Vapor−Liquid Equilibrium for Binary System of Diethyl Sulfide + *n*-Heptane and Diethyl Sulfide + 2,2,4-Trimethylpentane at (363.15 and 353.15) K

Erlin Sapei,*,† Anna Zaytseva,† Petri Uusi-Kyyny,† Kari I. Keskinen,†,‡ and Juhani Aittamaa†

Department of Chemical Technology, Helsinki University of Technology, P.O. Box 6100, FI-02015 HUT, Finland, and Neste Jacobs Oy, P.O. Box 310, FI-06101, Porvoo, Finland

Isothermal vapor−liquid equilibrium (VLE) for diethyl sulfide + *n*-heptane and diethyl sulfide + 2,2,4-trimethylpentane at (363.15 and 353.15) K were measured with a circulation still. Maximum pressure azeotropes were found in both systems. The experimental results were correlated with the temperature-dependent Wilson model and also compared with the original UNIFAC and COSMO-RS predictive models. The measured diethyl sulfide + *n*-heptane VLE have been used simultaneously with the excess enthalpy from literature for a correlation of temperature-dependent Wilson parameters. Analyses of liquid- and vapor-phase composition were determined with a gas chromatograph and a refractometer. All VLE measurements passed the three thermodynamic consistency tests used.

Introduction

Increasing concerns on air pollution have led many countries to adopt more stringent regulations, which impose an ultralow concentration of sulfur in gasoline.[1] Design of separation processes to accomplish the removal of sulfur requires the knowledge of the vapor−liquid equilibrium (VLE) of sulfur compounds with hydrocarbons. Real gasoline is a rather complex hydrocarbon mixture composed of alkanes, olefins, cycloalkanes, and aromatics ranging from C_5 to C_{14}.

Sulfides are one of the major impurities present in crude oils and are also found in distillates and in products from cracking, coking, and alkylation processes.[2] The quantities of these compounds in the distillates are varying, depending on oil source and distillation operation.

The VLE measurements of sulfides and hydrocarbon mixtures are very scarce in the literature. In this work, isothermal VLE measurements for binary system of diethyl sulfide + *n*-heptane and of diethyl sulfide + 2,2,4-trimethylpentane were performed at (363.15 and 353.15) K with a circulation still. Similar measurements studied in this work were not found in the open literature.

Lecat[3] has measured the azeotropic point of diethyl sulfide + *n*-heptane at 101.32 kPa by using the distillation method. Didaoui-Nemouchi and Ait Kaci[4] have measured the excess molar enthalpies of diethyl sulfide with heptane at 303.15 K. Desty and Fidler[5] have measured the azeotropic point of diethyl sulfide + 2,2,4-trimethylpentane at 101.32 kPa by using the distillation method.

Experimental Section

Materials. Diethyl sulfide, *n*-heptane, 2,2,4-trimethylpentane, and toluene were purchased from Sigma Aldrich, Finland. The purities of the chemicals were checked with a gas chromatograph (GC) equipped with a flame ionization detector. *n*-Heptane, 2,2,4-trimethylpentane, and toluene were dried over molecular sieves (Merck 3Å) for 24 h. Diethyl sulfide was used as purchased without further purification. The refractive index (n_D) of the pure liquids were measured at 298.15 K with automatic refractometer (ABBEMAT-HP, Dr. Kernchen, Germany) with accuracy ± 0.00002, and the water contents were determined with a Karl Fischer titrator (DL38, Mettler Toledo). 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

component	GC purity (mass %)	water content (mass %)	n_D (298.15 K) exptl	n_D (298.15 K) lit.[6]
diethyl sulfide	99.72	0.01	1.4400	1.4402
n-heptane	99.28	0.01	1.3853	1.3851
2,2,4-trimethylpentane	99.78	0.01	1.3890	1.3890
toluene	99.97	0.02	1.4939	1.4941

Apparatus. The VLE runs were carried out with a circulation still of the Yerazunis-type[7] built at the glass workshop of the Helsinki University of Technology with minor modifications to the original design.[8] The experimental setup is described in detail in previous works.[8,9] Approximately 80 mL of reagent was 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) with an accuracy of ± 0.02 K, and 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 pressure transducer (PMP 4070, Druck) (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

---

* Corresponding author. E-mail: sapei@cc.hut.fi.
† Helsinki University of Technology.
‡ Neste Jacobs Oy.

10.1021/je060351e CCC: $37.00

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}, T_{max})

component	diethyl sulfide	*n*-heptane	2,2,4-trimethylpentane
T_c[a]/K	557.15	540.26	543.96
P_c[a]/MPa	3.962	2.736	2.568
ω[a]	0.294	0.351	0.303
V_i[a]/$cm^3 \cdot mol^{-1}$	108.363	147.014	165.452
A	7.0397[b]	6.9848[c]	6.7960[c]
B	2896.000[b]	2911.0373[c]	2896.0492[c]
C	−54.4934[b]	−57.4210[c]	−53.3543[c]
T_{min}/K	333.82	338.47	338.06
T_{max}/K	365.05	371.75	372.05

[a] Ref 6. [b] Ref 13. [c] Antoine parameters fitted from the measurements in this work: $P^S/\text{MPa} = \exp(A - [B/(T/\text{K} + C)])$.

Table 3. Experimental Vapor Pressure of *n*-Heptane and 2,2,4-Trimethylpentane

n-heptane		2,2,4-trimethylpentane	
T/K	P/kPa	T/K	P/kPa
371.75	102.91	372.05	101.32
369.49	96.10	369.85	95.03
367.39	90.13	368.06	90.13
364.91	83.48	364.60	81.27
360.77	73.29	360.21	71.15
355.44	61.71	355.56	61.51
349.40	50.45	350.06	51.53
342.90	40.26	345.38	44.13
338.47	34.34	338.06	34.27

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 Diethyl Sulfide (1) + *n*-Heptane (2) System at (363.15 and 353.15) K (GC Analysis)

at 363.15 K					at 353.15 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	79.09		1.00	0.000	0.000	57.34		1.00
0.032	0.049	80.56	1.30	1.00	0.038	0.059	58.75	1.33	1.00
0.069	0.102	82.24	1.27	1.00	0.088	0.131	60.44	1.29	1.00
0.111	0.157	84.00	1.24	1.00	0.149	0.208	62.30	1.25	1.01
0.159	0.217	85.80	1.22	1.01	0.214	0.284	64.04	1.21	1.01
0.204	0.268	87.38	1.20	1.01	0.280	0.352	65.61	1.18	1.02
0.254	0.320	88.98	1.17	1.02	0.345	0.415	66.96	1.15	1.04
0.299	0.366	90.31	1.15	1.03	0.410	0.474	68.11	1.12	1.05
0.354	0.419	91.74	1.14	1.04	0.473	0.527	69.06	1.10	1.07
0.417	0.477	92.99	1.11	1.05	0.530	0.576	69.79	1.08	1.09
0.477	0.531	94.23	1.09	1.06	0.595	0.628	70.23	1.06	1.12
0.568	0.605	95.64	1.06	1.10	0.667	0.687	70.78	1.04	1.15
0.652	0.674	96.56	1.04	1.13	0.735	0.744	71.09	1.02	1.19
0.721	0.732	97.06	1.03	1.17	0.798	0.797	71.21	1.01	1.24
0.779	0.781	97.40	1.02	1.21	0.855	0.849	71.16	1.01	1.29
0.826	0.823	97.40	1.01	1.24	0.905	0.897	70.94	1.00	1.33
0.865	0.859	97.30	1.01	1.27	0.945	0.938	70.68	1.00	1.38
0.901	0.894	97.10	1.00	1.31	0.976	0.973	70.41	1.00	1.41
0.932	0.925	96.91	1.00	1.33	1.000	1.000	70.20	1.00	
0.959	0.954	96.59	1.00	1.36					
0.981	0.979	96.35	1.00	1.40					
1.000	1.000	95.99	1.00						

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.

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

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 Diethyl Sulfide (1) + 2,2,4-Trimethylpentane (2) System at (363.15 and 353.15) K (GC Analysis)

at 363.15 K					at 353.15 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	77.77		1.00	0.000	0.000	57.11		1.00
0.044	0.068	79.98	1.30	1.00	0.044	0.069	58.71	1.32	1.00
0.100	0.146	82.49	1.27	1.00	0.098	0.148	60.61	1.31	1.00
0.178	0.245	85.67	1.23	1.01	0.165	0.232	62.63	1.26	1.01
0.260	0.337	88.58	1.20	1.01	0.242	0.318	64.70	1.22	1.02
0.361	0.431	91.53	1.14	1.04	0.316	0.391	66.32	1.17	1.03
0.459	0.519	93.89	1.11	1.06	0.398	0.469	67.96	1.14	1.05
0.550	0.595	95.56	1.08	1.09	0.450	0.513	68.75	1.12	1.06
0.644	0.671	96.62	1.05	1.14	0.540	0.587	69.93	1.08	1.09
0.711	0.725	97.20	1.03	1.18	0.622	0.653	70.75	1.06	1.13
0.775	0.778	97.47	1.02	1.22	0.703	0.717	71.25	1.04	1.18
0.830	0.826	97.49	1.01	1.27	0.776	0.777	71.49	1.02	1.24
0.877	0.870	97.37	1.01	1.31	0.839	0.833	71.49	1.01	1.29
0.919	0.911	97.12	1.00	1.35	0.895	0.886	71.23	1.00	1.35
0.953	0.947	96.75	1.00	1.39	0.940	0.932	70.91	1.00	1.41
0.981	0.978	96.41	1.00	1.42	0.976	0.972	70.50	1.00	1.45
1.000	1.000	95.89	1.00		1.000	1.000	70.11	1.00	

After equilibration, the pressure 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 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). For the diethyl sulfide + *n*-heptane system, the GC column used was a HP-1 dimethylpolysiloxane (60.0 m × 250 μm × 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 mL·min^{-1}, and the inlet split ratio was 100:1. First, the initial oven temperature was held at 50 °C, and the temperature was increased subsequently to 90 °C at a rate of 6 °C·min^{-1} and was held at 90 °C for 3 min. After that time, it was increased again to 140 °C at a rate of 15 °C·min^{-1} and was held at 140 °C for 1 min. The total run time was 14 min.

For the diethyl sulfide + 2,2,4-trimethylpentane system, the GC column used was a HP-1701 14% cyano-propylphenyl methyl polysiloxane (60.0 m × 250 μm × 0.25 μm). 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 the inlet split ratio was 100:1. First, the initial oven temperature was held at 70 °C, and the temperature was increased subsequently to 90 °C at a rate of 6 °C·min^{-1} and was held at 90 °C for 3 min. After that time, it was increased again to 140 °C at a rate of 20 °C·min^{-1}. The total run time was 8.83 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 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

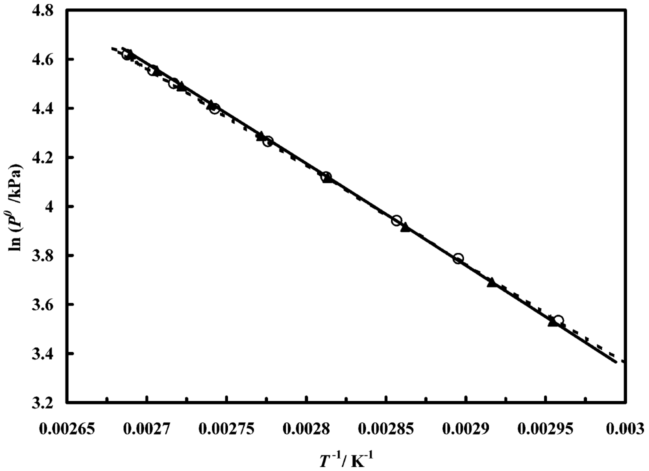

Figure 1. Measured vapor pressures of pure substances in this work: ▲, *n*-heptane; ○, 2,2,4-trimethylpentane. Measured vapor pressure from literature: —, *n*-heptane;[14] - - -, 2,2,4-trimethylpentane.[14]

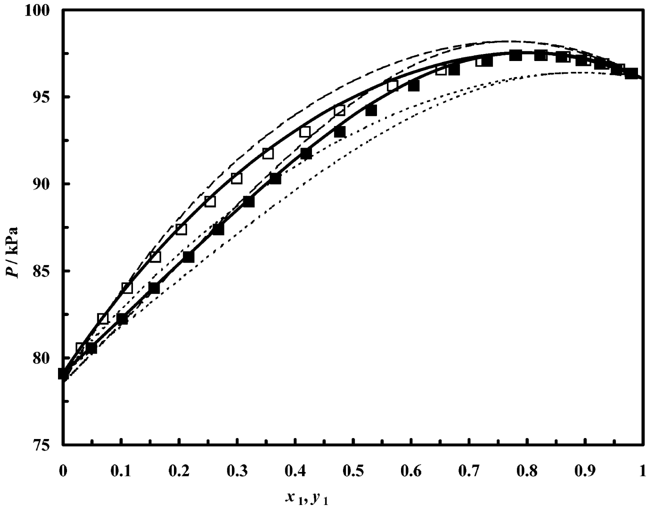

Figure 2. Pressure−composition diagram for the diethyl sulfide (1) + *n*-heptane (2) system at 363.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson model-extended data (parameter sets W_1); - - -, UNIFAC; — —, COSMO-RS.

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

where A_1 and A_2 are the areas 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.

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 the refractive indexes were measured at 293.15 K (n_D^{20}). 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[10] 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 the Turbomole program[11] (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.[12] In the COSMO-RS calculations, several conformers were taken into account for diethyl sulfide, *n*-heptane, and 2,2,4-trimethylpentane.

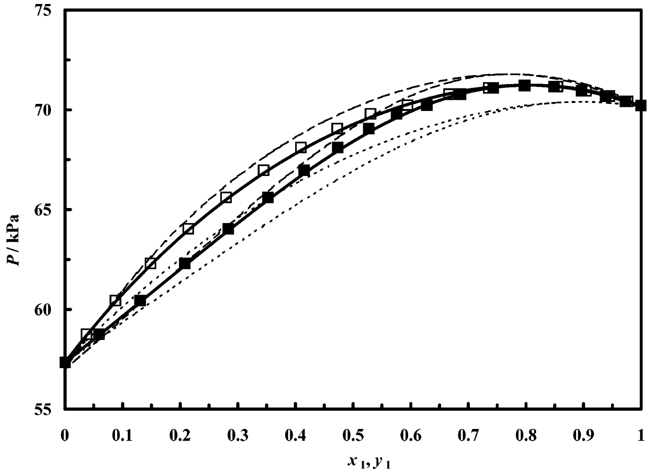

Figure 3. Pressure−composition diagram for the diethyl sulfide (1) + *n*-heptane (2) system at 353.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson model-extended data (parameter sets W_1); - - -, UNIFAC; — —, COSMO-RS.

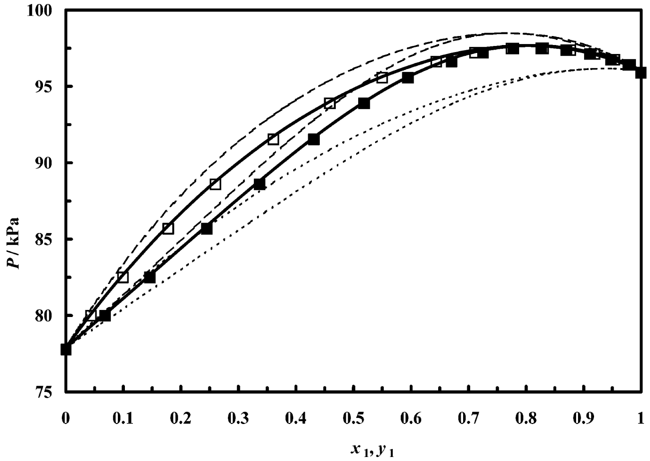

Figure 4. Pressure−composition diagram for the diethyl sulfide (1) + 2,2,4-trimethylpentane (2) system at 363.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson model-extended data; - - -, UNIFAC; — —, COSMO-RS.

Results and Discussion

Vapor Pressure Measurements. Diethyl sulfide vapor pressures were measured in the previous work.[13] The Antoine constants for *n*-heptane and 2,2,4-trimethylpentane 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.[6] The absolute average deviation (AAD) of pressure between experimental and literature correlation[6] for *n*-heptane and for 2,2,4-trimethylpentane were (0.66 and 0.35) kPa, respectively. Measured vapor pressures of *n*-heptane and of 2,2,4-trimethylpentane are in line with the ones

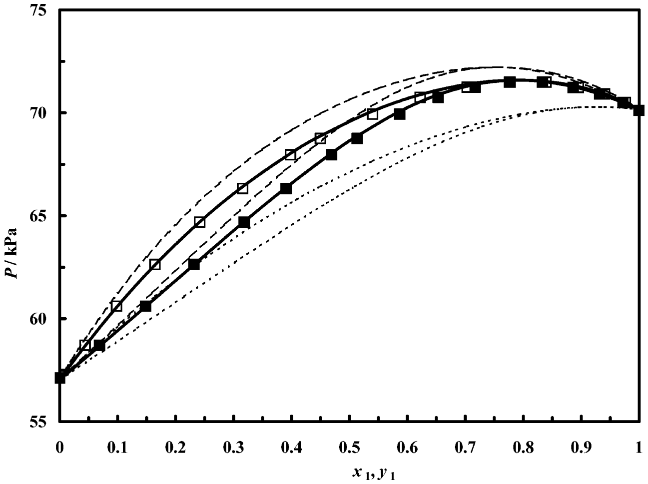

Figure 5. Pressure−composition diagram for the diethyl sulfide (1) + 2,2,4-trimethylpentane (2) system at 353.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson model-extended data; - - -, UNIFAC; — —, COSMO-RS.

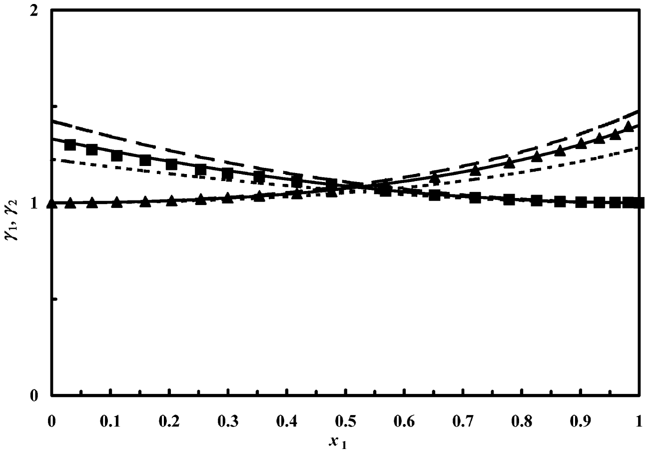

Figure 6. Activity coefficient−composition diagram for the diethyl sulfide (1) + *n*-heptane (2) system at 363.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from the Wilson model-extended data (parameter sets W_1); - - -, γ_1 and γ_2 from UNIFAC; — —, γ_1 and γ_2 from COSMO-RS.

measured by Willingham et al.[14] 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) 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 liquid and vapor compositions measured with refractometer, refractive indexes (liquid and vapor phases), and calculated activity coefficients of the systems measured are reported in the Supporting Information. The agreement between the results from the chromatographic and refractometric analysis was good: an absolute average deviation of 0.001 in mole fraction was observed.

The activity coefficients γ_i were calculated from

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

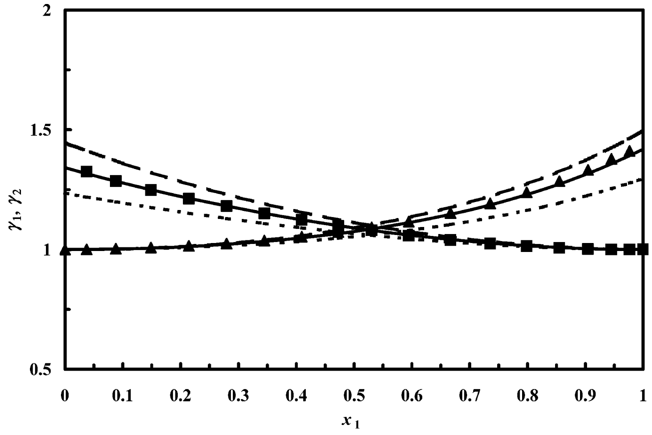

Figure 7. Activity coefficient−composition diagram for the diethyl sulfide (1) + *n*-heptane (2) system at 353.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from the Wilson model-extended data (parameter sets W_1); - - -, γ_1 and γ_2 from UNIFAC; — —, γ_1 and γ_2 from COSMO-RS.

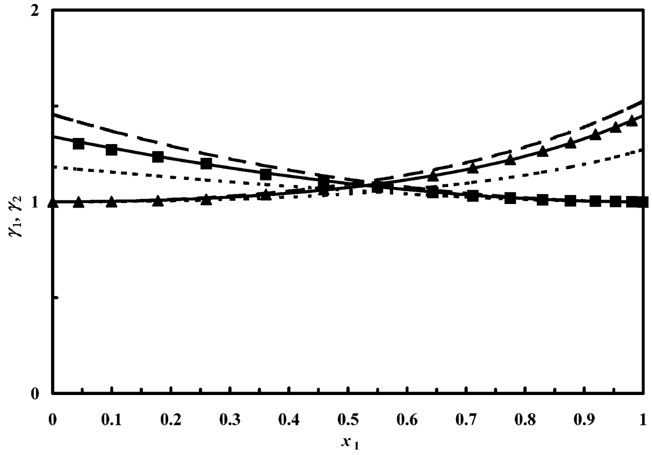

Figure 8. Activity coefficient−composition diagram for the diethyl sulfide (1) + 2,2,4-trimethylpentane (2) system at 363.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from the Wilson model-extended data; - - -, γ_1 and γ_2 from UNIFAC; — —, γ_1 and γ_2 from COSMO-RS.

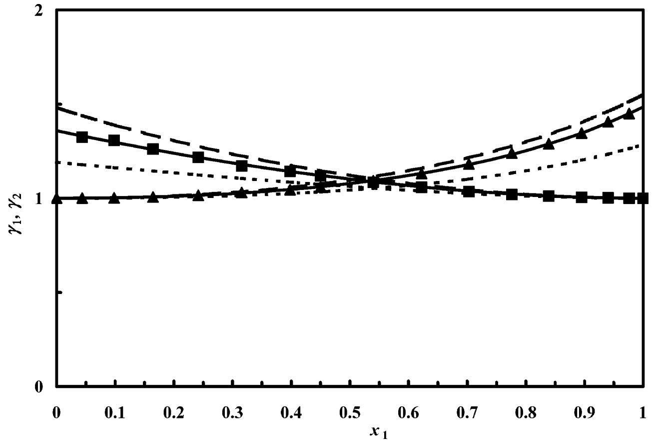

Figure 9. Activity coefficient−composition diagram for the diethyl sulfide (1) + 2,2,4-trimethylpentane (2) system at 353.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from the Wilson model-extended data; - - -, γ_1 and γ_2 from UNIFAC; — —, γ_1 and γ_2 from COSMO-RS.

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 liquid phase at the system temperature, T is temperature in Kelvin, and R is the universal gas constant (8.31441 J·K^{-1}·mol^{-1}).

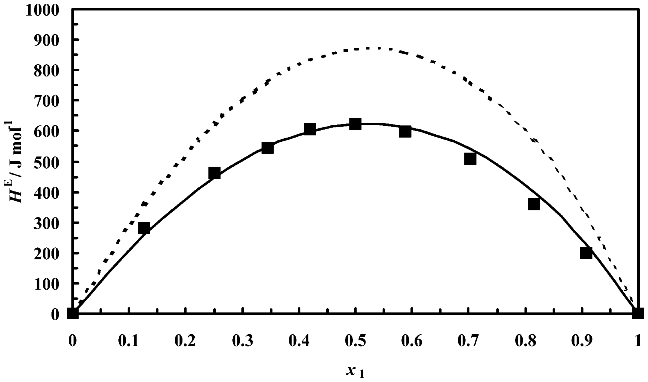

Figure 10. Excess molar enthalpy for the diethyl sulfide (1) + *n*-heptane (2) system at 303.15 K: ■, measured;[4] —, from the Wilson model (VLE this work + H^E literature,[4] parameter sets W_1); - - -, from the Wilson model (VLE this work, parameter sets W_2).

Table 6. Excess Molar Enthalpy for the Diethyl Sulfide (1) + *n*-Heptane (2) System at 303.15 K

x_1[a]	$H^E_{measured}$[a]/J·mol^{-1}	H^E_{model}/J·mol^{-1}	ΔH^E [b]/J·mol^{-1}
0.000	0.0	0.0	0.0
0.127	279.6	259.0	−20.6
0.251	461.9	447.7	−14.2
0.345	545.3	546.7	1.4
0.420	606.3	597.2	−9.1
0.500	623.3	622.3	−1.0
0.588	597.1	613.8	16.7
0.703	509.1	542.4	33.3
0.817	360.2	399.1	38.9
0.909	199.5	226.2	26.7
1.000	0.0	0.0	0.0

[a] Ref 4. [b] $\Delta H^E = H^E_{model} - H^E_{measured}$.

The VLEFIT program[15] was used for processing all the 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 the 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 of the diethyl sulfide + *n*-heptane system and the diethyl sulfide + 2,2,4-trimethylpentane system at (363.15 and 353.15) K were correlated with the Wilson[18] model with the temperature-dependent parameters. The objective function[15] (OF) used for fitting of the activity coefficient parameters is given by eq 4, where N_{VLE} is the number of points used in the fit:

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

Table 8. Activity Coefficients at Infinite Dilution (γ_i^∞) and Azeotropic Composition (x_{1az}, T_{az}, P_{az}) for Diethyl Sulfide (1) + *n*-Heptane (2) at 363.15 K (System 1), Diethyl Sulfide (1) + *n*-Heptane (2) at 353.15 K (System 2), Diethyl Sulfide (1) + 2,2,4-Trimethylpentane (2) at 363.15 K (System 3), and Diethyl Sulfide (1) + 2,2,4-Trimethylpentane (2) at 353.15 K (System 4)

system	γ_1^∞	γ_2^∞	x_{1az}	T_{az}/K	P_{az}/kPa	source
1			0.7965	363.15	97.28	this work
	1.33	1.40	0.8002	363.15	97.47	Wilson
	1.43	1.48	0.7821	363.15	98.19	COSMO-RS
	1.23	1.29	0.8903	363.15	96.39	UNIFAC
			0.7975	<364.95	101.32	ref 3
2			0.7912	353.15	71.15	this work
	1.34	1.42	0.8050	353.15	71.17	Wilson
	1.45	1.50	0.7816	353.15	71.78	COSMO-RS
	1.24	1.30	0.8963	353.15	70.39	UNIFAC
3			0.7984	363.15	97.47	this work
	1.34	1.40	0.8054	363.15	97.60	Wilson
	1.46	1.52	0.7765	363.15	98.35	COSMO-RS
	1.18	1.27	0.9413	363.15	96.15	UNIFAC
			0.8090	364.59	101.32	ref 5
4			0.7815	353.15	71.43	this work
	1.36	1.48	0.7907	353.15	71.52	Wilson
	1.48	1.55	0.7626	353.15	72.12	COSMO-RS
	1.19	1.28	0.9295	353.15	70.26	UNIFAC

In addition, the measured VLE data of the diethyl sulfide + *n*-heptane system at (363.15 and 353.15) K and excess enthalpy (H^E) data[4] at 303.15 K have been fitted simultaneously to obtain the temperature-dependent parameter sets of the Wilson model. The following objective function was used:

$$\mathrm{OF} = \frac{1}{N_{VLE}} \sum_{i=1}^{N_{VLE}} \left(\frac{|\gamma_{i,calc} - \gamma_{i,exp}|}{\gamma_{i,exp}} \right) + \frac{1}{N_{HE}} \sum_{i=1}^{N_{HE}} \frac{|H^E_{i,calc} - H^E_{i,exp}|}{\mathrm{kJ \cdot mol^{-1}}} \tag{5}$$

The H^E data are important to describe the temperature dependence of the activity coefficients following the Gibbs−Helmholtz equation:

$$H^E_{calc} = -RT^2 \left(\sum_{i=1}^{NC} x_i \frac{\partial(\ln \gamma_{i,calc})}{\partial T} \right)_{P,x} \tag{6}$$

The temperature dependence of the Wilson parameters (Wilson extended model) is described by the following expression:

$$\Delta\lambda_{ij} = a_{0,ij} + a_{1,ij}(T/\mathrm{K}) + a_{2,ij}(T/\mathrm{K})^2 \tag{7}$$

Wilson temperature-dependent interaction parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) for diethyl sulfide + *n*-heptane obtained from measured VLE and excess enthalpies data[4] (parameter sets W_1), diethyl sulfide + *n*-heptane obtained from measured VLE data (parameter sets W_2), and diethyl sulfide + 2,2,4-trimethylpentane (parameter sets W_3) are given in Table 7. Good agreement between measurements and model were achieved for all systems. The parameter sets W_1 were used in the calculations to describe diethyl sulfide + *n*-heptane system.

Table 7. Wilson Interaction Parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) for Diethyl Sulfide (1) + *n*-Heptane (2) (Extended, System W_1), Diethyl Sulfide (1) + *n*-Heptane (2) (Extended, System W_2), and Diethyl Sulfide (1) + 2,2,4-Trimethylpentane (2) (Extended, System W_3)

system	$a_{0,12}$ / J·mol^{-1}	$a_{1,12}$ / J·mol^{-1}·K^{-1}	$a_{2,12}$ / J·mol^{-1}·K^{-2}	$a_{0,21}$ / J·mol^{-1}	$a_{1,21}$ / J·mol^{-1}·K^{-1}	$a_{2,21}$ / J·mol^{-1}·K^{-2}
W_1[a]	5746.383	−30.783	0.048	987.415	−0.325	−0.006
W_2[b]	5734.660	−28.817	0.042	918.751	3.196	−0.014
W_3	5705.352	−27.728	0.041	1000.520	0.406	−0.009

[a] VLE this work + H^E data from ref 4. [b] VLE this work: $\lambda_{12} - \lambda_{11} = a_{0,12} + a_{1,12}T + a_{2,12}T^2$; $\lambda_{21} - \lambda_{22} = a_{0,21} + a_{1,21}T + a_{2,21}T^2$.

Table 9. Results of Integral Test and Infinite Dilution Test; Averages of Absolute Vapor Fraction Residuals (Δy_{aver}) and Averages of Absolute Pressure Residuals (ΔP_{aver}) for the Wilson Model; and Residual for UNIFAC for the Measured Systems: Diethyl Sulfide (1) + *n*-Heptane (2) at 363.15 K (System 1), Diethyl Sulfide (1) + *n*-Heptane (2) at 353.15 K (System 2), Diethyl Sulfide (1) + 2,2,4-Trimethylpentane (2) at 363.15 K (System 3), and Diethyl Sulfide (1) + 2,2,4-Trimethylpentane (2) at 353.15 K (System 4)

		integral test	infinite dilution test (%)		point test (Wilson)		residuals (UNIFAC)	
system	Wilson parameter set used	D/%	$x_1 = 0$	$x_1 = 1$	$\lvert\Delta y_{aver}\rvert$	$\lvert\Delta P_{aver}\rvert$/kPa	$\lvert\Delta y_{aver}\rvert$	$\lvert\Delta P_{aver}\rvert$/kPa
1	W_1	3.9	−3.4	−0.6	0.0011	0.18	0.0049	1.00
2	W_1	3.8	4.8	−7.1	0.0010	0.07	0.0055	0.95
3	W_3	2.4	−10.5	−1.0	0.0007	0.14	0.0079	1.59
4	W_3	1.2	3.0	1.0	0.0004	0.07	0.0086	1.37

The comparison between the measured excess molar enthalpy and the one calculated by the Wilson extended model with parameter sets W_1 is presented in Table 6 and shown in Figure 10. Good agreement is obtained between experimental and calculated results. The calculated excess enthalpy by using the Wilson extended model with parameter sets W_2 are included in Figure 10. The agreement between experimental and calculated excess molar enthalpy can be considered typical for the VLE measured with this apparatus.[19]

The VLE of diethyl sulfide (1) + *n*-heptane (2) system at 101.32 kPa were calculated with Wilson temperature-dependent parameter sets W_1 and also with parameter sets W_2. The VLE calculated with parameter set W_1 show good agreement with the VLE calculated with the parameter set W_2. The absolute average deviation of vapor composition and temperature between VLE calculated with parameters W_1 and W_2 are 0.001 mole fractions and 0.05 K, respectively.

The diethyl sulfide + *n*-heptane system and the diethyl sulfide + 2,2,4-trimethylpentane system at (363.15 and 353.15) K were predicted with the original UNIFAC[20] model with the parameters on the level of Wittig et al.[21] and COSMO-RS. The results are presented in Figures 2 to 9. Original UNIFAC and COSMO-RS models gave poor prediction for the systems studied.

All systems show positive deviations from Raoult's law. Diethyl sulfide + *n*-heptane and diethyl sulfide + 2,2,4-trimethylpentane systems measured at (363.15 and 353.15) K show maximum pressure azeotropes. The compositions, pressures, and temperatures of the azeotropes are summarized in Table 8 together with the literature values.[3,5] The activity coefficients at infinite dilution (γ_i^∞) are also presented in Table 8.

The following thermodynamic consistency tests were applied to the measured VLE data: integral test,[22] point test,[22] and infinite dilution test.[23] The results were summarized in Table 9. The measurements passed all the consistency tests applied.

Conclusions

Vapor pressure of *n*-heptane and of 2,2,4,-trimethylpentane were measured and compared with the literature values. Isothermal VLE were measured for diethyl sulfide + *n*-heptane and diethyl sulfide + 2,2,4-trimethylpentane at (363.15 and 353.15) K with a circulation still. Liquid- and vapor-phase composition were determined with gas chromatography and refractometry. The agreement between the results from the chromatographic and refractometric analysis was good: an absolute average deviation of 0.001 in mole fraction was observed.

Maximum pressure azeotropy was found in both systems. All systems measured passed the thermodynamic consistency tests. The experimental data of diethyl sulfide + *n*-heptane system have been fitted using temperature-dependent Wilson parameters, which allow the simultaneous description of the VLE and excess enthalpy behavior. The excess molar enthalpy calculated from diethyl sulfide + *n*-heptane VLE data are in good agreement with the literature data. The Wilson model gave good correlation for all systems whereas original UNIFAC and COSMO-RS prediction gave poor predictions for the systems studied.

Acknowledgment

The authors acknowledge CSC (Finnish Information Technology Center for Science) for the supplied computing resources in this project and Ms. Piia Haimi for measurements of pure component water content.

Supporting Information Available:

Refractive indexes (n_D) calibration data for diethyl sulfide (1) + *n*-heptane (2) and diethyl sulfide (1) + 2,2,4-trimethylpentane (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) Lecat, M. Azeotropes of sulfides and halides. *Bull. Cl. Sci. Acad. R. Belg.* **1947**, *33*, 160−182.
(4) Didaoui-Nemouchi, S.; Ait Kaci, A. Excess molar enthalpies of binary mixtures of thiophene and diethyl sulfide with *n*-alkanes. *J. Therm. Anal.* **2002**, *69*, 669−680.
(5) Desty, D. H.; Fidler, F. A. Azeotrope formation between sulfur compounds and hydrocarbons. *Ind. Eng. Chem.* **1951**, *43*, 905−910.
(6) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill: New York, 1999.
(7) Yerazunis, S.; Plowright, J. D.; Smola, F. M. Vapor−liquid equilibrium determination by a new apparatus. *AIChE J.* **1964**, *10*, 660−665.
(8) 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.
(9) Pokki, J.-P.; Řehák, K.; Kim, Yh.; 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.
(10) Eckert, F.; Klamt, A. Fast solvent screening via quantum chemistry: COSMO-RS approach. *AIChE J.* **2002**, *48*, 369−385.
(11) 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.
(12) Eckert, F.; Klamt, A. *COSMOtherm*, Version C2.1, Release 01.05; COSMOlogic GmbH &Co. KG: Leverkusen, Germany, 2005.
(13) Sapei, E.; Zaytseva, A.; Uusi-Kyyny, P.; Younghun, K.; Keskinen, K. I.; Aittamaa, J. 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.
(14) 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.

(15) Aittamaa, J.; Pokki, J.-P. *User Manual of Program VLEFIT*; Helsinki University of Technology: Espoo, 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) Pokki, J.-P. Development of Vapour Liquid Equilibrium Calculation Methods for Chemical Engineering Design. Dissertation, Helsinki University of Technology, 2004; pp 24−28.

(20) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibria Using UNIFAC−A Group Contribution Method*; Elsevier: Amsterdam, 1977.

(21) 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.

(22) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series, Vol. 1, Part 1; DECHEMA: Frankfurt/Main, 1977.

(23) Kojima, K.; Moon, H.; Ochi, K. Thermodynamic consistency test of vapor−liquid equilibrium data. *Fluid Phase Equilib.* **1990**, *56*, 269−284.

Received for review August 8, 2006. Accepted October 31, 2006. The authors acknowledge Neste Jacobs Oy, Neste Oil Oyj, and TEKES (National Technology Agency of Finland) for the financial support.

JE060351E