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# Vapor−Liquid Equilibrium for Binary System of 1-Propanethiol, Thiophene, and Diethyl Sulfide with Toluene at 90.03 kPa

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Isobaric vapor−liquid equilibrium (VLE) for three systems with different organic sulfur compounds (1-propanethiol + toluene, thiophene + toluene, and diethyl sulfide + toluene) were measured at 90.03 kPa with a circulation still. The experimental results were compared with original UNIFAC, UNIFAC-Dortmund, and COSMO-RS predictive models. All systems showed nearly ideal behavior. VLE data sets measured passed the point consistency test.

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## Introduction

The regulation for sulfur contents in gasoline has become stricter recently. The new allowable levels vary; 30 ppm in Canada from 2004, 50 ppm in Europe from 2005, and 10 ppm in the United States from 2006.[1] As a consequence, the sulfur removal processes play an important part in refinery plant operations.

Thiols, sulfides, and thiophenes are the major impurities present in crude oils and are also found in distillates and in products from cracking, coking, and alkylation processes.[2] Design of separation processes to accomplish the removal of sulfur compounds requires the knowledge of the VLE of sulfur compounds with hydrocarbons.

In this work, isobaric VLE data for binary system of 1-propanethiol + toluene, thiophene + toluene, and diethyl sulfide + toluene were measured by using a circulation still at 90.03 kPa. The diethyl sulfide + toluene system studied in this work was not found in the open literature. Kilner et al.[3] measured VLE of 1-propanethiol + toluene at mole fraction from 0 to 0.2 over a temperature range from (323 to 373) K by using a static apparatus. Two VLE literature data sets of thiophene + toluene measured at (100 and 101.3) kPa were found in data compilations.[4,5]

## Experimental Section

***Materials.*** 1-Propanethiol, diethyl sulfide, thiophene, and toluene were provided by Sigma Aldrich, Finland; *o*-xylene was purchased from Fluka, Finland. The purity of all substances was checked by gas chromatography (GC) equipped with a flame ionization detector. Toluene and *o*-xylene were dried over molecular sieves (Merck 3A) for 24 h. The sulfur compounds were used as purchased without further purification.The refractive index ($n_D$) of the pure liquids were measured at 298.15 K with ABBEMAT-HP automatic refractometer (Dr. Kernchen, Germany) with accuracy ± 0.00002, and the water content was determined with a DL38 KF titrator (Mettler Toledo). The water content determination of 1-propanethiol was not possible directly as the iodine oxidizes the SH group of the compound very quickly. The purity, water content, and measured refractive indexes are presented in Table 1. The measured refractive indexes corresponded well with literature values.[6]

**Table 1. Purity, Water Content, and Refractive Indexes ($n_D$) of Pure Components**

| | GC purity | water content | $n_D$ (298.15 K) | |
|---|---|---|---|---|
| component | (mass %) | (mass %) | exptl | literature[6] |
| 1-propanethiol | 99.98 | | 1.4353 | 1.4353 |
| thiophene | 99.98 | 0.02 | 1.5255 | 1.5257 |
| diethyl sulfide | 99.72 | 0.00 | 1.4400 | 1.4402 |
| toluene | 99.95 | 0.02 | 1.4939 | 1.4941 |
| *o*-xylene | 99.33 | 0.02 | 1.5026 | 1.5029 |

***Apparatus.*** The VLE runs were conducted with a circulation still of the Yerazunis-type[7] built at the glass workshop of Helsinki University of Technology with minor modifications to the original design.[8] Experimental setup is described in detail in the previous works.[8,9] Approximately 80 mL of reagents was needed to run the apparatus.

Temperatures were measured with Pt-100 resistant temperature probe, which was located at the bottom of the packed section of the equilibrium chamber and connected to Thermometer F200 (Tempcontrol) with an accuracy of ± 0.02 K and the calibration uncertainty was ±0.01 K. The uncertainty of the whole temperature measurement system is estimated to be ± 0.05 K.

Pressure was measured with a Druck pressure transducer PMP 4070 (0 to 100 kPa) connected to a Red Lion panel meter. The inaccuracy of the instruments was reported to be ± 0.07 kPa by the manufacturer. The pressure measurement system was calibrated against BEAMEX PC 105-1166 pressure calibrator. The inaccuracy of the whole pressure measurement system including the calibration uncertainty is expected to be less than ± 0.17 kPa. To improve mixing in the sampling chambers and mixing chamber of the condensed vapor phase and the liquid phase, DC electric motors (Graupner speed 400) were equipped with magnetic stirrer bars, which deliver stirring action in the chambers.

***Experimental Procedures.*** Pure component 1 was introduced in the circulation still, and its vapor pressure was measured at several temperatures. Then component 2 was introduced into the circulation still. It took approximately from (15 to 30) min to achieve constant temperature. The temperature was held constant for approximately (30 to 45) min before sampling.

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After equilibration, the temperature in the equilibrium cell was measured, and then vapor and liquid samples were withdrawn with a 1 mL Hamilton Sample Lock syringe and after that injected into the cooled 2 mL autosampler vial containing approximately 1 mL of *o*-xylene. The compositions of both samples were immediately measured by gas chromatography (GC). To prevent spreading of the unpleasant odor of the sulfur compounds, the GC was placed in a closed and ventilated cupboard.

***Analysis and GC Calibration.*** The liquid and vapor samples were analyzed with a HP 6850A gas chromatograph equipped with an autosampler and a flame ionization detector (FID). The GC column used was a HP-1 dimethylpolysiloxane (60.0 m × 250 $\mu$m × 1.0 $\mu$m). The injector and FID were set at 250 °C. Helium was used as the carrier gas at a constant flow rate of 1 mL·min$^{-1}$ and inlet split ratio 100:1. The initial oven temperature was held at 70 °C for 2 min and then increased subsequently to 150 °C at rate of 8 °C·min$^{-1}$ and was held at 150 °C for 5 min. The total run time was 17 min.

The pure components were used to determine the retention times, after that the GC was calibrated with 15 mixtures of known composition that were prepared gravimetrically. To reduce the volume of the sample, *o*-xylene was used as solvent.

The response factor of component 2 ($F_2$) was calculated from eq 1:

$$\frac{m_2}{m_1}\frac{A_1}{A_2} = F_2 \tag{1}$$

Therefore, the vapor or liquid composition of component 1 can be calculated from

$$x_1 = \frac{\dfrac{A_1}{M_1}}{\dfrac{A_1}{M_1} + \left(F_2\dfrac{A_2}{M_2}\right)} \tag{2}$$

where $A_1$ and $A_2$ are the GC peak areas; $M_1$ and $M_2$ are the molar masses; and $m_1$ and $m_2$ were masses in the gravimetrically prepared sample of components 1 and 2, respectively. The maximum error of liquid and vapor composition measurements is estimated to be 0.003 mole fraction.

***Data Reduction.*** The activity coefficients $\gamma_i$ were calculated from

$$\gamma_i = \frac{y_i P \phi_i}{x_i P_i^{\mathrm{s}} \phi_i^{\mathrm{s}}} \exp\int_P^{P_i^{\mathrm{s}}} \frac{V_i^{\mathrm{L}}}{RT}\,\mathrm{d}P \tag{3}$$

where $y_i$ is the mole fraction of component $i$ in the vapor phase, $P$ is the total pressure of the system, $\phi_i$ is the fugacity coefficient of component $i$ in the vapor phase, $x_i$ is mole fraction of the component $i$ in the liquid phase, $P_i^{\mathrm{s}}$ is the vapor pressure of pure component $i$ at the system temperature, $\phi_i^{\mathrm{s}}$ is the pure component saturated liquid fugacity coefficient at the system temperature $T$, $V_i^{\mathrm{L}}$ is the molar volume of pure component $i$ in liquid phase at the system temperature and pressure, $T$ is temperature in Kelvin, and $R$ is the universal gas constant (8.31441 J·K$^{-1}$·mol$^{-1}$).

The VLEFIT program[10] was used for processing all the data. The Soave−Redlich−Kwong equation of state with quadratic mixing rules in the attractive parameter and linear in co-volume was used for vapor-phase fugacity coefficient calculation.[11] The binary interaction parameter in the quadratic mixing rules was set to zero. The Rackett equation[12] was used to calculate the liquid molar volume in the pointing factor. The Antoine parameters for vapor pressure, critical temperature, critical pressure, acentric factor, and liquid molar volume for each component used in the calculations are presented in Table 2.

**Table 2. Physical Properties of the Pure Components Used in Calculations**[a]

| component | 1-propanethiol | thiophene | diethyl sulfide | toluene |
|---|---|---|---|---|
| $T_c$[b]/K | 536.00 | 579.35 | 557.15 | 591.79 |
| $P_c$[b]/MPa | 4.63 | 5.690 | 3.962 | 4.109 |
| $\omega$[b] | 0.235 | 0.193 | 0.294 | 0.264 |
| $\upsilon_i$[b]/cm$^3$·mol$^{-1}$ | 91.068 | 79.477 | 123.739 | 106.556 |
| $A$[c] | 7.0174[d] | 7.0923[e] | 6.9925[f] | 6.7321[g] |
| $B$[c] | 2724.9699[d] | 2869.0277[e] | 2894.0403[f] | 2869.7197[g] |
| $C$[c] | −47.9846[d] | −51.4575[e] | −53.3224[f] | −65.4951[g] |
| $T_{\mathrm{min}}$/K | 310.52 | 328.01 | 333.82 | 335.00 |
| $T_{\mathrm{max}}$/K | 375.24 | 380.89 | 383.32 | 379.44 |

[a] Critical temperature ($T_c$), critical pressure ($P_c$), acentric factor ($\omega$), liquid molar volume ($\upsilon_i$) at 298.15 K, pure component vapor pressure equation parameters ($A$, $B$, and $C$) for the Antoine equation. Vapor pressure data measured; recommended temperature range of the vapor pressure correlation ($T_{\mathrm{min}}$), ($T_{\mathrm{max}}$). [b] Ref 6. [c] Antoine parameters fitted from the measured data in this work using additional data points from literature. $P^{\mathrm{s}}/\mathrm{MPa} = \exp(A - [B/(T/\mathrm{K} + C)])$. [d] 1-Propanethiol, this work combined with literature values[16] from (120.79 to 270.10) kPa at (346.49 to 375.24) K. [e] Thiophene, this work combined with literature values[17] from (101.29 to 198.55) kPa at (357.31 to 380.89) K. [f] Diethyl sulfide, this work combined with literature values[18] from (120.78 to 169.06) kPa at (371.22 to 383.32) K. [g] Toluene, this work combined with literature values[19] from (19.92 to 34.90) kPa at (335 to 350.09) K.

***COSMO-RS Calculation.*** The COSMO-RS calculations were performed using a continuum model with density functional theory (RI-DFT) using BP functional with TZVP basis set as it was implemented in Turbomole program[13] (version 5.7). Geometry optimization for the molecules under investigation was performed with Turbomole software as well. Subsequent COSMO-RS calculations were done with COSMOtherm-C12-0105.[14]

In the COSMO-RS calculations, several conformers were taken into account for 1-propanethiol and diethyl sulfide. For toluene and thiophene, only one stable conformer was found and then used for further calculations. To improve the description of these sulfur compound systems, the van der Waals interaction term from surface binary interaction energy was excluded.[15]

## Results and Discussion

***Vapor Pressure Measurements.*** The vapor pressures of pure components measured in this work are shown in Figure 1 and presented in Table 3. The measured vapor pressure of each component was compared with literature correlation[6] and COSMO-RS prediction. The absolute average deviation of pressure between experimental and literature correlation[6] for 1-propanethiol, thiophene, diethyl sulfide, and toluene were (0.39, 0.18, 0.8, and 0.36) kPa, respectively. Measured vapor pressures of 1-propanethiol, thiophene, diethyl sulfide, and toluene are inline with ones measured by Pennington et al.,[16] Waddington et al.,[17] Scott et al.,[18] and Willingham et al.,[19] respectively.

The Antoine constants for all compounds were regressed from the vapor pressures measured in this work using additional data points from literature.These parameters with the recommended temperature range of the vapor pressure equations are presented in Table 2. The vapor pressure correlation for 1-propanethiol was slightly extrapolated to 377.84 K.

Pure component's vapor pressures predicted with COSMO-RS were higher than experimental ones. As an example the esti-

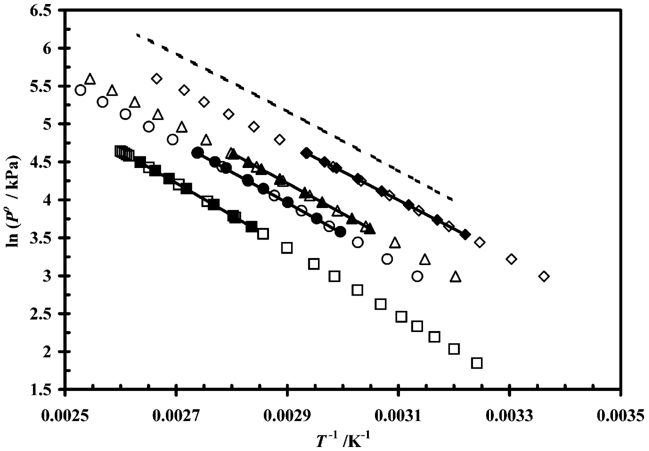

**Figure 1.** Measured vapor pressures of pure substances in this work: ◆, 1-propanethiol; ▲, thiophene; ●, diethyl sulfide; ■, toluene. Measured vapor pressure from literature: ◇, 1-propanethiol;[16] △, thiophene;[17] ○, diethyl sulfide;[18] □, toluene;[19] —, calculated from literature correlation;[6] - - -, 1-propanethiol, COSMO-RS.

**Table 3. Experimental Vapor Pressure of 1-Propanethiol, Thiophene, Diethyl Sulfide, and Toluene**

| 1-propanethiol | | thiophene | | diethyl sulfide | | toluene | |
|---|---|---|---|---|---|---|---|
| $T$/K | $P$/kPa | $T$/K | $P$/kPa | $T$/K | $P$/kPa | $T$/K | $P$/kPa |
| 340.63 | 101.19 | 356.73 | 99.99 | 365.05 | 101.92 | 379.44 | 90.03 |
| 337.03 | 90.03 | 353.38 | 90.03 | 361.02 | 90.03 | 375.63 | 80.42 |
| 334.62 | 83.15 | 350.46 | 82.01 | 358.41 | 83.03 | 372.12 | 72.27 |
| 330.38 | 72.02 | 346.44 | 71.92 | 353.56 | 71.09 | 367.88 | 63.37 |
| 325.73 | 61.23 | 341.13 | 60.12 | 350.02 | 63.30 | 361.31 | 51.31 |
| 320.68 | 51.03 | 337.52 | 53.02 | 344.70 | 52.89 | 356.84 | 44.23 |
| 315.47 | 41.96 | 331.52 | 42.75 | 338.63 | 42.73 | 352.64 | 38.32 |
| 310.52 | 34.60 | 328.01 | 37.50 | 333.82 | 35.84 | | |

**Table 4. Isobaric VLE Data, Liquid Phase ($x_1$), and Vapor Phase ($y_1$) Mole Fractions, Temperature ($T$), and Activity Coefficient ($\gamma_i$) for the Diethyl Sulfide (1) + Toluene (2) System at 90.03 kPa**

| $x_1$ | $y_1$ | $T$/K | $\gamma_1$ | $\gamma_2$ | $x_1$ | $y_1$ | $T$/K | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.000 | 0.000 | 379.45 | | 1.00 | 0.488 | 0.623 | 369.25 | 1.01 | 0.99 |
| 0.012 | 0.020 | 379.20 | 1.00 | 1.00 | 0.580 | 0.701 | 367.74 | 1.00 | 1.00 |
| 0.046 | 0.074 | 378.42 | 1.00 | 1.00 | 0.643 | 0.755 | 366.68 | 1.00 | 1.00 |
| 0.081 | 0.128 | 377.61 | 1.00 | 1.00 | 0.712 | 0.809 | 365.51 | 1.00 | 1.00 |
| 0.121 | 0.185 | 376.75 | 1.00 | 1.00 | 0.782 | 0.860 | 364.36 | 1.00 | 1.01 |
| 0.167 | 0.252 | 375.73 | 1.00 | 1.00 | 0.853 | 0.909 | 363.18 | 1.01 | 1.01 |
| 0.219 | 0.318 | 374.65 | 0.99 | 1.00 | 0.899 | 0.938 | 362.50 | 1.01 | 1.01 |
| 0.282 | 0.397 | 373.35 | 1.00 | 1.00 | 0.960 | 0.976 | 361.56 | 1.01 | 1.01 |
| 0.343 | 0.464 | 372.14 | 0.99 | 1.01 | 1.000 | 1.000 | 361.03 | 1.00 | |
| 0.413 | 0.544 | 370.75 | 1.00 | 1.00 | | | | | |

mated vapor pressure of 1-propanethiol was presented in Figure 1. The absolute average deviation of pressure of 1-propanethiol between COSMO-RS prediction and experimental was 27 kPa. Similar behavior was shown as well by the other compounds. Thus, the experimentally determined pure component vapor pressures were used in the COSMO-RS calculations.

***Vapor−Liquid Equilibrium Measurements.*** The measured isobaric equilibrium data ($T$, $x_1$, and $y_1$) and calculated activity coefficients are reported in Tables 4 to 6 and presented in Figures 2 to 4. All systems show nearly ideal behavior, and no azeotropes were found in the systems.

Comparisons of the experimental data and VLE at 90.03 kPa predicted with original UNIFAC[20] with the parameters on the level of Wittig et al.[21] and COSMO-RS models are shown in Figures 2 to 4. In both models all interactions between molecules in liquid phase are considered as interactions pairwise contacting molecular surfaces. However, in COSMO-RS the interactions are based on molecule surface screening charge densities, calculated by quantum mechanical method (COSMO) for a single molecule in a conductor surrounding.[22] In UNIFAC interaction parameters of the molecule functional groups are treated as parameters fitted empirically to extensive experimental data collection. Considering a single molecule as an entity enables COSMO-RS to take into account intermolecular interactions.

**Table 5. Isobaric VLE Data, Liquid Phase ($x_1$), and Vapor Phase ($y_1$) Mole Fractions, Temperature ($T$), and Activity Coefficient ($\gamma_i$) for the 1-Propanethiol (1) + Toluene (2) System at 90.03 kPa**

| $x_1$ | $y_1$ | $T$/K | $\gamma_1$ | $\gamma_2$ | $x_1$ | $y_1$ | $T$/K | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.000 | 0.000 | 379.44 | | 1.00 | 0.493 | 0.778 | 352.05 | 1.01 | 1.03 |
| 0.021 | 0.065 | 377.84 | 1.01[a] | 1.00[a] | 0.559 | 0.822 | 349.55 | 1.01 | 1.03 |
| 0.065 | 0.182 | 374.61 | 1.00 | 1.01 | 0.632 | 0.862 | 347.14 | 1.01 | 1.04 |
| 0.122 | 0.318 | 370.84 | 1.02 | 1.00 | 0.694 | 0.892 | 345.12 | 1.01 | 1.05 |
| 0.176 | 0.416 | 367.16 | 1.01 | 1.02 | 0.747 | 0.916 | 343.59 | 1.00 | 1.05 |
| 0.211 | 0.479 | 365.41 | 1.01 | 1.00 | 0.818 | 0.944 | 341.56 | 1.00 | 1.06 |
| 0.258 | 0.545 | 362.79 | 1.01 | 1.01 | 0.850 | 0.956 | 340.63 | 1.01 | 1.05 |
| 0.311 | 0.607 | 360.19 | 1.00 | 1.02 | 0.898 | 0.971 | 339.42 | 1.01 | 1.07 |
| 0.354 | 0.655 | 358.03 | 1.00 | 1.03 | 0.936 | 0.982 | 338.49 | 1.00 | 1.07 |
| 0.393 | 0.695 | 356.19 | 1.01 | 1.02 | 0.986 | 0.996 | 337.32 | 1.00 | 1.06 |
| 0.446 | 0.741 | 353.95 | 1.01 | 1.03 | 1.000 | 1.000 | 337.03 | 1.00 | |

[a] The vapor pressure correlation of 1-propanethiol was slightly extrapolated.

**Table 6. Isobaric VLE Data, Liquid Phase ($x_1$), and Vapor Phase ($y_1$) Mole Fractions, Temperature ($T$), and Activity Coefficient ($\gamma_i$) for the Thiophene (1) + Toluene (2) System at 90.03 kPa**

| $x_1$ | $y_1$ | $T$/K | $\gamma_1$ | $\gamma_2$ | $x_1$ | $y_1$ | $T$/K | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.000 | 0.000 | 379.44 | | 1.00 | 0.395 | 0.581 | 366.62 | 1.00 | 1.01 |
| 0.010 | 0.020 | 379.09 | 1.01 | 1.00 | 0.468 | 0.654 | 364.63 | 1.01 | 1.01 |
| 0.025 | 0.051 | 378.52 | 1.02 | 1.00 | 0.529 | 0.708 | 363.08 | 1.01 | 1.01 |
| 0.039 | 0.078 | 378.03 | 1.02 | 1.00 | 0.604 | 0.770 | 361.32 | 1.01 | 1.00 |
| 0.059 | 0.116 | 377.31 | 1.00 | 1.00 | 0.694 | 0.834 | 359.27 | 1.01 | 1.00 |
| 0.086 | 0.165 | 376.32 | 1.00 | 1.00 | 0.743 | 0.865 | 358.29 | 1.01 | 1.00 |
| 0.111 | 0.207 | 375.43 | 1.00 | 1.00 | 0.791 | 0.892 | 357.32 | 1.00 | 1.01 |
| 0.146 | 0.264 | 374.20 | 1.00 | 1.00 | 0.835 | 0.918 | 356.43 | 1.00 | 1.01 |
| 0.204 | 0.355 | 372.21 | 1.02 | 1.00 | 0.905 | 0.951 | 355.23 | 1.00 | 1.09 |
| 0.255 | 0.423 | 370.62 | 1.01 | 1.00 | 0.925 | 0.965 | 354.74 | 1.00 | 1.02 |
| 0.317 | 0.500 | 368.61 | 1.02 | 1.01 | 1.000 | 1.000 | 353.38 | 1.00 | |

At present original UNIFAC and especially UNIFAC-Dortmund[23] with parameters on the level of Wittig et al.[24] have been extensively refined, providing good prediction for the systems, where the group interaction parameters are available. However, the original UNIFAC interaction parameter for sulfides ($CH_2S$) and toluene (ACH) binary pair is not available, hence the original UNIFAC prediction for diethyl sulfide + toluene system is not possible. As can be seen from Figure 2, the prediction of COSMO-RS is close to experimental results.

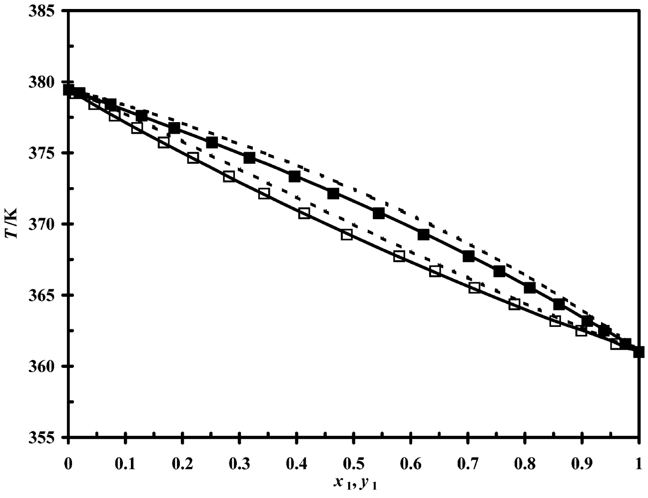

**Figure 2.** Temperature−composition diagram for the diethyl sulfide (1) + toluene (2) system at 90.03 kPa: □, $x_1$ measured; ■, $y_1$ measured; —, COSMO-RS, modified; - - -, COSMO-RS.

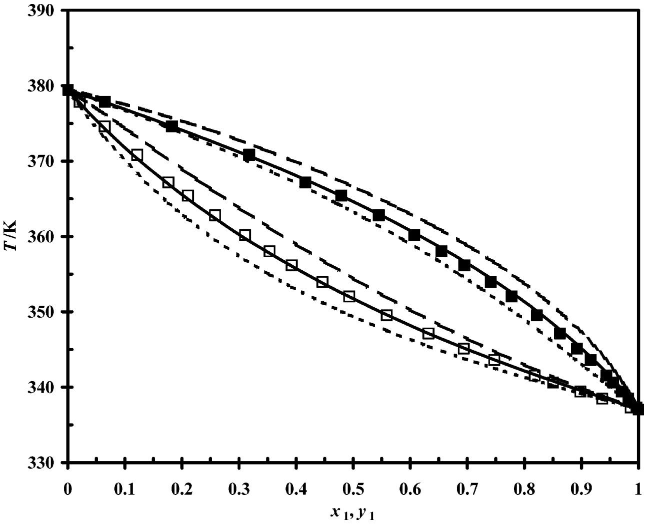

**Figure 3.** Temperature−composition diagram for the 1-propanethiol (1) + toluene (2) system at 90.03 kPa: □, $x_1$ measured; ■, $y_1$ measured; —, COSMO-RS, modified; − −, COSMO-RS; - - -, UNIFAC.

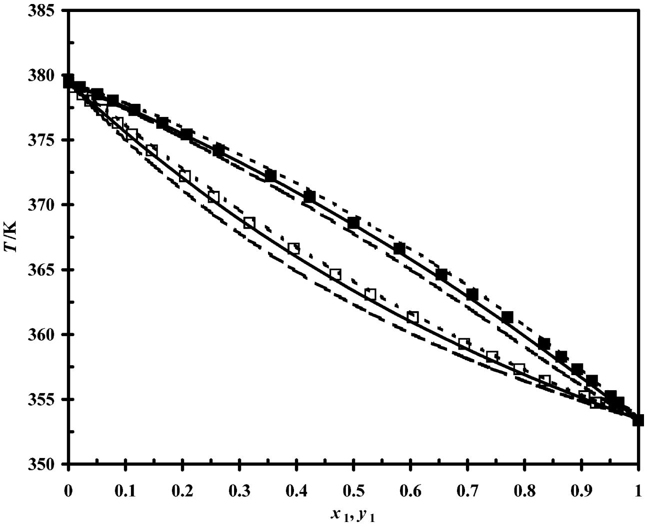

**Figure 4.** Temperature−composition diagram for the thiophene (1) + toluene (2) system at 90.03 kPa: □, $x_1$ measured; ■, $y_1$ measured; —, UNIFAC-Dortmund; − −, UNIFAC; - - -, COSMO-RS.

**Table 7. Averages of Absolute Vapor Molar Fraction Residual $\Delta y_{ave}$ and Temperature Residuals $\Delta T_{ave}$ for the Wilson Fits for the Measured Systems at 90.03 kPa**

| systems | $\Delta y_{ave}$ | $\Delta T_{ave}$/K |
|---|---|---|
| diethyl sulfide (1) + toluene (2) | 0.0008 | 0.07 |
| 1-propanethiol (1) + toluene (2) | 0.0037 | 0.12 |
| thiophene (1) + toluene (2) | 0.0012 | 0.08 |

In Figure 3, the predictions of original UNIFAC and COSMO-RS for the 1-propanethiol + toluene system are comparable even though they do not match well with experimental data.

The thiophene + toluene system was predicted using UNIFAC-Dortmund and COSMO-RS models. From the Figure 4, it is shown that the predictions with COSMO-RS are slightly better as compared to UNIFAC-Dortmund, while original UNIFAC gave unsatisfactory results.

For the sulfur-containing systems, the modification of the COSMO-RS model by exclusion of the van der Waals interaction from binary surface interaction energy improves the quality of the prediction. The results of the prediction of our VLE systems with the modified COSMO-RS are shown in Figures 2 to 4. The COSMO-RS model with the modification gave very accurate prediction of VLE also in very diluted regions for all systems.

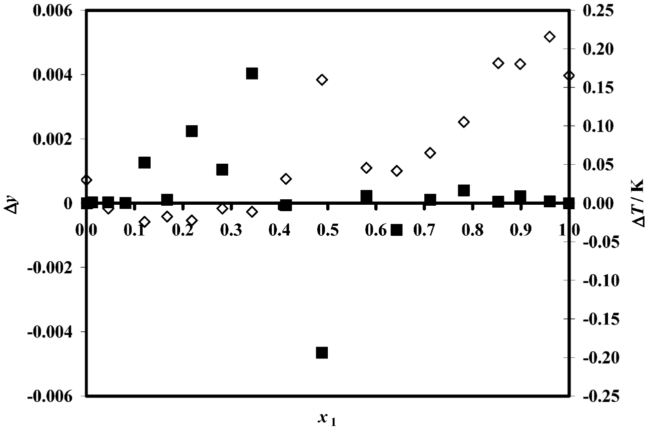

**Figure 5.** Point test for the diethyl sulfide (1) + toluene (2) system at 90.03 kPa (Wilson model): ■, Δ*y*; ◇, Δ*T*.

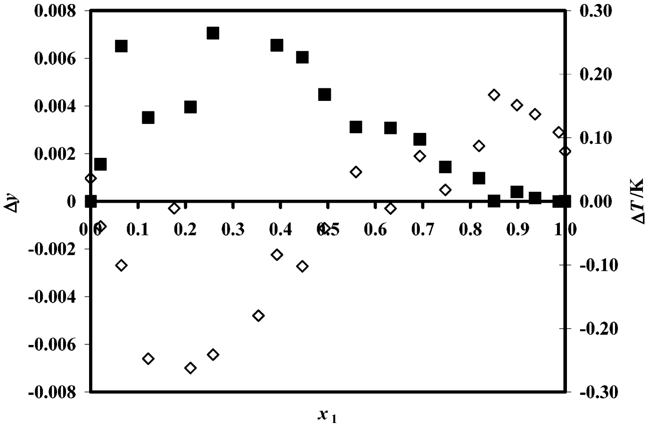

**Figure 6.** Point test for the 1-propanethiol (1) + toluene (2) system at 90.03 kPa (Wilson model): ■, Δ*y*; ◇, Δ*T*.

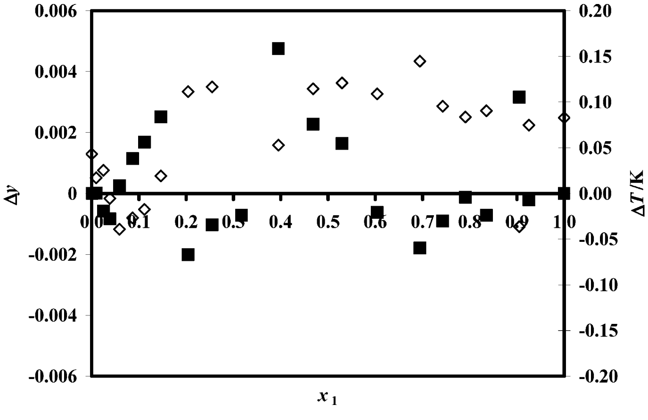

**Figure 7.** Point test for the thiophene (1) + toluene (2) system at 90.03 kPa (Wilson model): ■, Δ*y*; ◇, Δ*T*.

The results of the point test[25] for all systems using fitted small $\lambda$ parameters for the Wilson[26] model are presented in Table 7 and shown in Figures 5 to 7. The objective function[10] (OF) used for fitting of the activity coefficient parameters is given by eq 4, where *N* is the number of points used in the fit:

$$\mathrm{OF} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{|\gamma_{i,\mathrm{model}} - \gamma_{i,\mathrm{meas}}|}{\gamma_{i,\mathrm{meas}}}\right) \tag{4}$$

The data sets are considered consistent if the absolute average deviations between the measured and calculated mole fractions of the vapor phase are smaller than 0.01. These measured data sets passed the point test. The integral test[25] is not applicable here because the activity coefficient range is very close to 1.

## Conclusions

Vapor pressure of 1-propanethiol, thiophene, diethyl sulfide, and toluene were measured and compared with the literature data. Isobaric VLE data were measured for the systems 1-propanethiol + toluene, thiophene + toluene, and diethyl sulfide + toluene at 90.03 kPa with a circulation still. All of the systems show almost ideal behavior. The VLE data of the binary systems were predicted using original UNIFAC, UNIFAC-Dortmund, and COSMO-RS predictive models. The original UNIFAC gave the worse predictions as compared to UNIFAC-Dortmund. Exclusion of the van der Waals surface interaction term from COSMO-RS calculations improved the VLE prediction of these sulfur compound systems. VLE data sets measured passed the point consistency test.

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