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Vapor−Liquid Equilibrium for Binary System of Diethyl Sulfide + *n*-Hexane at (338.15 and 323.15) K and Diethyl Sulfide + 1-Hexene at (333.15 and 323.15) 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*-hexane at (338.15 and 323.15) K and diethyl sulfide + 1-hexene at (333.15 and 323.15) K were measured with a circulation still. All systems exhibit a slight positive deviation from ideality. No azeotropic behavior was found in any of the systems studied. The experimental results were correlated with the Wilson model and also compared with the original UNIFAC and the COSMO-RS predictive models. The measured diethyl sulfide + *n*-hexane VLE have been used simultaneously with the excess enthalpy from literature for a correlation of temperature-dependent Wilson parameters. Excess molar enthalpies at 318.15 K for the diethyl sulfide + 1-hexene system were calculated from the VLE data. Analyses of liquid- and vapor-phase compositions were determined with gas chromatography. All VLE measurements passed the thermodynamic consistency tests that were used (integral, infinite dilution, and point test).

Introduction

Sulfides are one of the common impurities present in crude oils and are also found in distillates and in products from cracking, coking, and alkylation processes.[1] Organosulfur impurities in gasoline cause severe environmental problems. Consequently, most countries have applied stricter regulations to lower the sulfur specification in gasoline.[2] Design of separation processes to accomplish the removal of organic sulfur compounds requires the knowledge of the vapor−liquid equilibrium (VLE) of sulfur compounds with hydrocarbons. The knowledge is also important in the thermodynamic model development and creation of new estimation methods.

In this work, isothermal VLE measurements for the binary system of diethyl sulfide + *n*-hexane were performed at (338.15 and 323.15) K, and diethyl sulfide + 1-hexene were measured at (333.15 and 323.15) K with a circulation still. No other VLE of binaries studied in this work were found in the literature search. Excess molar enthalpies of diethyl sulfide with *n*-hexane have been measured at 318.15 K.[3]

Experimental Section

Materials. Diethyl sulfide, *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 and dried over molecular sieves (Merck 3A) for 24 h. 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 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.[4]

Apparatus. The VLE runs were carried out with a circulation still of the Yerazunis-type[5] built at the glass workshop of the Helsinki University of Technology with minor modifications to the original design.[6] The experimental setup is described in detail in our previous works.[6,7] Approximately 80 mL of reagent was needed to run the apparatus.

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.[4]
diethyl sulfide	99.75	0.01	1.4400	1.4402
n-hexane	99.93	0.01	1.3723	1.3723
1-hexene	99.95	0.01	1.3852	1.3850
toluene	99.97	0.02	1.4939	1.4941

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 the 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 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 the mixing chamber of the condensed vapor phase and the liquid phase, DC electric motors (Graupner speed 400) were equipped with magnetic stirrer bars.

Experimental Procedures. Pure component 1 was introduced in the circulation still, and its vapor pressure was measured. 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.

After equilibration, the temperature in the equilibrium cell was measured, and then vapor and liquid samples were

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

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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	diethyl sulfide	*n*-hexane	1-hexene
$T_c{}^a$/K	557.15	507.43	504.03
$P_c{}^a$/MPa	3.962	3.012	3.140
ω^a	0.294	0.305	0.28
$V_i{}^a$/cm^3·mol^{-1}	108.363	131.306	126.103
A	7.0397^b	6.9802^c	6.9000^c
B	2896.000^b	2724.9601^c	2655.0085^c
C	−54.4934^b	−47.7364^c	−47.6225^c
T_{min}/K	333.82	307.31	298.99
T_{max}/K	365.05	342.00	336.04

[a] Ref 4. [b] Ref 11. [c] Ref 12. $P^S/\text{MPa} = \exp(A - [B/(T/\text{K} + C)])$.

Table 3. 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*-Hexane (2) System at (338.15 and 323.15) K

338.15 K					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	90.46		1.00	0.000	0.000	54.26		1.00
0.038	0.026	89.29	1.41	1.00	0.025	0.017	53.74	1.49	1.00
0.099	0.066	87.43	1.36	1.00	0.077	0.050	52.76	1.43	1.00
0.166	0.109	85.26	1.31	1.01	0.140	0.089	51.58	1.36	1.01
0.229	0.149	83.12	1.26	1.02	0.212	0.132	50.09	1.30	1.02
0.301	0.193	80.55	1.21	1.03	0.291	0.179	48.34	1.24	1.03
0.369	0.238	78.00	1.18	1.05	0.377	0.231	46.38	1.18	1.06
0.428	0.276	75.62	1.14	1.07	0.460	0.285	44.23	1.14	1.08
0.494	0.319	72.87	1.11	1.09	0.544	0.341	42.01	1.10	1.13
0.559	0.367	69.90	1.08	1.12	0.637	0.409	39.29	1.06	1.19
0.658	0.440	65.55	1.03	1.20	0.708	0.469	37.10	1.03	1.25
0.719	0.502	62.01	1.02	1.23	0.750	0.520	35.37	1.03	1.26
0.832	0.642	55.02	1.01	1.32	0.810	0.592	33.01	1.01	1.32
0.878	0.719	51.65	1.00	1.35	0.865	0.675	30.66	1.00	1.38
0.919	0.799	48.62	1.00	1.37	0.914	0.767	28.31	1.00	1.43
0.952	0.867	46.05	1.00	1.43	0.951	0.853	26.45	1.00	1.48
0.980	0.940	43.73	1.00	1.47	0.979	0.933	24.91	1.00	1.52
1.000	1.000	42.02	1.00		1.000	1.000	23.76	1.00	

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 toluene. The compositions of both samples were analyzed immediately with 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-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 1.0 mL·min^{-1}, and the inlet split ratio was 100:1. First, the initial oven temperature was held at 60 °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 1 min; after that, it increased again to 140 °C at a rate of 15 °C·min^{-1}. The total run time was 9.33 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 eq 1:

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

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) + 1-Hexene (2) System at (333.15 and 323.15) K

333.15 K					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	90.85		1.00	0.000	0.000	64.83		1.00
0.040	0.020	88.89	1.23	1.00	0.038	0.018	63.44	1.26	1.00
0.093	0.046	86.35	1.20	1.00	0.093	0.045	61.59	1.22	1.00
0.163	0.081	83.10	1.16	1.01	0.155	0.076	59.43	1.20	1.01
0.236	0.122	79.42	1.15	1.01	0.231	0.114	56.86	1.16	1.01
0.317	0.168	75.45	1.12	1.02	0.311	0.157	54.12	1.13	1.03
0.493	0.281	66.42	1.07	1.05	0.396	0.207	51.02	1.11	1.04
0.577	0.343	61.87	1.04	1.07	0.482	0.263	47.84	1.09	1.06
0.647	0.405	58.01	1.03	1.09	0.629	0.377	41.42	1.04	1.09
0.719	0.478	53.81	1.01	1.12	0.697	0.442	38.63	1.02	1.11
0.783	0.555	49.85	1.00	1.14	0.743	0.489	37.08	1.02	1.15
0.841	0.640	46.10	1.00	1.17	0.766	0.521	35.66	1.02	1.14
0.893	0.734	42.62	1.00	1.19	0.828	0.612	32.68	1.01	1.16
0.936	0.826	39.64	1.00	1.22	0.859	0.660	31.37	1.01	1.19
0.973	0.919	37.04	1.00	1.23	0.886	0.711	29.83	1.00	1.19
1.000	1.000	34.98	1.00		0.911	0.761	28.76	1.01	1.21
					0.935	0.813	27.38	1.00	1.23
					1.000	1.000	23.76	1.00	

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 the GC peak; 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 was estimated to be 0.001 mole fraction.

COSMO-RS Calculation. The COSMO-RS[8] 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[9] (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.[10] In the COSMO-RS calculations, several conformers were taken into account for diethyl sulfide, *n*-hexane, and 1-hexene.

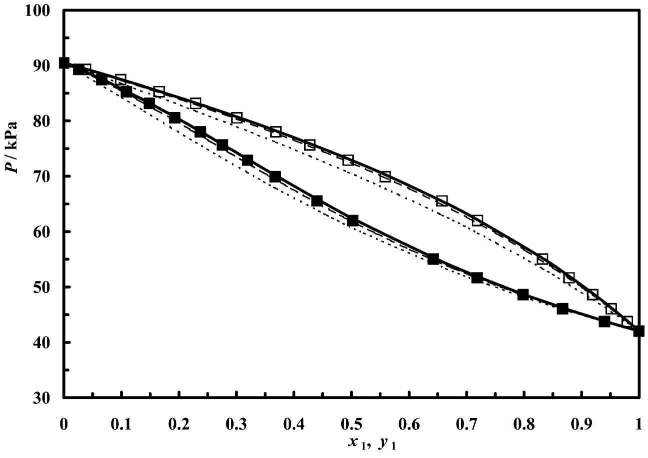

Figure 1. Pressure−composition diagram for the diethyl sulfide (1) + *n*-hexane (2) system at 338.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, UNIFAC; − −, COSMO-RS.

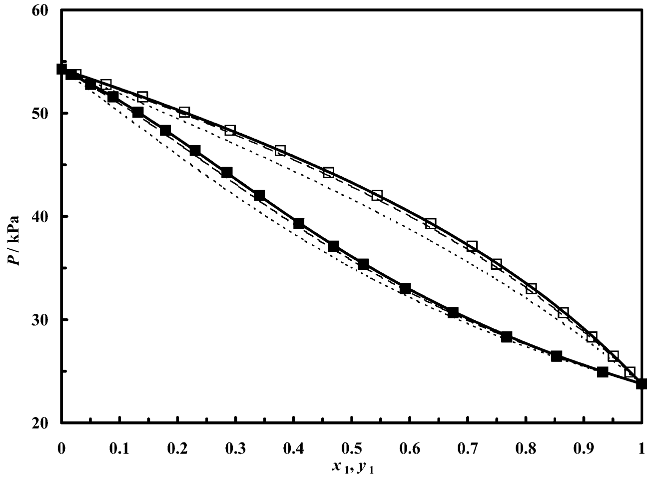

Figure 2. Pressure−composition diagram for the diethyl sulfide (1) + *n*-hexane (2) system at 323.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, UNIFAC; — —, COSMO-RS.

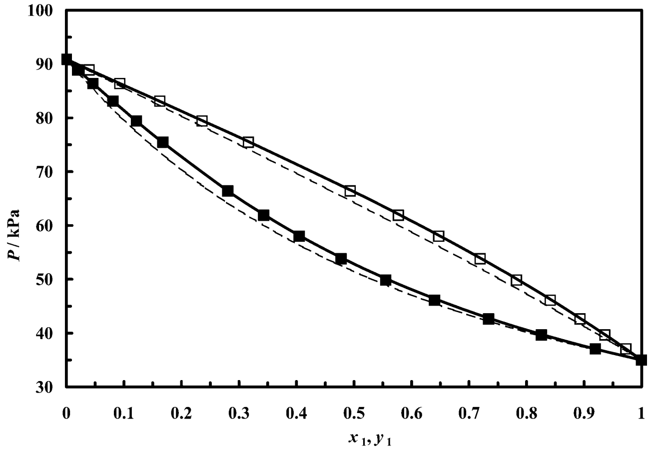

Figure 3. Pressure−composition diagram for the diethyl sulfide (1) + 1-hexene (2) system at 333.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; — —, COSMO-RS.

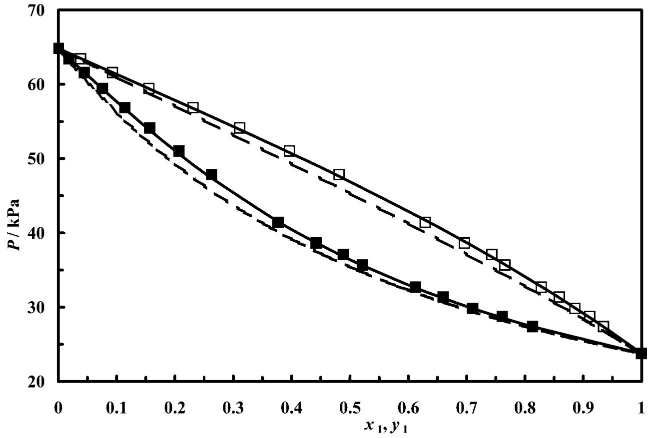

Figure 4. Pressure−composition diagram for the diethyl sulfide (1) + 1-hexene (2) system at 323.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; — —, COSMO-RS.

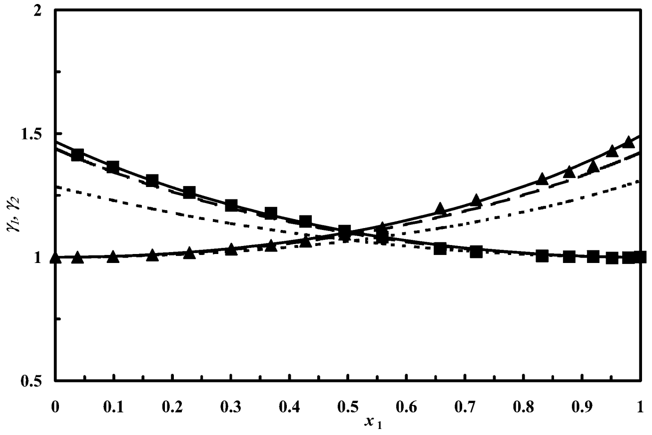

Figure 5. Activity coefficient−composition diagram for the diethyl sulfide (1) + *n*-hexane (2) system at 338.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from Wilson model; - - -, γ_1 and γ_2 from UNIFAC; — —, from COSMO-RS.

Table 5. Excess Molar Enthalpy at 318.15 K for the Diethyl Sulfide (1) + *n*-Hexane (2) System and Diethyl Sulfide (1) + 1-Hexene (2) System

	diethyl sulfide (1) + *n*-hexane (2)			diethyl sulfide (1) + 1-hexene (2)
	H^E_{measured}[a]	H^E_{model}	$\Delta H^{E\,b}$	H^E_{model}
x_1[a]	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}
0.000	0.0	0.0	0.0	0.0
0.060	122.0	118.6	−3.4	108.7
0.119	226.0	221.9	−4.1	202.8
0.176	309.0	309.1	0.1	281.6
0.233	381.0	383.7	2.7	348.2
0.288	441.0	443.5	2.5	401.0
0.342	491.0	490.4	−0.6	441.6
0.395	525.0	524.7	−0.3	470.7
0.447	547.0	547.0	0.0	488.6
0.498	555.0	557.7	2.7	495.9
0.548	557.0	557.0	0.0	493.1
0.597	549.0	545.5	−3.5	480.6
0.645	529.0	523.5	−5.5	459.1
0.693	497.0	490.5	−6.5	428.1
0.739	450.0	448.5	−1.5	389.4
0.784	393.0	397.2	4.2	343.1
0.829	329.0	335.4	6.4	288.2
0.873	260.0	264.6	4.6	226.2
0.916	184.0	185.3	1.3	157.5
0.958	99.0	97.8	−1.2	82.7
1.000	0.0	0.0	0.0	0.0

[a] Ref 3. [b] $\Delta H^E = H^E_{\text{model}} - H^E_{\text{measured}}$.

Results and Discussion

Diethyl sulfide, *n*-hexane, and 1-hexene vapor pressures were measured in the previous work.[11,12] The Antoine constants parameters with the recommended temperature range of the vapor pressure equations are presented in Table 2. They are used in the COSMO-RS and activity coefficient calculations.

The isothermal VLE measurements (P, x_1, and y_1) and calculated activity coefficients are reported in Tables 3 and 4, and $P-x_1-y_1$ diagrams are presented in Figures 1 to 4. All systems show slight positive deviations from Raoult's law. No azeotropic behavior was found in any of the systems studied.

The activity coefficients γ_i were calculated from

$$\gamma_i = \frac{y_i P \phi_i}{x_i P_i^S \phi_i^S} \exp \int_P^{P_i^S} \frac{V_i^L}{RT} dP \qquad (3)$$

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

Table 6. Wilson Interaction Parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) for Diethyl Sulfide (1) + *n*-Hexane (2) (Extended, System W$_1$), Diethyl Sulfide (1) + 1-Hexene (2) at 333.15 K (System W$_2$)

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]	5688.186	−31.061	0.051	969.830	1.139	−0.011
W$_2$	5689.861	−32.124	0.052	970.040	0.951	−0.007

[a] VLE this work + H^E data from ref 3.

Table 7. 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, Residual for UNIFAC, and Activity Coefficients at Infinite Dilution for the Measured Systems Diethyl Sulfide (1) + *n*-Hexane (2) at 338.15 K (System 1), Diethyl Sulfide (1) + *n*-Hexane (2) at 323.15 K (System 2), Diethyl Sulfide (1) + 1-Hexene (2) at 333.15 K (System 3), and Diethyl Sulfide (1) + 1-Hexene (2) at 323.15 K (System 4)

system	Wilson parameter set used	integral test	infinite dilution test (%)		point test (Wilson)		residuals (UNIFAC)			
		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	γ_1^∞	γ_2^∞
1	W$_1$	0.9	1.7	−27.0	0.0014	0.15	0.0095	1.24	1.47	1.49
2	W$_1$	0.1	−4.1	−21.7	0.0010	0.06	0.0113	0.70	1.51	1.55
3	W$_2$	3.3	−3.4	−27.1	0.0010	0.11			1.25	1.24
4	W$_2$	8.3	−12.0	0.2	0.0020	0.12			1.27	1.27

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

The VLEFIT program[13] was used for processing the measurements. The Soave−Redlich−Kwong equation of state with quadratic mixing rules in the attractive parameter and linear in covolume was used to calculate vapor-phase fugacity coefficient.[14] The binary interaction parameter in the quadratic mixing rules was set to zero. The Rackett equation[15] 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

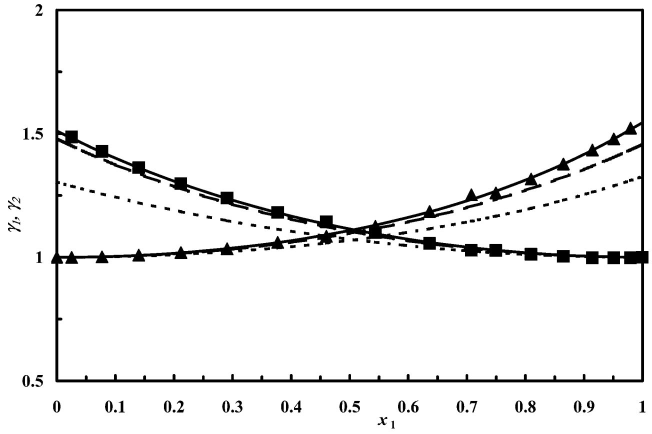

Figure 6. Activity coefficient−composition diagram for the diethyl sulfide (1) + *n*-hexane (2) system at 323.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from Wilson model; - - -, γ_1 and γ_2 from UNIFAC; − −, from COSMO-RS.

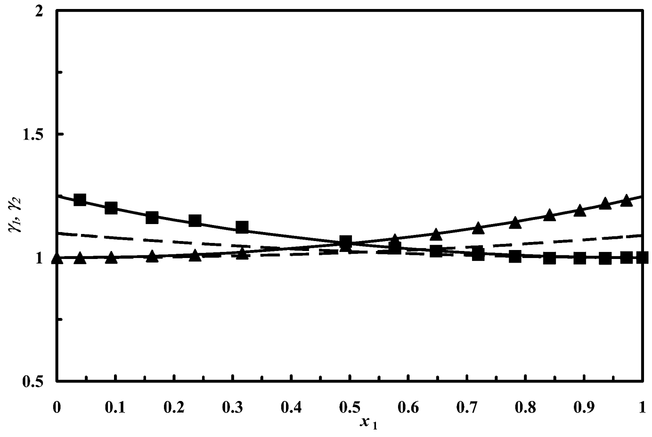

Figure 7. Activity coefficient−composition diagram for the diethyl sulfide (1) + 1-hexene (2) system at 333.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from Wilson model; − −, γ_1 and γ_2 from COSMO-RS.

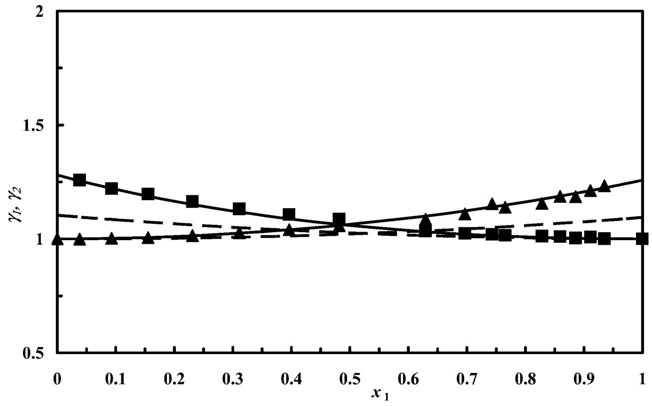

Figure 8. Activity coefficient−composition diagram for the diethyl sulfide (1) + 1-hexene (2) system at 323.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from Wilson model; − −, γ_1 and γ_2 from COSMO-RS.

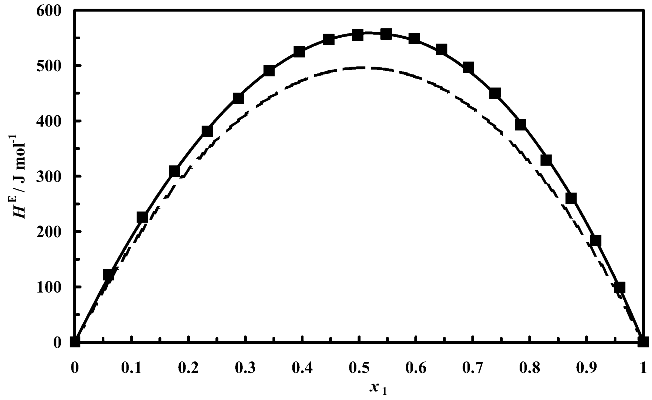

Figure 9. Excess molar enthalpy for the diethyl sulfide (1) + *n*-hexane (2) system at 318.15 K: ■, measured;[3] —, from the Wilson model-extended data. Excess molar enthalpy for the diethyl sulfide (1) + 1-hexene (2) system at 318.15 K: − −, calculated from the Wilson model-extended data.

each component used in the calculations are presented in Table 2.

The liquid phase activity coefficients of diethyl sulfide + 1-hexene system at (333.15 and 323.15) K were correlated with the Wilson[16] model with the temperature-dependent parameters. The objective function[13] (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:

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

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

$$\Delta\lambda_{ij} = a_{0,ij} + a_{1,ij}(T/\text{K}) + a_{2,ij}(T/\text{K})^2 \tag{5}$$

The temperature-dependent parameters of the Wilson model for diethyl sulfide + *n*-hexane system have been fitted by using simultaneously the measured VLE data at (338.15 and 323.15) K and excess enthalpy (H^{E}) data[3] at 318.15 K. The following objective function was used:

$$\text{OF} = \frac{1}{N_{\text{VLE}}} \sum_{i=1}^{N_{\text{VLE}}} \left(\frac{|\gamma_{\text{i,calc}} - \gamma_{\text{i,exp}}|}{\gamma_{\text{i,exp}}} \right) + \frac{1}{N_{\text{HE}}} \sum_{i=1}^{N_{\text{HE}}} \frac{|H^{\text{E}}_{\text{i,calc}} - H^{\text{E}}_{\text{i,exp}}|}{\text{kJ}\cdot\text{mol}^{-1}} \tag{6}$$

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

$$H^{\text{E}}_{\text{calc}} = -RT^2 \left(\sum_{i=1}^{NC} x_i \frac{\partial(\ln \gamma_{i,\text{calc}})}{\partial T} \right)_{P,x} \tag{7}$$

The comparison between the measured excess molar enthalpy and the one calculated by using the parameters from Wilson extended model for diethyl sulfide + *n*-hexane system is presented in Table 5 and shown in Figure 9. Good agreement is obtained between experimental and calculated results. The excess enthalpies at 318.15 K for diethyl sulfide + 1-hexene system were calculated from the VLE data. The results are shown in Table 5 and Figure 9.

Wilson interaction parameters with temperature-dependent ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) for diethyl sulfide + *n*-hexane (parameters W_1) and diethyl sulfide + 1-hexene (parameters W_2) are given in Table 6. Good agreement between measurements and model were achieved for all systems.

Diethyl sulfide + *n*-hexane system at (338.15 and 323.15) K were predicted with the original UNIFAC[17] model with the parameters on the level of Wittig et al.[18] and COSMO-RS. The results are presented in Figures 1, 2, 5, and 6. COSMO-RS predictions are quite close to the experimental results and show better prediction as compared to the original UNIFAC.

The original UNIFAC interaction parameter for the diethyl sulfide (CH_2S group) and 1-hexene ($CH_2{=}CH$ group) binary pair is not available; hence the original UNIFAC prediction is not possible for diethyl sulfide + 1-hexene system. As can be seen from Figures 3, 4, 7, and 8, the COSMO-RS gave poor prediction for these systems.

The following thermodynamic consistency tests were applied to the measured VLE data: integral test,[19] point test,[19] and infinite dilution test.[20] The results are summarized in Table 7 including the activity coefficients at infinite dilution (γ_i^∞). The measurements passed all consistency tests applied.

Conclusions

Isothermal VLE were measured for diethyl sulfide + *n*-hexane at (338.15 and 323.15) K and for diethyl sulfide + 1-hexene at (333.15 and 323.15) K with a circulation still. The liquid- and vapor-phase compositions were determined with gas chromatography. All systems show slight positive deviations from Raoult's law. No azeotropic behavior was found in any of the systems studied. The experimental data of the diethyl sulfide + *n*-hexane 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*-hexane VLE data are in good agreement with the literature data. The excess enthalpies of diethyl sulfide + 1-hexene system at 318.15 K were calculated from the VLE data. The Wilson model gave good correlation for all systems. COSMO-RS gave better prediction as compared to the original UNIFAC for the diethyl sulfide + *n*-hexane system, but poor prediction for the diethyl sulfide + 1-hexene system. All systems measured passed the thermodynamic consistency tests that were used.

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