



## Phase equilibria on five binary systems containing 1-butanethiol and 3-methylthiophene in hydrocarbons

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### ABSTRACT

Isothermal vapor–liquid equilibrium (VLE) of the following systems was measured with a recirculation still: 1-butanethiol + methylcyclopentane at 343.15 K, 1-butanethiol + 2,2,4-trimethylpentane at 368.15 K, 3-methylthiophene + toluene at 383.15 K, 3-methylthiophene + *o*-xylene at 383.15 K, and 3-methylthiophene + 1,2,4-trimethylbenzene at 383.15 K. 1-Butanethiol + methylcyclopentane and 1-butanethiol + 2,2,4-trimethylpentane systems exhibit positive deviation from Raoult's law, whereas systems containing 3-methylthiophene in aromatic hydrocarbons exhibit only slight positive deviation from Raoult's law. A maximum pressure azeotrope was found in the system 1-butanethiol + 2,2,4-trimethylpentane ( $x_1 = 0.548$ ,  $P = 100.65$  kPa,  $T = 368.15$  K). The experimental results were correlated with the Wilson model and compared with original UNIFAC and COSMO-SAC predictive models. Raoult's law can be used to describe the behavior of 3-methylthiophene in aromatic hydrocarbons at the experimental conditions in this work. Liquid and vapor-phase composition were determined with gas chromatography. All measured data sets passed the thermodynamic consistency tests applied. The activity coefficients at infinite dilution are also presented.

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### 1. Introduction

Stringent air quality regulations impose the use of ultra-low sulfur gasoline and diesel in many countries [1]. In Europe, the sulfur level in gasoline and diesel should be lower than 10 ppm beginning from 2009 [2]. New developments on sulfur separation process design to further decrease the sulfur level have become one of the major challenges to the refining industry [3]. Design of separation processes to accomplish the removal of sulfur compounds requires the knowledge of the behavior of sulfur compounds in hydrocarbons. Information of such systems is scarce and experimental work is required. 1-Butanethiol and 3-methylthiophene are typical organic sulfur compounds present in the hydrocarbon streams originating from the fluid catalytic cracker (FCC) [4,5].

In this work, we measured vapor–liquid equilibrium (VLE) for the systems 1-butanethiol + methylcyclopentane at 343.15 K, 1-butanethiol + 2,2,4-trimethylpentane at 368.15 K, 3-methylthiophene + toluene at 383.15 K, 3-methylthiophene + *o*-xylene at 383.15 K, and 3-methylthiophene + 1,2,4-trimethylbenzene at 383.15 K with a recirculation still. No other VLE data of the binary

systems studied in this work have been found in the literature search.

In the previous studies, Sapei et al. [6,7] measured VLE data for the systems 3-methylthiophene + 2,2,4-trimethylpentane at 368.15 K, 3-methylthiophene + 2,4,4-trimethyl-1-pentene at 368.15 K, 3-methylthiophene + cyclohexane at 348.15 K, 3-methylthiophene + 1-hexene at 333.15 K, 3-methylthiophene + 2-methylpentane at 333.15 K, 3-methylthiophene + *n*-hexane at 333.15 K, 3-methylthiophene + methylcyclopentane at 343.15 K, and 3-methylthiophene + methylcyclohexane at 373.15 K. Kilner et al. [8] measured vapor–liquid equilibrium for system 1-butanethiol + *n*-hexane and 1-butanethiol + toluene for mole fractions  $x = 0$ –0.2 of 1-butanethiol at temperatures between 323 and 373 K.

### 2. Experimental

#### 2.1. Materials

1-Butanethiol, 3-methylthiophene, methylcyclopentane, 2,2,4-trimethylpentane, toluene, *o*-xylene, and 1,2,4-trimethylbenzene were provided by Sigma–Aldrich, Finland. The purity of all substances was checked by gas chromatography (GC) equipped with a flame ionization detector (FID). All chemicals were dried over molecular sieves (Merck 3Å) for 24 h. The refractive indexes,  $n_D$ ,

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**Table 1**  
Purity and refractive indexes ( $n_D$ ) of pure components.

Component	GC purity (mass%)	$n_D$ (298.15 K)	
		Experimental	Literature [9]
1-Butanethiol	99.40	1.4400	1.4403
3-Methylthiophene	99.78	1.5172	1.5176
Methylcyclopentane	99.92	1.4070	1.4070
2,2,4-Trimethylpentane	99.78	1.3888	1.3890
Toluene	99.98	1.4940	1.4941
<i>o</i> -Xylene	99.99	1.5028	1.5029
1,2,4-Trimethylbenzene	99.12	1.5020	1.5024

of the pure liquids were measured at 298.15 K with ABBEMAT-HP automatic refractometer (Dr. Kernchen, Germany) with accuracy  $\pm 0.00002$ . The purity and measured refractive indexes are presented in Table 1. The measured refractive indexes corresponded well with literature values [9].

## 2.2. Apparatus

The VLE runs were conducted with a circulation still of the Yerazunis-type [10] built at the glass workshop of Helsinki University of Technology with minor modifications to the original design [11]. Experimental setup is described in detail in the previous works [11,12]. Approximately 80 ml of reagents were needed to run the apparatus.

Temperatures were measured with a Pt-100 resistance temperature probe, which was located at the bottom of the packed section of the equilibrium chamber and connected to Thermometer (F200, Tempcontrol) which has a manufacturer's stated accuracy of  $\pm 0.02$  K and the calibration uncertainty was  $\pm 0.01$  K. The uncertainty of the whole temperature measurement system is estimated to be  $\pm 0.05$  K.

Pressure was measured with a Druck pressure transducer PMP 4070 (0–100 kPa) connected to a Red Lion panel meter. The inaccuracy of the instruments was reported to be  $\pm 0.07$  kPa by the manufacturer. The pressure measurement system was calibrated against a BEAMEX PC 105-1166 pressure calibrator. The uncertainty of the whole pressure measurement system including the calibration uncertainty is expected to be less than  $\pm 0.17$  kPa.

## 2.3. Experimental procedures

Pure component 1 was introduced in the recirculation still and its vapor pressure was measured at several temperatures. Then component 2 was introduced into the recirculation still. It took approximately from 45 min to 60 min to achieve constant temperature. The temperature was held constant for approximately 30–45 min before sampling. Constant temperature indicated that phase equilibrium was reached.

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 auto-sampler vial containing approximately 1 ml solvent (used as diluent). 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.

## 2.4. Analysis and GC calibration

The liquid and vapor samples were analyzed with Agilent 6850A gas chromatograph equipped with an auto-sampler and a flame ionization detector (FID). The GC-column used was a HP-1 dimethylpolysiloxane (60.0 m  $\times$  250  $\mu$ m  $\times$  1.0  $\mu$ m). The injector

**Table 2**  
Solvent used in GC analysis.

Systems	Solvent
1-Butanethiol + methylcyclopentane	<i>o</i> -Xylene
1-Butanethiol + 2,2,4-trimethylpentane	<i>o</i> -Xylene
3-Methylthiophene + toluene	<i>o</i> -Xylene
3-Methylthiophene + <i>o</i> -xylene	2,2,4-Trimethylpentane
3-Methylthiophene + 1,2,4-trimethylbenzene	Toluene

and FID were set at 250 °C. Helium was used as the carrier gas at a constant flow rate of 1 ml min<sup>-1</sup> and inlet split ratio 100:1.

For the systems 1-butanethiol + methylcyclopentane, 1-butanethiol + 2,2,4-trimethylpentane, 3-methylthiophene + toluene, and 3-methylthiophene + *o*-xylene, 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<sup>-1</sup> and was held at 150 °C for 3 min. The total run time was 15 min.

For the system 3-methylthiophene + 1,2,4-trimethylbenzene, the initial oven temperature was held at 90 °C for 2 min and then increased subsequently to 175 °C at rate of 8 °C min<sup>-1</sup> and was held at 175 °C for 3 min. The total run time was 15 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, the solvent was added. The solvent used in each system is given in Table 2.

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

$$\frac{m_2 A_1}{m_1 A_2} = F_2 \quad (1)$$

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

$$x_1 = \frac{A_1/M_1}{A_1/M_1 + (F_2(A_2/M_2))} \quad (2)$$

where  $A_1$  and  $A_2$  are the GC peak areas,  $M_1$  and  $M_2$  are the molar masses, and  $m_1$  and  $m_2$  are 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.

## 3. Results and discussion

### 3.1. Vapor pressure measurements

Vapor pressure of 3-methylthiophene, methylcyclopentane, 2,2,4-trimethylpentane, toluene, and *o*-xylene were measured in the previous studies [6,7,13–15]. The Antoine parameters for 1-butanethiol and 1,2,4-trimethylbenzene were regressed from the vapor pressures measured in this work. These parameters with the recommended temperature range of the vapor pressure equations are presented in Table 3. The average absolute deviation of pressure ( $|\Delta P^S|_{aver}$ ) between measured ( $P_{i,exp}$ ) and values calculated with regressed parameters of the Antoine equation ( $P_{i,calc}$ ) for 1-butanethiol and 1,2,4-trimethylbenzene measured in this work and also the values obtained from earlier measurements with the same equipment are presented in Table 3.

The vapor pressures of 1-butanethiol and 1,2,4-trimethylbenzene measured in this work are shown in Fig. 1 and presented in Table 4. The measured vapor pressures were compared with literature correlation [9]. The absolute average deviation of pressure between experimental and literature correlation for 1-butanethiol and 1,2,4-trimethylbenzene were 0.27 kPa and 0.57 kPa, respectively. Measured vapor pressures of 1-butanethiol and 1,2,4-trimethylbenzene agree with those

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