and chlorobenzene, respectively.

***Apparatus and Procedure.*** A microcalorimeter DAK-1-1 of Calvet-type was used for measurements of excess enthalpies at 298.15 K. The details of the calorimetric procedure and the reproducibility test of this calorimetric system were described previously.[15,16] The uncertainty of the excess enthalpies was estimated to be <2%, as the result of the chemical and electrical calibration.

The boiling temperature−liquid mole fraction ($T-x$) measurements were performed by means of a semimicroebulliometer. The experimental arrangement and the procedure of determining the $T-x$ relation were described previously.[17,18] Uncertainties of the boiling temperature measurements were estimated to be <0.05 K. Equilibrium pressure was measured by a mercury manometer. The absolute accuracy of these measurements is probably within 13 Pa.

All mixtures were prepared by weight. Uncertainties of mole fraction composition of a liquid mixture ($x_i$) were evaluated to be $<5 \times 10^{-4}$.

## Results and Discussion

Validation measurements of binary $H^E$ at 298.15 K over the whole mole fraction range showed that the average relative deviations between our results and those of Tanaka and Benson[5,6] for all constituent binaries were <1.0%, with a maximum deviation 1.5%. Therefore, the data of Tanaka and Benson were fitted with eq 1, and the coefficients $A_i$ were used in this work for calculation of the ternary system.

$$H^E/(\text{J}\cdot\text{mol}^{-1}) = \boldsymbol{x}_1(1-\boldsymbol{x}_1)\sum_{i=0}^{k-1} A_i(2\boldsymbol{x}_1-1)^i \qquad (1)$$

The $A_i$ values are given in Table 1 together with those of standard deviations

$$\sigma(H^E)/(\text{J}\cdot\text{mol}^{-1}) = [\sum (H^E_{\text{calc}} - H^E_{\text{exp}})^2/(N-k)]^{1/2} \qquad (2)$$

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10.1021/je020186c CCC: $25.00

**Table 1. Coefficients of Eq 1 and Standard Deviations Calculated by Eq 2**

| $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma(H^E)$ |
|---|---|---|---|---|---|
| Toluene (1) + Ethylbenzene (2) | | | | | |
| −36.83 | −1.987 | 0.196 | 0.805 | - | 0.04 |
| Toluene (1) + Chlorobenzene (2) | | | | | |
| −475.07 | −34.42 | 2.14 | 5.58 | 6.69 | 0.15 |
| Ethylbenzene (1) + Chlorobenzene (2) | | | | | |
| −614.45 | −5.24 | 23.38 | −8.69 | −22.09 | 0.26 |

**Table 2. Experimental and Calculated Molar Excess Enthalpies ($H^E$) for the Ternary System Toluene (1) + Ethylbenzene (2) + Chlorobenzene (3) at 298.15 K**

| molar fractions | | | $H^E$/J·mol$^{-1}$ | |
|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | exp | calc |
| | | $x_1/x_2 = 1.0$ | | |
| 0.500 | 0.500 | 0.000 | −9.2 | −9.2 |
| 0.381 | 0.381 | 0.238 | −107 | −107 |
| 0.3465 | 0.3465 | 0.307 | −125 | −123 |
| 0.3405 | 0.3405 | 0.319 | −126 | −125 |
| 0.335 | 0.335 | 0.330 | −128 | −127 |
| 0.2955 | 0.2955 | 0.409 | −133 | −137 |
| 0.2595 | 0.2595 | 0.481 | −134 | −140 |
| 0.219 | 0.219 | 0.562 | −131 | −136 |
| 0.1845 | 0.1845 | 0.631 | −127 | −127 |
| 0.179 | 0.179 | 0.642 | −123 | −125 |
| 0.125 | 0.125 | 0.750 | −101 | −100 |
| 0.116 | 0.116 | 0.768 | −98 | −95 |
| 0.115 | 0.115 | 0.770 | −97 | −95 |
| | | $x_1/x_3 = 1.0$ | | |
| 0.500 | 0.000 | 0.500 | −119 | −119 |
| 0.371 | 0.258 | 0.371 | −131 | −130 |
| 0.335 | 0.330 | 0.335 | −128 | −128 |
| 0.3135 | 0.373 | 0.3135 | −126 | −126 |
| 0.267 | 0.466 | 0.267 | −118 | −117 |
| 0.223 | 0.554 | 0.223 | −107 | −106 |
| 0.1715 | 0.657 | 0.1715 | −89 | −89 |
| 0.1275 | 0.745 | 0.1275 | −72 | −70 |
| | | $x_2/x_3 = 1.0$ | | |
| 0.000 | 0.500 | 0.500 | −153 | −154 |
| 0.277 | 0.3615 | 0.3615 | −135 | −134 |
| 0.330 | 0.335 | 0.335 | −128 | −128 |
| 0.508 | 0.246 | 0.246 | −104 | −105 |
| 0.522 | 0.239 | 0.239 | −102 | −102 |
| 0.725 | 0.1375 | 0.1375 | −65 | −66 |

where $N$ is the number of experimental points and $k$ is the number of parameters.

The ternary $H^E$ was calculated as the sum of binary terms with an added ternary contribution as described in previous work,[19]

$$H^E_{calc} = H^E_{12} + H^E_{23} + H^E_{31} + H^E_{123} \tag{3}$$

where

$$H^E_{123} = x_1x_2x_3[C_0 + C_1x_1^m + C_2x_2^m + C_3x_3{}^m] \tag{4}$$

Taking an optimum value of $m = 4$, the coefficients $C_0$, $C_1$, $C_2$, and $C_3$ were calculated by a least-squares method; they are equal to −61.35, 3.10, −401.26, and 0, respectively, with standard deviation 2.65 J·mol$^{-1.}$

The experimental results of excess enthalpies of the ternary system are summarized in Table 2 together with calculated values of $H^E$. The mean absolute relative error between calculated and experimental results was equal to 1.26%.

The experimental values of boiling temperature measurements for binary systems at the pressures (26.66, 53.33, 79.99, and 101.32) kPa are reported in Table 3.

**Table 3. Isobaric Vapor−Liquid Equilibrium Data: Liquid Phase Mole Fraction ($x_1$) and Boiling Temperatures ($T$) in Binary Systems**

| | $T$/K at pressure $P$/kPa | | | |
|---|---|---|---|---|
| $x_1$ | $P = 26.66$ | $P = 53.33$ | $P = 79.99$ | $P = 101.32$ |
| | Toluene (1) + Ethylbenzene (2) | | | |
| 0.000 | 365.86 | 386.94 | 400.70 | 409.31 |
| 0.188 | 360.27 | 381.34 | 395.07 | 403.63 |
| 0.316 | 357.03 | 377.91 | 391.40 | 399.88 |
| 0.323 | 356.78 | 377.68 | 391.30 | 399.80 |
| 0.379 | 355.73 | 376.48 | 389.97 | 398.43 |
| 0.434 | 353.90 | 374.66 | 388.23 | 396.67 |
| 0.447 | 353.73 | 374.36 | 387.90 | 396.30 |
| 0.513 | 352.10 | 372.72 | 386.16 | 394.47 |
| 0.606 | 350.23 | 370.67 | 384.07 | 392.38 |
| 0.702 | 348.12 | 368.52 | 381.78 | 389.83 |
| 0.773 | 346.68 | 366.97 | 380.16 | 388.37 |
| 0.872 | 344.99 | 365.13 | 378.23 | 386.37 |
| 1.000 | 342.65 | 362.63 | 375.66 | 383.76 |
| | Toluene (1) + Chlorobenzene (2) | | | |
| 0.000 | 361.57 | 382.63 | 396.37 | 404.90 |
| 0.286 | 355.40 | 376.10 | 389.68 | 398.09 |
| 0.419 | 352.54 | 373.22 | 386.60 | 394.97 |
| 0.492 | 351.18 | 371.69 | 385.13 | 393.45 |
| 0.611 | 348.98 | 369.33 | 382.67 | 390.94 |
| 0.717 | 347.09 | 367.39 | 380.67 | 388.89 |
| 0.793 | 345.86 | 366.06 | 379.23 | 387.47 |
| 1.000 | 342.65 | 362.63 | 375.66 | 383.76 |
| | Ethylbenzene (1) + Chlorobenzene (2) | | | |
| 0.000 | 361.57 | 382.63 | 396.37 | 404.90 |
| 0.119 | 362.12 | 383.16 | 396.90 | 405.45 |
| 0.303 | 362.95 | 383.99 | 397.73 | 406.26 |
| 0.502 | 363.73 | 384.82 | 398.59 | 407.16 |
| 0.704 | 364.61 | 385.72 | 399.46 | 408.09 |
| 0.853 | 365.17 | 386.33 | 400.13 | 408.76 |
| 1.000 | 365.86 | 386.94 | 400.70 | 409.31 |

**Table 4. Fitted Coefficients of the Modified Wilson Equation (Eq 5) and Calculated Absolute Mean Errors ($\Delta P$) and Standard Deviations ($\sigma P$) of Pressure for Binary Systems**

| $a_{12}$ | $b_{12}$ | $a_{21}$ | $b_{21}$ | $\Delta P$/% | $\sigma P$/kPa |
|---|---|---|---|---|---|
| Toluene + Ethylbenzene | | | | | |
| 0.162 10 | −46.534 | −0.076 16 | 37.961 | 0.24 | 0.23 |
| Toluene + Chlorobenzene | | | | | |
| −0.223 78 | 308.555 | 0.673 41 | −544.956 | 0.09 | 0.08 |
| Ethylbenzene + Chlorobenzene | | | | | |
| −0.808 0 | 408.923 | 1.121 43 | −538.575 | 0.06 | 0.04 |

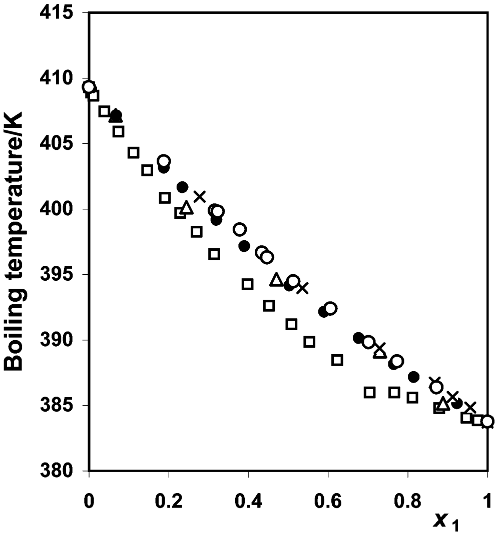

**Figure 1.** Boiling temperature−composition diagram for toluene (1) + ethylbenzene (2) at 101.32 kPa: ○, this work; ×, Wohland and Pape;[11] □, Kutsarov et al.;[12] △, Makh and Azarova;[9] ●, Martirosyan et al.[10]

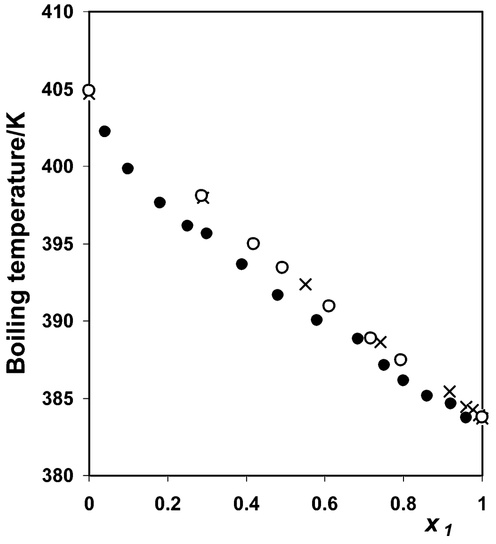

**Figure 2.** Boiling temperature−composition diagram for toluene (1) + chlorobenzene (2) at 101.32 kPa: ○, this work; ×, Wohland and Pape;[11] ●, Borisova et al.[13]

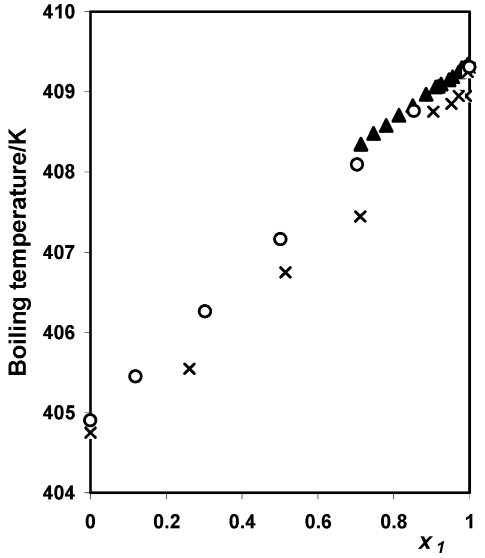

**Figure 3.** Boiling temperature−composition diagram for ethylbenzene (1) + chlorobenzene (2) at 101.32 kPa: ○, this work; ×, Wohland and Pape;[11] ▲, Machova et al.[14]

**Table 5. Coefficients for the Antoine Vapor Pressure Equation (kPa, K) (Eq 6)**

| component | $A_i$ | $B_i$ | $C_i$ | temp range/K |
|---|---|---|---|---|
| toluene | 14.084 06 | 3148.177 | −51.1715 | 342−384 |
| ethylbenzene | 13.707 77 | 3083.502 | −70.0678 | 365−410 |
| chlorobenzene | 14.095 35 | 3326.021 | −53.9457 | 361−405 |

Our results are compared with literature data available at 101.32 kPa in Figures 1−3. $T-x$ data obtained for toluene + ethylbenzene agree with those of Makh and Azarova[9] and Martirosyan et al.[10] The results for both binary systems containing toluene are in agreement with data obtained by Wohland and Pape,[11] as shown in Figures 1 and 2. The $T-x$ data for ethylbenzene + chlorobenzene, illustrated in Figure 3, agree in the ethylbenzene-rich region with data reported by Machova et al.[14] The boiling points reported by Wohland and Pape[11] are lower than our measurements within the overlapped uncertanties.

The $T-x$ data of binary systems were fitted with the Wilson model,[20] which is traditionally used when VLE data have to be reduced. We have used the modified form of this

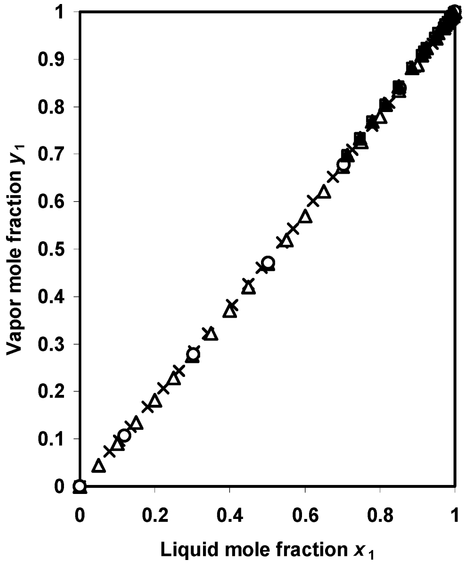

**Figure 4.** Vapor composition−liquid composition diagram for ethylbenzene (1) + chlorobenzene (2) at 101.32 kPa: ○, this work; ×, Hawkins and Brent;[23] △, Gardy and Bugarel;[22] ▲, Machova et al.[14]

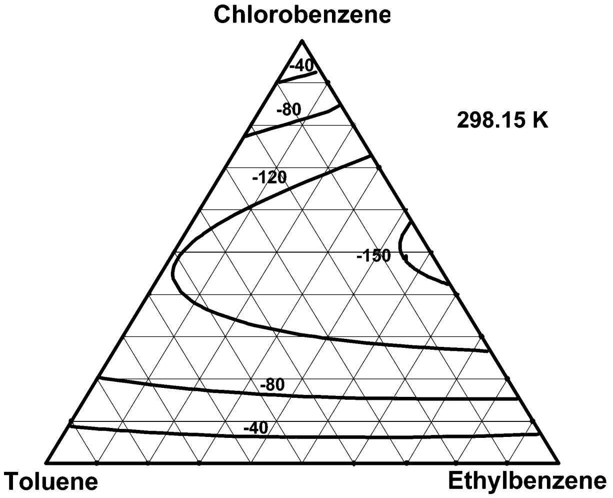

**Figure 5.** Calculated isoenthalpic curves for the ternary system toluene + ethylbenzene + chlorobenzene at 298.15 K.

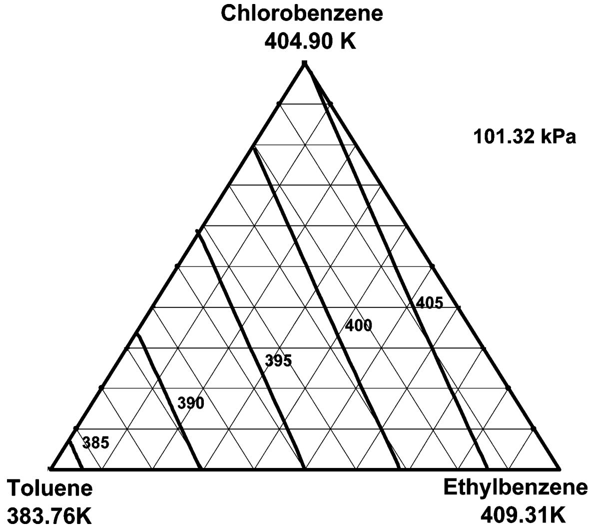

**Figure 6.** Calculated boiling temperature isotherms for the ternary system toluene + ethylbenzene + chlorobenzene at 101.32 kPa.

**Table 6. Experimental Vapor−Liquid Equilibria Data for the Ternary System Toluene (1) + Ethylbenzene (2) + Chlorobenzene (3) at Four Pressures and Values Calculated by the Modified Wilson Equation[21] of Activity Coefficients ($\gamma_1$, $\gamma_2$, and $\gamma_3$), Vapor Mole Fractions ($y_1$ and $y_2$), Excess Gibbs Energy ($G^E$), Pressure ($P_{calc}$), and Boiling Temperature ($T_{calc}$)**

| experimental data | | | calculated values | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| liquid mole fraction | | boiling temp | activity coefficients | | | vapor mole fraction | | Gibbs energy | pressure | boiling temp |
| $x_1$ | $x_2$ | $T_{exp}$/K | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $y_1$ | $y_2$ | $G^E$/J·mol$^{-1}$ | $P_{calc}$/kPa | $T_{calc}$/K |
| $P = 101.32$ kPa | | | | | | | | | | |
| 0.530 | 0.235 | 393.46 | 0.988 | 0.975 | 0.983 | 0.685 | 0.147 | −52.8 | 101.30 | 393.47 |
| 0.759 | 0.120 | 388.35 | 0.998 | 0.957 | 0.969 | 0.863 | 0.063 | −35.2 | 101.11 | 388.42 |
| 0.232 | 0.384 | 400.88 | 0.965 | 0.991 | 0.995 | 0.356 | 0.302 | −45.0 | 101.36 | 400.87 |
| 0.334 | 0.333 | 398.45 | 0.975 | 0.986 | 0.993 | 0.483 | 0.242 | −51.9 | 101.91 | 398.24 |
| 0.195 | 0.537 | 402.53 | 0.960 | 0.995 | 0.993 | 0.309 | 0.442 | −42.1 | 101.72 | 402.39 |
| 0.492 | 0.339 | 394.62 | 0.985 | 0.980 | 0.983 | 0.655 | 0.220 | −55.5 | 101.23 | 394.65 |
| 0.702 | 0.199 | 389.83 | 0.996 | 0.964 | 0.971 | 0.827 | 0.110 | −42.9 | 101.46 | 389.78 |
| 0.352 | 0.432 | 398.16 | 0.975 | 0.989 | 0.989 | 0.509 | 0.314 | −53.9 | 101.26 | 398.18 |
| 0.251 | 0.250 | 400.23 | 0.969 | 0.987 | 0.997 | 0.376 | 0.190 | −43.4 | 102.32 | 399.87 |
| 0.400 | 0.200 | 396.29 | 0.981 | 0.979 | 0.991 | 0.552 | 0.136 | −50.7 | 101.53 | 396.22 |
| 0.606 | 0.131 | 391.50 | 0.993 | 0.966 | 0.980 | 0.747 | 0.076 | −46.4 | 101.28 | 391.51 |
| 0.126 | 0.748 | 405.01 | 0.951 | 0.999 | 0.988 | 0.211 | 0.664 | −29.8 | 101.45 | 404.96 |
| $P = 79.99$ kPa | | | | | | | | | | |
| 0.530 | 0.235 | 385.11 | 0.988 | 0.975 | 0.983 | 0.690 | 0.144 | −51.8 | 79.99 | 385.11 |
| 0.759 | 0.120 | 380.12 | 0.998 | 0.957 | 0.968 | 0.866 | 0.062 | −34.5 | 79.83 | 380.19 |
| 0.232 | 0.384 | 392.40 | 0.965 | 0.991 | 0.995 | 0.360 | 0.299 | −43.5 | 80.07 | 392.36 |
| 0.334 | 0.333 | 389.97 | 0.974 | 0.987 | 0.992 | 0.488 | 0.239 | −50.5 | 80.43 | 389.78 |
| 0.195 | 0.537 | 393.99 | 0.960 | 0.995 | 0.993 | 0.313 | 0.439 | −40.3 | 80.30 | 393.86 |
| 0.492 | 0.339 | 386.22 | 0.985 | 0.981 | 0.982 | 0.659 | 0.217 | −54.0 | 79.88 | 386.27 |
| 0.702 | 0.199 | 381.52 | 0.996 | 0.964 | 0.971 | 0.830 | 0.108 | −41.9 | 80.02 | 381.51 |
| 0.352 | 0.432 | 389.68 | 0.975 | 0.989 | 0.989 | 0.514 | 0.310 | −52.3 | 79.89 | 389.72 |
| 0.251 | 0.250 | 391.72 | 0.968 | 0.987 | 0.996 | 0.381 | 0.188 | −42.4 | 80.75 | 391.39 |
| 0.400 | 0.200 | 387.88 | 0.980 | 0.980 | 0.991 | 0.557 | 0.134 | −50.0 | 80.16 | 387.81 |
| 0.606 | 0.131 | 383.23 | 0.993 | 0.967 | 0.979 | 0.750 | 0.075 | −46.0 | 80.05 | 383.20 |
| 0.126 | 0.748 | 396.47 | 0.951 | 0.999 | 0.989 | 0.215 | 0.660 | −28.5 | 80.15 | 396.40 |
| $P = 53.33$ kPa | | | | | | | | | | |
| 0.530 | 0.235 | 371.67 | 0.988 | 0.976 | 0.981 | 0.697 | 0.140 | −50.8 | 53.28 | 371.70 |
| 0.759 | 0.120 | 366.90 | 0.998 | 0.958 | 0.965 | 0.870 | 0.060 | −34.0 | 53.21 | 366.97 |
| 0.232 | 0.384 | 378.78 | 0.965 | 0.992 | 0.995 | 0.368 | 0.294 | −42.1 | 53.42 | 378.73 |
| 0.334 | 0.333 | 376.39 | 0.974 | 0.988 | 0.991 | 0.496 | 0.234 | −49.2 | 53.62 | 376.21 |
| 0.195 | 0.537 | 380.30 | 0.960 | 0.996 | 0.993 | 0.321 | 0.433 | −38.5 | 53.53 | 380.18 |
| 0.492 | 0.339 | 372.77 | 0.985 | 0.981 | 0.981 | 0.668 | 0.211 | −52.2 | 53.27 | 372.81 |
| 0.702 | 0.199 | 368.24 | 0.996 | 0.965 | 0.968 | 0.836 | 0.104 | −40.6 | 53.35 | 368.23 |
| 0.352 | 0.432 | 376.13 | 0.975 | 0.990 | 0.988 | 0.523 | 0.303 | −50.4 | 53.29 | 376.15 |
| 0.251 | 0.250 | 378.12 | 0.967 | 0.989 | 0.996 | 0.388 | 0.185 | −41.8 | 53.89 | 377.78 |
| 0.400 | 0.200 | 374.39 | 0.980 | 0.982 | 0.990 | 0.565 | 0.131 | −49.8 | 53.47 | 374.31 |
| 0.606 | 0.131 | 369.92 | 0.993 | 0.968 | 0.976 | 0.756 | 0.073 | −46.0 | 53.42 | 369.87 |
| 0.126 | 0.748 | 382.79 | 0.952 | 0.999 | 0.990 | 0.221 | 0.654 | −26.9 | 53.53 | 382.67 |
| $P = 26.66$ kPa | | | | | | | | | | |
| 0.530 | 0.235 | 351.03 | 0.988 | 0.978 | 0.975 | 0.710 | 0.133 | −51.5 | 26.58 | 351.12 |
| 0.759 | 0.120 | 346.64 | 0.998 | 0.960 | 0.957 | 0.877 | 0.056 | −34.4 | 26.63 | 346.67 |
| 0.232 | 0.384 | 358.04 | 0.964 | 0.993 | 0.992 | 0.381 | 0.285 | −42.8 | 26.87 | 357.82 |
| 0.334 | 0.333 | 355.69 | 0.973 | 0.989 | 0.988 | 0.511 | 0.225 | −49.9 | 26.93 | 355.41 |
| 0.195 | 0.537 | 359.41 | 0.960 | 0.996 | 0.991 | 0.335 | 0.421 | −38.0 | 26.84 | 359.22 |
| 0.492 | 0.339 | 352.11 | 0.985 | 0.982 | 0.976 | 0.682 | 0.201 | −51.2 | 26.62 | 352.16 |
| 0.702 | 0.199 | 347.87 | 0.996 | 0.966 | 0.961 | 0.845 | 0.098 | −39.7 | 26.68 | 347.85 |
| 0.352 | 0.432 | 355.27 | 0.975 | 0.990 | 0.984 | 0.539 | 0.291 | −49.5 | 26.59 | 355.35 |
| 0.251 | 0.250 | 357.40 | 0.965 | 0.989 | 0.994 | 0.401 | 0.179 | −43.8 | 27.12 | 356.92 |
| 0.400 | 0.200 | 353.73 | 0.978 | 0.983 | 0.986 | 0.579 | 0.125 | −52.1 | 26.78 | 353.60 |
| 0.606 | 0.131 | 349.48 | 0.992 | 0.971 | 0.970 | 0.768 | 0.069 | −48.3 | 26.74 | 349.40 |
| 0.126 | 0.748 | 361.87 | 0.952 | 0.999 | 0.988 | 0.232 | 0.643 | −25.7 | 26.87 | 361.65 |

equation,[21] that uses a linear dependence of the parameters ($\lambda_{ij}-\lambda_{ii}$) on temperature. In this case, the coefficients $\Lambda_{ij}$ can be expressed as

$$\Lambda_{ij} = \exp\left[a_{ij} + \frac{b_{ij}}{T}\right] \tag{5}$$

where the parameters $a_{ij}$ and $b_{ij}$ include molar volumes of components and the gas constant.

The parameters $a_{ij}$ and $b_{ij}$ calculated by a Newton iteration method are recorded in Table 4.

The vapor pressure of pure components was calculated by the Antoine equation

$$\ln(P_i^{\circ}/\mathrm{kPa}) = A_i - \frac{B_i}{T/\mathrm{K} + C_i} \tag{6}$$

where $A_{\mathrm{i}}$ , $B_i$, and $C_i$ and the applicable temperature range are reported in Table 5. The values of these coefficients were calculated on the basis of experimental data of this work, using measured boiling temperatures of pure components at four pressures (Table 3).

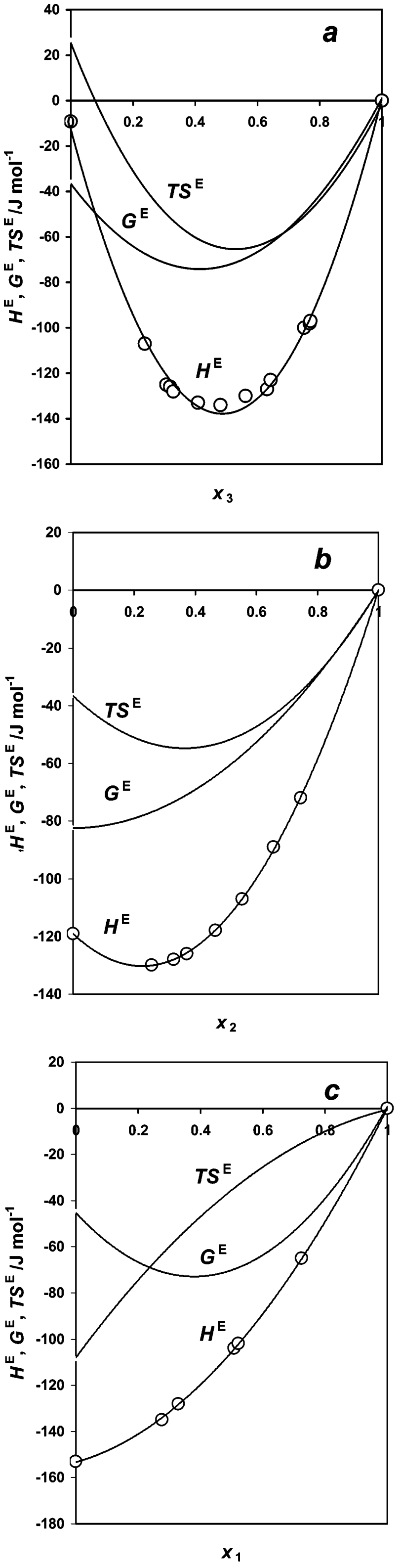

**Figure 7.** Experimental excess enthalpy, $H^E$, calculated using the modified Wilson equation,[21] Gibbs energy, $G^E$, and excess entropy, $TS^E = H^E - G^E$, at 298.15 K for the ternary system toluene (1) + ethylbenzene (2) + chlorobenzene (3) along the secants $x_1/x_2 = 1$ (a), $x_1/x_3 = 1$ (b), and $x_2/x_3 = 1$ (c).

In addition to comparison of $T-x$ relations for ethylbenzene + chlorobenzene in Figure 3, vapor phase mole fraction ($y_i$) versus liquid mole fraction ($x_i$) values of ethylbenzene at 101.32 kPa are compared in Figure 4. As seen from Figure 4, the experimental data of other authors[14,22,23] are in good agreement with our correlations.

The isobaric VLE data for the ternary system are given in Table 6. Listed along with $T-x$ experimental data are the calculated values of activity coefficients, vapor compositions, excess Gibbs energy, temperatures, and total pressures predicted by the modified Wilson equation using the binary parameters from Table 4.

It is observed that the ternary system shows negative deviations from Raoult's law, as seen from the values of activity coefficients which are smaller than unity for each component, and negative values of $G^E$ at all four investigated pressures. No ternary azeotrope was found in this investigation, either from experimental data or calculated by the Wilson equation results.

Comparison of experimental and calculated boiling temperatures and total pressures showed that the modified Wilson equation gave good predictions in a wide range of temperatures, (342 to 410) K. Mean absolute deviations between experimental and calculated temperature and pressure were equal to 0.10 K and 0.19 kPa, respectively.

For illustration, the isoenthalpic curves for the ternary system at 298.15 K are shown in Figure 5, and the calculated boiling temperature isotherms at 101.32 kPa are presented in Figure 6, both in the form of the Gibbs triangle.

According to the calculation results, it is implied that the modified Wilson equation also predicts satisfactorily VLE behavior at 298.15 K. In Figure 7, the calculated values of excess molar Gibbs energy versus composition are shown together with experimental values of excess molar enthalpy of the ternary system at 298.15 K. Excess entropy $TS^E$ curves calculated from $H^E - G^E = TS^E$ are also plotted. The composition of the ternary system changes along the secants $x_i/x_j = 1$.

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Received for review October 2, 2002. Accepted April 10, 2003. Financial support of this work by the Estonian Ministry of Education under the theme no. 0351456s00 is gratefully acknowledged.

JE020186C