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Phase equilibria for systems containing dimethyl disulfide and diethyl disulfide with hydrocarbons at 368.15 K

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ABSTRACT

Isothermal vapor–liquid equilibrium (VLE) for dimethyl disulfide + toluene, dimethyl disulfide + 2,2,4-trimethylpentane, dimethyl disulfide + 2,4,4-trimethyl-1-pentene, and diethyl disulfide + 2,2,4-trimethylpentane at 368.15 K were measured with a recirculation still. All systems exhibit positive deviation from Raoult's law. Dimethyl disulfide + toluene system shows only slight positive deviation from Raoult's law, while dimethyl disulfide + 2,2,4-trimethylpentane, dimethyl disulfide + 2,4,4-trimethyl-1-pentene, and diethyl disulfide + 2,2,4-trimethylpentane systems show larger positive deviation from Raoult's law. Maximum pressure azeotropes were found in systems: dimethyl disulfide + toluene ($x_1 = 0.632$, $P = 66.4$ kPa, $T = 368.15$ K), dimethyl disulfide + 2,2,4-trimethylpentane ($x_1 = 0.311$, $P = 95.8$ kPa, $T = 368.15$ K), and dimethyl disulfide + 2,4,4-trimethyl-1-pentene ($x_1 = 0.295$, $P = 88.4$ kPa, $T = 368.15$ K). No azeotropic behavior was observed in system diethyl disulfide + 2,2,4-trimethylpentane at 368.15 K. The experimental results were correlated with the Wilson model. Original UNIFAC was used to predict dimethyl disulfide + 2,2,4-trimethylpentane and diethyl disulfide + 2,2,4-trimethylpentane systems at 368.15 K. COSMO-SAC predictive model was used to predict infinite dilution activity coefficients for all systems measured. Liquid and vapor-phase composition were determined with gas chromatography. All VLE measurements 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]. New developments on sulfur separation process design to further decrease the sulfur level have become one of the major challenges to the refining industry [2]. 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.

Dimethyl disulfide and diethyl disulfide are among the organic sulfur compounds present in the hydrocarbon streams originating from the Fluid Catalytic Cracker (FCC) [3,4]. Experimental work with dimethyl disulfide requires appropriate occupational health measures due to the toxicity of the compound. In this work, we measured vapor–liquid equilibrium (VLE) for systems dimethyl disulfide + toluene, dimethyl disulfide + 2,2,4-trimethylpentane, dimethyl disulfide + 2,4,4-trimethyl-1-pentene, and diethyl disulfide + 2,2,4-trimethylpentane at 368.15 K with a recirculation still. No other VLE data of the binary systems studied in this work have been found in the literature search. Excess enthalpy measurements at 298.15 K for systems containing dimethyl disulfide with *n*-hexane, *n*-octane, *n*-dodecane, and *n*-hexadecane and also for systems diethyl disulfide + *n*-octane, diethyl disulfide + *n*-dodecane, and diethyl disulfide + *n*-hexadecane were found in the literature [5]. Additionally, solubility data for the systems dimethyl disulfide in hexadecane at 298.15 K was found [6].

2. Experimental

2.1. Materials

Dimethyl disulfide, diethyl disulfide, toluene, 2,2,4-trimethylpentane, 2,4,4-trimethyl-1-pentene, and *o*-xylene (used as diluent) 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 3 Å) for 24 h. The refractive indexes, n_D, of the pure liquids were measured at 298.15 K with ABBEMAT-HP automatic refractometer (Dr. Kernchen, Germany) with accuracy ±0.00002. The purity and measured refractive indexes are pre-

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

Component	Purity		n_D (298.15 K)	
	Manufacturer (mass %)	GC (mass %)	Experimental	Literature [7]
Dimethyl disulfide	≥99	99.66	1.52284	1.5230
Diethyl disulfide	99	99.74	1.50451	1.5047
Toluene	≥99.5	99.95	1.49393	1.4941
2,2,4-Trimethylpentane	≥99	99.78	1.38902	1.3890
2,4,4-Trimethyl-1-pentene	99	99.46	1.40621	1.4060
o-Xylene (used as diluent)	≥99	99.43	1.50264	1.5029

sented in Table 1. The measured refractive indexes corresponded well with literature values [7].

2.2. Apparatus

The VLE runs were conducted with a circulation still of the Yerazunis-type [8] built at the glass workshop of Helsinki University of Technology with minor modifications to the original design [9]. Experimental setup is described in detail in the previous works [9,10]. 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 ±0.02 K and the calibration uncertainty was ±0.01 K. The uncertainty of the whole temperature measurement system is estimated to be ±0.05 K.

Pressure was measured with a Druck pressure transducer PMP 4070 (0–100 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 uncertainty of the whole pressure measurement system including the calibration uncertainty is expected to be less than ±0.17 kPa.

In order to improve mixing in the sampling chambers and mixing chamber of the condensed vapor-phase and the liquid-phase DC electric motors (Graupner speed 400) were equipped with magnetic stirrer bars, which deliver stirring action in the chambers.

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 to 60 min to achieve constant temperature. The temperature was held constant for approximately 30–45 min before sampling. Steady temperature was assumed as an indication 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 × 250 μm × 1.0μm). The injector and FID were set at 250 °C. Helium was used as the carrier gas at a constant flow rate of 1 ml min^{-1} and inlet split ratio 100:1. The initial oven temperature was held at 70 °C for 2 min and then increased subsequently to 150 °C at rate of 8 °C min^{-1} and was held at 150 °C for 3 min. The total run time was 15 min.

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}), and average of the absolute pressure residuals ($\left|\Delta P^S\right|_{aver}$) between measured ($P_{i,exp}$) and values calculated with regressed parameters of the Antoine equation ($P_{i,calc}$).

Component	Dimethyl disulfide	Diethyl disulfide	Toluene	2,2,4-Trimethylpentane	2,4,4-Trimethyl-1-pentene
T_c[a] (K)	606.00	642.00	591.79	543.96	553.00
P_c[a] (MPa)	5.36	3.870	4.109	2.568	2.630
ω[a]	0.265	0.346	0.264	0.303	0.270
V_i[a] (cm^3 mol^{-1})	89.118	123.739	106.556	165.452	157.915
A[b]	7.1352[c]	7.1466[c]	6.7321[d]	6.7960[e]	6.9288[f]
B[b]	3080.0182[c]	3421.9951[c]	2869.7197[d]	2896.0492[e]	2999.2728[f]
C[b]	−55.7933[c]	−64.0675[c]	65.4951[d]	−53.3543[e]	−49.1179[f]
T_{min} (K)	332.19	366.97	335.00	338.06	329.03
T_{max} (K)	382.02	426.39	379.44	372.05	374.18
$\left|\Delta P^S\right|_{aver}$ (kPa)[g]	0.21	0.15	0.08	0.09	0.03

[a] Ref. [7].

[b] $P^S \text{ (MPa)} = \exp\left(A - \left[B/(T/K + C)\right]\right)$

[c] This work.

[d] Ref. [11].

[e] Ref. [12].

[f] Ref. [13].

[g] $\left|\Delta P^S\right|_{aver} = \dfrac{\sum_{i=1}^{N}\left|P_{i,calc}-P_{i,exp}\right|}{N}$

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