Phase Equilibria for Separation of Organic Sulfur Compounds for Cleaner Fuels

Erlin Sapei, Piia Haimi, Anna Zaytseva, Petri Uusi-Kyyny, Kari I. Keskinen, Juhani Aittamaa

Abstract— **The infinite dilution activity coefficients (γ^∞) of sulfur compounds in hydrocarbons are very important in the reliable design of sulfur removal processes producing cleaner gasoline. We determined 23 γ^∞ of sulfur compounds from vapor-liquid equilibrium (VLE) binary systems measurements with recirculation still and 7 infinite dilution activity coefficients of systems containing different sulfur compounds in selected hydrocarbons with comparative ebulliometers. The γ^∞ of sulfur compounds in water is very essential for modeling the sour water removal in distillation column. We measured infinite dilution activity coefficient of 4 sulfur compounds in water determined over a range of temperature from 288.15 K to 333.15 K with inert gas stripping method.**

Index Terms— **fuels, infinite dilution activity coefficient, phase equilibrium, sulfur compounds, UNIFAC.**

I. INTRODUCTION

Increasing concerns on air pollution have led many countries to adopt more stringent regulations, which impose an ultra-low concentration of sulfur in gasoline [1]. These regulations place many challenges on the refining industry [2]. The accurate knowledge of sulfur behavior in hydrocarbons requires the VLE information of sulfur compounds in hydrocarbons, in particular infinite dilution activity coefficients of sulfur compounds, which are important for the optimum design of

sulfur separation processes. However, the experimental data of VLE of hydrocarbon containing organic sulfur compounds are scarce in the literature. As a consequence, current available thermodynamic models are inadequate to predict both phase equilibrium and physical properties of mixtures containing the sulfur compounds in the dilute range.

We have measured 23 VLE binary and 7 infinite dilution activity coefficients of systems containing different sulfur compounds in selected hydrocarbons with recirculation still [3]–[8] and comparative ebulliometer [9], respectively.

Sour water coming from distillation, fluid catalytic cracking, coking and hydrotreating processes in refineries typically contains pollutants such as H_2S, low-molecular-weight sulfur compounds, hydrocarbons, ammonia, and phenol. The presence of sour water in the distillation column causes phase splitting. Hence, in this work we have measured the infinite dilution activity coefficient of 4 sulfur compounds in water determined over a range of temperature from 288.15 K to 333.15 K with the inert gas stripping method [10].

II. EXPERIMENTAL SECTION

A. Materials

1-propanethiol, 2-propanethiol, 1-butanethiol, thiophene, ethyl methyl sulfide, diethyl sulfide, *n*-hexane, cyclohexane, *n*-heptane, toluene, 2,2,4-trimethylpentane, and toluene were purchased from Sigma Aldrich, Finland. The chemicals were used as purchased. 2-Ethoxy-2-methylpropane was supplied by Neste Oil Oyj, Finland and was further purified by distillation and extraction of alcohol impurities with distilled water. All chemicals were dried over molecular sieves (Merck 3A) for 24 h. The purities of the chemicals were checked with a gas chromatograph (GC) equipped with a flame ionization detector. 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 measured refractive indexes corresponded well with literature values [11].

B. Apparatus and Procedures

- Recirculation still

The VLE runs were conducted with a circulation still of the Yerazunis-type [12] built at the glass workshop of Helsinki University of Technology (HUT) with minor modifications to the original design [13]. Experimental procedure is described in

detail in the previous works [3]–[8]. The schematic of experimental setup is presented in Fig. 1. 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 minutes to achieve constant temperature. The temperature was held constant for approximately 30 – 45 minutes 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 and after that injected into the cooled 2 ml auto sampler vial containing approximately 1 ml of solvent. 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.
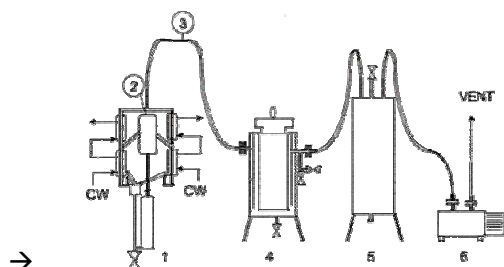

Fig. 1 The experimental setup for circulation still apparatus: (1) recirculation still; (2) temperature probe (Pt-100); (3) pressure transducer; (4) liquid nitrogen trap; (5) buffer tank; (6) vacuum pump.

- Comparative ebulliometers

The equipment used for the determination of γ^∞ is shown in Fig. 2 schematically. Experimental procedure is described in more details in [9]. The measurements were conducted with 4 Swietoslawski-type ebulliometers [14] in parallel, which allow the determination of activity coefficient for several solutes simultaneously. The temperature differences were measured between the ebulliometer containing pure solvent and the ones containing the mixtures. The apparatus is made of glass and equipped with a Cottrell pump. The apparatus can be operated from 15 kPa to atmospheric pressure. The differences of the boiling temperatures at equilibrium were measured by using a Thermometer F200 (Tempcontrol) with an accuracy of ± 0.02 K. A mixture of 2-propanol and water was used as a cooling medium for condenser at 277.15 K.
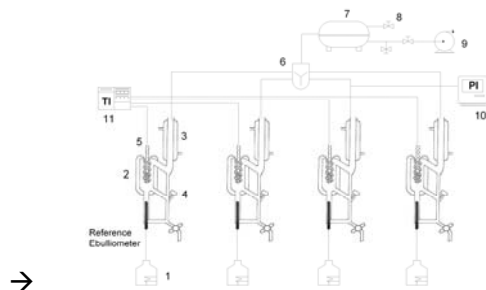

Fig. 2 Overall design of system used to measure activity coefficients by differential ebulliometry: (1) heating units; (2) equilibrium cell; (3) condenser; (4) injection port; (5) thermometer; (6) N$_2$ trap; (7) 50 dm^3-ballast; (8) manual valve; (9) vacuum pump; (10) pressure indicator; (11) temperature indicator.

- Inert gas stripping method

The experimental set-up is presented schematically in Fig. 3. The experimental procedure is described in details in [10]. A gas chromatograph (Agilent 6890N) equipped with a flame ionization detector was used in the measurements. The GC was equipped with a pneumatic six-port gas-sampling valve (loop size 250 μl). The temperature of the sampling valve could be controlled independently and it was set from 373.15 K to 403.15 K. The capillary column used was HP-5, length 30 m, inner diameter 0.32 mm with a film thickness of 0.25 μm. The GC-run was isothermal and the oven temperature was set to 383.15 K. The equilibrium cell used was of the type described by Hovorka *et al*. [15]. The cell was constructed at the HUT glass workshop. The device consists of a full-jacketed presaturator and a dilution cell. The volume of the presaturator was about 0.005 dm^3 and it was filled with the solvent used and spring packing. The total volume of the dilution cells was 0.235 dm^3. The volume of the solvent used in the measurements varied from 0.202 dm^3 to 0.218 dm^3. The temperature of the jacket was kept under isothermal (±0.2 K) conditions with a temperature controlled water bath (Lauda E200). Tap water was used as a cooling agent for the runs below room temperature. Inert stripping gas (N$_2$) was introduced through a mass flow control unit (Bronkhorst Hi-Tech; E-7500-DBB), to provide constant flow. The flow rate was measured with a soap-bubble flow meter after the pneumatic valve. Typical flow rates used in the measurements were 3 – 8 cm^3/min. The cell was connected to the sampling valve via an independently heated transfer line.
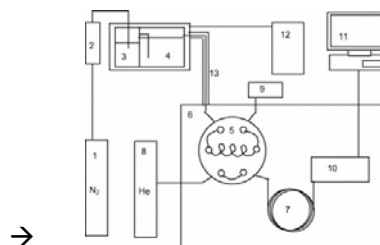
Fig. 3 Schematic experimental setup for inert gas stripping method: (1) stripping gas source; (2) mass flow meter; (3) presaturator; (4) dilution cell; (5) six port gas-sampling valve; (6) GC gas chromatograph; (7) capillary column; (8) GC carrier gas source; (9) soap-bubble flow meter; (10) flame ionization detector; (11) computer; (12) thermostated bath; (13) heated transfer line.

III. RESULTS AND DISCUSSIONS

- γ^∞ determined from VLE measurements with recirculation still

The consistent VLE experimental results carried out with recirculation still were correlated with the Wilson [16] model and the extrapolated infinite activity coefficients were presented in Table 1. The extrapolated γ^∞ were compared with the γ^∞ predicted with original UNIFAC [17] in the level of [18], UNIFAC-Dortmund [19] in the level of [20], and COSMO-RS [21] predictive models.

The systems of 1-propanethiol, thiophene, and diethyl sulfide with toluene were carried out at 90.03 kPa [3]. The systems

thiophene + n-hexane were measured at 323.15 K and 338.15 K. The systems thiophene + 1-hexene were measured at 323.15 K and 333.15 K. The systems diethyl sulfide + n-heptane and diethyl sulfide + 2,2,4-trimethylpentane were measured at 353.15 and 363.15 K [5]. The systems diethyl sulfide + n-hexane were carried out at 323.15 K and 338.15 K. The systems diethyl sulfide + 1-hexene were carried out at 323.15 K and 333.15 K [6]. The systems diethyl sulfide + cyclohexane were measured at 343.15 K and 353.15 K. The systems diethyl sulfide + 2-ethoxy-2-methylpropane were measured at 333.15 K and 343.15 K [7]. The systems thiophene + 2,2,4-trimethylpentane were carried out at 343.15 K and 353.15 K. The systems thiophene + 2-ethoxy-2-methylpropane were measured at 333.15 and 343.15 K [8].

Table 1 Activity coefficients at infinite dilution determined from VLE measurements with recirculation still; Methods: A, extrapolation of experimental VLE with the Wilson model; B, UNIFAC; C, UNIFAC-Dortmund; D, COSMO-RS

system	γ_1^∞	γ_2^∞	method
1-propanethiol (1) + toluene (2) isobaric, P = 90.03 kPa	1.04	1.06	A
thiophene (1) + 1-hexene (2) isothermal, T = 323.15 K	1.63	2.0	A
thiophene (1) + 1-hexene (2) isothermal, T = 333.15 K	1.57	1.89	A
thiophene (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 333.15 K	1.21 1.44	1.40 1.88	A D
thiophene (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 343.15 K	1.20 1.43	1.38 1.84	A D
thiophene (1) + toluene (2) isobaric, P = 90.03 kPa	1.00	1.03	A
thiophene (1) + n-hexane (2) isothermal, T = 323.15 K	1.96 2.15	2.71 3.36	A C
thiophene (1) + n-hexane (2) isothermal, T = 338.15 K	1.82 1.73 2.18	2.49 2.40 3.61	A B C
thiophene (1) + 2,2,4-trimethylpentane (2) isothermal, T = 343.15 K	1.72 1.53 1.68 2.68	2.62 2.59 3.34 4.77	A B C D
thiophene (1) + 2,2,4-trimethylpentane (2) isothermal, T = 353.15 K	1.68 1.50 1.71 2.56	2.54 2.52 3.55 4.43	A B C D

Table 1 (*continued*)

system	γ_1^∞	γ_2^∞	method
diethyl sulfide (1) + n-hexane (2) isothermal, T = 323.15 K	1.51	1.55	A
diethyl sulfide (1) + n-hexane (2) isothermal, T = 338.15 K	1.47	1.49	A
diethyl sulfide (1) + 1-hexene (2) isothermal, T = 323.15 K	1.27	1.26	A
diethyl sulfide (1) + 1-hexene (2) isothermal, T = 333.15 K	1.26	1.25	A
diethyl sulfide (1) + cyclohexane (2) isothermal, T = 343.15 K	1.38	1.34	A
diethyl sulfide (1) + cyclohexane (2) isothermal, T = 353.15 K	1.36	1.32	A
diethyl sulfide (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 333.15 K	1.13	1.17	A
diethyl sulfide (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 343.15 K	1.13	1.17	A
diethyl sulfide (1) + toluene (2) isobaric, P = 90.03 kPa	1.00	1.00	A
diethyl sulfide (1) + n-heptane (2) isothermal, T = 353.15 K	1.34 1.45 1.24	1.42 1.50 1.30	A D B
diethyl sulfide (1) + n-heptane (2) isothermal, T = 363.15 K	1.33 1.43 1.23	1.40 1.48 1.29	A D B
diethyl sulfide (1) + 2,2,4-trimethylpentane (2) isothermal, T = 353.15 K	1.36 1.48 1.19	1.47 1.55 1.28	A D B
diethyl sulfide (1) + 2,2,4-trimethylpentane (2) isothermal, T = 363.15 K	1.34 1.46 1.18	1.45 1.52 1.27	A D B

The original UNIFAC and UNIFAC-Dortmund group contribution models have been widely applied in the estimation of the VLE of organic mixtures, as it includes almost all the functional groups involved in the organic substances. However, the applications of the predictive models are limited since some important interaction parameters for sulfur and hydrocarbon functional group are unavailable because of little

or no experimental data available. The important UNIFAC sulfur and hydrocarbon group interactions are shown in the Table 2. The missing interaction parameters of the functional group CH_3SH with C=C, CH_2S with C=C, ACH, $ACCH_2$, CH_2O, and C_4H_4S with C=C, CH_2O in UNIFAC model can be correlated using experimental data.

Table 2 Important UNIFAC sulfur and hydrocarbon group interactions

sulfur / hydrocarbon	CS_2	CH_3SH	CH_2S	C_4H_4S
CH_2	√	√	√	√
C=C	√	–	–	–
ACH	√	√	–	√
$ACCH_2$	√	√	–	√
CH_2O	√	√	–	–

(√) available; (–) not available

When the original UNIFAC and UNIFAC-Dortmund group contribution methods are not applicable, COSMO-RS is used as an alternative method for the prediction of vapor-liquid equilibrium. As can be seen from Table 1, in general, the infinite dilution activity coefficients for systems containing organic sulfur compounds with hydrocarbons predicted with COSMO-RS model show larger deviation than the original UNIFAC and UNIFAC-Dortmund methods.

- γ^∞ from comparative ebulliometry

The infinite dilution activity coefficients of 1-propanethiol, ethyl methyl sulfide, and thiophene in toluene, *n*-heptane, and 2,2,4-trimethyl-pentane at 90 kPa are presented in Table 3. The measured infinite dilution activity coefficients were compared with the predictive original UNIFAC group contribution model. The experimental results show quite good agreement with original UNIFAC prediction.

Table 3 Experimental values of γ^∞ determined with comparative ebulliometry together with original UNIFAC estimation

Solute (1)	Solvent (2)	T (K)	γ_1^∞	original UNIFAC
thiophene	toluene	379.53	1.04	1.13
	n-heptane	367.47	1.31	1.54
	2,2,4-trimethyl-pentane	368.11	1.46	1.47
1-propanethiol	*n*-heptane	367.47	1.04	1.31
	2,2,4-trimethyl-pentane	368.11	1.23	1.25
ethyl methyl sufide	*n*-heptane	367.47	1.18	1.20
	2,2,4-trimethyl-pentane	368.11	1.17	1.14

- γ^∞ from inert stripping method

γ^∞ values determined in the temperature range from 288.15 K to 333.15 K are presented in Table 4 together with the estimated solubility values (x_1), literature solubility values, and Henry's constant. The γ^∞ values for sulfur compounds varied from 1095 for thiophene to 6042 for 1-butanethiol. There seems to be very weak temperature dependence in the measured temperature range, except for 1-butanethiol, which also has the longest chain length. Przyjazny *et al.* [22] have measured distribution coefficients (K_i) for thiophene and *n*-propanethiol in water with the headspace gas chromatographic technique. The γ^∞ values were estimated from the K_i values. The values were lower than our values especially for 1-butanethiol [25]. The γ^∞ value differs from our measurements by 9%.

IV. CONCLUSION

23 infinite dilution activity coefficients were determined from VLE binary systems measurements with a recirculation still and 7 infinite dilution activity coefficients of systems containing different sulfur compounds in selected hydrocarbons with comparative ebulliometers. New experimental data gave new information about sulfur behavior in hydrocarbons. However, more experimental work for various systems containing higher sulfides, higher molecular weight thiols and branched thiophenes is needed in order to model the behavior of sulfur compounds in multicomponent separation processes.

The measured infinite dilution activity coefficients were compared with original UNIFAC, UNIFAC-Dortmund, and COSMO-RS predictive models. Original UNIFAC is adequate to describe the organic sulfur compound behavior in hydrocarbons even though its application is limited due to the availability of the functional group interaction parameters. COSMO-RS gave poor prediction for all systems studied, thus currently, it is not a suitable method to predict the systems containing sulfur compounds.

The infinite dilutions of several sulfur compounds in water were measured at different temperatures from 288.15 K to 333.15 K. The measurements showed that the water solubility estimations of organic sulfur compounds show significant uncertainties.

Table 4 Infinite dilution activity coefficients for the investigated solutes (1) in water (2) in the temperature range from 288.15 K to 333.15 K, calculated solubility values (x_1), literature solubility values (x_1 literature), and Henry's constants (H_{12})

Solute	T (K)	γ_1^∞	γ_1^∞ (literature)	x_1 (mol)	x_1 (literature)	H_{12} (Mpa)
thiophene	288.15	1263 ± 46		7.92E-04		8.05
	298.15	1272 ± 43	1200 [22]	7.92E-04	6.48E-04 [23], 4.66E-04 [23]*, 3.68E-04 [24]	13.34
	308.15	1314 ± 46		7.60E-04		21.8
	318.15	1291 ± 51		7.73E-04		32.71
	333.15	1095 ± 49		9.08E-04		49.48
1-butanethiol	288.15	6027 ± 221		1.66E-04		21.75
	298.15	6042 ± 244	6600 [25]	1.65E-04	1.20E-04 [26], 2.09E-04 [23]*, 5.12E-04 [24]	36.65
			8330 [23]			
	308.15	5834 ± 266		1.71E-04		57.13
	318.15	5338 ± 293		1.86E-04		81.40
	333.15	4140 ± 302		2.38E-04		115.63
1-propanethiol	288.15	1423 ± 51		7.01E-04		18.53
	298.15	1495 ± 56	1100 [22]	6.56E-04	8.75E-04 [23]	30.72
	308.15	1455 ± 60		6.86E-04		45.53
	318.15	1448 ± 69		6.93E-04		66.89
	333.15	1309 ± 79		7.54E-04		103.00
2-propanethiol	288.15	1116 ± 41		8.96E-04		27.00
	298.15	1135 ± 46		8.80E-04	14.69E-04 [23]	41.98
	308.15	1188 ± 56		8.42E-04		64.94
	318.15	1127 ± 63		8.80E-04		88.49

*Calculated using correlation Ref [27].

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