Vapor−Liquid Equilibrium for Binary System of Thiophene + *n*-Hexane at (338.15 and 323.15) K and Thiophene + 1-Hexene at (333.15 and 323.15) K

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Isothermal vapor−liquid equilibrium (VLE) for thiophene + *n*-hexane at (338.15 and 323.15) K and thiophene + 1-hexene at (333.15 and 323.15) K were measured with a circulation still. Maximum pressure azeotropes were found in the thiophene + *n*-hexane system. Azeotropic behavior was not found for the thiophene + 1-hexene system. The experimental results were correlated with Wilson model and also compared with original UNIFAC, UNIFAC−Dortmund, and COSMO-RS predictive models. Analyses of liquid and vapor-phase composition were determined with gas chromatograph and refractometer. All VLE measurements passed the three thermodynamic consistency tests used.

Introduction

Organosulfur impurities in gasoline cause severe environmental problems. Sulfur present in gasoline results in SO_x air pollution and is directly responsible for increased levels of NO_x in automotive exhaust. They also act as poisons for many of the catalytic converters in automobiles. In order to minimize the negative healthy and environmental effects of automotive exhaust emissions, stricter regulations on sulfur levels in gasoline have been applied in most countries.[1]

Thiophene is one of the major impurities present in crude oils and also found in distillates and in products from cracking, coking, and alkylation processes[2] in concentrations up to (0.5 to 1.5) wt %.[3] Thiophene and its derivatives contribute to the overall sulfur content of a particular fraction and to the amount of the corrosive sulfur oxides formed during combustion. Design of separation processes to accomplish the removal of thiophene requires the knowledge of the VLE of sulfur compounds with hydrocarbons.

In this work, isothermal VLE measurements for the binary system thiophene + *n*-hexane were performed at (338.15 and 323.15) K, and thiophene + 1-hexene were measured at (333.15 and 323.15) K with a circulation still. Similar measurements studied in this work were not found in the open literature. Desty and Fidler[4] have measured the azeotropic point of thiophene + *n*-hexane at 101.32 kPa by using the distillation method.

Experimental Section

Materials. Thiophene, *n*-hexane, 1-hexene, and toluene were purchased from Sigma Aldrich, Finland. The purities of the chemicals were checked by gas chromatograph (GC) equipped with a flame ionization detector. *n*-Hexane, 1-hexene, and toluene were dried over molecular sieves (Merck 3A) for 24 h. Thiophene was used as purchased without further purification. The refractive index (n_D) of the pure liquids was measured at 298.15 K with an ABBEMAT-HP automatic refractometer (Dr. Kernchen, Germany) with accuracy ± 0.00002, and the water contents were determined with a DL38 KF titrator (Mettler Toledo). The purity, water content, and measured refractive indexes are presented in Table 1. The measured refractive indexes corresponded well with literature values.[5]

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[5]
thiophene	99.98	0.02	1.5255	1.5257
n-hexane	99.99	0.01	1.3724	1.3723
1-hexene	99.98	0.01	1.3851	1.3850
toluene	99.97	0.02	1.4939	1.4941

Apparatus. The VLE runs were carried out with a circulation still of the Yerazunis-type[6] built at the glass workshop of the Helsinki University of Technology with minor modifications to the original design.[7] Experimental setup is described in detail in previous works.[7,8] Approximately 80 mL of reagent was needed to run the apparatus.

Temperatures were measured with a 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. The calibration uncertainty was ± 0.01 K. The uncertainty of the whole temperature measurement system was 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 a 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 the mixing chamber of the condensed vapor phase and the liquid phase, DC electric motors (Graupner speed 400) were equipped with magnetic stirrer bars to mix the liquids 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

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Table 2. Critical Temperature (T_c), Critical Pressure (P_c), Acentric Factor (ω), Liquid Molar Volume (v_i) at 298.15 K, Pure Component Vapor Pressure Equation Parameters (A, B, and C) for the Antoine Equation, Recommended Temperature Range of the Vapor Pressure Correlation (T_{min}) and (T_{max})

component	thiophene	*n*-hexane	1-hexene
$T_c{}^a$/K	579.35	507.43	504.03
$P_c{}^a$/MPa	5.690	3.012	3.140
ω^a	0.193	0.305	0.28
$v_i{}^a/\text{cm}^3\cdot\text{mol}^{-1}$	79.477	131.306	126.103
A	7.1055[b]	6.9802[c]	6.9000[c]
B	2869.0003[b]	2724.9601[c]	2655.0085[c]
C	−51.8054[b]	−47.7364[c]	−47.6225[c]
T_{min}/K	323.15	307.31	298.99
T_{max}/K	356.73	342.00	336.04

[a] Ref 5. [b] Ref 12. [c] Antoine parameters fitted from the measurements in this work: $P^S/\text{MPa} = \exp(A - [B/(T/\text{K} + C)])$.

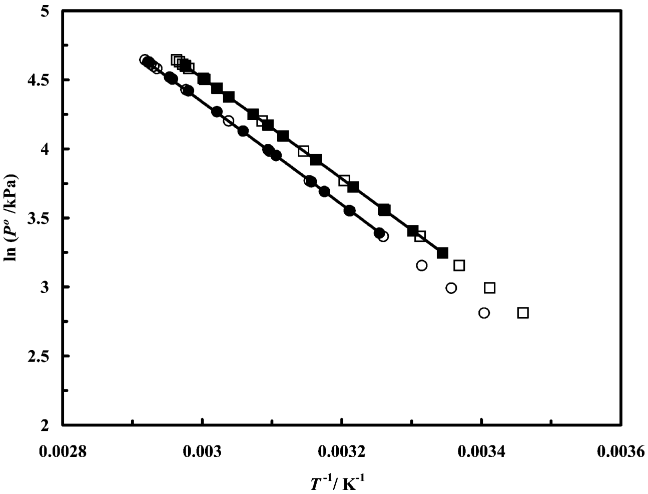

Figure 1. Measured vapor pressures of pure substances in this work: ●, *n*-hexane; ■, 1-hexene. Vapor pressure from literature: ○, *n*-hexane;[13] □, 1-hexene;[14] —, calculated from literature correlation.[5]

Table 3. Experimental Vapor Pressure of *n*-Hexane and 1-Hexene

n-hexane		1-hexene	
T/K	*P*/kPa	*T*/K	*P*/kPa
342.00	102.27	336.04	99.73
338.59	91.73	333.15	90.94
338.15	90.44	332.94	90.24
335.54	83.09	330.99	84.63
331.00	71.39	329.11	79.46
326.94	62.11	325.41	70.09
323.15	54.25	323.15	64.82
321.97	52.02	320.92	59.91
316.81	43.01	316.17	50.46
314.93	40.02	310.90	41.41
311.36	34.86	306.73	35.19
307.31	29.67	302.85	30.13
		298.99	25.68

Table 4. Isothermal VLE Measurements, Liquid-Phase (x_1) and Vapor-Phase (y_1) Mole Fractions, Pressure (P), and Activity Coefficient (γ_i) for the Thiophene (1) + *n*-Hexane (2) System at (338.15 and 323.15) K (GC analysis)

at 338.15 K					at 323.15 K				
x_1	y_1	P/kPa	γ_1	γ_2	x_1	y_1	P/kPa	γ_1	γ_2
0.000	0.000	90.44		1.00	0.000	0.000	54.25		1.00
0.045	0.052	90.58	1.88	0.99	0.039	0.044	54.59	1.97	1.00
0.098	0.100	90.75	1.67	1.00	0.080	0.083	54.70	1.80	1.00
0.146	0.142	90.73	1.61	1.01	0.117	0.117	54.75	1.74	1.01
0.193	0.181	90.55	1.55	1.02	0.159	0.153	54.72	1.68	1.01
0.241	0.219	90.20	1.49	1.03	0.213	0.197	54.54	1.60	1.03
0.289	0.253	89.72	1.43	1.04	0.255	0.228	54.33	1.54	1.04
0.335	0.286	89.12	1.39	1.06	0.303	0.261	54.00	1.48	1.06
0.379	0.316	88.39	1.35	1.08	0.355	0.295	53.52	1.42	1.08
0.420	0.343	87.59	1.30	1.10	0.404	0.326	52.97	1.36	1.10
0.508	0.399	85.73	1.23	1.16	0.462	0.362	52.22	1.30	1.14
0.567	0.436	84.09	1.18	1.22	0.511	0.393	51.46	1.26	1.18
0.616	0.469	82.53	1.15	1.27	0.575	0.430	50.34	1.20	1.25
0.670	0.505	80.50	1.11	1.34	0.638	0.469	49.03	1.15	1.33
0.725	0.546	78.07	1.08	1.43	0.708	0.516	47.43	1.10	1.45
0.785	0.594	74.94	1.04	1.58	0.762	0.553	45.70	1.06	1.59
0.826	0.641	72.48	1.03	1.67	0.813	0.604	43.78	1.04	1.72
0.881	0.705	68.77	1.01	1.90	0.858	0.660	41.80	1.03	1.86
0.902	0.748	66.52	1.01	1.92	0.901	0.727	39.35	1.02	2.02
0.923	0.778	64.38	1.00	2.06	0.931	0.777	37.54	1.00	2.26
0.939	0.814	62.61	1.00	2.13	0.952	0.832	35.80	1.00	2.35
0.956	0.854	60.77	1.00	2.23	0.970	0.886	34.23	1.00	2.46
0.978	0.916	57.93	1.00	2.43	0.986	0.936	32.80	1.00	2.69
0.987	0.953	56.24	1.00	2.35	1.000	1.000	31.21	1.00	
1.000	1.000	54.27	1.00						

to achieve constant temperature. The temperature was held constant for approximately (30 to 45) min before sampling.

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. The vapor and liquid samples were analyzed with GC and refractometer. The refractive indexes of both samples were measured right away, and the rest of the samples were injected into the cooled 2 mL autosampler vial containing approximately 1 mL of toluene. The compositions of both samples were immediately measured by GC. To prevent spreading of the unpleasant odor of the sulfur compounds, the GC was placed in a closed and ventilated hood.

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 m × 1.0 μm). The injector and FID were set at 250 °C. Helium was used as the carrier gas at a constant flow rate of 1.8 mL·min^{-1}, and the inlet split ratio was 150:1. First, the initial oven temperature was held at 55 °C for 2 min, and the temperature was increased subsequently to 100 °C at a rate of 10 °C·min^{-1} and was held at 100 °C for 2 min; after that, it increased again to 150 °C at a rate of 10 °C·min^{-1} and was held at 150 °C for 1 min. The total run time was 14.5 min.

The pure components were used to determine the retention times of GC peaks, after that the GC was calibrated with 12 mixtures of known composition that were prepared gravimetrically. To reduce the volume of the sample, toluene was used as the solvent.

The response factor of component 2 (F_2) was calculated from

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

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 area of GC peak; 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 was estimated to be 0.001 mole fraction.

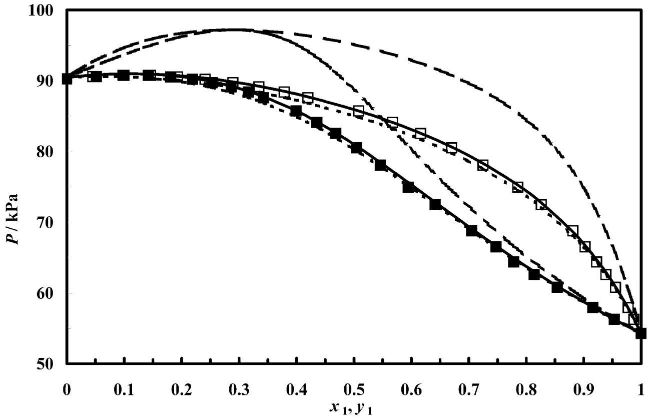

Figure 2. Pressure−composition diagram for the thiophene (1) + *n*-hexane (2) system at 338.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, UNIFAC; − −, COSMO-RS.

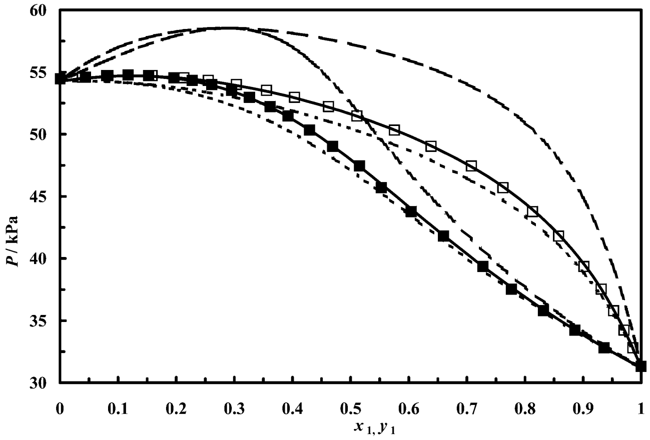

Figure 3. Pressure−composition diagram for the thiophene (1) + *n*-hexane (2) system at 323.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, UNIFAC; − −, COSMO-RS.

Table 5. Isothermal VLE Measurements, Liquid-Phase (x_1) and Vapor-Phase (y_1) Mole Fractions, Pressure (P), and Activity Coefficient (γ_i) for the Thiophene (1) + 1-Hexene (2) System at (333.15 and 323.15) K (GC analysis)

at 333.15 K					at 323.15 K				
x_1	y_1	P/kPa	γ_1	γ_2	x_1	y_1	P/kPa	γ_1	γ_2
0.000	0.000	90.94		1.00	0.000	0.000	64.82		1.00
0.056	0.043	89.78	1.51	1.00	0.113	0.085	63.11	1.50	1.01
0.160	0.119	87.41	1.41	1.01	0.221	0.160	61.15	1.40	1.02
0.247	0.181	85.17	1.36	1.02	0.311	0.216	59.40	1.31	1.05
0.309	0.220	83.57	1.29	1.04	0.368	0.254	58.06	1.27	1.06
0.357	0.254	81.96	1.27	1.05	0.425	0.289	56.80	1.23	1.09
0.411	0.287	80.20	1.22	1.07	0.539	0.365	53.70	1.15	1.15
0.475	0.329	78.09	1.18	1.10	0.611	0.412	51.50	1.11	1.21
0.536	0.367	75.94	1.14	1.15	0.691	0.472	49.00	1.07	1.30
0.615	0.424	72.75	1.09	1.21	0.761	0.537	46.28	1.04	1.40
0.634	0.446	71.51	1.10	1.20	0.817	0.598	43.67	1.02	1.49
0.683	0.473	69.56	1.05	1.28	0.868	0.672	40.90	1.01	1.58
0.714	0.511	67.72	1.06	1.29	0.916	0.757	37.87	1.00	1.71
0.753	0.541	65.98	1.04	1.36	0.980	0.925	32.96	1.00	1.94
0.815	0.617	61.96	1.03	1.43	1.000	1.000	31.21	1.00	
0.924	0.788	53.40	1.00	1.66					
0.959	0.870	49.96	1.00	1.77					
0.985	0.946	47.15	1.00	1.86					
1.000	1.000	45.44	1.00						

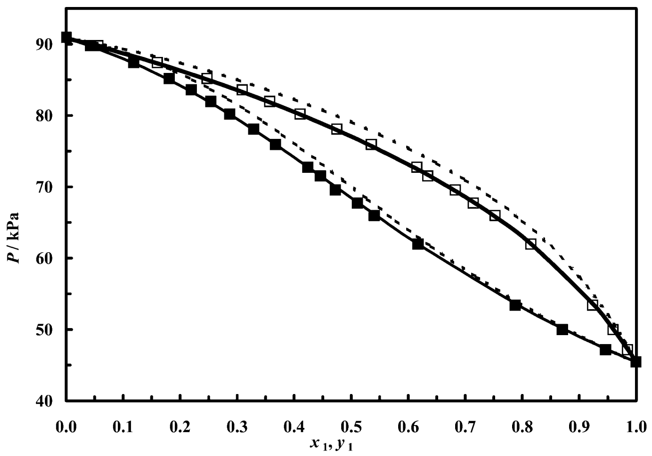

Figure 4. Pressure−composition diagram for the thiophene (1) + 1-hexene (2) system at 333.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, COSMO-RS.

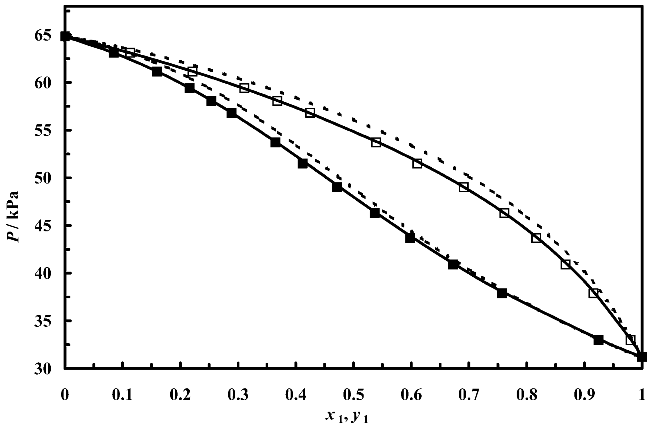

Figure 5. Pressure−composition diagram for the thiophene (1) + 1-hexene (2) system at 323.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, COSMO-RS.

Analysis and Refractive Indexes Calibration. Seventeen mixtures of known compositions were prepared gravimetrically for each binary system. The compositions covered the whole concentration range and were measured at 293.15 K. The measured refractive indexes of the calibration curves were fitted with a third-order polynomial. The compositions of VLE liquid and vapor samples were determined from the calibration curves. The accuracy in the compositions with this procedure is estimated to be 0.001 mole fraction. The refractive index−composition calibration data for the studied systems are presented in the Supporting Information.

COSMO-RS Calculation. The COSMO-RS[9] 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[10] (version 5.7). Geometry optimization of the molecules under investigation was performed with Turbomole software as well. Subsequent COSMO-RS calculations were done with COSMOtherm-C12-0105.[11]

In the COSMO-RS calculations, several conformers were taken into account for *n*-hexane and 1-hexene. For thiophene, only one stable conformer was found and then used for further calculations.

Results and Discussion

Vapor Pressure Measurements. Thiophene vapor pressures were measured in the previous work.[12] The Antoine constants for *n*-hexane and 1-hexene 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 2. The vapor pressures of pure components are shown in Figure 1 and presented in Table 3.

The measured vapor pressure of each component was compared with literature correlation[5] and COSMO-RS predic-

Table 6. Correlation of Wilson Parameters, Activity Coefficients at Infinite Dilution (γ_i^∞), and Azeotropic Composition (x_{1az}, T_{az}, P_{az}) for Systems Thiophene (1) + *n*-Hexane (2) at 338.15 K (System 1), Thiophene (1) + *n*-Hexane (2) at 323.15 K (System 2), Thiophene (1) + 1-Hexene (2) at 333.15 K (System 3), and Thiophene (1) + 1-Hexene (2) at 323.15 K (System 4)

	λ_{12}	λ_{21}				T_{az}	P_{az}
system	J·mol^{-1}	J·mol^{-1}	γ_1^∞	γ_2^∞	x_{1az}	K	kPa
1					0.1102[a]	338.15[a]	90.68[a]
	1407.728[b]	1160.497[b]	1.82[b]	2.49[b]	0.1108[b]	338.15[b]	90.90[b]
			1.73[c]	2.40[c]	0.0631[c]	338.15[c]	90.77[c]
			2.18[d]	3.61[d]	0.2479[d]	338.15[d]	94.11[d]
					0.1130[e]	341.61[e]	101.32[e]
2					0.1174[a]	323.15[a]	54.75[a]
	1516.417[b]	1173.183[b]	1.96[b]	2.71[b]	0.1224[b]	323.15[b]	54.66[b]
			2.15[d]	3.36[d]	0.1967[d]	323.15[d]	55.57[d]
3	1162.172[b]	602.481[b]	1.57	1.89[b]			
4	1192.359[b]	669.6368[b]	1.63	2.00[b]			

[a] This work. [b] Wilson model. [c] UNIFAC. [d] UNIFAC−Dortmund. [e] Ref 4.

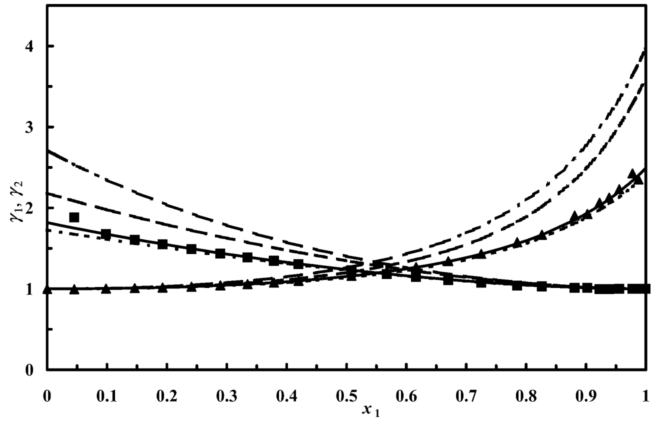

Figure 6. Activity coefficient−composition diagram for the thiophene (1) + *n*-hexane (2) system at 338.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from Wilson model; - - -, γ_1 and γ_2 from UNIFAC; − −, from UNIFAC−Dortmund; − - −, from COSMO-RS.

tion. The absolute average deviation (AAD) of pressure between experimental and literature correlation[5] for *n*-hexane and 1-hexene were (0.43 and 0.11) kPa, respectively. Measured vapor pressures of *n*-hexane and 1-hexene are in line with the ones measured by Willingham et al.[13] and Camin and Rossini,[14] respectively. The experimentally determined pure component vapor pressures were used in the COSMO-RS calculations.

Vapor−Liquid Equilibrium Measurements. The isothermal VLE measurements (P, x_1, and y_1) analyzed with GC, and calculated activity coefficients are reported in Tables 4 and 5, and $P-x_1-y_1$ diagrams are presented in Figures 2 to 5. The refractive indexes (liquid and vapor phases) and calculated activity coefficients of the systems measured with refractometer are reported in the Supporting Information. The absolute average deviations of liquid and vapor composition analyzed with GC and refractometer were 0.001 mole fraction.

All systems show positive deviations from Raoult's law. Thiophene + *n*-hexane systems measured at (338.15 and 323.15) K show maximum pressure azeotropes, while no azeotropes were found in the thiophene + 1-hexene systems. The compositions, pressures, and temperatures of the azeotropes are summarized in Table 6 together with the literature values.[4]

The activity coefficients γ_i were calculated from

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

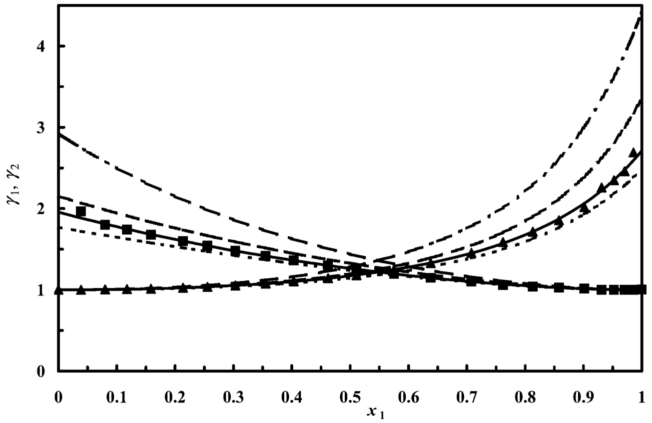

Figure 7. Activity coefficient−composition diagram for the thiophene (1) + *n*-hexane (2) system at 323.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from Wilson model; - - -, γ_1 and γ_2 from UNIFAC; − −, from UNIFAC−Dortmund; − - −, from COSMO-RS.

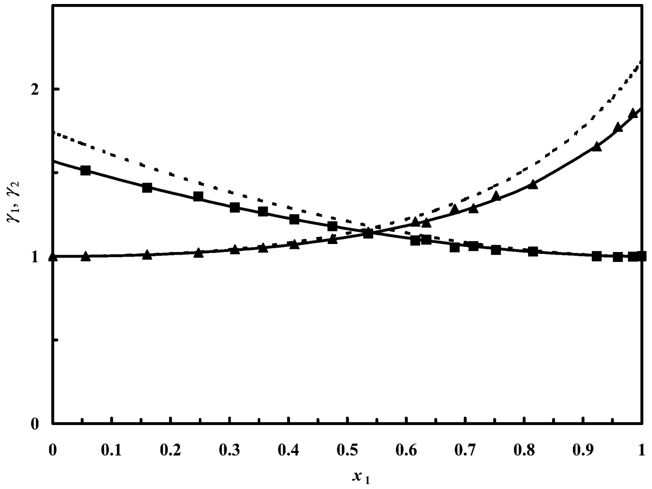

Figure 8. Activity coefficient−composition diagram for the thiophene (1) + 1-hexene (2) system at 333.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from Wilson model; - - -, γ_1 and γ_2 from COSMO-RS.

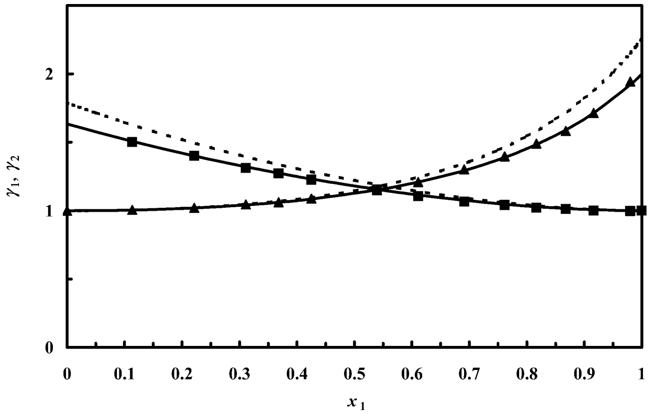

Figure 9. Activity coefficient−composition diagram for the thiophene (1) + 1-hexene (2) system at 323.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from Wilson model; - - -, γ_1 and γ_2 from COSMO-RS.

where y_i is the mole fraction of component i in the vapor phase, P is the total pressure of the system, ϕ_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^s is the vapor pressure of pure component i at the system temperature, ϕ_i^s is the pure component-saturated liquid fugacity coefficient at the system temperature T, V_i^L is the molar volume of pure component i in

Table 7. Results of Integral Test and Infinite Dilution Test and Averages of Absolute Vapor Fraction Residuals (Δy_{aver}) and Averages of Absolute Pressure Residuals (ΔP_{aver}) for the Wilson Model, UNIFAC, and UNIFAC−Dortmund for the Measured Systems Thiophene (1) + *n*-Hexane (2) at 338.15 K (System 1), Thiophene (1) + *n*-Hexane (2) at 323.15 K (System 2), Thiophene (1) + 1-Hexene (2) at 333.15 K (System 3), and Thiophene (1) + 1-Hexene (2) at 323.15 K (System 4)

	integral test	infinite dilution test (%)		point test (Wilson)		UNIFAC		UNIFAC−Dortmund	
system	D %	$x_1 = 0$	$x_1 = 1$	$\lvert\Delta y_{\mathrm{aver}}\rvert$	$\lvert\Delta P_{\mathrm{aver}}\rvert$/kPa	$\lvert\Delta y_{\mathrm{aver}}\rvert$	$\lvert\Delta P_{\mathrm{aver}}\rvert$/kPa	$\lvert\Delta y_{\mathrm{aver}}\rvert$	$\lvert\Delta \mathrm{P}_{\mathrm{aver}}\rvert$/kPa
1	0.02	−6.2	−5.7	0.0017	0.15	0.0043	0.44	0.0224	4.09
2	0.85	5.0	−4.9	0.0012	0.07	0.0065	0.77	0.0126	1.28
3	1.76	4.6	−7.9	0.0021	0.13				
4	0.80	5.5	−13.4	0.0013	0.07				

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[15] was used for processing all measured data. The Soave−Redlich−Kwong equation of state with quadratic mixing rules in the attractive parameter and linear in co-volume was used to calculate vapor-phase fugacity coefficient.[16] The binary interaction parameter in the quadratic mixing rules was set to zero. The Rackett equation[17] was used to calculate the liquid molar volume in the Poynting factor. The critical temperature, critical pressure, acentric factor, liquid molar volume, and Antoine parameters for vapor pressure for each component used in the calculations are presented in Table 2.

The liquid-phase activity coefficients were correlated with the Wilson[18] model. The objective function[15] (OF) used for fitting the activity coefficient parameters is given by eq 4, where N is the number of points used in the fit:

$$\mathrm{OF} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{|\gamma_{i,\mathrm{calc}} - \gamma_{i,\mathrm{exp}}|}{\gamma_{i,\mathrm{exp}}}\right) \qquad (4)$$

The Wilson parameters (λ_{12} and λ_{21}) and the activity coefficients at infinite dilution, γ_i^{∞}, are given in Table 6. Good agreement between measurements and model were achieved for all systems.

Thiophene + *n*-hexane system at (338.15 and 323.15) K were predicted with the original UNIFAC[19] model with the parameters on the level of Wittig et al.,[20] UNIFAC−Dortmund[21] with the parameters on the level of Wittig et al.,[22] and COSMO-RS. The results were presented in Figures 2, 3, 6, and 7.

Original UNIFAC shows better prediction for the system at 338.15 K as compared with predictions for the system at 323.15 K, whereas UNIFAC−Dortmund and COSMO-RS gave unsatisfactory prediction for both systems.

The original UNIFAC and UNIFAC−Dortmund interaction parameter for the thiophene (C_4H_4S group) and 1-hexene (CH_2═CH group) binary pair is not available; hence the original UNIFAC prediction and UNIFAC−Dortmund for thiophene + 1-hexene system is not possible. As can be seen from Figures 4, 5, 8, and 9, the COSMO-RS prediction is close to the experimental results.

The following thermodynamic consistency tests were applied to the measured VLE data: integral test,[23] point test,[23] and infinite dilution test.[24] The results are summarized in Table 7. The measurements passed all consistency tests applied.

Conclusions

Vapor pressure of *n*-hexane and 1-hexene were measured and compared with the literature values. Isothermal VLE were measured for thiophene + *n*-hexane at (338.15 and 323.15) K and for thiophene + 1-hexene at (333.15 and 323.15) K with a circulation still. The liquid- and vapor-phase compositions were determined with gas chromatography and refractometry. Maximum pressure azeotropy was found in thiophene + *n*-hexane system. Azeotropic behavior was not found in the thiophene + 1-hexene system. All systems measured passed the thermodynamic consistency tests. The Wilson model gave satisfactory correlation for all systems. Original UNIFAC prediction gave good prediction for thiophene + *n*-hexane as compared to UNIFAC−Dortmund and COSMO-RS. COSMO-RS prediction for thiophene + 1-hexene were close to experimental data.

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Supporting Information Available:

Refractive indexes (n_D) calibration data for thiophene (1) + *n*-hexane (2) and thiophene (1) + 1-hexene (2) at 293.15 K, the isothermal VLE measurements (P, x_1, and y_1), the refractive indexes (liquid and vapor phases), and the calculated activity coefficients of the systems measured with refractometer. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Twu, C. H.; Tassone, V.; Sim, W. D. Accurately predict the VLE of thiol-hydrocarbon mixture. *Chem. Eng. Prog.* **2004**, *100* (9), 39−45.

(2) Kenneth, J. C. *Process Analyzer Technology*; Wiley: New York, 1986.

(3) Leflaive, P.; Lemberton, J. L.; Perot, G.; Mirgain, C.; Carriat, J. Y.; Colin, J. M. On the origin of sulfur impurities in fluid catalytic cracking gasoline—reactivity of thiophene derivatives and of their possible precursors under FCC conditions. *Appl. Catal., A* **2002**, *227*, 201−215.

(4) Desty, D. H.; Fidler, F. A. Azeotrope formation between sulfur compounds and hydrocarbons. *Ind. Eng. Chem.* **1951**, *43*, 905−910.

(5) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill: New York, 1999.

(6) Yerazunis, S.; Plowright, J. D.; Smola, F. M. Vapor−liquid equilibrium determination by a new apparatus. *AIChE J.* **1964**, *10*, 660−665.

(7) Uusi-Kyyny, P.; Pokki, J.-P.; Aittamaa, J.; Liukkonen, S. Vapor−liquid equilibrium for the binary systems of 3-methylpentane + 2-methyl-2-propanol at 331 K and + 2-butanol at 331 K. *J. Chem. Eng. Data* **2001**, *46*, 754−758.

(8) Pokki, J.-P.; Řehák, K.; Kim, Y.; Matouš, J.; Aittamaa, J. Vapor−liquid equilibrium data at 343 K and excess molar enthalpy data at 298 K for the binary systems of ethanol + 2,4,4-trimethyl-1-pentene and 2-propanol + 2,4,4-trimethyl-1-pentene. *J. Chem. Eng. Data* **2003**, *48*, 75−80.

(9) Eckert, F.; Klamt, A. Fast solvent screening via quantum chemistry: COSMO-RS approach. *AIChE J.* **2002**, *48*, 369−385.

(10) Schafer, A.; Klamt, A.; Sattel, D.; Lohrenz, J. C. W.; Eckert, F. COSMO implementation in TURBOMOLE: extension of an efficient quantum chemical code towards liquid systems. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2187−2193.

(11) Eckert, F.; Klamt, A. *COSMOtherm*, Version C2.1, Release 01.05; COSMOlogic GmbH & Co. KG: Leverkusen, Germany, 2005.

(12) Sapei, E.; Zaytseva, A.; Uusi-Kyyny, P.; Younghun, K.; Keskinen, K. I.; Aittamaa, J. V. Vapor−liquid equilibrium for binary system of 1-propanethiol, thiophene, and diethyl sulfide with toluene at 90.03 kPa. *J. Chem. Eng. Data* **2006**, *51*, 1372−1376.

(13) Willingham, C. B.; Taylor, W. J.; Pignocco, J. M.; Rossini, F. D. Vapor pressures and boiling points of some paraffin, alkylcyclopentane, alkylcyclohexane, and alkylbenzene hydrocarbons. *J. Res. Natl. Bur. Stand.* **1945**, *35*, 219−244.

(14) Camin D. L.; Rossini, F. D. Physical properties of the 17 isomeric hexenes of the API research series. *J. Phys. Chem.* **1956**, *60*, 1446−1451.
(15) Aittamaa, J.; Pokki, J.-P. *User Manual of Program VLEFIT*; Helsinki University of Technology: Espoo, Finland, 2003.
(16) Soave, G. Equilibrium constants from a modified Redlich−Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.
(17) Rackett, H. G. Equation of state for saturated liquids. *J. Chem. Eng. Data* **1970**, *15*, 514−517.
(18) Wilson, G. M. Vapor−liquid equilibrium. XI: A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.
(19) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibria Using UNIFAC—A Group Contribution Method*; Elsevier: Amsterdam, 1977.
(20) Wittig, R.; Lohmann, J.; Gmehling, J. Vapor−liquid equilibria by UNIFAC group contribution. 6. Revision and extension. *Ind. Eng. Chem. Res.* **2003**, *42*, 183−188.
(21) Gmehling, J.; Li, J.; Schiller, M. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.
(22) Wittig, R.; Lohmann, J.; Gmehling, J. Prediction of phase equilibria and excess properties for systems with sulfones. *AIChE J.* **2003**, *49*, 530−537.
(23) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series, Vol. 1, Part 1; DECHEMA: Frankfurt/Main, 1977.
(24) Kojima, K.; Moon, H.; Ochi, K. Thermodynamic consistency test of vapor−liquid equilibrium data. *Fluid Phase Equilib.* **1990**, *56*, 269−284.

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